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# An Overview of Climatic Elements

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**March 2007**

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## Acknowledgments

Many people, through many years of effort and dedication, have contributed to the development of knowledge and the storage of wisdom. These are the intrepids, the developers, the servers, the historians, the researchers, and those who publish and distribute the collected wisdom.

This survey of the contributions of those mentioned above presents only a small portion of the collected and available information on climatic elements. The inspiration of Dr. Helmut E. Landsberg was fundamental. The guidance, suggestions, and urging by Dr. Oskar M. Essenwanger is appreciated. It was planned that Elsevier Scientific Publishing, as part of the series, *World Survey of Climatology*, would publish this material. Under that presumption permissions to quote from, abstract, or copy material were sought. Elsevier now has declined to publish this survey. It is hoped that those who granted permission will extend their permission to permit the publication of their material by other means.

My dear wife, Clarice, and my daughters, Sharron and Carol, enthusiastically supported me. Their steadfast support and encouragement have been extraordinary. My grandson, Gregory Gebhardt, and his wife, Dawnell, have contributed their time and efforts preparing this material for publication.

I tender acknowledgments to journals, books, groups, and organizations; wherever possible, attribution has been made. In each case, journals and publications have given their permission. In some cases, quotation marks are used to show excerpted remarks. There may be some cases of error and inadvertent omission. I offer apologies in these cases.

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## FOREWORD

This publication was originally intended as a contribution to a 15-volume series in *World Survey of Climatology* as a part of V. 1. A previous contribution was a small chapter in V. 4 in 1969. Work on this was begun in 1977. The subject was climatic elements. Trace gases have become increasingly important in the study of climatology. Here, climatic elements include trace gases as well as measures of the expected physical elements—wind, temperature, precipitation, radiation, and others. There are many references. The requisite permissions were obtained. The expected publishers indicate that they do not wish to publish this material. Therefore, this procedure is chosen to place the material in your hands. You will find the material to be informative and useful. Since the principal author assembled the technical contents given within this publication over a number of years, some of the technical content may not be representative of the latest state-of-the art information.

## SURVEYOR



As this is a survey and has no original research done especially for the survey, you probably are interested in some information about the surveyor. Perhaps it will make the survey more interesting.

Harold Lee Crutcher was born at Cheraw, CO, November 18, 1913. His father was a schoolteacher, school administrator, farmer, and stockman. His mother was a housewife, farmer, and a teacher. The family lived in southeastern Colorado near the Arkansas River, in the San Luis Valley west of the Continental Divide, and in Denver, CO. At age 9, the family moved to the Cheyenne River Agency and a Sioux Reservation. Both his parents worked for the Bureau of Indian Affairs. His father was an administrator for Indian Schools and his mother was a teacher. In a small, one-room school he was taught the story of Continental Drift. There were 15 students and eight grades in the one room. The teacher was an admirer of and perhaps a disciple of Alfred Wegener, a German geophysicist. Four years later, the father was transferred to the Kiowa Indian Reservation near Anadarko, OK. In 1930, the father was again transferred, this time to Durant, OK, as an Indian Agent for the Five Civilized Tribes of Eastern Oklahoma. Here, Harold started college at the now Southeastern State University of Oklahoma. In 1933 and 1934, respectively, he obtained BA and BS degrees. In 1935 he spent some time in the Army Air Corps and then started teaching school for which he had been trained. He had obtained majors in Latin, mathematics, education, and chemistry with minors in instrumental music, manual training, physical education, library science, and modern languages. In an extracurricular sense, he had absorbed some of the Spanish, Lakota, and Kiowa languages. He taught school during the normal school years and attended Oklahoma University at Norman, OK. There, he completed course work for a Doctorate in Physical Chemistry before entering the U.S. Weather Bureau in 1939. He was never assigned to Oklahoma City. He would have been able to attend the University of Oklahoma at Norman, OK, a scant 15 miles away. Without such an assignment and with no job or income, it would have taken 2 years to start and finish a dissertation on the aging of colloids. There were no U.S. or State Government grants in those days. Indeed it would have been a hungry time. Assignments in the Weather Bureau intervened. World War II also intervened.

He spent a year in Little Rock, AR, learning the techniques of making weather observations. There he learned to plot weather maps, hang up the printed teletype weather reports, analyze weather maps, and brief pilots. This was in the days before frontal analysis became fashionable and required. To serve his upward mobility, he was transferred to Atlanta, GA, to learn the new weather observation procedures for radiosonde observations. The U.S. Weather Bureau was expanding its atmospheric observation program. In 1940 he was sent to establish the Swan Island, WI, permanent upper air observing station. That location had served as an outpost station during the hurricane season. The well-known Joseph Cline of New Orleans manned the stations prior to 1939. It was manned by Herbert Rahmlow in 1939. Eight months there and Harold was assigned to the North Atlantic Weather Patrol. Ships of the U.S. Coast Guard and the U.S. Navy were the observing platforms. There was a teaching assignment at the Washington National Airport. He was one of about eight instructors and had six students—two from Canada, two from Mexico, and two ladies. The Canadians were transitioning from the chronometric type to the modulated type radiosonde in use today; Gerry Gill was one of the Canadians. The two ladies were being trained to replace the male observers who were being sent to northern outlying stations. One of the ladies was Florence Rohde. The two Mexican observers were being trained to lead some of the radiosonde work in Mexico. These two observers were Señores Ernesto Domingues and Armando Ojeda. In late 1942 Harold was assigned to Mexico. The Mexican Meteorological Service was establishing networks of surface stations, upper air stations, and radiosonde observation stations. That Service needed help both in a material way and in training. The assignment to Mexico lasted more than 3 years. After returning from Mexico, there were assignments in forecasting and then in climatology. A transfer to San Juan, Puerto Rico, and Central America was followed by a 3½-year assignment to Lima, Peru, and the northern and western countries of South America. This assignment was as a member of a State Department and a Civil Aeronautics assigned team to help those countries establish their Civil Aviation potential after World War II. There might be as many as nine people involved in a team in each country, such as airport engineers, air safety, airport controllers, weather personnel, and communications. Sometimes there was a single member.

He had married while in Mexico. His wife was a former meteorological observer. They had met while working together at the Washington National Airport forecast office. In 1950 they returned to the United States of America. He obtained a master's degree in meteorology. In 1951 he was reassigned to the Office of Climatology in Washington, DC. His assignment was to work with the U.S. Naval Service. He was involved in the formation of the National Weather Records Center at Asheville, NC. The three major participants were and are the U.S. Weather Bureau (Service), the U.S. Naval Weather Service, and the U.S. Air Force Weather Service Detachment. Due to reorganizations, these names have changed. Their missions have not changed. He was Science Advisor to the Director of the National Weather Records Center. This is now the National Climatic Data Center. The name changed through the years but the function remained essentially unchanged. His main work involved the production of the long series of Marine Climatic Atlases. These include upper air atlases. It takes about 5 years from initiation to publication of each atlas. Initially, punched cards were the medium to store and compute the material for the atlases and other work. Gradually, the use of punched cards dwindled due to the development and use of electronic computers.

In 1955 he received a 9-month assignment to New York University College of Engineering. He finished the necessary course work for a doctorate. He returned to Asheville to work. During vacations and weekends, he spent his time working on his dissertation. His wife and family were quite supportive. The title of his dissertation is "Statistical Grouping of Climates and the Statistical Discrimination Among Climatic Groups." He received his Ph.D. in 1960. He retired from Government service in 1977. He still lives in the Asheville area. During his employment with the U.S. Weather Bureau, over 100 publications were published. The following is a list of some of the professional organizations to which he belongs. This may give you an idea of the depth of his knowledge, expertise, and interests:

- American Chemical Society.
- American Institute of Chemists—Certified Chemist and a Fellow.

- American Meteorological Society—Certified Consulting Meteorologist.
- American Society for Quality—Certified Reliability Engineer (ret) and a Fellow.
- American Society for Testing.
- American Statistical Association.
- American Water Resources Association.
- International Union of Pure and Applied Chemistry (IUPAC).
- International Water Resources Association.
- Royal Meteorological Society.

This survey was started in 1978 at the request of Dr. H.E. Landsberg. He has died. In the interim, in the early 1980s he asked that trace gases be surveyed. That section discussion has essentially doubled the size of this survey. Some of the earlier portion of the survey has been updated. But as time goes on, there will be more opportunity to update by someone else.

The survey has not had a complete “peer review.” The reader’s indulgence is appreciated.





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## LIST OF ACRONYMS, SYMBOLS, AND ABBREVIATIONS

AFCRL	Air Force Cambridge Research Laboratory
AGR	astronomical global radiation
APOB	aircraft meteorograph observation
Ar	argon
ASTM	American Society for Testing Materials
BIPM	International Bureau of Weights and Measures
BP	before present
CD-ROM	compact disk-read only memory
CF <sub>2</sub> Cl <sub>2</sub>	halocarbon
CFCl <sub>3</sub>	halocarbon
CFC	chlorofluorocarbon
cgs	centimeter-gram-second
CH <sub>4</sub>	methane
CHCl <sub>3</sub>	chloroform
Cl	chlorine
CLICOM	climate computing
CLINO	climatic normal data
CO <sub>2</sub>	carbon dioxide
COESA	Committee on the Extension to the Standard Atmosphere
CQC	complex quality control
D	deuterium
D <sub>2</sub> O	heavy water
DBMS	database management system
DoD	Department of Defense
ERB	Earth radiation budget
ESADS	Earth Science and Applications Data
FOV	field of view
GATE	GARP Atlantic Tropical Experiment
GWP	global warming potential
H	hydrogen
H <sub>2</sub> O	water
ICSU	International Council of Scientific Unions

## LIST OF ACRONYMS, SYMBOLS, AND ABBREVIATIONS (Continued)

IEEE	International Electrical and Electronics Engineers
Ih	ice in its general occurrence and normal hexagonal form
MKS	meter-kilogram-second
MKSA	meter-kilogram-second-ampere
msl	mean sea level
MTS	meter-ton-second
N <sub>2</sub>	nitrogen gas
N <sub>2</sub> O	nitrous oxide
Na	sodium
NaCl	table salt
NASA	National Aeronautics and Space Administration
NBS	National Bureau of Standards
NCDC	National Climatic Data Center
NDC	National Data Center
NESDIS	National Environmental Satellite, Data, and Information Service
NMR	nuclear magnetic resonance
NO <sub>2</sub>	nitrous oxide
NOAA	National Oceanic and Atmospheric Administration
NPL	National Physical Laboratory
NPRA	National Petroleum Reserve in Alaska
O <sub>2</sub>	oxygen
O <sub>3</sub>	ozone
OLR	outgoing, longwave radiation
OWS	Ocean Weather Station
PC	personal computer
PMSE	polar mesospheric summer echo
PPI	planned position indicator
PVT	pressure-volume-temperature
QC	quality control
RE	rough error
RGR	reflected global radiation
SBUV	solar backscatter ultraviolet
SEASAT	first orbiting satellite for remote sensing of oceans
SI	International System of Units

## LIST OF ACRONYMS, SYMBOLS, AND ABBREVIATIONS (Continued)

SMAR	Summary of Marine Aerological Records
SN	Standardization News
SRI	Stanford Research Institute
STP	standard temperature and pressure
Sv	sverdrup
T	tritium
TOMS	total zone mapping spectrometer
TP	Technical Publication
TQM	Total Quality Management
USA	United States of America
USAF	United States Air Force
WCDP	World Climate Data Programme
WDC	World Data Center
WMO	World Meteorological Organization



## NOMENCLATURE

$a$	zonal component
$C$	proportional constant; cooling degree day
$c$	velocity/speed of light
$E$	energy
$H$	Hamiltonian operator
$H$	heating degree days
$h$	Planck's constant
$h\nu$	magnitude of a photon (unit)
$k$	Boltzmann's constant; radioactivity constant
$L$	length
$M$	mass; magnitude quantum number; any third body
$m_s$	electron spin quantum number
$N$	Avagadro number
$n$	number of moles of gas; quantum number
$n_0$	number of $^{14}_6\text{C}$ present
$P$	power
$p$	pressure
$p_i$	probability of finding the system in a state "i"
$Q_h$	rate of heat exchange between ocean and atmosphere
$q$	probability of zeros or of origin
$R$	constant; precipitation
$R_a$	gas constant for air
$R_H$	Rydberg constant
$R_v$	gas constant for water
$S$	thermodynamic entropy
$T$	temperature; time
$t$	time
$t_0$	time zero
$u$	wind component
$V$	volume
$v$	frequency; meridional component
$x$	orthogonal axis; cummulative probability of nonoccurrence

## NOMENCLATURE (Continued)

$y$	orthogonal axis
$z$	orthogonal axis
$\gamma$	probability function
$\varepsilon$	function of wavelenth
$\lambda$	wavelength
$\tilde{\nu}$	wave number
$\sigma$	Boltzmann's constant
$\theta$	temperature (energy)

## TECHNICAL PUBLICATION

### AN OVERVIEW OF CLIMATIC ELEMENTS

#### 1. INTRODUCTION

The Earth, including its gaseous envelope, is a very small interactive part of the solar system. As such, it is also a part of the interactive dynamic structure of the galaxy and the universe. Existing within this dynamic material and energetic macrocosm, the Earth is subject to varying forces and energy fields. Though the Earth, in turn, affects the macrocosm, its effect is small indeed.

Answers to questions concerning climate and its changes are difficult to formulate. Why? Because many authors have tried to define the “climate” and have a different understanding of what climate is. Until one can define climate adequately and its characteristics can be stated, and the definition is accepted, prediction of changes or any future state will be relatively untenable. There probably are as many definitions of climates as there are of readers interested in climate. Hann (1903, 1910, 1911) describes climate as the sum total of the meteorological phenomena that depict the average atmospheric condition at a point on the Earth’s surface. The statement by Landsberg (1958) may serve your needs. Landsberg states, “One may define climate as the collective state of the Earth’s atmosphere for a given place within a specified interval of time.” Individual states or the state at any specified instant of time may be termed weather. Physical and chemical measurements of various weather elements may be made. These characterize or describe the instantaneous states of weather. It is collectives of these data, such as temperatures, precipitation, lack of precipitation, etc., that may be used to make some definitive statements about the climate in which these were measured. The user must not forget that it is the total ensemble of all subcollectives that constitute a measure of the climate. The collective state includes the potential to determine departures from norms (normals), the relationships among the information packets, and the inherent variabilities that these contain. Guttman (1989) writes on the climate’s statistical descriptors. The works of Hann (op. cit.) and Landsberg (op. cit.) among many others are referenced. If some weather element has not been measured or is as yet undefined, then the climate collective is deficient. The user may not be aware of such a deficiency. Even the field of climatology—the study of climate—has its proponents for different phases of the climate. Their arguments, though seemingly precise in themselves, may be biased and may not provide an accurate picture or perspective of climate.

The genesis of Earth’s climate in its varied and changing form lies in the galaxies with their dynamic physical forms and energy fields. Time and distance imply that the galaxy in which the Earth is embedded is of more immediate effect. The solar system, in turn, is effective in the state of “here and now.” Landsberg’s statement need not be changed, but it becomes more apparent that to understand climate, attention must be given to the chemistry and physics of the atmosphere, oceans, Earth, and to the dynamic interactions within and among these, with the regions outside the atmosphere, and with man’s activity in the environment. Today, in particular, this is mandatory with respect to radiation absorption and emission and to all the gases with their molecular, atomic, and radical forms. In addition, these—besides being elements in the physical and chemical sense—are elements in the weather and climate sense. The climatologist must become a multidisciplinary student. The alternative is disappearance.

With the above statements in mind, an abbreviated section on the atmospheric gases is included.

Physical considerations imply that the Sun and its system provide the most immediate and interactive influence with the Earth and Moon system. From an energy viewpoint, the heat (energy) contributed by the Earth itself is probably no more than five ten-thousandths of the atmospheric heat or radiation budget. The Earth intercepts about five ten-billionths of the solar output. This solar output and the throughput to the Earth vary as to amount, intensity, and wavelength or frequency. Often, within a small range, the solar output is treated as a constant. Approximately  $2 \text{ cal cm}^2 \text{ min}$  ( $4.18 \text{ J cal}$ ) are intercepted at the top of the Earth's atmosphere. It is this energy, generally concentrated in the ultraviolet, near ultraviolet, visible, and near infrared, that helps to drive the atmosphere. Eddy (1977) discusses the possibility of a 1 percent variation in solar output effect as well as variation in the Earth's magnetic field. Coulson (1975) describes both solar and terrestrial radiation. NASA, cited by Coulson (1975), established a standard of  $1.940 + 0.03 \text{ cal cm}^{-2} \text{ min}^{-1}$ . These values may change with the continuing observation of and reduction of data as the latter are obtained. See also Henderson (1977) in his treatise on sunlight and its spectrum. More extensive and broader research about this phenomenon continue.

For a review, table A-1 (in app. A) provides some measures of the physical constants of the Sun, Earth, and Moon.

Controversies continue with respect to solar output variation both in totality and in wavelengths. The Maunder Minimum, about 1640 to 1715 (Moore and Hunt (1983) and Oliver and Fairbridge (1987)), is one recorded extreme in sunspot history. The solar activity maximum of the period 1950–1960 and the present maximum culminating in 1990 are extremes of the 20th century. These and the recently reported downward trend in total irradiance during the period 1980–1985 (Willson et al. (1986)) are features of the solar activity. The reader is urged to consider that the downward trend during 1980–1985 should not be considered extraordinary as it parallels the sunspot activity. These may be taken to be indicative of the output itself, though this is not certain. Even the corrections or changes in the reported solar output may be just indications of ongoing slow variation of the present series. The reader may refer to Kessler (1985), volume 1A, of the *World Survey of Climatology*. See chapter 2.

Small though the amount of energy received by the Earth compared to the total solar energy output may be from a climatic point of view, without it the Earth's atmosphere would be an essentially very thin solid sheet of inert form composed of near frozen gases, their crystallized forms, either singly or in physical-chemical complexes. Even a cessation in receipt of energy for a short period of years would presumably stop nearly all life processes as we know them today.

The budget of this energy flow remains a master control. An assessment of this budget is, in a sense, mandatory if an understanding of climate and its variability is to be reached. It is a master climatic element, but it is composed of many components or subsidiary elements. Though temperature is only a measure of energy present, it is often considered an element. Temperature is simply an indication of the molecular activity of a substance or mixture, such as air, water, or soil. The gain, loss, or no-gain of energy is particularly meaningful. These constantly changing flows need to be observed, measured, recorded, studied, and stored for future reference and use. The present network of surface observation points (land and sea) needs expansion into those regions where no observations are made. The development of satellite techniques beyond the present available system is needed. This does not suggest the replacement of present-day basic measurements. Such ground truth existence is required, yet the satellite observations can be an important supplementary source. The budget is important. It is crucial. Models of the energy budget flow need to be developed further, continually reviewed, and updated. These should be dynamic, viable, and useful in the sense of their application.

The Earth itself is the main modifier of the energy it receives. As it spins on its axis, as its axis is inclined to the ecliptic plane, as its axis wobbles (as its motion precesses), with its magnetic field and the induced drag, as it revolves about the Sun, as it interacts with the Moon, with a smooth, consistent surface, the Earth could produce a fairly predictable, though slowly changing, climate. But the Earth is a complex system in itself.

The surface of the Earth is far from smooth insofar as climate is concerned. The continents appear, in the long, long, long term, to move about in a random fashion, being jostled and carried by vast and massive, extremely slow turbulent flow within the total structure. On the long term, as contrasted to the long, long, long term, these movements may be measured in centimeters or even millimeters per year. But the inexorable results are evident, on the one side, in the slow separation of continents by the midocean fractures and the formation of the midocean ridges, the development of rift valleys, the development of mountain ranges, and on the other side, the collision buckling of continents and the sliding of one plate under another (subduction) or the sliding of one plate along the edge of another. With these go the development of and the destruction of oceans and seas. See Habicht (1979) and Ledley (1987).

Climate, in toto, has been broken down into defined bits, pieces, and parcels that might be studied by a specialized individual or group of individuals. Thus, there are many disciplinary fields that study climate and its variability from the very narrow confines of the discipline. There are attempts to break this strangling action in the formation of committees, the convening of meetings, and the formulation and publication of reports. The works of Pitlock et al. (1978), Mitchell (1965), and of Landsberg (1969–1988) are only three of the many that could be mentioned. Schneider (1988) extends these arguments. He discusses some of the interfacial problems and difficulties associated with cross-disciplinary efforts.

Pitlock (op. cit.) (1978) indicates that the study of climatic change and its variability involves a great range of disciplines, interests, and techniques. Included in these might be the needs of those organisms, plants, and animals that have lived, live, and might live within the framework of Earth's climate(s).

The availability of and use of adequate instrumentation and data therefrom has been equally uncertain. The inability to provide complete, useful results meeting the needs of all has led to the search for other ways to measure or understand the important effective climate influences.

Therefore, the reader may be surprised to see in reference to, in later sections, and perhaps to accept the use of proxy data or even new ideas as measures of climate, such as the increasing amounts of trace gases of the atmosphere. In a sense, then, the reader may accept these as climatic elements in themselves. Most of these are put to use in trying to provide information about those elementary elements with which the reader is most familiar.

Life, in itself, may be considered to be a development against the usual argument of the second law of thermodynamics. It is counterentropic. Ephemeral and fleeting at best, from an individual's point of view, it is the only thing going for the individual. From a galactic point of view, the Earth's climate suitable for life exists within severely restricted constraints: a very real microcosm. In order to understand climate and, thereby, to make decisions reasonably favorable for living, one tries to obtain information, to assemble information, to arrange information, and to extract small informational kernels that convey the idea of climate.

In the uncertain fields of climate, weather, hydrodynamics, etc., every effort must be made to reduce that uncertainty. For practical purposes, if the statistical distribution—the normal distribution model—has been shown to hold for air temperatures at a specified point and time period, only the mean and the standard deviation are required to reproduce the distribution. Thus, partial certainty is available but uncertainty remains in the ability to identify the time of occurrence of a single temperature of the data set or its relationship with any of its neighbors or with any other parameter. All of this does not resolve the problems facing the climatologist but it does indicate the needed care in observing, recording, and using data of the climatic elements. The recommendations of the World Meteorological Organization (WMO) are all designed to help reduce the uncertainties.

Climate is the totality but how does one study such a totality? Clearly, the totality is not available. Without question, all that is available are samples that are incomplete and biased. Good and dependable databases are

a necessity. Until these are available and until climate can be defined adequately, practical predictions of future climates, much less changes in climate, will be essentially limited. Climatic change is discussed in the WMO Technical Note No. 79, climatic change (U.N. WMO (1966)). There are many other sources—really too numerous to mention all of them, for there are thousands. The present series of 15 volumes of the *World Survey of Climatology* is among them. Here are a few more, without any indication of which are the most important from all viewpoints. See Kincer (1933), Brooks (1949), Milankovitch (1957), Mitchell (1968), Lamb (1972a,b), U.S. National Academy of Science (1975), and Eddy (1979, 1980, 1983).

An individual's perception, thinking, and understanding are generally linear and one-dimensional—one thing at a time. Rare is the individual who thinks in other than a linear sense, although there are those who do attempt to do so. Rare, too, for these reasons, is an assessment of climate elements, their dynamics, their actions, and their interactions even in the restricted multidimensional set of  $x, y, z, t$ . (These axes are the usual three orthogonal axes,  $x, y$ , and  $z$ , while  $t$  is the time.) Models that are developed to try to explain climatic features suffer these restrictions. The requisite climatic matrix, and particularly the techniques to manipulate the extensive matrix or matrices, in real time, have not been developed. When developed, it is not certain that computer hardware will be adequate.

Added to the above, and making the problem still more complex, is the necessity to include the capability to manipulate linear and nonlinear features in these data matrices. The principles of hydrodynamics have yet to be developed to their optimum. Much remains to be learned. Lorenz (1958, 1959) showed that linear techniques do not do as well as nonlinear techniques in predicting future states of some of the features of atmospheric dynamics, either in terms of climate sequences or in weather snapshots. Lorenz (1960, 1963a,b, and 1964) continues his assault on the seemingly intractable maelstroms of uncertainty in the field of hydrodynamics. According to Lorenz (1960), "Since the study of energy transformations and the numerical integration of simplified equations are sometimes used as alternatives to the same physical problems it is often desirable that the simplified equations conserve total energy under reversible adiabatic processes . . ." In Lorenz (1963a), he states, "Finite systems of deterministic ordinary nonlinear differential equations may be designed to represent forced dissipative hydrodynamic flow. Solutions of these equations can be identified with trajectories in phase space. For those systems with bounded solutions, it is found that nonperiodic solutions are ordinarily unstable with respect to small modifications, so that slightly differing initial states can evolve into considerably different states . . ." In Lorenz (1963b), he discusses "The Mechanics of Vacillation."

Lorenz (1964) turns his and our attention to "the problem of deducing the climate from the governing equations." He, in his abstract, states, "The climate of a system is identified with the set of long-term statistical properties. Methods of deducing the climate from the equations which govern the system are enumerated. These methods are illustrated by choosing a first order quadratic difference equation in one variable as a governing equation. The equation contains a single parameter . . ." He further states, "Climate is not universally identified with averages over infinite time intervals. Many investigators are concerned with averages over long but finite time intervals." He does concern himself with averages and other statistics over infinite time intervals as the lengths of the intervals approach infinity. Lorenz (1964) continues, "In the special case of the atmosphere, theory alone does not tell us that a climate exists. Recourse to observations is not much more enlightening." Lorenz (1964) argues that the weather (climate) of this century does not resemble the weather (climate) of the past century nor does the weather of this period, the interglacial period, resemble the weather of the last well-marked ice age.

Lorenz (1965) continues his arguments in the attempt to present his ideas of the situation(s) facing those attempting to define and deduce climate. He critically examines the oft-accepted hypothesis that physical laws that govern atmospheric behavior determine a unique climate. Even if they did, to the writer the variable input and control from the outside presumably would not permit the establishment and maintenance of such a matchless state. He, Lorenz, suggests the possibility that long-term climatic changes may result from the almost intransitivity of the atmosphere rather than from environmental changes. He defines transitive systems, intransitive systems, and

almost intransitive systems that may be examined and chooses the last. The first—the transitive—arises in the way the problem is formulated, the deterministic form of the system equations. With a specified set of initial conditions determining a time-dependent solution, a long-term statistics set ensues. The second—the intransitive—arises when two different sets of random initial conditions will produce two long-term statistics sets. The third—the almost intransitive system—produces statistics that, taken over infinitely long time intervals, are independent of the initial conditions, and taken over finite time intervals, statistics which are highly dependent on the initial conditions. This allows an infinite time interval to have successive long-term periods with quite different statistics. Lorenz (1965) in summary concludes that climate may or may not be deterministic. As is usual in such situations, only further development of mathematical and statistical theory and of better realistic nonlinear models will enable us to assess the probabilities of our opinions.

Lorenz (1983) discusses irregularity as a fundamental property of the atmosphere. If, as inferences are made of Lorenz's and others' papers, irregularity or even uncertainty is a function of the nonlinear hydrodynamic forces governing the Earth, the prediction of a future state must carry with it a measure of this uncertainty.

Lorenz's concept in the papers referenced above indicates that, in the nonlinear world of turbulent dynamic systems, such as the Earth's seeming solid, liquid, and gaseous features, different end states may evolve. The evolution may be gradual or made in a seeming jump; time considerations are important here. A fairly well-known feature of many studies is that the addition or extraction of energy in any form in an experiment will change the hydrodynamic state such as from (to) laminar to (from) turbulent flow and that the transitions may be smooth or abrupt.

The problem of sensing or deducing patterns in apparently random fields is difficult. An example, perhaps not a good one, is the art of camouflage, the art of disorganization. Colors and structure may be used. In this case, those individuals who are colorblind do not sense the constructed disorganization. Mandelbrot (1977, 1980) in his development of fractals might just represent a step-function jump in our understanding of dynamic systems. His contributions in turn were sparked by chance encounters with others in other disciplines. Thus, in what may be seemingly completely disorganized fields, there may be patterns that can be detected. In the converse sense, they may be functions which develop seemingly disorganized end results simply because these are beyond the immediate comprehension of the beholder. This might occur because a deficient phase space is used. If so, it would be helpful to increase the dimensions of the phase space. See also Kadanoff (1986), Peitgen and Richter (1986), Stewart and Thompson (1986), Dewdney (1987), and Sander (1987).

Chaos seemingly faces all in all disciplines that wish to advance. Every effort is made to reduce the uncertainties. Thus, the titles of several papers and books over the past two or three decades may start with the word chaos followed by a subheading indicating an attempt to deduce regularity, patterns, or purpose from a chaotic field. These titles all present the idea that there is not really chaos but something not seen or only dimly seen or sensed that drives and maintains the system. For interesting reading on the subject of chaos, see Stewart and Thompson (1986) and Gleick (1987). Also, as Lorenz in the above-referenced papers used the words "deterministic chaos," these now form the title of a recently revised book (Schuster (1987)). Poole (1989) attributes the use of the word chaos to York. Krasner (1990) edits contributions of 19 authors or groups of authors on the chaotic behavior in systems and on nonlinear theories.

Rosby (1939) and collaborators started the use of the average wind in the 35° N. to 55° N. latitude as a measure of the strengths of the westerlies. Namias ((1950) and earlier) was one of those who stressed the value of this "zonal" index in climatic forecasting in the near term. The use of the index lessened with the introduction of the concept of random variation of the zonal indices. Lorenz (1985) indicates that initially the index cycle was thought to be a manifestation of that randomness. However, the once popular technique may once again be used but from the viewpoint of chaos rather than a random function. In interaction, the climatologist must become familiar with the concepts of chaos in order to understand some of climate's vagaries or excursions.

Schuster (1988) brings the reader up to date on the intriguingly powerful techniques in these studies. Bridges are provided between the information of and entropic theories of Shannon's measure of information (Shannon and Weaver (1949)), the Kolmogorov (1959) entropy 10 yr later, and the fundamental concepts of Lorenz (1963a). Briefly, thermodynamic entropy  $S$  measures the disorder in a given system and, as such, is a measure of the degradation of the system. The second law of thermodynamics may be stated in many ways, such as that above (Lewis and Randall (1923), Getman and Daniels (1931), Barton (1935), Shannon (1949), Shannon and Weaver (1949), Zemansky (1951), Brunt (1952), and Billingsley (1965)). This is discussed again in section 4.1.4. Shannon et al. (1949) defines the entropy  $S$  as the negative summation of the products of the probabilities ( $p_i$ ) and the logarithms of those same probabilities, where  $p_i$  is the probability of finding the system in a state " $i$ ". Kolmogorov's (1959) concept, entropy  $K$ , is a measure of this loss of information; i.e., it is proportional to the loss rate.

The main thrust of these arguments is that, in general, in deducing the means, variances, and other distribution characteristics of climatological (meteorological) sequences, measures of the phase state(s) are being estimated. These are important in the past tense and vitally important in the near future. But these generally are couched in linear stationary stochastic terms or concepts and interpretations in these terms may not be the best.

Therefore, those climatologists (meteorologists) really interested in the long-term climates and their changes can make themselves familiar with the concepts embodied in disorder (entropy) and development of new understanding of the so-called chaotic regimes. As has been stated before, an increase in information is a decrease in uncertainty. See Billingsley (1965).

Apparently the systems producing the noted turbulent features do tend to a point in the phase space, perhaps some stability. The words and the point are "strange attractors," apparently first introduced by Lorenz in his early writing. It would seem to this writer that perhaps this point or "strange attractor" would not be a singular point but a singular region of uncertainty. Small it may be. The reader may find pursuit of these ideas about the nonlinear hydrodynamical systems rewarding. In the least, the reader will find that there are others who are trying to understand the complexities facing all disciplines. Especially, the climatologist will develop, not a sense of frustration, but a sense of how the efforts and results of endeavors will really add to the science of climatology. There will be added importance to the observing of the reporting of and the exploitation of climatic element measurements. Within the long, very long finite time intervals or even the infinite time intervals envisioned, the "strange attractor" may move somewhat with the development of and the dissolution of Pangea, itself a manifestations of a drive to order with "chaos." Thus, we are left with the problem of trying to determine where we are and where we are going. We are, therefore, challenged to learn as much about our climate system as possible. This requires attention to those climate elements that portray climate and to the measurement, recording, and use of their characteristics that enable that portrayal.

This field of "chaos" in itself may be a "strange attractor" for it is an expanding field with respect to the sciences, including those of climatology and weather. Tsonis (1989) and Tsonis and Elsner (1989) reviews some of the recent literature in their articles, "Chaos, strange attractors and weather." They present some new numerical techniques to analyze weather data. Nicolis and Nicolis (1984) following Lorenz's (1963a) contribution, make some applications to climate studies. They use isotopic records of deep sea cores. They do not attempt to establish the validity of climatic models but they do attempt to establish the restraints or constraints of any model. Their results seem to indicate that about four variables seem to be sufficient in any of these models. By coincidence, perhaps, four variables in linear multiple regression seem to also contain the maximum contribution to variance in a model. Due to the inherent correlation among many variables in climate (weather) data sets, it does not seem to be important which four variables are used or selected. Usually, the four that are eventually selected are those for which data are easily available and for which data may be expected to be available in the future. Whether this holds true in the nonlinear cases is not known. Fraedrich (1986, 1987) presents features of these nonlinear systems with respect to



climate (weather). See also discussions by Shaw (1987) on the periodic structure of the natural record and nonlinear dynamics.

With all the complexities facing the climatologist, it is reiterated that measures of climatic elements be carefully defined, observed, recorded, disseminated, and used. Careless work or ineptitude can only aggravate the situation. The problems of the biosphere and the development of sciences of the environment imply that many items not considered as climatic elements may need to be considered as such. This includes the phenotypes which display some of the interactions of the usually considered climatic elements, and for a simplistic illustration, the migration of fishes in the search for food which is a measure of the conditions favorable for the production of their food. For example, see Hopp and Blair (1973) for phenology and Sharp and Csirke (1983) for neritic fish resources. See Muller (1982) for climatic data, climagrams, a software program to construct climagrams, and the Koppen-Geiger and Troll-Paffen climatic zone charts for Eurasia in color plates.

Constraints of the physical world and our present capabilities prevent depiction of climate in all but the most elementary sense. Until some abstract mode of thinking and presentation is developed, propagated, and accepted, discussions must be limited mostly to simple linear ideas, even in the face of ideas briefly mentioned in the foregoing paragraphs. For example, few information presentations are made in more than the one element case. Some attempts have been made to develop some function that is a combination of several climatic elements. A simple example is air density. Although it is a mass per unit volume ratio, often it is computed indirectly by means of the gas equation. This requires a knowledge of the atmospheric constituents, their temperatures, and their pressure. Density (specific gravity) in water is just as complicated in its assessment unless measured accurately and precisely with a pycnometer. The weather or climate forecast is composed of a forecast, generally element by element, for that is all the forecaster and the user can comprehend and utilize. It is a one-step process. Usually, these forecasts are given separately, e.g., temperature and precipitation. The user either must supply or be supplied an interpretation of the interaction between the two. The interactive matrix seldom is shown and even less is it requested.

The distribution of one climatic element—a phase state of one—is a simple marginal distribution of the total set of climatic elements. A distribution of two interacting climatic elements is also a marginal distribution of the total climatic element set. Presumably, the interactions could be “chaotic” and nonlinear in terms of the foregoing discussions. Under present states of knowledge of information processing and of information presentation, in order to begin to understand the total interactive climatic element data package, simplest of the marginal data sets are studied. The reader may be interested in the concepts of entropy (information) as discussed by Shannon (1948, 1949), Shannon and Weaver (1949), Brillouin (1963), Billingsley (1965), Bartlett (1966), Feller (1966), Crutcher (1969a), and Wyner (1981).

Yet, in order to attain some measure of understanding of climate, it is still necessary for most persons to first examine each marginal element one by one.

Elements of climate or its science, climatology, are discussed by Landsberg (1958). The following, which establishes the general format of this Technical Publication (TP), includes some of those discussed by Landsberg:

- Spheres.
- Data and instrumentation.
- Planet Earth.
- Atmospheric heat budget.
- Temperature.
- Pressure.
- Winds.
- Precipitation.

- Clouds.
- Drought and evaporation.
- Atmospheric composition.
- Aerosols.
- Extremes.
- Data publications.

Gases have always been present in climate. Water in its three states—solid, liquid, and gas—continues and always will be a salient determiner of our climate. Oxygen (O<sub>2</sub>), nitrogen (N<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), ozone (O<sub>3</sub>), and methane (CH<sub>4</sub>) have always been important, but in view of today's high interest in potential climatic change, an understanding of these and the so-called trace gases is of vital concern.

Not all the elements may be discussed in detail in this TP for those have been discussed in other parts of the World Survey of Climates (Landsberg (1969–1989)). Specifically and admittedly, the study of a single climatic element at a point, region, or globally provides a very narrow parochial look at the climate totality. However, it may be a very important look to answer an urgent vital question. Iterating, that look may be considered a view along a single line, and at other times, it may be a thin sheet of two dimensions. Rarely does it take on a three-dimensional look, much less a still higher dimensional aspect, thin and tenuous as it may be. Hopefully, if the viewer has a multitude of single element presentations, an abstract idea of how these elements fit together might be obtained. In this case, no information can be provided as to the internal time and/or space correlations within and between elements. Decisions are made individually and collectively, often times in a “here and now” situation with whatever information is available, limited and sketchy as it may be.

Efforts to understand and model climate have intensified recently. Knowledge that climate is not static but everchanging and variable further opens an uncertain field. Increasing knowledge of the amounts of trace gases in the atmosphere and oceans and a knowledge of their potential in changing the temperature climate is one factor in changing risk assessments. But from a reliability point of view, interactions are an important feature of the Earth's climatic system and of any model thereof. No one is yet able to provide an acceptable model that would provide a moderately probable assessment of future climate. For example, simply not enough is known about all elements of climate to describe some future climate state. Conjectures and supposedly educated guesses are made. Continuing, given that the increasing amounts of trace gases with their infrared absorption and emission characteristics will tend to initially increase the atmospheric temperatures, no generally accepted model of subsequent conditions exists. That the end effect will be a so-called runaway greenhouse phenomenon lies in a broad range of uncertainty. Aperiodically, and in this range, the threat of an ice age with the increasing covering and continental burdens of ice in the polar regions is envisioned. No one knows the end result of initially increased oceanic evaporation, formation of clouds, with a potential increase of albedo and wind, distribution of water in vapor, liquid, and solid form. No one knows but one can postulate the effect of change in atmospheric ozone in both troposphere and the stratosphere.

Man, animals, and plants have to adjust to climate or cease to exist. Relocation to a more suitable climate sometimes is an answer. For man, the answer sometimes has been a change in shelter (house) design, impoundment, storage, and distribution of water to alleviate flooding, to provide power (energy), and to facilitate agriculture (food production). Transportation and distribution of food and materials also are alleviation modes.

As more knowledge is gained and as new items are added to the list of climatic elements to be considered, such as atmospheric gases, decision processes become more involved. Eventually, these lead to group, national, and international policy concerns. White (1990) assesses these problems in his article, “The Great Climate Debate.” It is against or within, depending upon the reader's viewpoint, the realm of uncertainties that this debate continues. Until sufficient data and information have been garnered and distributed so as to reduce this uncertainty will it be known whether actions taken are correct.

## 2. DATA AND INSTRUMENTATION

### 2.1 Design of Quality

There is always the question, “How good is this information?” Good and reliable information is needed. Quantification of information permits easier assessment of its value and use. This applies to climatic data just as much as in any other disciplines.

Reliability and quality assurance of information are mandatory. Clearly, quality cannot be engineered into an already collected data set. (An out-of-focus photograph is most difficult, if not impossible, to process and arrive at a picture which would have been obtained if the camera had been correctly focused in the first place.) Therefore, management must be involved and supportive—even demanding—of quality. Quality must be designed into a project, editing and remedial action must be provided, and budgeting and finance must be provided on a sufficient continuous long-term basis. To determine long-term climate characteristics, databases longer than the long term are needed.

Establishment of good benchmark stations is a necessary goal. Figure 2-1 shows a recent ensemble of the worldwide network of climatological stations. See Mitchell (1953) for problems associated with climatological data. See also Swartz (1956) on “A Climatological Benchmark Network” program. Due to many factors, that program has suffered slow deterioration. The structure has changed considerably. Figure 2-2 shows the present location status of the USA “Reference Climatological Station Network” for surface observations.

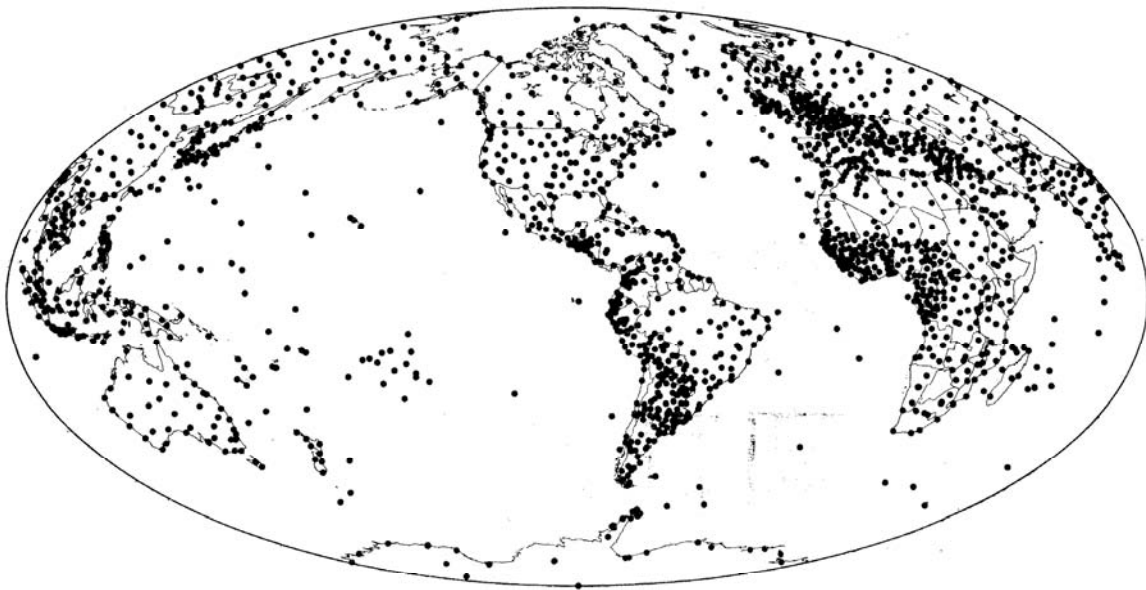


Figure 2-1. Ensemble of worldwide climatological stations (courtesy of WMO and NCDC, Asheville, NC).

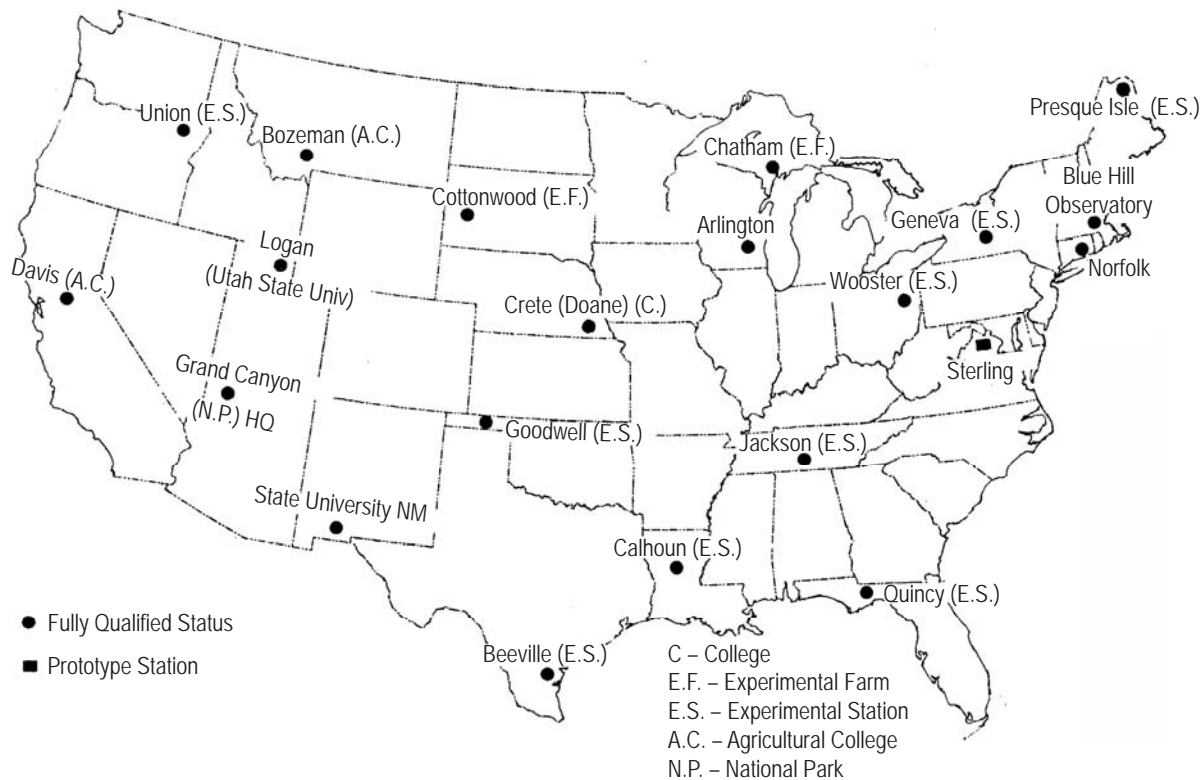


Figure 2-2. Ensemble of present climatological benchmark stations for the U.S. surface observations—1991 (courtesy of WMO and NCDC, Asheville, NC).

Professional organizations exist dedicated to the activity, quality assurance, and control over any discipline, any business, or any activity. One is the American Society for Quality with headquarters in Milwaukee, WI. An international organization and other national organizations exist throughout the world. Innovations and progress are continual. Deming (1950, 1986), Juran (1974, 1987, 1988), and Taguchi and Wu (1980) are internationally known individuals. The work of these people provides extensive and valuable guidance to the beginner and the experienced. There are many others. Juran (1988) emphasizes the quality trilogy—quality planning, quality control, and quality improvement. He has stressed these points for many years. Crutcher (1970) lists (1) management, (2) design and reliability, and (3) quality assurance and quality control. Forward feed and backfeed of information are essential ingredients of any scheme or outline. Deming (1986), as he has for many years, expounds 14 points; but in this particular book, he stresses these points for a transformation in an organization. The organization may be a factory, a business, a national government organization, or an international organization. It need not be big business. Feigenbaum (1983) discusses total quality control. Recognition of one's work is always appreciated. In Japan, the "Deming Award" does this at a high industrial and a high government level. In the United States, such recognition in industry is provided from a government point of view by the U.S. Department of Commerce in its "Malcolm T. Baldrige Award." Ireson (1966), Proschan and Serfling (1974), and Mann, Schafer, and Singpurwalla (1974) provide excellent guidance in design and operation of reliability procedures.

In the Total Quality Management (TQM) aspect, total involvement is mandatory. For example, in a nation such as the United States of America, the measurement of climatological elements may be spread through many organizations. TQM therefore demands the oversight by and management by the executive and legislative bodies. Anything less is likely to produce a fragmented and, at best, a mediocre program.

Fillipov (1969) presents the World Meteorological Organization's (WMO's) view of quality control. But again, this is an attempt to check or audit the ongoing quality. The ongoing or outgoing quality can be improved only by commitment of and an active, not reactive, participation of top top-management and by redesign. Crutcher (1969a) in that same WMO publication discusses automatic data handling for climatological purposes. In the introduction by Julius F. Bosen in that proceedings, "Probably the most important idea to come out of the symposium was expressed first by Dr. Wallen and later expounded brilliantly by Prof. Godske: 'Climatology is meteorological research.' This is possibly the most obvious identity in the science of meteorology." The above papers and others were presented in 1968. Additionally, from the viewpoint of a here and now situation, meteorology can only provide snapshots or quick glances. Growing climatological research activities requires increased funding. Usually there is little funding for equipment replacement, observer training, quality assurance, and quality control. Unless there is good care of "ground truth" locations, those interested in "climate" and "climate change" will find it difficult to accurately assess situations. Some funding today is going to the study of atmospheric trace gases. Many scenarios are being presented. The relationship of climate and energy is the focus of many studies from the viewpoint of renewable, nonrenewable, and solar resources. However, there is no clearcut indication to the author that the researchers have considered an effective reliability and quality assurance to be made in this work. It cannot be taken for granted that no problems will occur. Hopefully, these activities will include the improvement of instrumentation and development of adequate reliability, quality design, quality assurance, and quality control procedures. In climatology (meteorology), there is no known national program designed for and documented for internal use in past, present, and future work. There may be sequestered cases where some editing techniques are embedded in other procedures, but it would be most difficult to isolate and to identify them.

Crutcher (1970) discusses briefly some centralized quality control and evaluation programs. Gandin (1988) surveys the so-called complex quality control (CQC) of meteorological information. This is the multivariate quality control technique in which the basic premises for some meteorological endeavors, notably for data entry into the forecasting algorithms, are made. The sense is that the information is of one mode, or that the errors may be treated as one modal distribution in the multivariate sense.

Gandin (1988) notes that though many items, parameters, or elements are discussed, the only CQC implemented is that which treats radiosonde height and temperature data at mandatory levels. That treatment is discussed in some detail. But Gandin (op. cit.) notes that only CQC relating to operational functions has been treated. However, for climatology, he strongly implies that the situation regarding the quality control (QC) of climatological data is not good. He states, "In non-operational applications, subjective QC methods have been used for a long time and still predominate today. As a result, many climatological data sets may be contaminated by rough errors (REs), especially old archives. Evidence does exist that the RE rate in some of these archives is very high." REs are defined as rough errors, exorbitant errors, or nonallowable errors. An example in climatological data would be a wind direction of 627°, though these might be permissible in (1) turning of the wind with time or height through more than 360°, or (2) in the automatic reduction of wind chart data through 540°, which prevents crossover at the 1° and 360° region. This is done to prevent "painting" of the charts leading to unreadability of the charts and/or the exhaustion of the ink supplies and loss of record. But, if in the original records a datum is excised or changed, it may be forever lost as an information bit. Another example for this century might be a recorded year of 2089, or an hour of the day of 36, or the day of the month as 42. Based on the writer's experience, the editing and remedial costs of many climatological studies is ≈80 percent of the total funds set aside; time must be devoted to producing a relatively "clean" data set before any definitive research can be affected.

Alduchov and Eskridge (1996) provide a present status of radiowind data CQC. Some work has been done on instrumentation problems with the radiosonde instruments. See Luers and Eskridge (1998). Much remains to be done in both fields.

Stankov (1998) discusses the use of a multiple sensing instrument. The use of these types of data will force the development of improved procedures for the study of these types of data. Interpretation techniques will be developed as experience is gained. The radiosondes for atmospheric pressures, temperatures, humidities, and trace gases and other chemicals are examples of present-day multisensor aids.

## 2.2 Units and Communications

The writer or surveyor of any one or set of scientific disciplines confronts arrays of definitions, descriptions, and units as well as languages both national, disciplinary, and to some extent, limited interdisciplinary sets. In all interdisciplinary language development there is a give-and-take process, and in some cases, no concession. The reader will note throughout this section that no deliberate attempt is made to use one and only one system where original work, charts, and tables are used or to which references may be made. These are generally considered in their original form. There is a risk, therefore, that to some readers, this section is derelict in some respect. However, the reader must share some responsibility. For example, the langley (ly)—a unit of radiation—may be defined as  $1 \text{ gm cal cm}^2$ . Usually a time interval of 1 min is used, such as 1 ly/min, which in turn may be written as  $6.98 \times 10^5 \text{ erg cm}^{-2} \text{ s}^{-1}$  (List (1958) and Coulson (1975)). The langley is not found in the International System of Units (SI) system. The SI recommends that the erg not be used. Nevertheless, the reader, here, will find occasional reference and use of these units as well as other units. Wherever possible, changes are made. However, some atmospheric charts will be in terms of millibars rather than pascals or kilopascals. Until a complete generation of people become immersed in the use of the SI, there will be those problems of communication.

Implicit in all discussions in section 2 is the need for and the existence of communications for the transfer of information and knowledge. Implicit in communications are both the mechanical and/or electrical modes to record and transfer information. Language modes are inherent. Included in the language modes are the units employed. From region to region, nation to nation, languages and units vary and still vary. Disciplines develop unique systems. Efforts to lessen these inherent problems continue. One problem is exemplified by the conversion of degrees of Fahrenheit temperatures to Celsius temperatures and back conversion. The return value may not be precisely the same as the original. Rounding errors develop. In data handling of large blocks of data, unless there is excellent source documentation, good complete algorithms, good attention to procedures, and quality editing is maintained, double conversion may occur. That is, the Fahrenheit temperatures may be converted to Celsius temperatures and these temperatures are considered as Fahrenheit and further converted to Celsius. Thus, a temperature of 32 °F might be converted to 0 °C and converted again to -17.7 °C. An individual instance generally would be detected if it is an extreme and an examination for extremes is employed.

There has been a general move to the metric system of units and on to the SI. But, here again, there is a language impediment. The French language is the internationally accepted language for these units. However, translation is necessary, therein, sometimes lie difficulties. The latest agreed-to definitions, symbols, etc., of the SI is that of 1985. This is the 5th edition (1985—revision of the 4th edition (1981)). It takes into consideration the decisions of the 17th General Conference on Weights and Measures (1983) and of the International Committee for Weights and Measures (1981, 1982, 1983, 1984) and the amendments made by the Consultative Committee for Units (1982, 1984). In the United States, the National Bureau of Standards (NBS) (now the National Institute of Technology) issued this 1985 version in 1986 as NBS Special Publication 330 (Goldman and Bell (1986)). This is a translation of the basic document in French, the fifth edition of “Le Systeme International d’Unites (SI)” issued by the International Bureau of Weights and Measures (BIPM). NBS Special Publication 330 is a collaborative effort of U.S. NBS and the National Physical Laboratory (NPL) in the United Kingdom. In order to make this booklet acceptable to a broad user community, it was necessary to recognize present U.S. practices and standards as they are found in the literature of the domestic voluntary standards organizations, such as the American Society for Testing Materials (ASTM) and the International Electrical and Electronics Engineers (IEEE) and to use American spelling of certain words. An example of word spelling is “meter” in lieu of “metre.” In climatology as well as in other disciplines, the

problems of conversion of data from one system to another is fraught with difficulties, including, those of understanding and comprehension. For instance, the measures and units of atmospheric air pressure have ranged in the experience and lifetime of this writer from inches of mercury to millibars and now to pascals. In most publications today, generally, if previous charts, maps, and tables in other systems are reproduced, the only changes made usually are relabeling. But the resultant labeling, except for certain values, may not be in whole numbers. Yet, the data used to produce these may still be available in original form. In some cases, only summarized data will be available. In both cases, conversion to the units of SI will have to be done with care if these are to be combined.

Tables A-2-1 through A-2-13 (app. A) provide several of the SI tables provided in NBS Special Edition 330 along with supplementary tables. For explicit definitions, please see the appropriate English or French format publications. The tables are divided into three classes—base units, derived units, and supplementary units. For example, there are seven well-defined units, which by convention are regarded as dimensionally independent—the meter, the kilogram, the second, the ampere, the kelvin, the mole, and the candela. Excepting the mole, three of the last four are measures of energy in one form or another. There are many systems which have been used, are existent in older published books, and which will be used by scientists until complete acceptance and use of one system has been made. There is the English system wherein the inch, the foot, the mile, etc., are well known and used. There is the metric system which utilizes the centimeter-gram-second (the CGS) system, and the meter-ton-second (MTS). Now there is increasing acceptance of the meter-kilogram-second (MKS) system and the meter-kilogram-second-ampere (MKSA) system.

### **2.3 Instrumentation**

There are many ways and instruments to measure or estimate a climatological element such as wind. But it is very difficult to have a group reach a consensus on standards for climatological (meteorological) equipment, including wind measuring equipment. An individual or an organization can usually specify the precision, accuracy, and maintainability of a needed system. Committees established within the ASTM are involved in trying to reach consensus standards for various climatological (meteorological) measuring instruments, including direction measuring and speed measuring equipment. See ASTM (1982, 1983, 1984a,b,c, 1985a,b, 1988a,b). These consensus standards must be reviewed every 5 yr, accepted again, modified, or rejected.

Consensus standards for climatological (meteorological) instruments are difficult to attain and to maintain. Certainly any individual, group, or service can establish a set of specifications for any one particular instrument for a specific use. First of all, the element or elements to be measured must be chosen. The range, accuracy, and precision wanted must be specified. The materials and their quality characteristics from which the instrument(s) is to be made must be indicated. The recording features must be set forth explicitly and correctly. The conditions under which the instruments are to be used must be specified. A reasonable lifetime for the instrument must be stipulated.

It is too much to expect that an instrument will perform properly forever under all conditions. An attempt to design, fabricate, and operate such an optimum instrument is doomed to failure—first, because it is perhaps impossible, and second, because it is prohibitively expensive. Therefore, the one who needs a climatological (meteorological) instrument must be selective in all aspects.

Sissenwine and Court (1951) prepared a study for climatic extremes for military equipment. In 1957, the U.S. Department of Defense (DoD) published updated material in MIL-STD-210A. Court and Salmela (1963) discuss the problem of improbable weather extremes. In 1974, Sissenwine and Cormier, in MIL-STD-210B, place in the hands of writers of specifications, the designer, and the user a still better guide.

Climate (weather) elements do not occur singly; i.e., wherever there is a temperature, there are also a pressure, humidity, gases, etc. Therefore, the design and specifications for an instrument should consider interaction of

these elements with the materials of the instrumentation. For example, though the design of the instrument may cover the extreme for a temperature, it need not cover the simultaneous occurrence of an extreme for another element for the two may not occur together. If so, that double extreme occurrence is still yet more improbable. On the other hand, the existence of corrosive gases or liquids and high moisture may require some attention in design. For example, the lifetime of some equipment is not great in the tradewind inversion levels of the islands' forests. Special equipment for these spots must be designed or the user must plan for fast obsolescence of equipment. (See Baynton (1969).) In the case of water gauges, the recording paper—if paper is used—must have the fibers aligned parallel to the length of the roll if measurements are to be made perpendicular to the roll length. This will minimize the expansion of the paper latitudinally and thereby reduce recording errors in this and only this respect. There may be other sources of error.

World Weather Records is a publication of the records submitted to the U.S. National Climatic Data Center (NCDC) for publication each decade. These may be used to gain some insight in temperature, pressure, and precipitation regimes at the locations indicated. Later in this Technical Publication (TP), table A-5-1 provides some measures of temperature and precipitation. Then table 13-1 provides measures of extremes of the same two elements as in table A-5-1 but also for many other elements.

The easier way to compare climatological (meteorological) elements in order to provide adequate assessment is to take measures of these elements, record, archive, process, and publish the measurements and the results. The instruments used are of so many types that a compilation and a discussion of each is beyond the scope of this TP.

The WMO's World Weather Watch, Planning Report, Collection, Storage, and Retrieval of Meteorological Data is an important survey, as its title implies.

The meters may be of many types for each individual element as indicated previously. For example, mercurial or alcohol (liquid-in-glass) thermometers, thermocouples, (bimetallic) strips, evacuated metallic tubes or discs, electric resistance, electrolytic, crystalline, gas, radiometers, etc., exist. For pressures, there are the barometers, mercurial, gas, aneroid, etc. For density, there are various types of pycnometers.

For details on equipment, the reader is referred to texts such as those of Middleton and Spilhaus (1953), Middleton (1969a,b), Fritschen and Gay (1979), and Lenschow (1987). Descriptions of the more interesting and important instruments are in the collection in the Smithsonian Museum of History and Technology. There are considerable changes and improvements since then, particularly in the sensors and recording systems, which depend on and further exploit the electromagnetic system potential.

Middleton (op. cit.) provides good histories and descriptions. Included are descriptions of the various radiosondes with sensors for varying elements, including radiation, humidity, gases, pressures, temperatures, etc. Fritschen and Gay (op. cit.) describe those that are most often used in studies of the environment. The user may obtain instrument catalogs. Some of these catalogs contain very good descriptions of the instruments and their ranges and statements of their expected performance. However, the responsibility rests with the purchaser to ascertain the appropriateness of the instruments, their precision, their viability, their maintainability, and their reliability, particularly with reference to usable output.

Rhodes and Hochheiser (1977) edit the proceedings of a symposium, the Data Validation Conference. Sponsored by the Environmental Protection Agency of the United States, this is a useful report on the problems of data procurement and validation in the environmental sensing.



Lenschow (1987) edits the material of the Sixth Symposium on Meteorological Observation and Instrumentation; there were 137 papers. This report is of interest to those involved in the new equipment types. Of intense interest are the comparisons of output data. For example, see Schmidlin and Finger (1987) and Lenschow (1987). See also the short discussion of scales in the discussion on temperature in section 5.

Near the end of the 19th century, sounding balloons led to the discovery of the cessation of the fall of temperature with altitude. This region, now called the tropopause, was considered to be isothermal until the higher soundings indicated a rise in temperature above the tropopause into the stratosphere. Through the years, kite soundings had supplied information on temperatures and relative humidity in the lower atmospheric surface layers. In time, these were replaced, in part, by meteorographs carried aloft by aircraft. The kites were still used in the United States until the 1920s while the aircraft meteorograph observations (APOBs) continued as a program until the 1940s. Today, these are occasionally used in research.

Moltchanoff (1928, 1930a,b, and 1936), in the words of Court (1942), a pioneer in radiosonde development, describes the beginning of radio transmission of balloon-carried sounding sensors. See also Weichmann and Moltchanoff (1931) and Schell and Stone (1937) cited by Court (op. cit.). This technique began to displace rapidly the kite, aircraft, and balloon-borne mechanical systems. Later, rocket-deployed instrumentation supported by parachutes augment and still augment the radiosonde transmission of temperatures, pressures, humidities, measurements of gases, particulates, and winds. For the last, winds may be determined by balloon positioning, by visual or radio tracking, by ground equipment, or by satellite tracking and positioning.

The reader may be interested in obtaining and studying the various manuals used by the National Meteorological Services. Ference (1951) and Bemis (1951) cite many references on instrumentation, particularly with reference to atmospheric soundings prior to 1950. They then bring the reader up to date historically and currently. Since then, of course, the space programs have introduced the rocket and satellite probes—direct and indirect. Satellite probes are mentioned briefly here and rockets will be mentioned again.

As mentioned previously, the present atmospheric composition has evolved, has changed, and continues evolution. Today, the atmospheric radiative characteristics assume great importance due to the natural and anthropogenic (man caused) loading of the atmosphere with essentially trace gases. In comparison, the atmosphere of Venus is heavily loaded with carbon dioxide ( $\text{CO}_2$ ). So much that the atmosphere is much deeper and much hotter and the surface atmospheric pressure is  $\approx 100$  times that of Earth. There is no sink for the  $\text{CO}_2$  such as exists on Earth in the oceans and in the solid carbonates. There is the long-term oscillation of temperatures and other physical aspects that permits or causes the exchange of the carbon compounds between prevailing sources and sinks.

The effect of man's activities is to augment the natural geophysical-chemical oscillations through the introduction of gases that may be physically radiative and chemically reactive. Thus, there is increasing attention given to potentially partially controlling these additions. It is necessary to develop new instrumentation and techniques to measure these radiatively and reactive gases that exist in trace amounts. Some of these exist only in  $10^{-12}$  or  $10^{-15}$ , pico- or femto, amounts. For most instrumentation, if available, these amounts are at or below their detection capabilities. There is another problem. The lifetime of some participants in the chemical reactions is very short due to their demise through reactivity. Radicals or unpaired electron configurations are such active participants. Ayers and Gillet (1990), with respect to the tropospheric chemical composition, present a selection survey for the detection measurement of selected atmospheric gases. Such measurements and others will not be discussed here due to the large scope of the problem. There is simply not enough space in this TP to adequately discuss the measurements. Present-day developments in instrumentation, information, and electronic data processing begins to provide capabilities to assemble and process information on elements previously beyond accurate and reliable measurement. Section 11 discusses in more detail some of the gases involved.

## 2.4 Data and Summaries

Only with the quantification of good, clean information will progress be made and continue to be made.

In view of previous comments, the discussion in this section may touch on elements with which the reader disagrees as to it being a climatic element. Similarly, the author may not treat a subject at all or not sufficiently for another person's definition and need.

Court (1968) edits and provides a preface to an interesting and informative selected subset of papers about certain facets of climatology. Meteorology, statistics, geography, geodesy, and oceanography diverged from the parent climatology. Today, the greatest advances arise whenever the specialists collaborate. Convergence produces the results. There are few people who are able to handle or understand the entire realm of diversity.

With respect to the elements usually thought of as climatic elements, some of these are temperatures and precipitation or lack of precipitation, clouds, sunshine, and others. These are, in a general sense, static. For example, temperature in itself is a measure of the molecular (or atomic) activity being measured. Such a measurement provides no dynamic sense to the flow of energy. The flow of energy, such as from the Sun, to its interception, absorption, and reradiation, must be considered an integral part of climate. It is extremely important to develop adequate models of this heat budget which controls the moment-to-moment conditions as well as the day-to-day, year-to-year, and longer periods. Thus, the heat budget is considered by many, including the author, to be a very important element of climate. Kessler (1985) is an excellent reference. Discussion of these and other elements (factors) will be made later.

Data are collected by many individuals, companies, government organizations, and by the meteorological services of each country. Some of these data are gathered into databanks within each country, but some still remain isolated and fragmented. One hundred years ago the development of the punched card permitted faster processing of data, particularly census data. Barger and Nyhan (1960) and Reid-Green (1989) provide short surveys of this development with reference to work within the Census Bureau. Barger and Nyhan (*op. cit.*) discuss the application to climatology. Sixty years ago the use of punched cards and electric accounting increased and gradually began to replace manual data processing. Increasingly, in some but not all areas today, electronic data processing has taken over the job from the collection of input of data on magnetic or optical cards, tapes, or disks to the needed output. Communication links among computers permit the transmission and exchange of data blocks.

The WMO is the entity that ties together the efforts of all the countries into a net of observation stations with standard programs to obtain, exchange, and produce weather and climate products. Apparently, three centers for climatology were originally established—one at Asheville, NC, USA, one at Novosibirsk, USSR, and one at Geneva, Switzerland. World Data Centers (WDCs) A, B, and C are located in the USA, USSR, and Europe. World Data Center A, at the present time, has nine sublocations with a coordination office at the National Academy of Sciences, Washington, DC. The disciplines covered and their locations are: (1) Glaciology, Boulder, CO, (2) Marine Geology and Geophysics, Boulder, CO, (3) Meteorology, Asheville, NC, (4) Oceanography, Washington, DC, (5) Rockets and Satellites, Greenbelt/Washington, DC, (6) Rotation of the Earth, Washington, DC, (7) Seismology, Golden/Denver, CO, (8) Solar-Terrestrial Physics, Boulder, CO, and (9) Solid Earth Geophysics, Boulder, CO.

World Data Center B, in Moscow, with headquarters in the Academy of Sciences, has two subcenters, B1 and B2. B1 comprises the discipline of Meteorology, Oceanography, Marine Geology and Geophysics, Glaciology, Rockets and Satellites, Rotation of the Earth, and Tsunami, Mean Sea Level, and Tides sections. This is operated by the All-Union Research Institute of Hydrometeorology. It is located in Obninsk, Kaluga, 249020, USSR. World Data Center B2 consists of sections on Solar-Terrestrial Physics and Solid Earth Geophysics.

World Data Center C1 consists of eight independent centers for various disciplines in Europe. There is no formal coordination mechanism. If no corresponding C2 center exists for a discipline, the European center is described simply as WDC-C. The C1 center representation on the International Council of Scientific Unions (ICSU) panel for World Data Centers is located at the present time at the Rutherford Appliance Laboratory, Chilton, Didcot, Oxon OX110QX UK. The eight C or C1 centers are: (1) Earth Tides, Brussels, Belgium, (2) Geomagnetism, Copenhagen, Denmark, (3) Geomagnetism, Edinburgh, UK, (4) Glaciology, Cambridge, UK, (5) Recent Crustal Movements, Prague, Czechoslovakia, (6) Solar Activity, Meudon, France, (7) Solar-Terrestrial Physics, Chilton, UK, and (8) Sun Spot Index, Brussels, Belgium. See publication on the ICSU, November 1987, part 1, the World Data Centers.

Under international agreement, for climatology (meteorology), the various nations send selected portions of their data to the National Oceanic and Atmospheric Administration (NOAA), Environmental Data Information Services, NCDC, Asheville, NC 28801, USA, for publication monthly in *Monthly Climatic Data of the World*. These data are reproduced as transmitted. The quality of the information remains the responsibility of the Service submitting the data, not the NCDC.

Various meteorological services and world organizations have their stated requirements of precision and bias (accuracy) for meteorological and climatological equipment. However, there are no national or international standards for the manufacture or buying and selling of meteorological or climatological instruments, including wind measuring instruments or systems. For a review of the general status and attempts to establish international agreements, see Standardization News (SN) of the ASTM, December 1986. The agreements and the standards agreed to are consensus agreements. Their application or nonapplication is the prerogative of the individual organization or service. These consensus agreements have “sunset” rules, which generally stipulate that the consensus agreement is valid for only 5 yr. Before the end of the period, review, modification, if necessary, and new agreement must be attained.

There is the ever-present argument as to the length of record required to portray climate adequately. These periods depend upon the element and the geographic location. Where there are quasi-dynamic centers of action, there may be some stability, but in other areas, the ever-changing and more dynamic regions produce more variability. These areas do change in both position and size. Trends will be quasi-periodic or simply aperiodic.

Apparent singularities appear. Whether these are viable is sometimes subject to bitter debate. Therefore, continual watch must be maintained. As previously implied, forecasting climate changes will be much more difficult. Perhaps a reasonable test would be the forecasting of today’s climate from a selected set of prior data. This might be designed as a blind or double blind test. Forecasting of climate cannot be made until climate and its variability has been defined and constraints have been determined. The variability of climate—the relative differing displacement of centers of action with respect to station location—all have their effect on what might be a wanted stability. On a longer timescale, essentially a “here and now” basis, a look at many diagrams of proxy data such as varves, tree rings, ice cores, etc., implies broad swings in climatic condition in both magnitude and time. On the other hand, on the relatively short timescale, as Court (1967) points out, different elements require different periods. He suggests the last 15- to 20-yr periods as probably better periods for norms for immediate practical use.

Ellsaesser et al. (1986) present Global Climatic Trends as revealed by recorded data. This is an extensive work and provides many references. In the near term, much concern has been expressed about induced warming by trace gases and aerosols. It will be difficult to separate these effects from what may be a return towards a longer term normal.

From a much longer term viewpoint, in the view of tectonics and continental drift and spin, very long-term climate with respect to the time involved must show a corresponding time change. Shorter time changes than

these are associated with the ice ages and the interglacial periods. Namias (1975) is recommended information and interesting reading.

The WMO, as a part of the United Nations complex, stipulates a 30-yr period for climatic normals. The first issue of climatic normal data (CLINO) was issued WMO/OMM-NO 117.TP.52, Climatological Normals (CLINO) for climatological (CLIMAT) and CLIMAT ship stations for the period 1931–1960. The next issue is scheduled for the period 1961–1990. Underway at the present time is the preparation of regional charts and maps for publication of data for the 1931–1960 period. Some of these are available now. Eventually, these may appear in hemispheric or global presentations. Until these and others are available to the user, the user may obtain various presentations in the open literature or in publications made by individuals, industries, or government organizations, local and national.

Previously, in the marine areas, there were the U.S. Navy products, the U.S. Weather Bureau products, the output of the British Meteorological Office, the German Weather Service Office, and the Hydrographic Office of the Russian government. Today, responsibility for a specific region has been assigned to a specific service within the WMO activities.

The climate of the free atmosphere is discussed in *World Survey of Climatology*, volume 4, 1969. These discussions are limited to the years prior to 1965. The periods used are, in general, less than the recommended 30 yr due to unavailability of data.

Remote sensing development and improvement are adding great increments to all databases. New databases are being established. Remote sensing has always been a part of our lives. Our own eyes, ears, skin, and nose are, in a way, sensors of objects near as well as far. From the idea generally held, for remote sensors, the sensor is some distance away and, in some fashion, reports back to some base. An observer in an aircraft reporting on what is seen is, in effect, a remote sensor. But still even further removed, the idea of the remote sensor is one that is devoid of life and is mechanical and/or electric (electronic) in concept, construction, and operation. It is the electromagnetic spectrum that is used and that is sensed. The electromagnetic spectrum is utilized to process, and if necessary, transmit and communicate the sensed portion of the spectra. There still remains the necessary interpretation. There are books and publications on these subjects, and the number exponentially increases. Concepts and foundations of electronic remote sensing are discussed by Lillesand and Kiefer (1979). In addition to the passive receptors, such as infrared and ultraviolet detectors for thermal imaging, there are the active systems of radar, lidar, and laser. These active systems propagate energy and determine reflected energy patterns. These are extremely useful to detect precipitation and agglomerative layers of pollutants in both gaseous and particulate form. Modulation and doppler techniques augment the usefulness of the above probes. Acoustic propagation and sensing plays an important part in all of these.

The development of adequate launching facilities has enabled the placement of many instrumental satellite platforms in synchronous, polar, and controllable orbits. The refinement of old types, the development of new sensors, the development of sensors for new types of information, and their placement on these platforms permits surveillance of the entire geosphere, including the surface aspects of the lithosphere and hydrosphere and the internal thermodynamic and dynamic structure of the atmosphere with its stratified spheres and pauses. The dynamic solar output may be monitored as well. Portions of that output are now monitored (Willson et al. (1986)).

The sensor output data volume is tremendous. It is so large that, as yet, viable information interpretive computer algorithms are not available to help assemble, store, and archive all the informational content in real time. Much information is lost. In many cases, the immediate real time value of the data has been realized and the information gathered for a particular immediate reason is no longer needed. The reality at the moment is that, though the value of the data for research is acknowledged, the majority of the data cannot be saved. The system yet is almost

entirely in an operational mode, striving for real time viability and no more. No reduction of these data sets to a few quantifiable, storable, and retrievable informational kernels has yet to be devised.

Today, satellites, using various portions of the electromagnetic spectrum, provide 24-hr coverage of the irradiances or reflectance from cloud systems (albedos); frontal boundaries; ocean wave structure, including the thermodynamic structure of the ocean's upper layers; temperatures and moisture configurations in clear air; hydrometeors, such as smoke and dust; surface temperatures, etc. The ability to interpret sensed signals is good in some cases and not so good in others. However, each year, improvements are made.

But with all this, the remote sensing platform information must be tied to ground truth. Ground truth procedures will and must always provide a check on the quality of the remotely sensed data. Ground truth requires the existence of surface stations—both continental and oceanic—that provide the basic air, water, and soil temperatures, humidity, clouds, wind, and radar information to validate and confirm the satellite sensor output. The loss of land (continental) benchmark stations and the loss of ocean platforms of the Ocean Weather Station (OWS) ships, “ground truthing” becomes difficult. Without such a tie-down structure, degradation of and outright output of false information will be undetectable in the short run and devastating in the long run unless corrected. Independent checks are needed against within-system checks which, though needed, are generally not trustworthy over time.

With respect to the satellite-borne microwave radiometers, Lovejoy and Austin (1980) provide a good summary and good set of references. In their conclusion they state, “Using the available literature and some GATE radar and thermodynamic data, we were able to estimate the potential accuracy of a microwave brightness-temperature to rainfall rate conversion as  $\pm 70\%$ .” They indicate that this is the case if the space and time resolution were perfect. In general, the procedures must be calibrated, as the average rainfall rate, given that it is raining, must be determined from the rain gauge records as a function of geographical location and season. These authors (Lovejoy and Austin (op. cit.)), also note that the microwave techniques need calibration, preferably with a radar. Reference is made to their table 7 (p. 273), “a comparison of rain estimation accuracy for different spatial scales (in %) estimation techniques and for each principal source of error.” The radar planned position indicator (PPI) accuracy ranges from a best of 20 to 90 percent, while for the radiometer field of view (FOV), the accuracy values range from the 70 percent best to 370 percent. The worst is the combination of all errors concerned. An update on this item is provided by Griffith (1987) in section 8.2.

Kahn (1988) discusses some of the problems associated with all the Earth science data. One terabit ( $10^{12}$  bits) of data per day per spacecraft will be produced. No estimate is provided here of the prodigious amounts of data being produced by all associated climate disciplines. There is more than an urgent need to process these data. Development of the kernel interrelationships in understandable, useful, and applicable terms is basic. If this is not done, one can only expect a slow, piecemeal, fragmented, and isolated—almost individualized—attempt to understand the meaning of the data themselves. Without question, this requires in an “a priori” context the goal of error-free instrumentation and data. This requires adequate design and budgetary funding before data are acquired. Kahn (1988) discusses the goals and suggested workshop task groups of the project, the Earth Science and Applications Data (ESADS) workshops. This group attempts to treat the data problems facing National Aeronautics and Space Administration (NASA) programs. But these same problems and others face the other disciplines.

## 2.5 Examples of Progress

The development of electronic computers has led to the establishment of large data centers. The computers have become larger in some instances, physically. In general, the capability to store larger amounts of data, process these data more rapidly and efficiently, and provide set information; i.e., the so-called “power” of the computers, has increased exponentially. In general, costs have also increased, placing the archived information beyond the reach of the single or small group of investigator(s).

The development of the so-called “PC”—personal computer—and the increasing capability of this type of computer does potentially bring the data archives within reach of these groups. The rapid development of better, more efficient, more powerful computer chips, computer languages, and partial acceptance of compatible computers make the options better. Development of computers using light rather than electricity provides a future avenue.

### **2.5.1 Climate Computing**

CLICOM is the acronym for a specially designed CLImate COMputing climate data monitoring system. This is the World Climate Data Programme (WCDP) project, “Transfer of Technology in Climate Data Management and User Services.” CLICOM emphasizes a “package” concept, user-friendly software, and training. The computer and peripheral equipment are the “hardware” of the system. The programmed instructions to and for the computer and peripheral equipment is the “software.” For convenience, computer hardware configurations and software packages developed specifically for this project are referred to as CLICOM-computer system and CLICOM-software. The World Climate Programme Data, WCDP-6, WMO/TD-No. 299 of the WMO, describes the program, the computer hardware configurations, and the software developed by the USA, National Climatic Data Center (NOAA-NESDIS/NCDC, Asheville, NC, USA. See also the National Climatic Center, U.S. CLICOM System descriptive manual. Development of the system was initiated by WMO through a contract with NCDC.

### **2.5.2 National Climatic Data Center**

CLICOM is a microbased climatological data processing system with the capability to digitize, quality control (edit), manage, and analyze data. It consists of a database management system (DBMS) to manage the data and a comprehensive set of FORTRAN programs to enter and validate the data and to produce various climatological products. At the present time, CLICOM is capable of managing seven types of data: Monthly, decadal, synoptic, hourly, 15 minute, and upper air observation. CLICOM meets two perceived needs in any nation—as a means to salvage aging and deteriorating climatological manuscript records and to provide a means of technology transfer for all nations. The PCs used must be IBM-compatible. Most microcomputers being manufactured today (1990) offer such compatibility.

A prospective CLICOM user must procure the necessary hardware and proprietary software packages. The Database Administration staff at the National Data Center (NDC) will provide the CLICOM-specific software at a cost sufficient to cover media and handling. Training is available in the installation and use of the system at the NCDC. Training usually requires 3 to 5 days. More specific information and up-to-date cost estimates may be obtained from the National Climatic Data Center, Data Base Administration, Federal Building, Asheville, NC 28801, USA.

Since 1951, there have been various summaries of meteorological observations available through the present NCDC and the groups preceding. These summaries all have their individual acronyms. One was and is the Summary of the Marine Aerological Records (SMAR). It is now available only in bulk paper printed forms and only for previous periods. Today, the summary of meteorological observations, surface products are available on magnetic tapes, printed forms. Today, the summaries are available from the NCDC in compact disk—read only memory (CD-ROM) form. These were prepared by the DoD, U.S. Navy, and U.S. Air Force groups at Asheville, NC. The data period ranges from 1973 to 1979. There are summaries of  $\approx 400$  stations. Per station, there are usually  $\approx 18$  hourly data summaries and  $\approx 26$  summaries of daily data. In the case of the hourly data, only the 3 hourly data are used in most instances. For most of the stations outside the USA, precipitation data are not available in this series. A print-out of these summaries for one station consists of  $\approx 350$  pages. A stack for all summaries reaches a height of more than 5 m. All of these summaries are available on just one disk, paper thin, and no more than 15 cm in diameter. The cost is about 61 USA. 1990 dollars. But of course the user must have a CD-ROM electronic player (reader) and an IBM-compatible PC.

There are many other types of databases being developed for summaries and many are already available for individual—not summarized—data. The original data for the summaries are available on magnetic tapes and disks. These can be supplied at cost not only by the NCDC but by several National Centers of the World. The reader, if interested, may place queries with the National Meteorological Services for information. Queries on the possible and actually available data sets at Asheville, NC, can be directed to the NCDC.

There are other data centers, such as those for nuclear data, ozone data, CO<sub>2</sub> data, acid precipitation data, solar radiation data, salinities, etc. The user must query the centers located as listed in section 2.4.





### 3. PLANET EARTH

#### 3.1 Anisotropic (Asymmetrical) Earth

The tacit assumption often is made that the Earth is symmetrical. If all things were symmetrical and the Earth's material was homogeneous, a consistent, constant climate might be expected to ensue. The fact that climate varies implies some existent asymmetry. In fact, wherever and whenever we pursue the subject, more aspects of the asymmetry and anisotropy emerge. Earthquakes indicate structural asymmetry and attempts at adjustment of stresses induced. The drift of continents, the rifting of continents, the downwelling of continents, and the upwelling and downwelling of the oceans are indicators. Asymmetries are noted in the Sun and its activity, including its magnetic field fluctuations and movement. This is imaged in part by the movement of the magnetic fields of the Earth and in the asymmetry of the magnetic poles; they are not 180° juxtaposed. The Earth is ellipsoidal in shape, with a bulge at the equator and a shortened vertical axis. Whether the other two axes are 90° apart and of the same physical length is not known. Whether the vertical axis is one straight line is not known. If not, then the oceans and internal stresses must strive to keep the balance. The continents and mountains are all indicators of asymmetry. The movement of the meteorological equator and the oceanographical equators are indicators. Magnetic and gravitational anomalies—known and previously unknown—have been detected and better located by means of satellite observations. The Earth at present is known to be somewhat pear shaped physically, so it is physically asymmetrical, but perhaps more mass symmetrical. The latter is certainly quite conjectural on the part of the writer. Internal symmetries do tend to develop as the winnowing (fractionating) in the differentiation processes of the interior materials continues.

Absolute symmetry and balance is not present. If present, life would perhaps soon not be possible. In some instances, one might want a little more symmetry. The reader undoubtedly has ideas of more asymmetrical aspects.

The tides of the Earth, ocean waters, and of the lithosphere are well known and documented. The belief that tides also exist in the molten liquid outer core seems to be true. In the viscous mantle, there is little doubt that these exist. The varying response times of these regions induce tremendous stresses in the total structure of the Earth. These asymmetric tides all produce asymmetries and internal resultant oscillations in their neighborhoods. This is a field in which indirect seismic probing has produced some knowledge. More needs to be done to expand the observational networks, to develop appropriate mathematical and statistical models and treatment procedures, and in particular, the quality assurance and control of the networks, the treatment procedures, and the archiving and retrieval of information. Data management is required. Quality assurance and control of this management can only come after adequate design and reliability procedures are in place.

#### 3.2 Lithosphere

The rock—lithosphere—is the thin crust floating on and surrounding the mantle. In analogy, it might be termed the slag, the crystallized material skim found on surfaces of pots of metal melt as these solidify. As the thin skin of the Earth, it contains an estimated 1 percent, and no more than 2 percent, of the Earth's total volume.

Most of the information available on the semisolid viscous portions of the Earth is indirect and inferential. Anderson (1989) asks the question, "Where on Earth is the crust?" The crust, at least the lower strata and the plates, is continually being carried downward into the mantle as a result of the slow, inexorable turbulent motion. The end

result of this is that at least the upper part of the mantle is a mixture of solid mantle material and melted and remelted pieces of former surface crust. An analogy might be that this might appear as cake or candy topping with admixing of large nuts or pieces of fruit. The mix is extremely heterogeneous from any point of view.

Even yet, after the more than 4 billion years of the Earth's existence—within the Earth's total structure—the winnowing (separating) of the elements and/or their compounds goes on. Though all these elements may have been thoroughly dispersed in beginning mix, presumably this was not the case, and today this is not the case. Though all elements, products of stellar development and explosion, exist in the Earth, the elements with mass numbers ranging from oxygen to iron predominate. These were the ones undergoing development or near development into iron prior to the stellar explosions long before the formation of the solar system more than 5 billion years ago. Iron, silicon, magnesium, and oxygen constitute slightly more than 90 percent of the Earth. The heavier elements have percolated towards the core, while the more mobile, lighter elements have risen to the surface. Inferentially, iron now constitutes the major portion of the core region, while the oxygen and silicon constitute the major portion of the crust.

Heating from release of gravitational energy, from radioactive decay, from the formation of less energy complexes in the eutectic mixes; i.e., crystallization, plastic congealing, or solidification, have all made their contribution to the separation of the heterogeneous mix into less heterogeneous structure. The important angular momenta have their effects in the spin separation processes, the establishment of relatively homogeneous regions in terms of their physical and chemical makeup, and in the establishment of separation discontinuities with their own unique structures, flow, and circulation. By definition, these discontinuities cannot have the exact characteristics of their neighboring shells.

The core, the mantle, and the crust and the transition discontinuities are all results of the winnowing or adjustment process. The hydrosphere and the atmosphere also produced in the winnowing process have their own unique structures, including separation zones. Some of these will be discussed in later sections. Within the mantle there are zones where the principal components are made up of oxygen-silicon-aluminum compounds, while the oxygen-silicon-magnesium compounds constitute another dominance region. The major portions of the crust have solidified from the basaltic molten magma and are termed igneous rocks. These generally contain oxygen-silicon-aluminum-magnesium and iron. These make up the ocean basins and the subcontinental portions. The masses that comprise the continents themselves are of granite combinations, generally of oxygen-silicon-aluminum and two of the alkaline metals—sodium and potassium. As a result, alkaline soils are extensive on the continents, particularly where much weathering of the rocks occurs. This weathering will change the trace gas and sediment mixtures. The continents float on the basalt and the two float on the mantle. The crust has a density slightly more than three and slightly less than three in the lower and upper portions, respectively.

The crust is not very thick, ranging from  $\approx 10$  km in the oceanic basins to  $\approx 40$  km in the continental regions. Discontinuities mark the differentiation with the mantle, one of them labeled the Mohorovicic, Moho, or simply M. Attempts to penetrate the crust to the Moho have declined in intensity. Deep gas wells (10 km) have been drilled in the Anadarko Basin (underlying Oklahoma, Texas, New Mexico, Colorado, and Kansas) in Oklahoma. Deep probes have been made into regions, such as the Kola Peninsula (Norway, Sweden, Finland, and Russia). See Y.A. Kozlovsky (1986, 1988). As the crust is thinner, the ocean basins offer the best chance to touch the Moho, but the obstacles are great. There, the drilling must be done from an ocean platform. Efforts to do so continue, but at a much lower pace. The drift of the continents is controlled heavily by the three-dimensionally moving mantle turbulent currents. This is not the fast turbulence of a storm or that seen in a pot of boiling water, but is the slow, but nevertheless turbulent, motion of an estimated fifth of a millimeter to perhaps a few centimeters per year. The visible continents often have been likened to icebergs. The major portion of the continent is below the surface. There seems to be a mirror image extending downward. In models, this extension is very deep, well into the mantle. These roots, as a keel on a boat, offer resistance to the mantle flow. Where deep roots might exist, the entire system could become

more responsive to the mantle's average flow and seemingly move against or across the surface flow. The shearing, turbulence, and accompanying eddies would be terrific. But this scenario is not generally accepted. More definite research needs to be done.

### 3.2.1 Rifting

Today, there is no doubt that continents and plates are moving and that oceans are being made larger in some cases and smaller in other cases. The insertion of navigation and other satellites into Earth's near space and maintained within Earth's orbit are new tools now available to keep tabs on these motions. It is now being done. At one time it is thought that the continents were all one. Whether these were formed in that way at the equator or were assembled piece by piece by jamming them together is not known. Whatever the stage before that time, the supercontinent then rode the crest of the turbulent mantle. Tied to the mantle through viscous boundaries and even perhaps some roots extending far down into the mantle's magma, apparently it eventually split in two. Those pieces, in turn, have been separating in some instances, and in others they have been thrust against each other again in turbulent slow motion. There are many scenarios.

At the present time, the Western Hemisphere is moving westward in a relative sense. But the northern and southern portions are in slow, different spins as they are floating on top of different large eddies of the mantle. On the western edges, they are overriding the Pacific plates. The Pacific plates are being forced downward in a subduction sense. Forced far downward, these are being remelted. This is a fractionation process and leads to the separation of elements. Thus, when these are brought to the surface in different ways, and at later times, heavy metals may be quite well separated from other materials.

In the subduction process, the overriding features are not smooth. The result is crumpling and buckling of the lithosphere in those regions. Mountain building progresses. For example, today, the fossils laid down in the ancient ocean beds will be found on the highest peaks of the Antarctic, the Andes of South America, and the Rockies of North America. Such fossils are also found in all the Plains states of the United States, with the general uplift of the continent. Volcanic activity went on and still goes on in the rifting and buckling regions. Earthquakes are common in these regions, but by no means restricted to them. West of the mountain chains are the deep trenches marking the subduction zones where the Pacific plate is being forced downward into the mantle. The same phenomena occur in other parts of the world.

In the middle of the Atlantic, rifting has occurred and continues to occur as the Western Hemisphere slides more rapidly westward than the eastern part of the Atlantic. In fact, the spin and slow northeastward movement of the North Africa plate helps to keep the eastern Atlantic region from moving relatively westward.

The stretching and thinning of the lithosphere, rather than the crashing together making mountains, permits the rifting and the development of valleys. The molten magma seeps through the breaks in this very thin region. The ferromagnetic metals well above the Curie point in the molten magma fall below the Curie point temperature as it cools. When it does, and while it is still viscous, the ferromagnetic materials take on the orientation of the Earth's magnetic field. The velocities of the rifting plates and the reversals of the Earth's magnetic fields can be deduced in their alternating magnetic strips running from the northern North Atlantic to the southern South Atlantic. However, subsequent remelting and recrystallizing under a different magnetic regime confuses the situation (McCabe and Elmore (1989)). Massive undersea mountain ranges are built in this way. Iceland is on the northern point of a rifting process. The same type of rifting occurs in the Pacific. Large rift valleys exist under the sea. In some instances, these rift valleys have been lifted as an entire plate has been lifted. A famous rift valley is in eastern Africa. The Island of Madagascar presumably has rifted from Africa and is moving northward—perhaps northeastward. The Indian subcontinent is assumed to have rifted from the African region and is being subducted, in a crash with Asia. The Himalaya mountain range, plateaus, and valleys are the result of this tremendous buckling. The Red Sea is said

to be a rift valley as the Arabian plate moves northeastward. It, too, may suffer the same sequence as the Indian subcontinent.

### 3.2.2 Vulcanism

Vulcanism is only briefly treated further here. This is the intrusion of the hot molten mantle magma through weak points into the lithosphere and its ejection upwards. These weak points may be at the:

- (1) Separation and thinning of the lithosphere by plate movements.
- (2) Collision of continents with subsequent buckling and rupture.
- (3) Shearing of continental and oceanic plates as the plates spin against each other.
- (4) Motion of thin plates over hot mantle magma. The evolution of the Hawaiian chain westward and northward toward Japan is one scenario of this process. But there are skeptics.

The earthquakes and tremors do cause changes that may be beneficial, or these may be damaging. It depends upon the point of view or the effects upon those things or persons affected. These do provide the release and propagation of energy for the essentially acoustic-like probes into the Earth's interior. Use of this indirect probing permits deduction in more detail of the Earth's internal structure(s). Often tsunamis, the great oceanic waves, are created which may be quite effective change agents.

Additionally, the volcanoes spew forth great amounts of material—solids, liquids, and gases. The immediate deposition of the larger particulate materials build the great cones with which one associates the physical structure of volcanoes.

A few of the many are Etna, El Chichon, Fujiyama, Hood, Kilimanjaro, Krakatoa, Mauna Loa, Orizaba, Pelee, Popocatepetl, Ranier, and Vesuvius. The finer solid particles are carried for some distance before falling on the Earth. In many instances, these are scavenged by precipitation. The gases of the nitrogen and sulfur compounds scavenged from the atmosphere are beneficial in small amounts and deleterious in larger amounts. More forceful explosions may eject and inject tremendous amounts of material—gaseous and particulate—through the troposphere and well into the stratosphere. Here the time element before deposition will be much longer. Change in some of the climate element characteristics should be expected. Temperatures are sensitive to the debris effects. See Mitchell (1982) for some details. Tilling (1989), editor, in “How Volcanoes Work” combines parts I, II, and III from the *Journal of Geophysical Research*, 1987 and 1988.

## 3.3 Hydrosphere

The oceans—the hydrosphere—cover almost three-fourths of the lithosphere. Those parts of the lithosphere not covered are the continents. Lakes, glaciers, rivers, and inland seas exist on portions of the continents. The impact, effect, or partial control on and of climate is without question.

The hydrosphere, composed of water, and also being eutectic in nature due to the added salts, with ions from the many admixed salts, has an influence on climate. It is very dynamic. Its thermodynamic influence is effective. Water is indispensable to life. Similar to other substances, reception or loss of sufficient energy permits—even forces—water to pass from one to either of the other two phases—liquid state, gas, or solid. With sufficient added energy from high-frequency radiation, it breaks down into hydrogen and hydroxyl ions. The three molecular states have different physical, thermal, and chemical characteristic capabilities and mobility. For example, under ordinary conditions of pressure, radiation, etc., in the vapor form, water mixes well with the atmosphere and flows as one with it. In its solid state, it generally appears as snow or ice crystals when it may be transported by the atmosphere, though these forms eventually precipitate or evaporate. In its solid form as snow or as ice, in favorable regions, it

exists as the cryosphere. Water on the Earth's surface is one of the greater climate-modifying elements. The energy exchange from the water vapor state to the liquid state is roughly five times that involved in going from the condensation point to the freezing point, and almost seven times that involved in the change of state at the freezing point. These energy exchanges are reversible.

A small calorie is the heat—energy—required to raise 1 g of water 1 °C under specified conditions. Often, one of these conditions is 15 °C. Another condition for the standard is 1 atm of pressure near 1 bar. More specifically, the energy involved in the change of state of 1 g of water—about two large liquid drops—from vapor to liquid at the condensation point of the vapor at 100 °C is ≈540 cal, from liquid at 100 to 0 °C is ≈100 cal, and the passage from liquid to solid at 0 °C is ≈80 cal. Thus, ≈720 cal are involved in the total process, the change between the vapor to solid states where this latent energy is released to the surrounding environment. The same amount of energy is required to take water from the ice state at 0 °C to the vapor state at 100 °C. It is important to point out that though each phase may exist in the energy realm of the other phases, it is the more stable form usually considered. For example, supercooled (subcooled) pure water may exist down to about -40 °C, though this is not usual. With considerable disturbance, the unstable form changes to ice; with contaminants in the water, the change may be almost instantaneous with almost no disturbance.

The paragraphs above consider water in a relative microscale context. The great fluid mass of the hydrosphere permits the large influence on climate. In essence, it becomes an enforcer. It acts as both a receiver and a disperser of energy. Most of the energy is received directly from the Sun. Most of the energy is lost to space through radiation in low-frequency form. The energy gain and loss is related directly to the changing season induced by the changing aspect of the Earth's surface to the Sun and to space.

Ubiquitous water by itself is a great change agent. A more or less steady state of climate might be envisaged if water and life were not present. Water changes all that. In the hydrosphere, ocean or sea currents transport heat from the sources (relative excess regions) to the sinks (relative deficits) and transport cool water from the sinks to the source regions. The heat capacity of water is phenomenal, near 1 cal/g (4.18 J/cal) per degree celsius in its liquid form. Its enthalpy, near zero at 0 °C and near 100 cal (418 J) per gram at 100 °C indicates the tremendous amounts of heat (energy) that can be absorbed, stored, transported, and released by the hydrosphere.

Tremendous eddies in both the hydrosphere and atmosphere are created by the absorption and loss of radiational energy, by the physical effects induced by the rotation of the Earth, and interaction with the continental ocean bottom configurations. Massive loop currents developed in the hydrosphere that transport surface energy excesses poleward and return deeper, cooler waters equatorward. There are many loops and regions of convergence and divergence where the great gyres of the various oceans are developed. These move with the seasons closely guided by the regions of excess and deficit energy. Cold and warm currents develop. Cold surface currents are often associated with the upwelling phenomena of cold, nutrient-rich waters rising to replace the warm waters moving away from the coasts. Most of these have special names, such as the Eastern South Pacific Peru (Humboldt) Current, the Eastern North Pacific California Current, and the Eastern South Atlantic Benguela Current. Warm currents develop, such as the Western North Atlantic Gulf Stream, the Western South Atlantic Brazil Current, and the West Pacific Kuroshio. These and allied items will be discussed in more detail later.

One of the proposed oceanic global circulation schemes is the surface flow of warm water from the North Pacific, the Indian Ocean, around the southern tip of Africa, thence northward to the North Atlantic where its continuing loss of energy through infrared (heat) radiation results in downwelling. A retracing return begins as a bottom current southward towards Africa, then to the Indian Ocean, and onward to the North Pacific where it slopes upwards, upswelling to again being warmed on its southward start of the loop for another sequence. This is discussed by Broecker (1987) and illustrates a feature of the radiation budget of the Earth and its atmosphere. Versions of this appear in the Lamont-Doherty advertisements in EOS and in a depiction by Hileman (1989), and Washington

(1990) discusses this feature and illustrates it. A potential problem—not in the model but in climate—may exist if cloudiness in the North Atlantic keeps the waters there from cooling, becoming denser, and down-welling. This would lessen or halt the “conveyor belt” system as Broecker calls this loop system. One scenario for this is the increase of radiative trace gases followed by increased temperatures and evaporation and the increase in cloudiness, rainfall, and glaciation. This process appears to be a slow feedback mechanism leading to glaciation.

Figure 3-1 is a sea surface temperature image for the first week of June 1984 of the western North Atlantic. Warmer hues denote warmer temperatures. The Gulf Stream in this particular image off Miami is  $\approx 27^\circ\text{C}$ . The warmer waters to the south of the Gulf Stream after it separates from Cape Hatteras are cold core rings, whereas the warmer eddies to the north of the Gulf Stream are warm core rings.

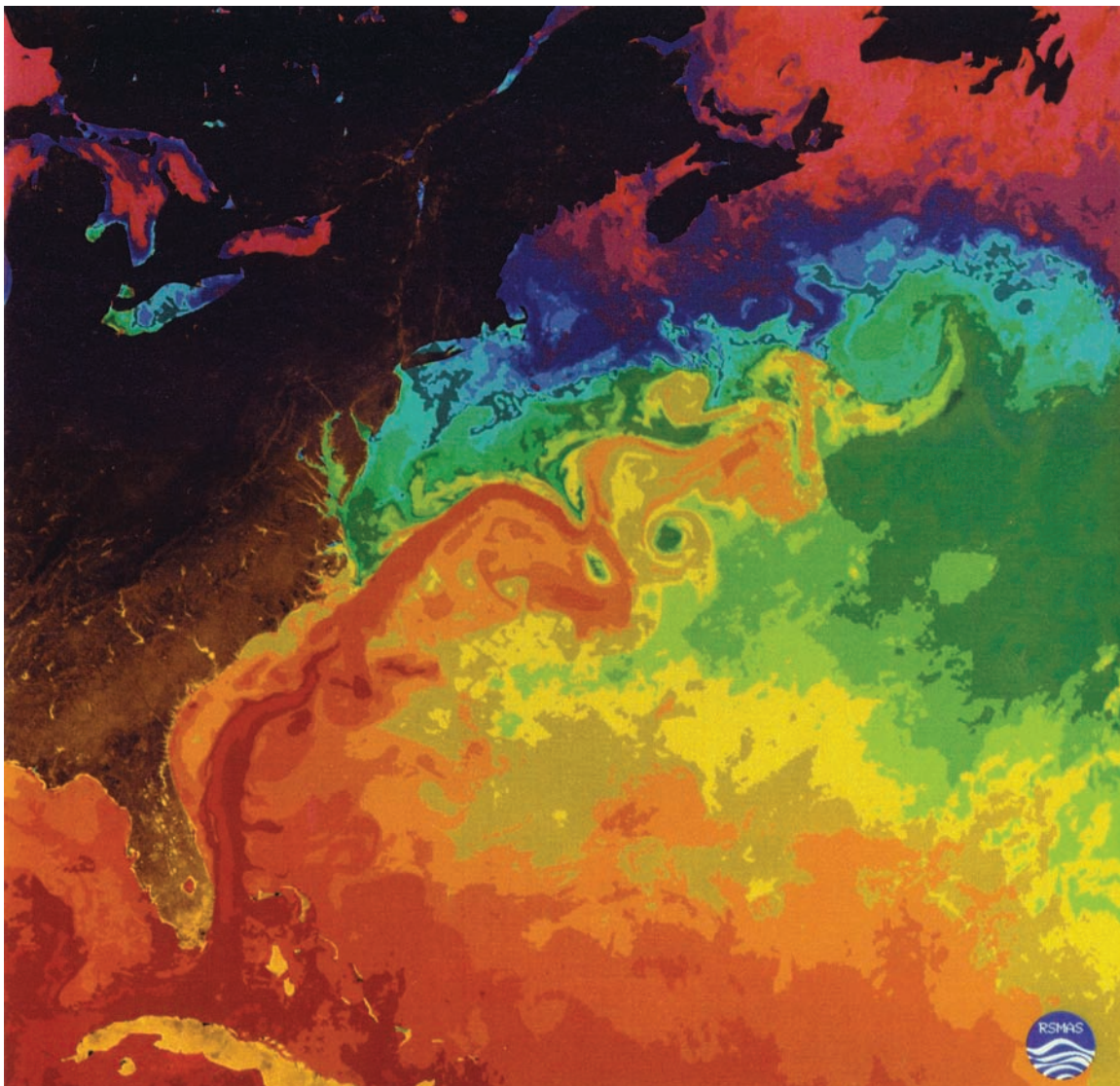


Figure 3-1. Sea surface temperature image for the first week of June 1984 of the western North Atlantic (courtesy of O. Brown, R. Evans, and M. Carle, University of Miami Rosenstiel School of Marine and Atmospheric Sciences).

Figure 3-2 is a sea surface temperature image for February 1985 of the Brazil Current confluence region off Uruguay and Argentina in the southwestern Atlantic Ocean. Warmest temperatures are denoted by warmest hues (red) while the coolest temperatures are denoted by the cooler tones (blue). Note the strong eddy activity in the Brazil Current as a pulse of warm water extends  $\approx 5^\circ$  S. from the main confluence. Although the Brazil Current is one of the weaker western boundary currents found in the world's oceans, eddies produced by this current are as strong as those observed in the Gulf Stream system.

Confluence Principal Investigators (1990) EOS (1990) present a report on an intensive multinational study of the southwestern Atlantic Basin. Argentina, Brazil, France, and the USA participated. Twelve principal individuals noted are Brown, Evans, Garcon, Garzoli, Memery, Maitland, Olson, Piola, Podesta, Provost, Takahashi, and Bianchi (1990). See figure 3-3.

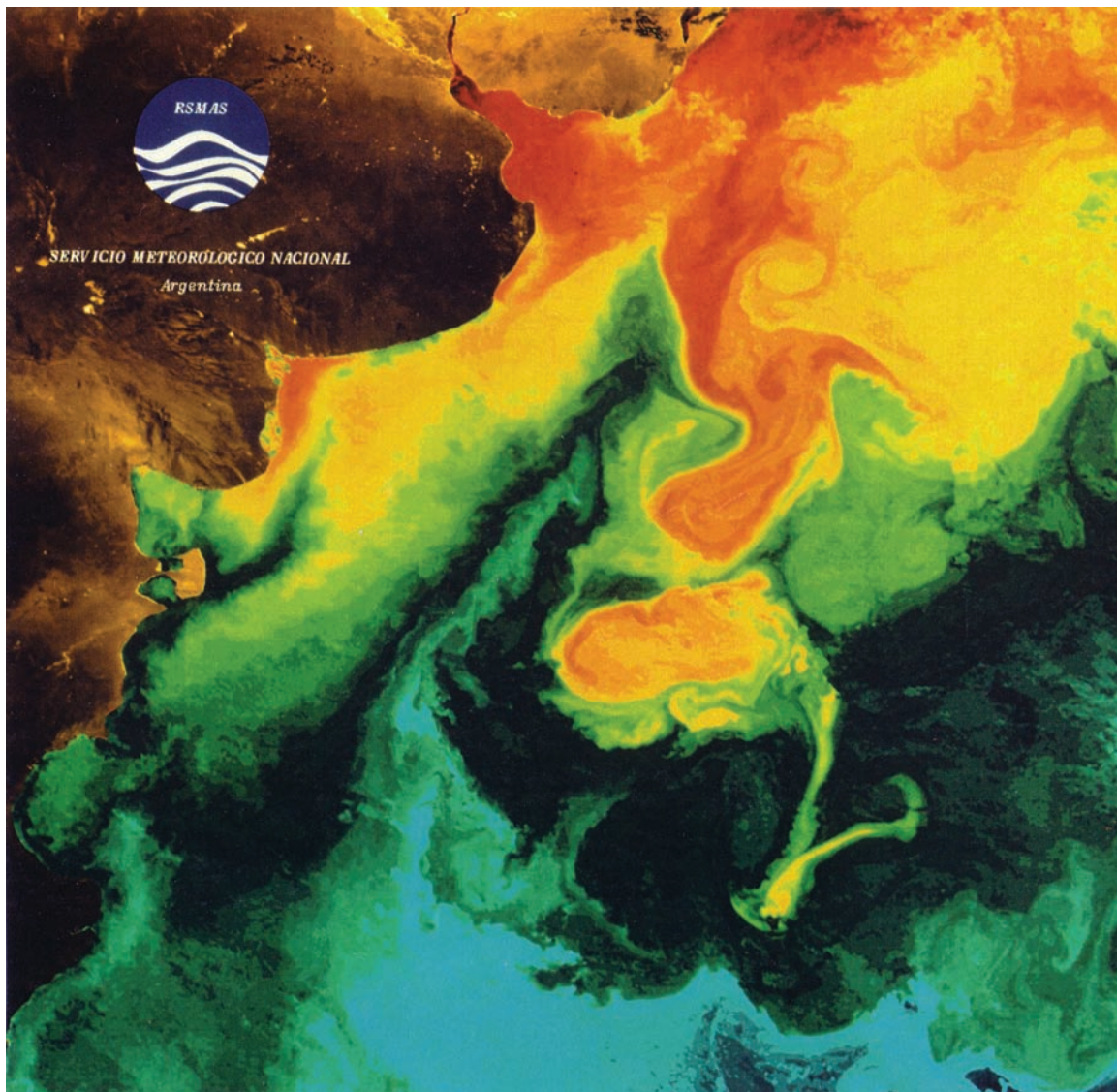
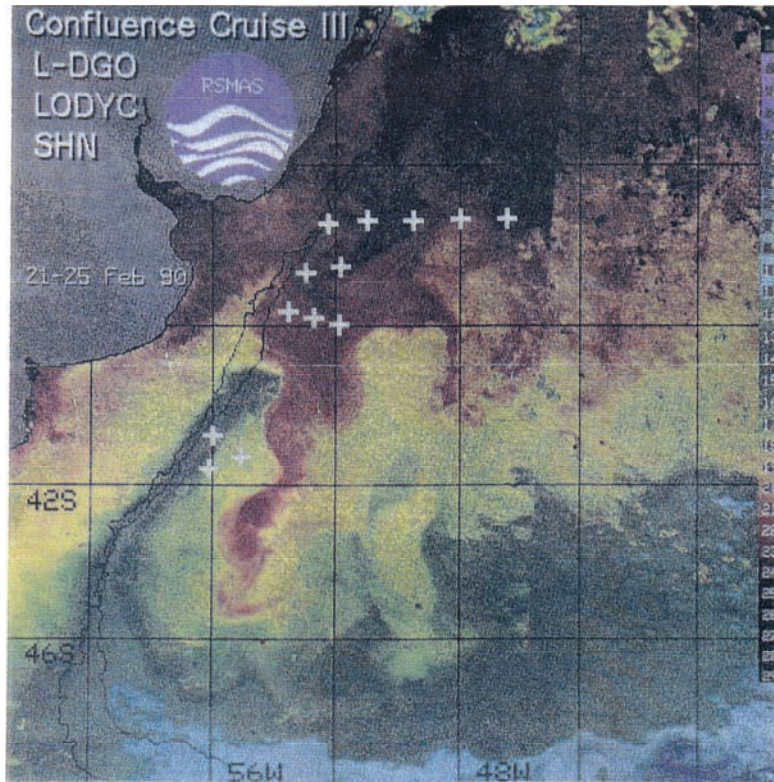
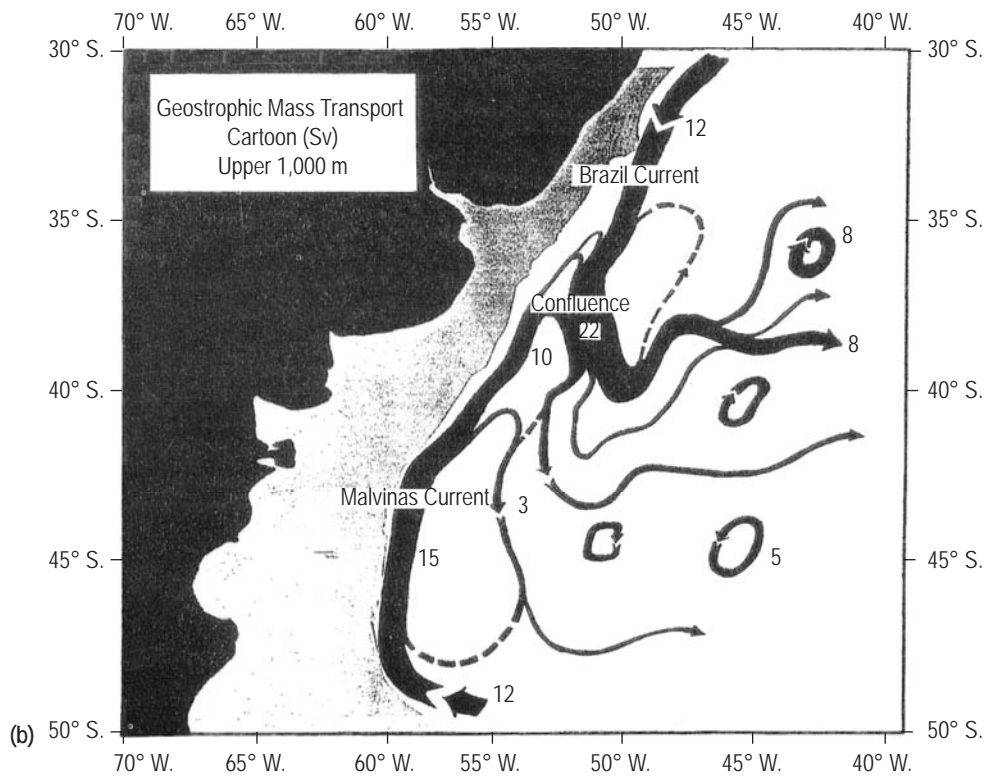


Figure 3-2. Sea surface temperature image for February 1985 of the Brazil Current confluence region off Uruguay and Argentina (courtesy of O. Brown, R. Evans, and M. Carle, University of Miami Rosenstiel School of Marine and Atmospheric Sciences).



(a)



(b)

Figure 3-3. Sea surface temperature off the Uruguay and Argentina coasts, February 21–25, 1985: (a) color and (b) black and white schematic flow pattern (from AGU EOS (1990) and confluence Principal Investigators).



The region under study borders the east coasts of Argentina, Uruguay, and Brazil. The major currents are the Malvinas and the Brazil. The Malvinas flows from the south before turning and flowing from the southwest, essentially parallel to the coast. The Brazil flows parallel to the coast from the north-northeast before meeting the Malvinas (Falklands). Their meeting and confluence during the period February 21–25, 1990, are near 39° S. and 54° W., latitude and longitude. Their mass transport is  $\approx 12$  Sv at the entrances. The immediately southeastward-flowing current after merging the transport is  $\approx 22$  Sv. A Sv is equivalent to  $1 \times 10^6 \text{ m}^3 \text{ s}^{-1}$ . The jet flow degenerates into an easterly 8 Sv flowing current along the 40° S. parallel with many small eddies (3–5 Sv) on either scale. Presumably, these eddies extend into the latitudes of 50° S. and 30° S. though these are not indicated. As indicated in the EOS (1990) report, the object of the study was:

- To monitor the variability of the dynamic topography in the area of the confluence of the Brazil and Malvinas Currents and to study the fluctuations in time and space of the associated thermalhaline front.
- To monitor the variations in transport of the Brazil Current in the vicinity of its separation from the boundary and to obtain the first estimates of the boundary currents in each water mass south of the confluence front.
- To obtain detailed water mass descriptions of the region during three different seasons, detect changes in water mass composition, and evaluate the water mass modifications due to small-scale mixing across the frontal region.
- To determine the strength of the carbon dioxide (CO<sub>2</sub>) sink in the region during wintertime.

Considerable detail of this confluence study is presented in the EOS (1990) article. The reader may wish to examine those details that include presentation of surface temperatures, salinities, oxygen saturation, and the CO<sub>2</sub> partial pressures of the CO<sub>2</sub>. The authors indicate that the total CO<sub>2</sub> concentration in the North Atlantic deep water range from 2,170 to 2,190 Mkg<sup>-1</sup> where those in the Antarctic bottom water range between 2,260 and 2,270 Mkg<sup>-1</sup>.

Presentations such as figure 3-1 may be known as “false” color images as the color delineations are arbitrary. As these are the result of computer processing, different delineation and different colors may be selected and used. Additionally, computer processing makes it very easy to combine “snapshots” into averages. In this way, the formation of the development of and the lifetime existence and the demise of the large general current and the eddies may be shown. This indicates the potential for using satellite observations in a determination of global climates. These particular presentations—in a qualitative sense—must be backed by “surface truth” comparisons and by the presentation of new statistics based on the separation of heterogeneous distributions into homogeneous subgroups and their attendant eddy correlation (diffusion) features. See Groenewoud, Hoaglin, Vitalis, and Crutcher (1967) for univariate, unimodal normal distribution and Crutcher and Joiner (1977a) for multivariate, multimodal distributions. Colton and Chase (1983) describe the interaction of the Antarctic circumpolar current with bottom topography using satellite altimetry. Fu and Holt (1983) provide some examples of detection of oceanic mesoscale eddies by sea satellite (SEASAT) synthetic-aperture radar. See also the inversion of ocean circulation models (Wilbrand and Wunsch (1990)).

There is no ready source of information of surface global currents which, based on observations, depict the global monthly mean of surface flow of oceans. There are many possible reasons, some of which are now mentioned:

- First and foremost is the lack of adequate observational coverage. That coverage is barely adequate even in the shipping lanes for which most of the data exist.

- For cost and space reasons, illustrations are kept to a minimum and texts, if they do have charts, usually contain one current chart. See Bowditch (1958).
- Coast pilots and pilot chart publications exist and are maintained though additional new data are rarely included.
- Quality editing of the data is difficult due to the paucity of the data that would allow the examination of extreme and other questionable values.

In general, the number of data on a global scale are insufficient to allow for the examination on a global month-by-month examination of the data. They are generally insufficient with respect to the mixed or heterogeneous normal multivariate distributions. From these, some idea of transport across the mean currents could be determined.

There are steps to help improve the data problems mentioned above. These are the programs that utilize moored and drifting buoys (NOAA (1990)), but it will be years before a coherent consistent picture can emerge. The period must cover  $\approx 45$  yr. This will allow for an initial coverage of some of the El Niño fluctuation.

Figure 3-4 depicts roughly only the (a) January and (b) July, respectively, global mean current flow. Mid-season and other months are not available. These two charts and their data are inadequate for a detailed presentation in scale, space, and time. These have been pieced together from a few available sources. Some of these are as follows.

These are products of the U.S. Department of Defense (DoD), U.S. Navy (Naval) Hydrographic Office Oceanographic Atlases, Atlas of the Polar Seas, Part I: Antarctic (1957), Part II: Arctic (1958), and North Atlantic (1965).

From the products of the U.S. DoD, U.S. Navy, U.S. Marine Climatic Atlas of the World program, Part II, Oceanography sections, V, I, II, III, IV, and V, respectively, Oceans of the North Atlantic, North Pacific, Indian Ocean, South Atlantic, and South Pacific. These sections were prepared by the U.S. Naval Hydrographic Office.

Texts and other sources were used as references and guides, but in general, these provided limited information. See also Sverdrup (1942), Sverdrup, Johnson, and Fleming (1942), and Neumann and Pierson (1966).

The U.S. Naval Oceanographic Office Special Publications in the 1400 series cover fairly well the surface currents of the oceans by  $1^\circ$  latitude and longitude quadrangles. Due to the low number count of observations, generally no isoline analyses are shown.

The depictions in figure 3-4(a) and (b) can only be considered to be approximate. Nothing but general directions are indicated by the lines. The spacing of the lines has no significance. No mean or average speeds above 4 kt are noted. In a few spots, the numbers indicating speeds have been placed on the continental margins. These will be noted near the maxima near the Florida Strait Gulf Stream, near the Madagascar-South Africa region, the Japanese Kuroshio stream, etc.

Between opposing jet streams, such as along the equatorial currents, eddies occur. A few of the larger ones are shown, such as in the Bay of Biscay. Between the near along-shore currents, such as between the shore and the major currents, between the major currents and the larger bodies of water, and between the surface and deeper waters, back currents and eddies inevitably are present. These cannot be shown on charts of this scale. Though figure 3-4(a) and (b) are not adequate, they are presented to the reader for concept. Lest the reader forget the point, the mass of water moving at slow speeds, probably averaging  $<1$  kt, is a tremendous mass and the momentum and heat

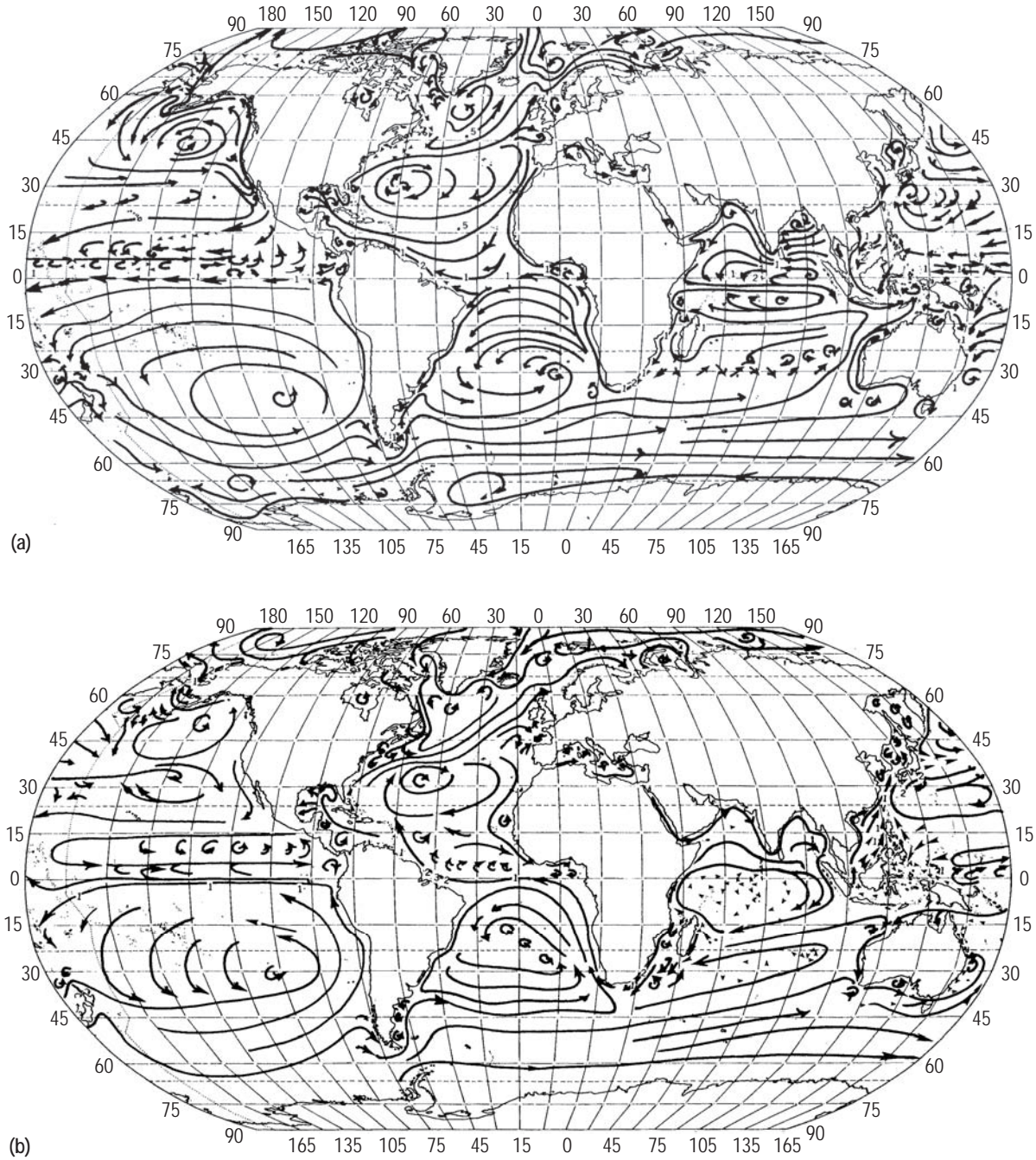


Figure 3-4. Depiction of approximate flow (knots) of global oceans for (a) January and (b) July.

(or lack of heat) transport (transfer) is astounding. The reader is referred to van Loon (1984). This extensive volume, *Climates of the Oceans*, is the 15th volume of the *World Survey of Climatology*. In thoughts expressed by the editor, van Loon, the fact that the Earth's oceans comprise three-fourths of the surface, the size of the volume, and the coverage of the details is extensive. The authors contributing to this volume are Hoflich (1974), Tucker and Barry (1984), Streten and Zeltman (1984), Terada and Hanzawa (1984), Taljaard and van Loon (1984), Ramage (1984), and Einarsson (1985). Each contributes to details and descriptions of selected ocean regions and their climates.

### 3.4 Cryosphere

Here, the cryosphere is treated only briefly, but will enter into later discussions. The cryosphere is one of the greater aspects of climate. The waxing and waning of the cryosphere through the ages occupy the thoughts of many professionals in a large number of disciplines. The waxing and waning are used as indications of changing climate.

Pressure and energy control water evaporation. Suspension or occlusion in water have their effect. Isotopic differences exert their influence. The lighter isotopes such as  $^1\text{H}_2^{14}\text{O}_1$  will evaporate more quickly than a heavier isotope such as  $^3\text{H}_2^{20}\text{O}_1$ . The water molecule  $^1\text{H}_2^{16}\text{O}_1$  is the predominant water molecule. See discussions in a later subsection. Mixed with the atmosphere and carried away by the air currents, water vapor transports vast amounts of heat in the latent form. This energy can only be released by a change of state from the vapor to the liquid or solid form. The capability of the atmosphere to retain moisture is a function of the temperature because the vapor pressure of water is a function of the temperature. With saturated air, cooling to lower and lower temperatures results in a continued change (decrease) of vapor pressure of water. A relative excess develops. A change of phase of state process (vapor to liquid) becomes more probable. Once this process begins, and with the accompanying decrease of vapor pressure with the decrease of temperature, there ensues the production of the liquid phase and the simultaneous release of the latent energy as sensible heat. If the air is not saturated, cooling continued to the condensation or dewpoint and then cooling below the dewpoint usually will initiate the change of state and release of heat of condensation (frost) or sublimation.

Continued loss of thermal energy takes the liquid water to a point where, in myriad forms, crystals develop. Some of these are snowflakes, ice needles, or simply ice crystals. For each gram of crystals formed,  $\approx 80$  cal of heat are released to the surroundings. These are equivalent to the energy absorbed in going from the solid state to the liquid state. Please refer to Bentley (1901, 1907), Humphreys (1928), Bentley and Humphreys (1931), Nakaya (1951), and Schaeffer (1951). Work by other investigators continues on the study of snow and ice crystalline forms.

Isotopic ratios in layers of snow deposition may then be used inferentially to produce so-called “proxy” data of former evaporative (temperature-pressure-circulation) regimes. In time, these may be used as “real” and not proxy data. These are transient information sources and should be tapped before they disappear in remelt processes. See figures 3-5 and 3-6 for maximal, mean, and minimal edges of ice for the Arctic and Antarctic regions.

The solid form, as snow within the atmosphere, may form directly by deposition of the vapor onto a particulate nucleus or it may first pass through a liquid phase, condensing onto a particulate nucleus. At the surface of the Earth, it may be deposited as frost directly onto some obstacle or energy-radiating point, such as a twig or blade of grass. It may also form in an associative or agglomerative process, water molecule to molecule.

The transport of moisture and heat (energy) to the polar regions goes on all the time. Though the polar regions receive more energy from the Sun during the high-latitude summers than do the equatorial regions, on a 24-hr basis, the changes of the length of the seasons over millennia have their effect. See Milankovich (1957) for ideas. With the deposition of snow in the polar regions and with insufficient energy to melt the snow, cumulations develop. Over time, great ice sheets have formed, disappeared, and formed again. The present period is often termed an interglacial period. The implication is that, in time, another ice age will be present. At the present time, the snow and ice fields are restricted to the polar regions, mainly Greenland and Antarctica. The high peaks of the world, including those of the tropics, have their glaciers, and there are the regions of the permafrost.

Simple calculations permit the assessment of the rise and fall of sea level with the formation of the great ice sheets. Some assessments range up to a 300-m change in sea level. Several times in the course of history recorded in varves, in coral, and by other fossils, the Mediterranean has been a dry lakebed of salt. The Persian Gulf has at

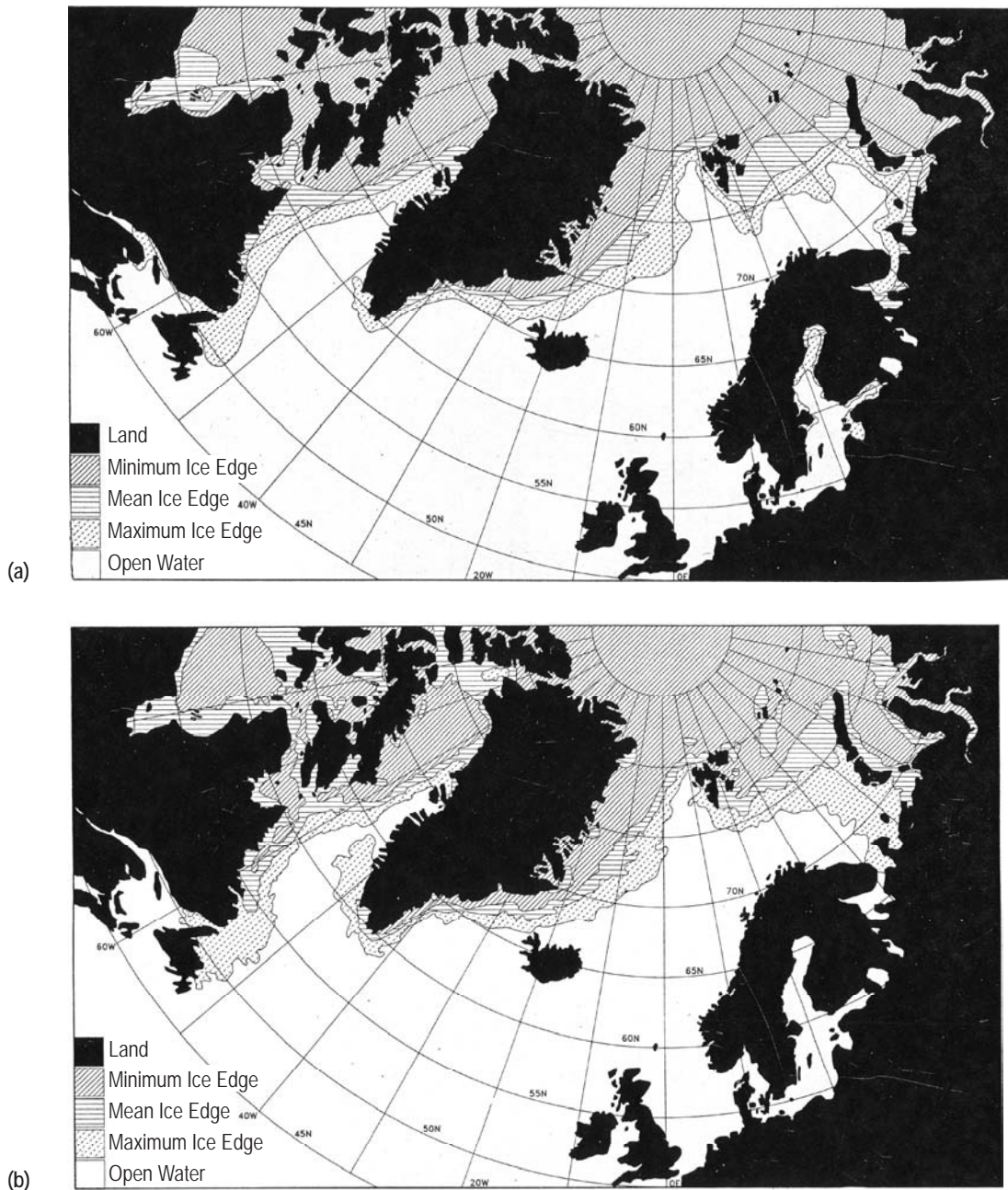


Figure 3-5. Arctic region maximum, mean, and minimum edges of ice for (a) winter (Dec. 15) and (b) summer (June 15) (NAVAIR-50-1C-540 (1985–1986)).

times also been nothing but a riverbed draining the present land forms bordering the Gulf. The assessment of the change of sea level is fraught with difficulties. The uplifting and sinking of vast regions complicate the determination of sea level changes. Just as necessary in assessments of climate itself, the establishment of reliable observing techniques is required for sea level measurements. For a chronology of fluctuating sea levels since the Triassic, see Haq, Hardenbol, and Vail (1987). The scales used are in terms of millions of years, which are much longer than the time periods with which present-day climatologists are interested. The usual basis for discussion is in terms of thousands of years. Thus, as indicated in the beginning of this publication, the time periods are of basic importance in any specific discussion and in climate definition.

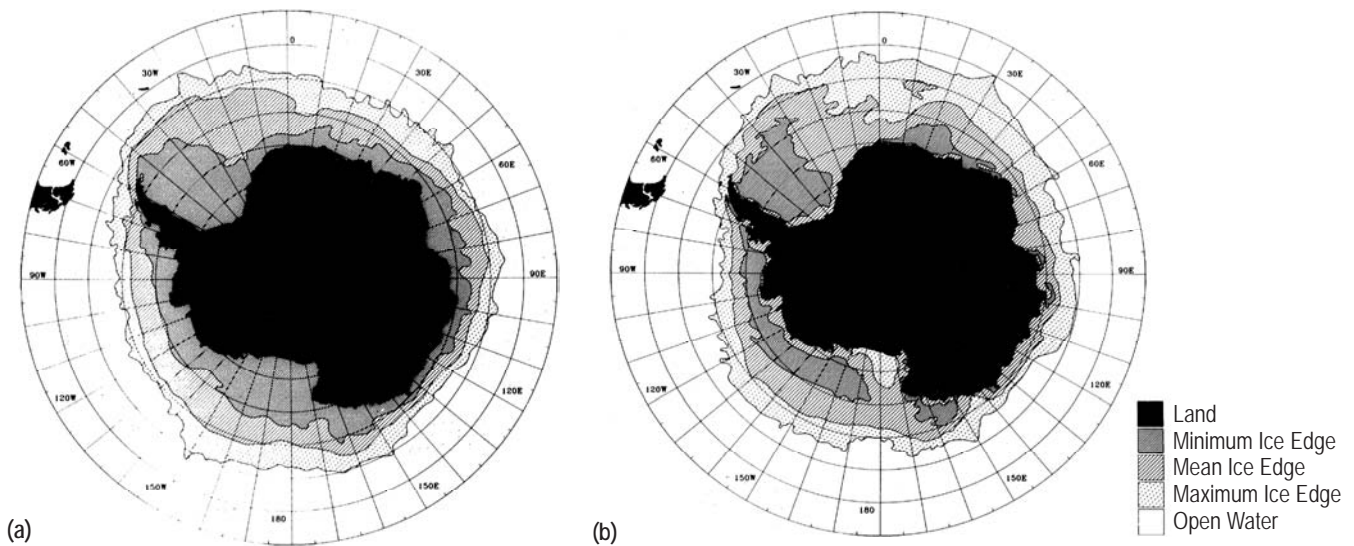


Figure 3-6. Antarctic region maximum, mean, and minimum edges of ice for (a) winter (June 15) and (b) summer (Dec. 15) (NAVAIR-50-1C-540 (1985–1986)).

A continuing point of emphasis here is that climate varies widely over regions with time. At least examination of the problem of the cryosphere will help to place some measures of variability on climate in its totality. The great ice sheets and glaciers of the polar regions affect the “status quo.” Icebergs and ice floes illustrate the dissolution, but the snow source continues. Only if the two balance will there be a continuation of the “status quo.” Zwally et al. (1983) present “Antarctic Sea Ice 1973–1976.” This is an excellent publication in which color presentations of the satellite passive microwave observations help the reader. Figures 3-5 and 3-6, respectively, show the June and December maximal and minimal ice edges of the Arctic and the Antarctic (NAVAIR 50-1C-540 (1985–1986)). The U.S. Naval Polar Oceanographic Center (1982) presents polar stereographic charts of the Antarctic ice sheets 1981–1982 and for the Arctic sea ice, eastern and western portions.

Zwally et al. (1989) and Zwally (1989), respectively, discuss the measurement of the Greenland ice sheet and the interpretation of this measurement. Satellite observational data are used. These papers attempt to make some assessments of the exchange of water (solid) from the Greenland and Antarctic ice sheets to the waters of the oceans and the passage of water (vapor) from the oceans to and the deposition of this vapor as ice on the Greenland and Antarctic ice fields and to the other world regions. The impact of their study is as follows: (1) The rise in sea level created by the melting of the ice sheets will be much, much less than present scenarios indicate, and (2) warming of the ocean waters will provide development and enlargement of the ice sheets.

Dunbar (1987) discussed an interesting phenomenon under the title, “Arctic Seas That Never Freeze.” He describes the aquatic oases known as polynyas. There, the air temperatures may be, as he indicates, near  $-37^{\circ}\text{C}$ . The water steams; i.e., the evaporating water, rising, becomes visible upon condensing. Dunbar (op. cit.) indicates that Antarctic polynyas exhibit haline convection. The implication is that haline convection also occurs in the Arctic polynyas. These polynyas can be as large as inland seas. These are food sources for prey and predator alike, including man. See also Dunbar (1987) for changes in the Canadian Arctic since 1800.

Comiso and Gordon (1987) and Gordon and Comiso (1988) also report on the Weddell polynyas of the Antarctic. Both coastal and open ocean polynyas are located in the Weddell Sea region. The coastal polynyas are extensive. It was not until 1973 that satellite passive microwave sensors opened up a new potential to survey the Earth. This opened a new window through which to observe the previously inaccessible regions. Open ocean polynyas

exist in the interior of the great polar ice sheets. These areas were at one time during the 3-yr period (1973–1976) base for this particular report, about 350 by 1,000 km in size, according to Gordon and Comiso (op. cit.). These large, open seas vent considerable energy, create vast food sources for the food chain participants, and influence and are influenced by the ocean currents. These polynyas do not form every year. Their appearance in the same neighborhood during recent years implies that favorable conditions for formation continue. An increase or decrease in the number of years of appearance would be an indication of a change in climate in the polyna region.

The authors (Gordon and Comiso) speculate that the bottom configuration in the neighborhood of the Maud Rise is a control in the maintenance of favorable formation and dissipation currents. This report by Gordon and Comiso (op. cit.) and others is simply exciting in the vast potential available to permit a better understanding of the exchange processes of the geosphere with a resultant better comprehension of the interactions creating, modifying, and controlling global climate.

Gordon and Comiso (op. cit.) describe the control and modification procedures of the oceanic currents in the neighborhood of this one large Antarctic open ocean polynya. Control of ocean temperatures to 2,600 m is indicated. The scenario of this ventilation is important to the understanding of the interaction of atmospheric and oceanic chemistry, physics, and frontal and mass characteristics of both the region. The exchange of gases, such as oxygen (O<sub>2</sub>), CO<sub>2</sub>, carbon monoxide (CO), and methane (CH<sub>4</sub>), is an important feature. The ionic exchange of elements occupies an important niche. All salts tend to be ionized and hydrated in water. For example, sodium (Na) is transported separately from chlorine (Cl). Their combination as in the dry state as NaCl cannot exist in water solution. On the other hand, changes of pH and assemblages of complexes may permit interaction. Various compounds may be dissociated or new compounds may be formed; e.g., CO<sub>2</sub> may be released or sequestered.

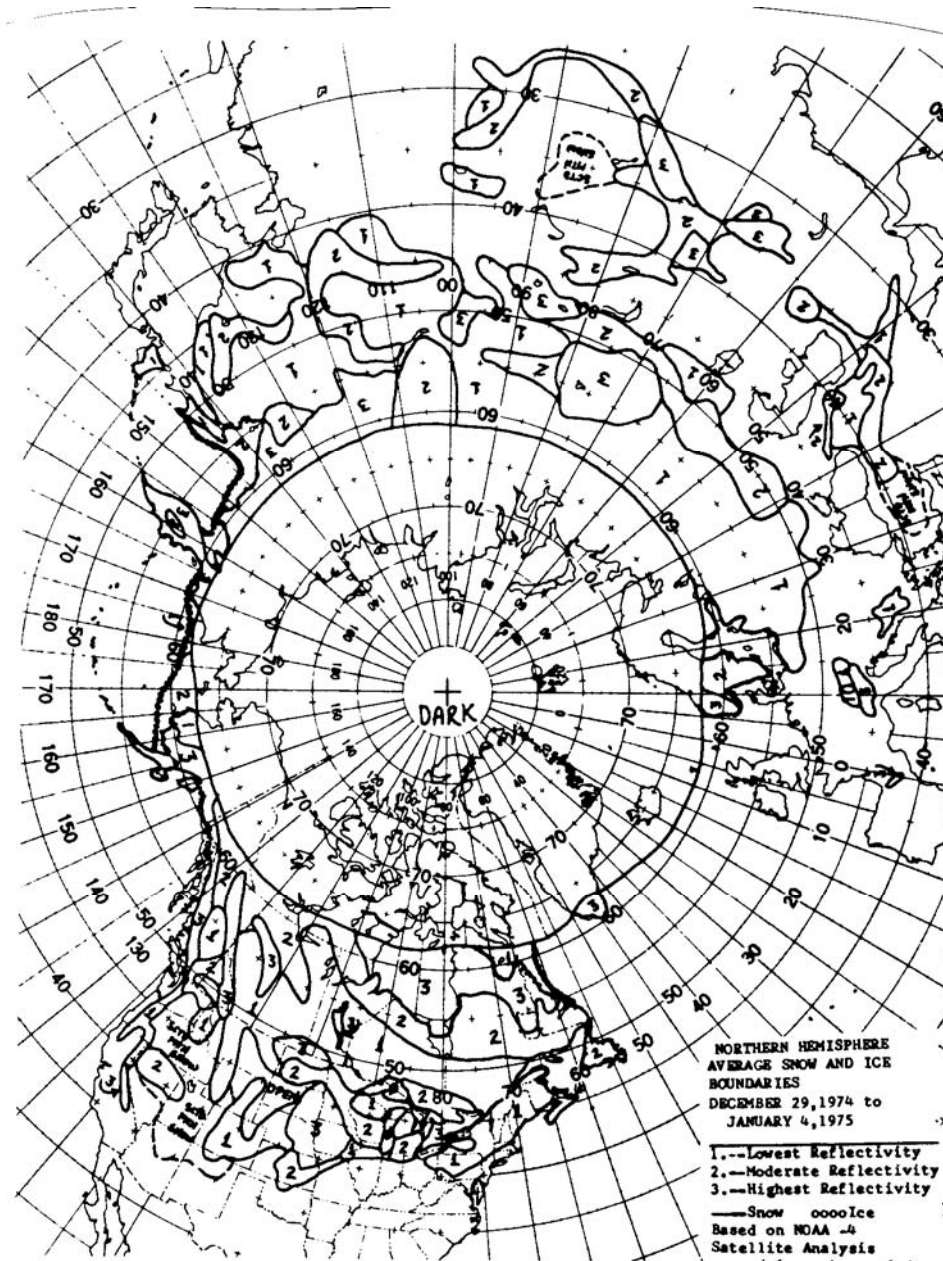
Schumacher et al. (1983) discuss the effects of a shelf polynya on flow and water properties in the northern Bering Sea in the vicinity of St. Lawrence Island. They infer from their study, among other things, that ice formation and the resulting brine rejection affects the flow in the vicinity of these polynya which often form. This brine rejection then is assumed to be an important component of the regional salt budget and in the production of deep, cold saline currents.

Topham et al. (1983) investigate a polynya in the Canadian Archipelago, who deduce that sufficient heat is lost through these polynyas to affect the water columns below. The water below is generally well above freezing temperatures and is brought into these areas by tidal currents flowing across the shallow sill connecting the Dundas and Devon Islands.

Complementing figures 3-5 and 3-6 (Matson, Ropelewski, and Varnadore (1986)) author the National Oceanic and Atmospheric Administration (NOAA) Atlas, an atlas of satellite-derived Northern Hemisphere snow cover frequency. They provide a listing of the NOAA/National Environmental Satellite, Data and Information Service (NESDIS) satellites and sensors used. The very high resolution radiometer, advanced very high resolution radiometer, and the visible infrared spin-scan radiometer primarily are available for North America. The program encountered the usual problems of instrumental variation, degradation, and drift. Their charts show the average snow and ice cover. Figures 3-7 and 3-8 taken from Matson et al. (op. cit.) show snow and ice information, respectively, for the periods December 29, 1974, to January 4, 1975, January 16–22, 1984, and the 15-yr period of 1967–1981. The authors also discuss the problems associated with the analyses. Other presentations show monthly seasonal and annual percentage frequencies in both digital and analyzed contour values of the digital numbers. The above figures show the digital map or chart printouts. By the time this Technical Publication reaches the reader, another decade or more of data will have become available. New analyses will permit a view between the Northern Hemisphere snow cover periods of 1967–1981 and the succeeding period.

Permafrost regions are a part of the cryosphere. These regions, due to their pressure depths and temperatures, are one of the many governors of climate. These regions, along with regions in ocean sediments, offer

potential vast storehouses of hydrocarbon and other gases. These are discussed in more detail in section 11.8, the section on CH<sub>4</sub>. Figure 3-9 is a map showing the depth to the base of the deepest ice-bearing permafrost as determined from well logs on the North Slope of Alaska: U.S. Geological Survey Oil and Gas Investigation Map OM-222, Collett et al. (1989) and Collett (1991). Note the 600-m depths just east of Prudhoe Bay. This is only one small portion of the Earth's permafrost regions.



(a)



### 3.5 Atmosphere

Thin and tenuous as it is, the atmosphere covers or surrounds the lithosphere and the hydrosphere. The combined depths of the atmosphere and the hydrosphere in relation to the globe of the Earth is as the thinness (thickness) of an orange peel to the orange it covers. The orange considered here is an orange with a thin skin.

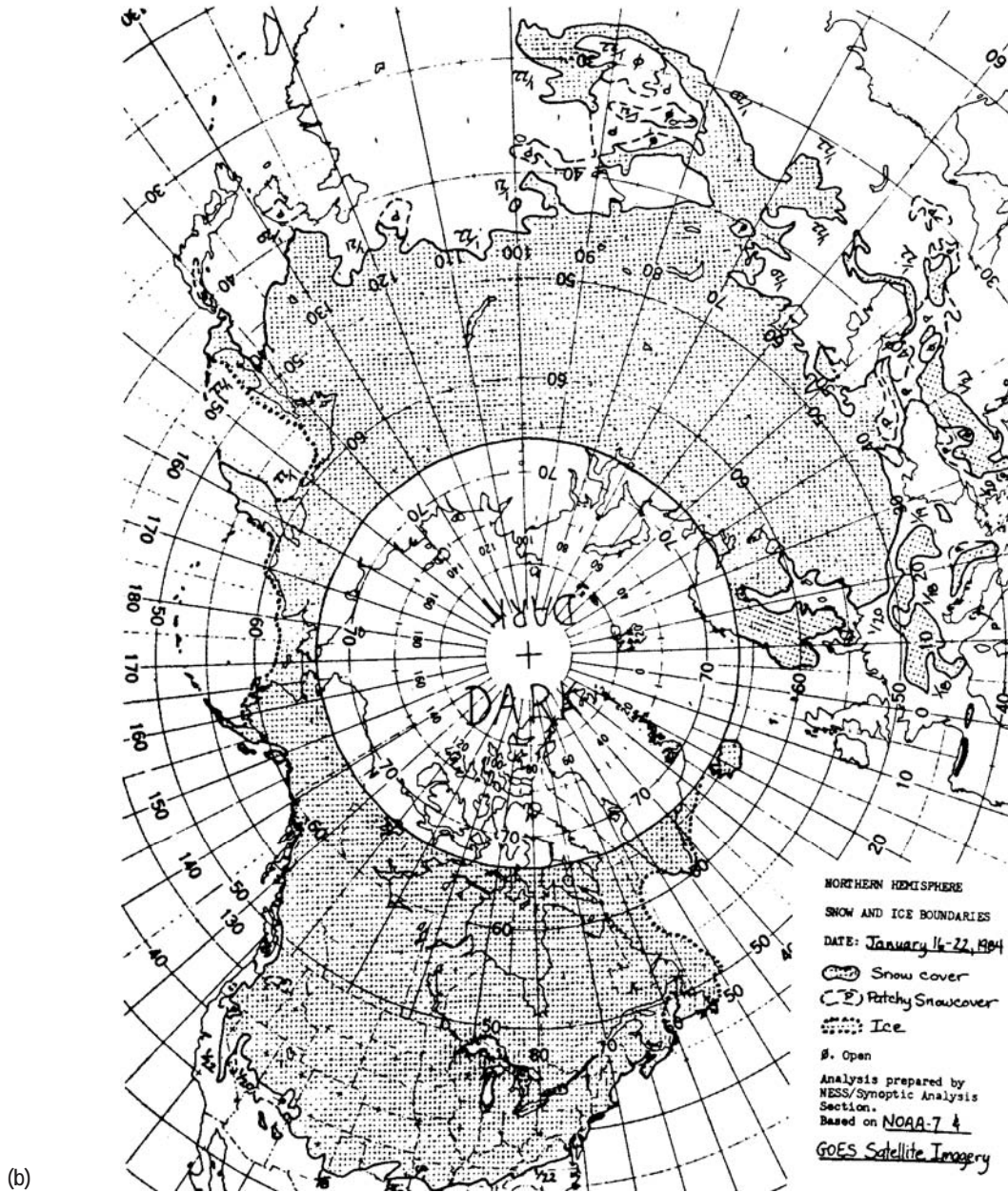


Figure 3-7. NESDIS Northern Hemisphere weekly snow and ice cover chart for (a) December 29, 1974, to January 4, 1975, and (b) January 16–22, 1984 (courtesy of NOAA; Matson, Ropelewski, and Varnadore (1986)).

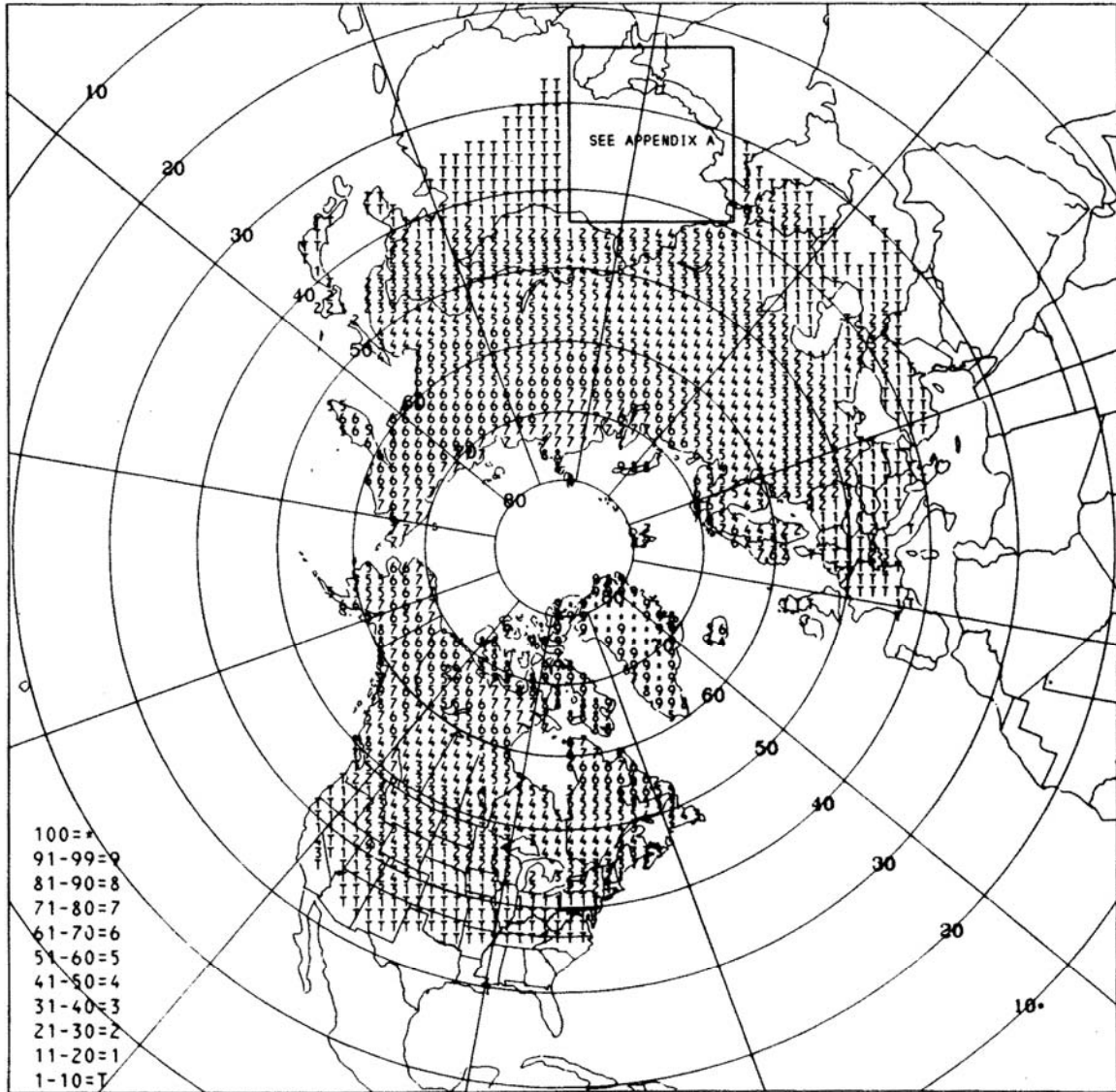


Figure 3-8. Fifteen-year annual snow cover frequency map (1967–1981)  
(courtesy of NOAA; Matson, Ropelewski, and Varnadore (1986)).

Walker (1977) discusses the evolution of the atmosphere. He discusses its chemistry with some of the more salient aspects of interaction. The Stanford Research Institute (SRI) (1961) study presents chemical reactions in the lower and upper atmosphere.

The reader is referred to volume 4 of the *World Survey of Climatology* for detailed discussion of the free atmosphere. The reader's attention is drawn to (1) the U.S. DoD Air Force Cambridge Research Laboratory (AFCRL), U.S. Air Force (USAF) publications, Handbook of Geophysics (1960, 1985), (2) Thomas F. Malone, Editor (1951), The American Meteorological Society 1951 Compendium of Meteorology, and (3) the U.S. Standard Atmosphere, 1976 joint publication of NOAA, NASA, and the USAF.

Just as the interior Earth has its various spheres, so does the atmosphere. Though these are covered in detail in the above references, the primary spheres are indicated again. The spheres are the tropo-, strato-, chemo-,

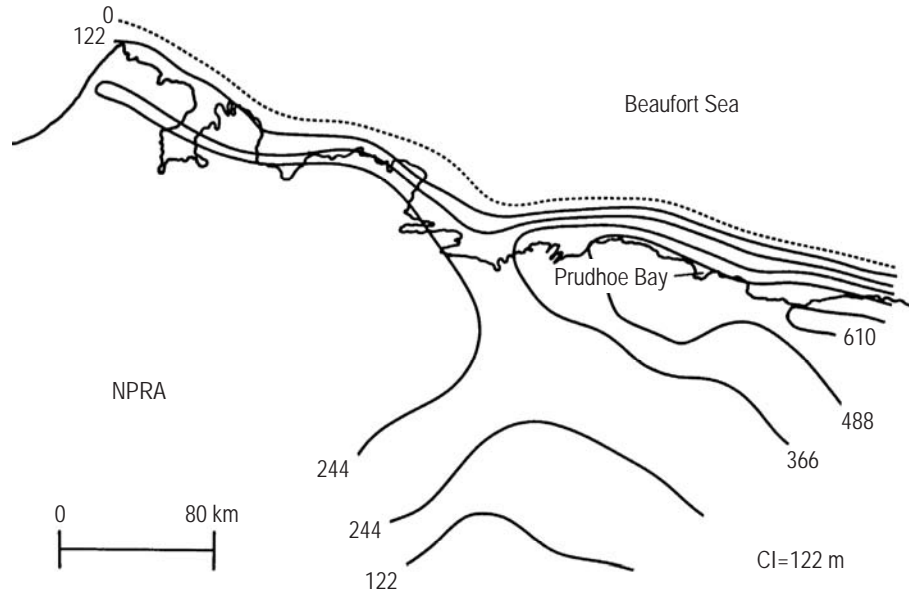


Figure 3-9. Permafrost map showing depth to the base of the deepest ice-bearing permafrost in the region of the National Petroleum Reserve in Alaska (NPRA) south of the Beaufort Sea. Prudhoe Bay lies near the maximum depths of the ice-bearing permafrost. Isoline depths are shown in increments of 122 m (adapted from Collett et al. (1989)).

homo-, iono-, thermo-, hetero-, and exosphere. Some of these, in their definitions, overlap others. Just as in the interior of Earth, there are discontinuities, sometimes rather tenuous in definition as well as existence, which separate the various spheres. These are the pauses, the tropo-, strato-, homo-, etc. Different authors classify some of these differently.

See U.S. DoD/USAF (1960, op. cit.) for details. The atmosphere is well-mixed in the troposphere, hence its name, but as greater altitudes are reached, such as those of the thermosphere and ionosphere, there is a tendency for the chemical elements and compounds to separate into layers determined by masses, gravitational forces, densities, and ionic forces. See also Smith et al. (1989).

Figure 3-10 and 3-11 show some of the spheres and pauses mentioned above. In addition to the single model temperature curve, averages and extremes are indicated by dashed lines and by symbols. The tabular atmosphere values available in volume 4 of this series are based on the 1962 U.S. Committee on the Extension to the Standard Atmosphere (COESA) model. This model atmosphere has been updated in the 1976 U.S. Standard Atmosphere mentioned above. Since tabular material is available in the last and, in a sense, duplicates the lower atmospheric portions, no tables are presented here. See section 6 for pressure. Warneck (1988) and Goody and Yung (1989) provide tables by height levels to 1,000 and 90 km, respectively, from the 1976 U.S. Standard Atmosphere. Those who need data by pressure levels may refer to the U.S. Standard Atmosphere. As these are for a global atmosphere, some supplementary atmospheres are available for different latitudes and for different seasons. See Sissenwine (1969). Sissenwine (1969) states, "The most unsophisticated, yet the most important, single presentation of upper air climatology is a Standard Atmosphere. To scientists, it is a starting point for any scientific endeavor that involves experimentation in the atmosphere." It becomes more important in today's intense interest in human interaction with the environment. Huschke (1959) defines the Standard Atmosphere as "a hypothetical vertical distribution of atmospheric temperature, pressure, and density which, by international agreement, is taken to be representative of the atmosphere for purposes of pressure altimetry calibration, aircraft performance calculations, aircraft and missile design, ballistic tables, etc."

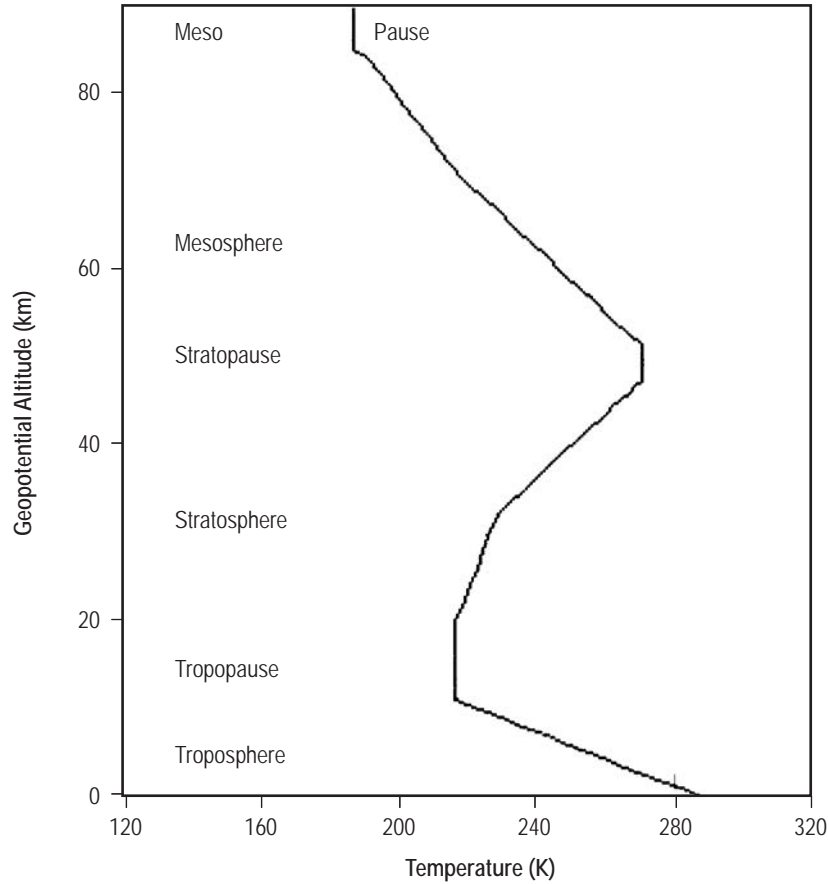


Figure 3-10. Temperature (K) versus geopotential altitude (km) illustration indicating some spheres and pauses (adapted from NOAA and others, U.S. Standard Atmosphere (1976)).

According to Minzer (1962), the French adopted a first version of a Standard Atmosphere. This was before the discovery of the tropopause phenomenon. Interest has been maintained and development continues in the updating of the Standard Atmosphere and supplementary material in both scope and material. For example, there are the supplemental atmospheres mentioned and given by Sissenwine (1969). In addition, molecular weights, speed of sound, mean free path, particle speed, collision frequency, thermal conductivity, etc., are provided. To these, it is almost certain that Standard Atmospheres will contain the vertical and global distributions of aerosols, electromagnetic radiation emission and absorption, atmospheric gases, and chemical species, notably the trace gases and radicals. The reader may refer to (1) the U.S. Standard Atmosphere (1962), (2) the U.S. Standard Atmosphere Supplements (1966), and (3) the U.S. Standard Atmosphere (1976). The editors or co-chairmen are, respectively, (1) Dubin, Sissenwine, and Wexler (1962), (2) Dubin, Sissenwine, and Teweles (1966), and (3) Dubin, Hull, and Champion (1976). See section 6 for a table of temperatures, pressures, densities, scale heights, number densities, and molecular weights versus altitudes.

As an approach to supplemental atmospheres, see the U.S. Navy publications, U.S. Marine Climatic Atlases, and the point (station) atmospheres produced by NASA.

The atmosphere is gaseous in nature though it does support some particulate matter. Dry air is composed of many gases (percent by volume and by mass), primarily the major gases nitrogen ( $N_2$ ) (78.09, 75.51), oxygen ( $O_2$ ) (20.95, 23.15), and argon (Ar) (0.93, 1.28) (Haurwitz (1941), E. Glueckauf (1951)). Trace amounts of

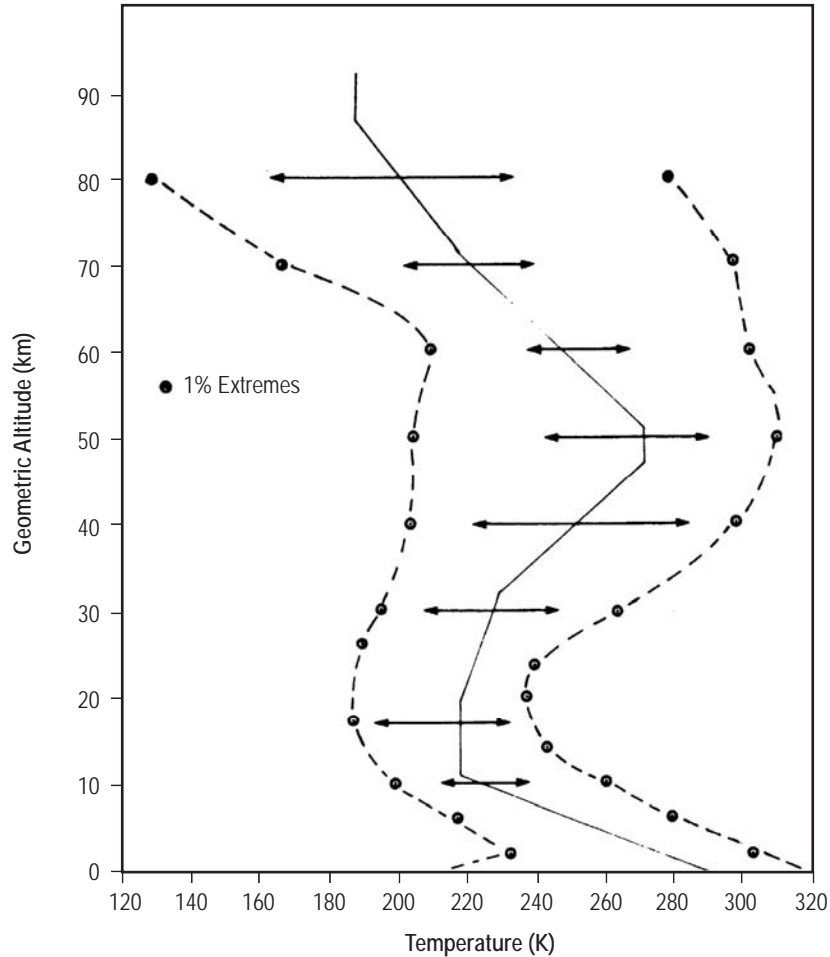


Figure 3-11. Temperature (K) versus geometric altitude (km). The horizontal arrows show the ranges of the monthly means over the globe. The estimated envelope (1 percent) covers the extremes for the warmest and coldest month irrespective of location (courtesy of NOAA and others, U.S. Standard Atmosphere (1976)).

other gases exist. Two gases in more than trace amounts, especially in their effects, are water ( $H_2O$ ) (0–4 percent) and  $CO_2$  (0.03, 0.05), and may be termed minor gases. See also the discussion by Miller (1960). As the amounts of  $H_2O$  and  $CO_2$ , the minor gases, change as well as the remaining trace gases and particulates change, the percentages given above must continually be adjusted. But the adjustments will be small. Because water occurs in the lithosphere, composes the major portion of the hydrosphere, and is an important minor constituent of the atmosphere, only from the viewpoint of quantity, it is discussed in more detail in later sections. Methane and the oxides of nitrogen and sulfur may play a larger role than many have considered. These, along with the triatomic oxygen, ozone, perhaps in their combined effect, are the greatest combination of natural climate markers and/or modifiers. Some of these may be in aerosol, colloidal, or hydrated form. Much has been written on each of these. The reader is referred to the general literature. These and other trace gases, such as radon, and their potentially considerable influences, will be discussed later. All atmospheric gases except water tend to remain in their most stable state, gas, within the lower portion of the atmosphere. This is because their phase change temperatures are lower than the usual temperatures of the atmosphere.

The speculative subject of a nuclear winter (Oliver and Fairbridge, pp. 625–627, op. cit.) or a tenfold increase in dust and aerosols from volcanic eruptions, are but two of the many potential scenarios which may be postulated. A review of the current literature discloses no consensus among the participants. See Turco et al. (1983), Covey, Schneider, and Thompson (1984), Malone et al. (1986), and Covey (1987) for opinions concerning particular scenarios. See Turco et al. (1990) for specific references to smoke with respect to a nuclear winter. This particular question may no longer be important if complete radiational devastation develops. Nothing animate will survive.

Earth, at least as far as is known now, is the only planet in this or any other star system that has regional climates hospitable to life as we know it. The aspects mentioned previously indicate that Earth system supporting climates is incredibly complex and interactive. Being such, any change at any one point will be transmitted, in time, through the system with all attendant interaction and reactions. This buffering and counterbuffering within the solar system and the Earth's geophysical and geochemical realms may seem to imply to some an animate system or a system with animate characteristics (Lovelock (1979)). The topography of the lithosphere provides constraints and restraints for the flow of the hydrosphere and the atmosphere. The valleys, ridges, trenches, basins, and the continental shelves forming the bottom topography of the hydrosphere, the cryosphere, and the continents themselves provide some of the constraints and restraints. Flow is stopped, impeded, slowed, increased, or redirected by these physical features. The motion imparted to the three spheres by the dynamic forces involved in the Earth's spin is modified by their interaction with the atmosphere as well as by the restraints and constraints mentioned above.

Each of the features discussed is important in itself. Not one of these can be considered, in the climate sense, by itself, for each interacts with the other. Buffering does occur. Weather and climate sense as we know them result from the actions and interactions of Earth's lithosphere, hydrosphere, atmosphere, and the energy received from the Sun. In iteration, weather is a state over a shorter time period than climate. Weather here is considered to be essentially an instantaneous state, while climate is a measure of state over any selected time period.

### 3.6 Water

Water of the hydrosphere is briefly discussed in section 3.3.

Inextricably water is an essential part of life and the climate in which life exists. It is present in the lithosphere, hydrosphere, and the atmosphere. It is present in any part of the universe where its ionic parts can merge and coalesce. According to estimates (Vinogradov and Linnell (1971)), in the lithosphere, it amounts to  $8 \times 10^{23}$  g as water of hydration, in the hydrosphere as  $14 \times 10^{23}$  g as liquid water, but in the atmosphere, it is a variable and erratic zero to 3–4 percent by volume. Almost by definition, it constitutes more than 96 percent of the hydrosphere. Its effect in the lithosphere, the hydrosphere, and the atmosphere is strong indeed.

In all three forms—vapor, liquid, and solid—water may be transported over all global regions. Transported within the atmosphere as vapor, it changes the radiative characteristics of the atmosphere as well as serves as an intercepting shield absorber, radiator, or filter for radiation. In the liquid and solid form in small sizes—visible to the eye—clouds intercept solar energy, reflecting—in both a backward and forward sense—portions of the energy, thereby changing the albedo over a particular geographic point. Clouds intercept, absorb, and reradiate the long wave terrestrial radiation, thereby acting as a blanket, conserving the energy between the Earth's surfaces and the clouds themselves. The passage of water from the hydrosphere to the atmosphere and its return to the hydrosphere directly through precipitation on the oceans, through percolation, through the rivers, and from the melting of the cryosphere, completes a cycle called hydrologic.

Thus, outside of the long-term astronomical, genetic, and solar system effects, water in its varied forms and mixtures and its transport serves as one of the greater, if not the greatest, immediate as well as long-term climate

modifier. Perhaps modifier is not the correct word. Only ammonia with a specific heat of 1.23 exceeds the specific heat of water defined as 1. Water's heat of vaporization is the highest of all known substances. Its electric constant is higher than almost all other pure liquids except hydrogen cyanide and some amides (Vinogradov and Linnell (1971)). Thus, water acts as a control or a mediator, though through its change of state process and transport, it certainly acts as a modifier. If not the greatest, at least in combination with the oxides, carbon, and nitrogen, along with methane, the four, as mentioned previously, may provide the greatest modifier combinations. Addition of particulates, of other aerosols, and of other trace gases certainly modifies the effects and may induce unexpected (to us) changes.

At this point, it is important to discuss in considerably more detail, but briefly, the truly wondrous pure water molecule in its gas, liquid, and solid forms. The single molecule as it is found in the vapor state now is considered. It consists of three atoms—one a central oxygen atom and two hydrogen atoms. There are seven isotopes of oxygen that are chemically alike but physically differ in mass. Three of these are differentiated usually as  $^{16}\text{O}$ ,  $^{17}\text{O}$ , and  $^{18}\text{O}$ . Similarly, there are three known isotopes of hydrogen but the heaviest,  $^3\text{H}$ , is unstable. These are usually designated as (1)  $^1\text{H}$ , (2)  $^2\text{H}$ , and (3)  $^3\text{H}$ , or (1) H, (2) D, and (3) T, respectively. The lightest of the three oxygen isotopes comprises  $\approx 99.757$  percent of the total oxygen (Ross (1975) and Malone (1951)). The lightest of the three hydrogen isotopes comprises  $\approx 99.99$  percent of the total hydrogen. These percentages are not consistently precise because the heavier forms are continually increasing here on Earth, on the one hand, through radiation (cosmic) and planetary accretion and evaporative processes. The heaviest is being destroyed through radioactive processes. Also, sampling techniques may not be sufficient to provide a base more precise with a well-determined measure of variability. But taking the above figures as they are, and under the assumption of independence, that may or may not be true, the product of the three probabilities  $(0.9999)(0.9999)(0.9976)$  gives a probability of the lightest water as 0.9974. Urey, Brickwedde, and Murphy (1932) report the detection of  $^2\text{H}$ , deuterium (D) while Oliphant, Hartek, and Rutherford (1934) report the detection of  $^3\text{H}$ , tritium (T). Hall and Jones (1936) and Gabbard and Dole (1937) indicate the ratios of H to D and T as being, respectively, 6,500 and  $10^{18}$ . See also Dorsay (1940) and Hamm (1965). Malone (1951) gives the relative abundance of the oxygen atoms as 99.757, 0.039, and 0.204. There is another interesting factor; i.e., the electron spins may differ. In the case of hydrogen, there are at least six effective forms of the hydrogen portion and three of oxygen. The reader readily can understand that in combining two of the six hydrogen atom forms with one oxygen atom, there exists an enormous number of combinations and permutations. As the above discussion implies, the probability of a molecule containing a heavier isotope of hydrogen or oxygen is, for most practical purposes, very small. For present-day climate researchers into water, ice, and snow, these provide crucial information. By a curious coincidence, the freezing point of  $\text{D}_2\text{O}$  (heavy water) is very near the temperature of the maximum density of ordinary water,  $\text{H}_2\text{O}$ . See extensive discussions by Vinogradov and Linnell (1971).

The usual model assumed for the water molecule is the triangular form in a tetrahedral field. The oxygen atom is central and surrounded by four faces and four vertices. There is a hydrogen atom at each of two vertices. Electron pair sharing bonding (valences) are available at the other two vertices. Limiting geometric considerations imply that the central angle between the two hydrogen atoms, with the oxygen atom being at the vertex, would have a minimum of  $90^\circ$  and a maximum of  $120^\circ$  (Mecke (1929), Slater (1931), and Dorsey (1940)). They infer that the repulsive forces between the hydrogen atoms requires that the angle be more than  $90^\circ$ . The atoms are known to be in ceaseless motion but constraining in their relative tetrahedral positions. Deming (1975) and Condon and Odishaw (1958) consider that the angle should be  $109^\circ 28'$ . Deming (1975) deduces further that the placement of the two hydrogens—one at each of two vertices—causes a weakening of their repulsive forces, allowing the angle to decrease to  $104^\circ 38'$ . There are other points of view. Maron and Lando (1974) indicate an angle of  $104^\circ 45'$ . Experimental data (Dorsey (1940)) and others provide values from  $96^\circ$  to  $111^\circ$  with the maximum observed frequency between  $103^\circ$  and  $105^\circ$ . The usual value quoted in most books today is  $105^\circ$  (Neumann and Pierson (1966) and Ross (1975)).

The vibrational modes, the presence of or near presence of other molecules, the impact or near impact of nearby water molecules, the absorption of different wavelength (or wave numbers) energies, the emission of energy, and the apparent randomness of motion place tremendous stress on an individual molecule and its three atoms—two of hydrogen and one of oxygen. Some of the effects have the more or less descriptive terms of stretching, bending, scissoring, wagging, rocking, and twisting (Hollas (1987)).

With the knowledge that a simple water molecule consists of a complex of one oxygen atom with two hydrogen atoms, one could just stop there. But even today, the actual structure of liquid water remains unknown (Vinogradov and Linnell (1971, p. 206)). Vinogradov and Linnell state, “Its complexities (water) has defied the efforts of many physical chemists over the last 30 to 40 years. Although a number of models of the structure of liquid water have been proposed, so far none have been found to be entirely satisfactory in the sense of being able to account for all the facts known about liquid water.” Jacoby (1923) cited by Dorsey (1940) concluded that in  $\text{H}_2\text{O}$ , one of the hydrogen atoms was not as strongly held by the oxygen atom as the other. This feature is important in the breakup of the molecule. The sense of hydration seems to be straightforward enough. As the water molecule is polar, it tends to break under stress into the  $\text{H}^+$  ion and the  $\text{OH}^-$  ion. Either of these, or both, may be hydrated, i.e., surrounded or enveloped by water molecules; the hydrated hydrogen ion  $\text{H}_3\text{O}^+$  is known as the hydronium ion. The hydrogens of one water molecule or an ion attract the oxygen (vertices) of the surrounding molecules. In the liquid state, a shell of such hydrating molecular forms is thought to be soon enveloped also by a second shell of looser fitting hydrating molecules. See Vinogradov and Linnell (op. cit.). This process is brought about by the hydrogen bonding processes. This same hydrogen bonding feature is considered in the hydration of all ions where sufficient water is available. Some of the features remain in salts recovered in evaporation—salts retain the waters of hydration. Other models of the processes have been proposed. Some now are known. Much research needs to be done. The formation of shells is discussed further in section 11.8 on methane.

The water molecule has a dipole. It has three moments of inertia. There are many forces that affect atoms and molecules; some are attractive while others are repulsive. In water, there are three bonds that are pertinent to the present discussion and to a later discussion on clathrates. The strongest of these bonds are the covalent bonds, the weakest are the van der Waal's bonds, and the intermediate are the hydrogen (proton) bonds. For treatment of these, see Chang (1986), Fessenden and Fessenden (1982), Huheey (1978), Sanderson (1960), Sloan (1990), and Vinogradov and Linnell (1971). The energies required to break these bonds, respectively, for the van der Waal, hydrogen, and covalent bonds are 0.3, 5, and 102 kcal mol<sup>-1</sup> (Sloan (1990)). The concept of bonding—van der Waal's—was originated by van der Waal in 1890. Latimore and Rodebush (1920) promulgated the hydrogen bond concept from Lewis and Randall's laboratories. Lewis and Randall (1923) present equations for the van der Waal's effects. These bonds are very important because they, along with the dipole-dipole interactions and the partial charges on the atoms, give to  $\text{H}_2\text{O}$  its great heat capacity. See Fessenden and Fessenden (1986) who note that hydrogen bonds increase the boiling point over the expected; i.e., they inhibit the vaporization of water. For comparison, please note tables A-11-2 and A-11-12, which provide characteristics, among other gases, for  $\text{H}_2\text{O}$  and  $\text{CH}_4$ .  $\text{CH}_4$  has no hydrogen bonds but does have the van der Waal's and the covalent bonds. Under normal atmospheric pressure, the melting points for  $\text{CH}_4$  and  $\text{H}_2\text{O}$ , respectively, are 90.7 and 273.2 K, while the boiling points are 111.7 and 373.2 K, respectively. Respective differences are 21 and 100 °C. The molecules of  $\text{H}_2\text{O}$ , in whatever form it may be, are assumed to be in continual motion. There is a continually changing aspect with relation to any fixed point and to any other molecule or group of molecules. Even the proximity of another molecule or group of molecules and their mutual interaction has an effect on the relative positions of the atoms within the molecule. The molecule's orientation is affected. Therefore, the determination of the configuration of the water molecules can only be an average effect over many molecules. This is most difficult to assess. Those reporting results do not provide measures of variability. Perhaps this cannot be done at the present time. The differing results can only be understood by the writer as indicative, in part, of the difficulties involved still remaining, the differing techniques employed, and the general run of expertise available.



Much of this uncertainty may be due to the interactions of the van der Waal's effects, the hydrogen bonding process, and the covalent bonding. Here, the hydrogen vertices align or orient themselves with respect to the oxygen atom of a nearby water molecule. Similarly, the oxygen atom is guided to orient itself with a hydrogen atom of the neighboring water molecule. Thus, chains of water molecules may form. Branches of molecules may develop from the chains, and if extensive, clumps may form. These can form easily when the vapor state is nearing the condensation or sublimation temperatures. Such chaining or clumping will change the optical characteristics of the various resultant mixes. As the van der Waals forces and hydrogen bonding are weaker than the covalent bonding, the chains and clumps are not secure. The chains and clumps are in a constant change in length, size, and orientation. They need not be straight chains, spherical shapes, or any other predetermined shape. In fact, they may be quite amorphous. The atoms are in constant motion. In water, these motions can set up a resonance in the bonding processes that does enhance the formation of and the breaking of the hydrogen bonds. Stillinger (1980) proposes a model consisting of a random three-dimensional network of hydrogen bonds. Contaminants in water—both electrolytes and nonelectrolytes—will deform the proposed tetrahedral configuration of the water molecule. At least, as indicated before, consensus seems to point to a variable central angle of  $\approx 105^\circ$  for the individual molecule, but there remains assessment of variability to be determined.

The discussion above serves to introduce, in part, the hydration phenomenon, which will be discussed in a later section on trace gases, including  $\text{CO}_2$  and  $\text{CH}_4$ .

There are many anomalous features of the water molecule and its association with others of its kind. See Dorsey (1940). It, as well as other chemical elements, exists with the thermal constraints imposed by its position in the universe. The three general states—gas, liquid, and solid—exhibit imposition of these constraints. As noted previously, the great heat capacity (specific heat) and the great range between the solid and gas phases; i.e., the liquid phase, freezing and boiling points, give water its great importance. These are greatly influenced by the polarity of the molecule, by the particle charges on the atoms. Both of these create high intermolecular attraction through dipole-dipole interaction and the formation of hydrogen bonds (protonic bridges) (Sanderson (1960)).

Another of the characteristics of water that plays a most important part in the climate process is the density and its changes. As water vapor approaches the condensation point, there is an accelerating process of coalescence or association of the molecules (Ellis (1931) and Honigmann (1932)). See Dorsey (1940), p. 55. Speculatively, clustering and hydration processes are involved at this point. The transition is quite sharp as the heat of condensation is released and condensation level is passed. From this point, as energy (thermal) is lost to the environment (as the water cools), the density increases because the molecules simply decrease their physical activity. They require less space. The mean free path decreases. In all stages, the water has been relatively free to flow, but the peculiar tetrahedral effects of the molecules interferes more and more as the energy decreases. The molecules tend to settle into closer fitting configurations, as the oxygen and hydrogen atoms align and hydrogen bonds (protonic bridges) develop. The configurations are certainly not the lattice arrangements one might expect if the atoms in the molecules were oriented along a straight line. The hydrogen bonding features permit the development of pairs; triplets; long, twisting chains of molecules; clumps and/or clusters. The tendency to attain a close physical fluid management increases as the temperature approaches  $4^\circ\text{C}$ . At about  $4^\circ\text{C}$ , the loss of energy does not permit such easy flow, and as the temperature falls still further, the molecules rearrange themselves in a more rigid framework as a function of their triangular (tetrahedral) form. Thus,  $4^\circ\text{C}$ —as a point of maximum density for pure water—becomes a prime climate forcer. As the water approaches  $0^\circ\text{C}$ , the liquid structure expands slightly in a quasi-crystalline configuration. The process is not assumed to be equally rapid at all points. The process presumably proceeds by means of small groups rearranging their neighborhood structures and connections. As the environment extracts still more thermal energy, the molecules assume minimal energy crystalline forms seen in snowflakes, ice crystals, and in ice. This leads to a rapid expansion of  $\approx 10$  percent in volume. At about  $-10^\circ\text{C}$ , the crystalline mass (ice) does begin to contract but only to a slight extent.

Nine or more crystalline forms exist (Vinogradov and Linnell (1971)). These exist in the cryosphere under various pressure ranges, such as on and within glaciers and ice fields like those found in the Antarctic, the Arctic, and in mountain ranges or on isolated mountain peaks. The cubic forms with pentagonal and hexagonal open-face lattice will be discussed in the sections dealing with clathrates. Of course, the expansion of the liquid water to its ice form leads to an associated decrease in density. Thus, ice in its general occurrence and normal hexagonal form, as  $I_h$ , will tend to float on water. There is a decrease in vapor pressure above the ice, and water vapor from liquid water will tend to flow to it, condense on it, and freeze if the temperature is below the freezing point. More importantly, the ice is a good insulator and impedes the passage of thermal energy from the water below to the atmosphere. Its reflective capabilities increase with respect to water. Thus, it will change the absorption of solar energy at the surface. Both of these effects act to prevent the warming of the atmosphere immediately above the ice. This leads to the development of cold, dry air over ice. A similar effect is noted when the water vapor is changed to snow and falls over land. Cold, dry air masses develop. For the most dense form of ice known, see Kamb and Davis (1964).

The feature of the maximum density of pure water at 4 °C permits a good reference point. Thus, density of water as 1 may be established for 4 °C and standard pressure. Some forms of ice exist only under pressure fields of 20 kbar or more, where 1 kbar = 987 atm. See Vinogradov and Linnell (1971). This is equivalent to 2 GPa. It is pointed out here that increased pressure will lower the freezing point of water. Under extreme pressure, the density of ice may reach 1.5 (Vinogradov and Linnell (1971)). Its crystal structure is quite different and the resultant colors are not the same as in ordinary ice.

If, under usual atmospheric conditions, the fall of temperature is not too rapid as the temperature approaches 4 °C and the density of pure water approaches its maximum, the increasingly dense water—if only slightly disturbed—will permit the slow downwelling of the cooling, more dense water. Thus, under the assumption of pure water in lakes, in ponds, and in shallow waters, the thermal structure of the entire body of water approaches the temperature profile associated with a constant maximum density vertical profile of 4 °C. Rapid lowering of surface temperatures usually creates rapid downwelling and counter upwelling. Thus, lakes, ponds, and shallow estuaries may experience rapid overturning with resultant mixing of the muddy bottom material throughout the water layer.

Only in the laboratory is it possible to isolate pure water. Even in such water, the hydrating effects and the changing energy fields surrounding the water help the groupings in continual flux. Pure water is a relatively active agent. Any addition of a foreign substance to the substance water changes the characteristics of the substance as well as those of water. Because of its potential to interact with other substances, it is almost impossible to keep a specimen of pure water in a pure state. There are many characteristics that are changed about which there is considerable information. Even the addition of essentially inert material, such as carbon or dust, will change some of the characteristics. A common example of other than inert material is the addition of a salt to water. The salt is dissociated. For example, common table salt (NaCl), presumably in ionic form in a crystal, dissociates further into more distant sodium and chloride ions. Each ion is enclosed within a shell of water molecules; i.e., it is hydrated. As far as is known, all physical characteristics of water are changed, however slightly or greatly, by the addition of any material or substance. Among these are the boiling (evaporating) point temperatures, the freezing (melting) point temperatures, the conductances, and the temperatures at which maximum density occurs. The freezing points are lowered while the boiling points are raised. The temperatures of the maximum density lower faster than the freezing point. Though the temperature of maximum density is nearly 4 °C above zero for pure water, the temperature of maximum density with salinity of 40 percent is nearly essentially equivalent to 4 °C below zero (Dorsey (1940)). A salinity of 40 percent is essentially equivalent to 40 g of salt per 1,000 g of pure  $H_2O$ . The freezing point of pure water under 1 atm of pressure is 0 °C (by definition), while the freezing point of 40 percent saline water at the same pressure is near 2 degrees below zero. The two lines representing these characteristics intersect near a salinity of 25 percent, more precisely 24.697. The importance here is that a fraction of the water portion of the saline mixture, representative of the oceans (35 percent), will begin to freeze out before the mixture reaches maximum density. The ice thus formed will float. Graphs are presented by Sverdrup (1942), Sverdrup, Johnson, and Fleming (1942),

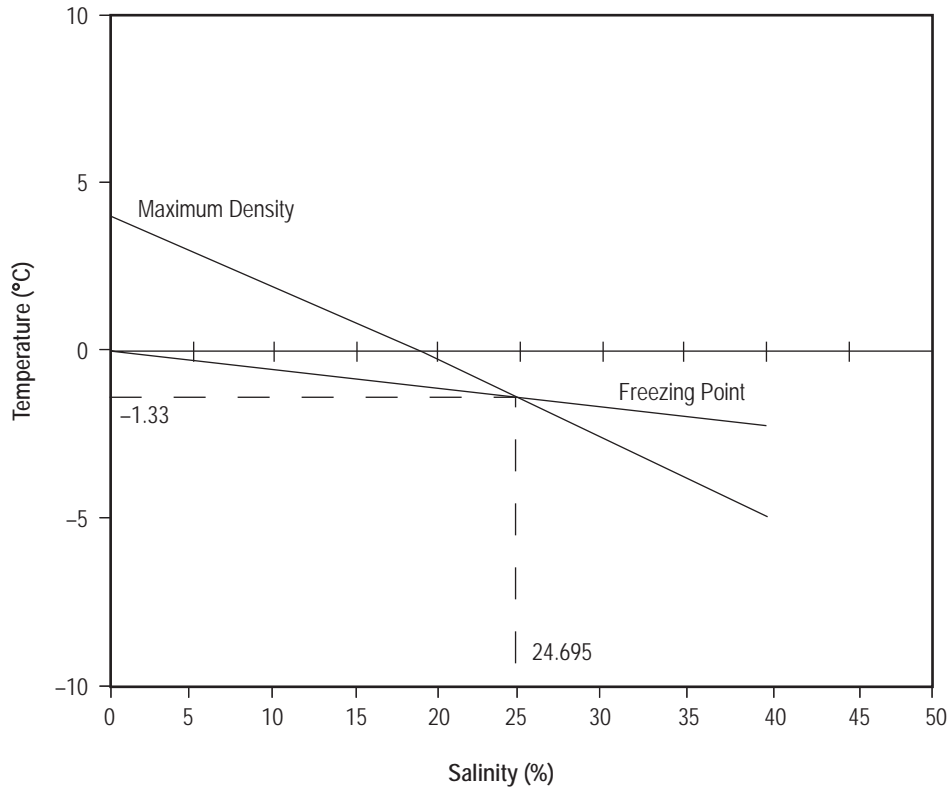


Figure 3-12. Temperature (°C) versus salinity (percent) showing freezing point with relationships to pure water and water with a salinity of 40 percent. Maximum density line is also shown (adapted from Neumann and Pierson (1966)).

Neumann and Pierson (1966), and Ross (1975). See figure 3-12 adapted from Neumann and Pierson (1966), apparently prepared from data given by Krummel (1907, 1911). By such fractionation, the ice crystals are surrounded with the remaining, more saline solution which will slowly percolate downward as more ice crystals form or as the ice crystals present an increase in size. In general, the forming ice crystal is separated from the hydrated ions so the parts that may touch are water to water. Thus, the ice crystal will tend to be composed of pure water surrounded by pure liquid water and by the hydrated ions. Water molecules in water, as indicated previously, may be broken apart; i.e., ionized into the hydrogen and the hydroxyl forms. This is infrequent but each of these ions may be and usually is hydrated. The hydrated salt ions and others—in the form of brine components—simply tend to flow downward due to their fluidity and density as compared to the crystalline water. If the freezing is too rapid, the brine may be captured and be held amongst the crystals. Subsequent repeated melting (thawing) and refreezing eventually will permit the brine to escape. In this manner, solids and particulates also are eliminated. Thus, one rarely finds such ice with sediment or other such impurities even in muddy rivers or lakes unless these have been deposited on top as dust after ice formation. By the same argument, almost pure water—suitable for drinking—may be found on the top of large ice sheets. The repeated thawing and freezing of the surface ice has essentially permitted all salts to percolate downward.

Millero and Scheiber (1983) provides an excellent update on the pressure-volume-temperature and thermochemical properties of sea water.



## 4. ATMOSPHERIC HEAT BUDGET

### 4.1 Thermodynamics

#### 4.1.1 General

There are several points at which this discussion might start. Statements concerning the energy and the thermodynamics of a system seem to be appropriate. “Planck refers to energy briefly as the facility to produce external effects” (Berry, Bollay, and Beers (1945)). Planck (1967, reprint) provides basic, interesting, and informative reading. As a general concept, this includes all those that are experienced knowingly or unknowingly—chemical, radiation, kinetic, mechanical, potential, radioactive, and other energies (following Holmboe, Forsythe, and Gustin (1945)). In terms of dimensional analysis where  $M$ ,  $L$ ,  $T$ , and  $\Theta$  represent mass, length, time, and temperature (energy), respectively, the dimensions of energy are  $[ML^2T^{-2}]$ . Huntley (1952) discusses dimensional analysis. In a qualitative way, appropriate body sensors could—or do—detect different energy levels. Thus, in a relative sense, a second body can be classified as cooler (colder), warmer (hotter), or the same. The temperature of one body can be said to be higher or lower than another. Heat is the energy transferred from one body to another. Temperature, then, can be said to be a measure of the internal energy of a body or system. As a measure of energy, the calorie, defined previously, or joule may be used. The calorie is  $\approx 4.186$  J of mechanical work. Of course, the calorie may be defined with any base, which is sometimes done.

Physical changes in material objects, solid, liquid, and gas were and are noted with varying degrees of qualitative “hotness” or “coldness.” These have been and are used to establish quantitative measures of the “hotness” or “coldness”; i.e., measures of the radiated energy.

Thermodynamic laws developed under the intense investigation of thermodynamic systems. There is no proof for any such statements but they indicate the way the systems seem to work. They are stated differently in each discipline, yet each of these must present the same salient idea.

#### 4.1.2 Zeroth Law

The zeroth law of thermodynamics:  $U(1) = U(2) = U(3)$ . “If two systems are both in thermal equilibrium with a third system then they are in thermal equilibrium with each other...systems in thermal equilibrium are said to have the same temperature” (Guggenheim (1950)).

“Two systems in thermal equilibrium with a third are said to be in thermal equilibrium with each other” (Zemansky (1951)).

#### 4.1.3 First Law

The first law of thermodynamics: (1)  $dQ = dU + pdv$ ; (2)  $dh = du + dw$ ; (3)  $w = U(2) - U(1)$ ; (4)  $dE = dQ - pdv$ ; and (5)  $Q = U_f - U_i + w$ . The first law of thermodynamics is a statement concerning the conservation of energy for a thermodynamic system. It is a statement of the physical changes that take place when heat (energy) is supplied to a system or when the system supplies energy to some other system. The internal energy is increased or decreased, respectively. The energy exchange during a change of state from or to a solid, liquid, or gas depends upon the path chosen.

“The first law, described equally well by each equation above, may be described also by the following statements. ‘If a system undergoes a small change in which it remains close to thermal equilibrium and the quantity of heat energy entering through the walls is  $dQ$  while the volume increases by  $dV$  against a pressure  $p$ , then the change in internal energy  $dU$  is given by  $dQ = dU + pdv$  which expresses the fact that the system only exchanges energy with its surroundings by taking in heat  $dQ$ , or by doing external work  $pdv$ ,” according to Condon (1958).

“Mechanical energy and heat are equivalent to each other and interconvertible” (Holmboe, Forsythe, and Gustin (1945)). “If a system is caused to change from an initial state to a final state by adiabatic means only, the work done is the same for all adiabatic paths connecting the two paths” (Zemansky (1951)). “The first law is merely a statement of the principle of the conservation of energy, according to which energy cannot be created nor destroyed” (Getman and Daniels (1931)). “The work required to bring a thermally insulated system from one completely specified state to a second completely specified state is independent of the source of work and of the path through which the system passes from the initial to the final state” (Guggenheim (1950)). “Heat added to the system between initial and final states equals the increase in internal energy of the system plus the work done by the system” (Berry, Bollay, and Beers (1945)). The first law is a statement of the physical changes that take place when heat (energy) is supplied to a system or when the system supplies energy to some other system. The internal energy is increased or decreased, respectively. The energy exchange during a change of state from or to a solid, liquid, or gas depends upon the path chosen.

#### 4.1.4 Second Law

The second law of thermodynamics,  $dQ = TdS$ , may be stated in several ways (Zemansky (1951) and Berry, Bollay, and Beers (1945)). As given by Kelvin and Planck, the Kelvin-Planck statement is, “It is impossible to construct an engine which, operating in a cycle, will produce no other effect than the extraction of heat from a reservoir, and the performance of an equivalent amount of work.” From the Entropy Principle, “As a result of natural processes, the entropy of the universe increases.” From the Probability Principle, it is given, “As a result of natural processes, the disorder of the universe is increasing.” The last may be restated as “A system tends toward a state of maximum probability.”

Insofar as the Earth and all parts of the solar system itself is concerned, the second law holds. But the Earth system does have a strong input of energy, though at the mean distance of the Earth from the Sun (1 astronomical unit (au)), it is only about  $5 \times 10^{-10}$  of the solar output. This is the Earth’s energy budget and is an amount fairly well assured each year. This amount does vary slightly, depending on the actual distance and on the internal nuclear activity, compaction, and radiational processes. Thus, the Earth becomes a way station, intercepting energy, using this energy in varying ways, building or permitting the buildup of small, seemingly counterentropic systems, such as organisms, plants, animals, and man. For the moment, when alive, these are counterentropic, but when dead, the entropic process is resumed once more.

#### 4.1.5 Third Law

The third law of thermodynamics: “If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature: every substance has a finite entropy, but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfectly crystalline substances” (Lewis and Randall (1923)). Stated in yet another way, the third law is, “The entropy of a crystal at absolute zero is zero” (Getman and Daniels (1931)). Another way to describe the third law is, “It is impossible by any procedure, no matter how idealized, to reduce any system to the absolute zero of temperature in a finite number of operations” (Zemansky (1951)). See also discussions by Miller (1951) on energy equations and by Beers (1945) on thermodynamics and statics.

Guggenheim (1950) discusses the third law in terms of monoatomic substance for these are less complicated than others. The reader may refer to the above and many other references for additional detailed discussion and, in particular, to the Nernst Heat Theorem.

The above three laws of thermodynamics are statements concerning the matrix and boundaries within which the Earth's climate develops and is maintained. There are many other equivalent statements for each of these three laws. Fundamentally, energy (heat) and the measure of the internal energy changes provide a glimpse or aspect of climate genesis.

The four thermodynamic laws above—the zeroth through the third—involve the emission, absorption, and reemission of energy. Every physical unit of the universe is affected. Except for the latent energy stored in radioactive materials, there is an incessant exchange of energy. This interchange may take place in a continuum or provide through discrete receptive or emissive gateways or windows. The emission need not be in the same form as the reception. For example, the physical unit may receive short-wave energy but emit long-wave energy. The electromagnetic spectrum describes the continuum.

Please see appendix A, tables A-4-1 through A-4-3, for measures of physical constants. Some are used in this subsection while the others are used in other subsections. Appropriate references are made.

## 4.2 Radiation

Kessler (1985), vol. 1A, Flohn (1969), vol. II, and Yao (1981) of the series, “*The World Survey of Climatology*” thoroughly discuss the subject of radiation with particular emphasis on general principles and global aspects along with the subject of net incoming radiant energy at the surface and the energy balance near the ground level. This section includes only a small amount of the same information.

The concerted efforts of many individuals provide progress. Any one or more diverse goals or ambitions drive or lead the individuals or groups. Many scenarios produce, display, critique, retract, modify, accept, are forgotten, or are well disseminated. The progress in the last century is extraordinary. The development of better and far-reaching communications and exchanges of concepts and ideas plays an important role.

Planck (1899, 1900) introduced the idea of quanta in order to resolve the mental quandary of energy exchange, yet Kirchoff (1859) previously provided a facet of insight immeasurably helpful. A statement of Kirchoff's law is, “The ratio of the intensity of emission to the fractional absorption of a slab is equal to the blackbody intensity at the same wavelength and intensity” (Charney (1945)). There are others. Stefan (1879) experimentally derived and Boltzmann (1884) theoretically from thermodynamics derived what is known today as the Stefan-Boltzmann constant ( $\sigma$ );  $5.67032 \times 10^{-5} \text{ erg cm}^{-2} \text{ s}^{-1} \text{ deg}^{-4}$ .  $\text{Wm}^{-2} \text{ K}^{-4}$  also expresses the dimensional units. It is best illustrated by the relationship

$$E = \epsilon \sigma T^4 , \tag{4.1}$$

where  $\epsilon < 1$  is the emissivity of a gray body.  $\epsilon$  actually is a function of wavelength (Forsythe (1937)) and  $T$  is temperature (K). See Yao (1981). If  $\epsilon = 1$ , this represents blackbody emissivity. In essence, blackbody radiation is not encountered as  $\epsilon$  is always  $< 1$ , giving a graybody effect. However, as the grayness may be difficult to assess, and may be an inappropriate term, generally the blackbody model is used. Planck's radiation law relationship may be written in several forms, one of which is

$$E = 2 hc^2 \lambda^{-5} (\exp(hcT\lambda^{-1}k^{-1}) - 1)^{-1} . \tag{4.2}$$

Here,

$h$  = Planck's constant with a value of  $6.626176 \times 10^{-27}$  erg s  
 $c$  = velocity of light,  $2.998 \times 10^{10}$  cm s<sup>-1</sup>  
 $k$  = Boltzmann's constant equal to  $1.380662 \times 10^{-16}$  erg deg<sup>-1</sup>  
 $T$  = absolute temperature (K) of the body.

Planck's and Boltzmann's constants, respectively, are  $6.626176 \times 10^{-34}$  Js and  $1.380662 \times 10^{-23}$  JK<sup>-1</sup>. Please see tables in appendix A-11. Here, the units are changed. Equation (4.2) for energy in terms of wavelength may be rewritten in terms of frequency ( $\nu$ ) as in equation (4.3):

$$E = 2 h \nu^3 c^{-2} (\exp(h\nu k^{-1} T^{-1}) - 1)^{-1} . \quad (4.3)$$

As certain combinations of terms are constant, equation (4.3) may also be written as

$$E_\lambda = \nu^2 c^{-1} E_\nu = C_1 \lambda^{-5} \pi^{-1} (\exp(C_2 \lambda^{-1} T^{-1}) - 1)^{-1} , \quad (4.4)$$

where

$$C_1 = 2\pi h c^2 \quad (4.5)$$

and

$$C_2 = h c k^{-1} . \quad (4.6)$$

See Goody and Yung (1989). Numerically,  $C_1 = 3.241832$  Wm<sup>-2</sup>, while  $C_2 = 1.4387863 \times 10^{-2}$  mK.

As these formulae are universally used in the physical sciences, many texts contain discussions. A few of the others follow here: Planck (1967, reprint of 1897), Getman and Daniels (1931), Petterssen (1940), Haurwitz (1941), Berry, Bollay, and Beers (1945), Guggenheim (1950), Zemansky (1951), and Brunt (1952). Various sources provide slightly different values of these constants.

Nondimensional Planck curves may be used (Chantry (1984)). The following equations (after Chantry, op. cit.) will do this:

$$x = 0.01438786 \tilde{\nu} / T , \quad (4.7)$$

$$y = x^3 (\exp(x) - 1) , \quad (4.8)$$

where  $\tilde{\nu}$  is the wave number (waves per meter) and  $T$  is the temperature (K). Figure 4-1 illustrates the nondimensional Planck curve as described by Chantry (1984) and given as his figure 2.12, p. 90. Dimensionality may be restored as needed. Doing this provides the radiant power curves usually seen for the various temperature-wave-number combinations. Various combinations are seen in different textbooks and sources, such as in Haurwitz (1941) and in Byers (1959). See also Goody and Yung (1989) (fig. 1.1, p. 4).

Figure 4-1(b) is the same as (a) with added comments included as to the constants used and the relations shown above. The dimensionality is restored through the use of equation (4.8):

$$P = 1.25631 \times 10^{-10} y T^3 , \quad (4.9)$$



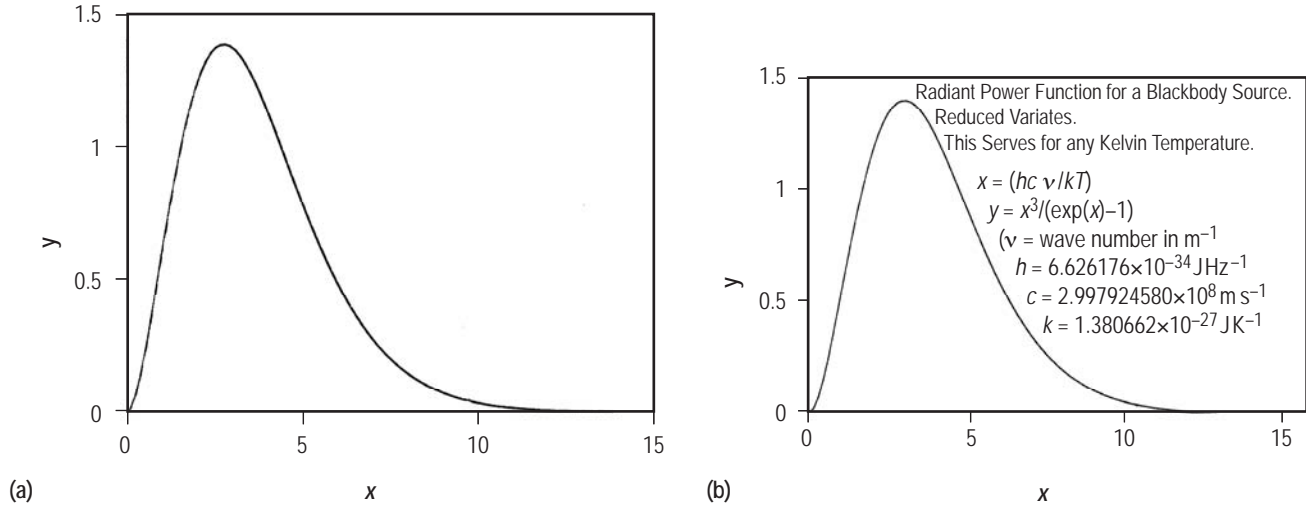


Figure 4-1. Nondimensional Planck radiation curve: (a) Abscissa and ordinate axes are in terms of reduced variables,  $x$  and  $y$ , so that a generalized curve shows. Here,  $x = 1.438786 \times 10^{-2} (\tilde{\nu})/T$  and  $y = x^3/(\exp(x)-1)^{-1}$ . The functional curve is  $F(\tilde{\nu}, T) = 1.25631 \times 10^{-10} y T^3$ .  $\tilde{\nu}$  is the wave number in  $m^{-1}$  (modified after Chantry (1984)).

which is equivalent to Chantry's (1984) equation (2.2.31), p. 89. The dimensions are wave number and  $P$  (power) in watts per square meter per meter ( $Wm^{-2}m^{-1}$ ). Figures 4-2(a)–(d) shows the families of curves, respectively, for 6,000, 5,000, 4,000, 3,000, and 2,000 K temperature ( $T$ ); 2,000, 1,500, and 1,000 K temperature; 1,000, 700, and 400 K temperature; and 400, 300, and 200 K temperature.

Figure 4-2(a) starts with the 6,000 K curve, which is the temperature usually associated with the radiating surface of the Sun. This same curve will be used later in the section on trace gases. Figure 4-2(d) illustrates the temperature curves of 400, 300, and 200 K, which encompass most of the radiating temperatures of the solid Earth, its atmosphere, and its ocean. See subsequent figures in section 4.5. These would indicate the radiation loss to the Earth if no intervening atmosphere or gases were present. The incoming radiation for the same temperatures would not suffer any loss either. However, the atmosphere does exist and, as such, absorbs radiation both on its way to and on its way away from the Earth. Relatively, the incoming solar radiation contains only a small fraction of the radiant power at small wave numbers (long wavelengths). The situation is reversed for the outgoing terrestrial radiation.

The nondimensionality indicated in figure 4-1(a) allows one to change the scaling, say with respect to figures 4-2(a) and 4-2(d). Thus, modification to these two curves can result in the two curves seeming to be almost the same if superposed. Some texts carry such representations. Care must be exercised to compare the energies involved.

Here, scaling features may change the shape of the curves. For example, if the wavelength is used as the abscissa, the radiation curves would show the inverse relationship where the wavelength is the reciprocal of the frequency. In either case, the shift of the maximum with temperature or radiant energy is clearly seen. Wien (Circa 1894) showed this relationship as

$$\lambda_{\max} T = \text{constant} \quad (4.10)$$

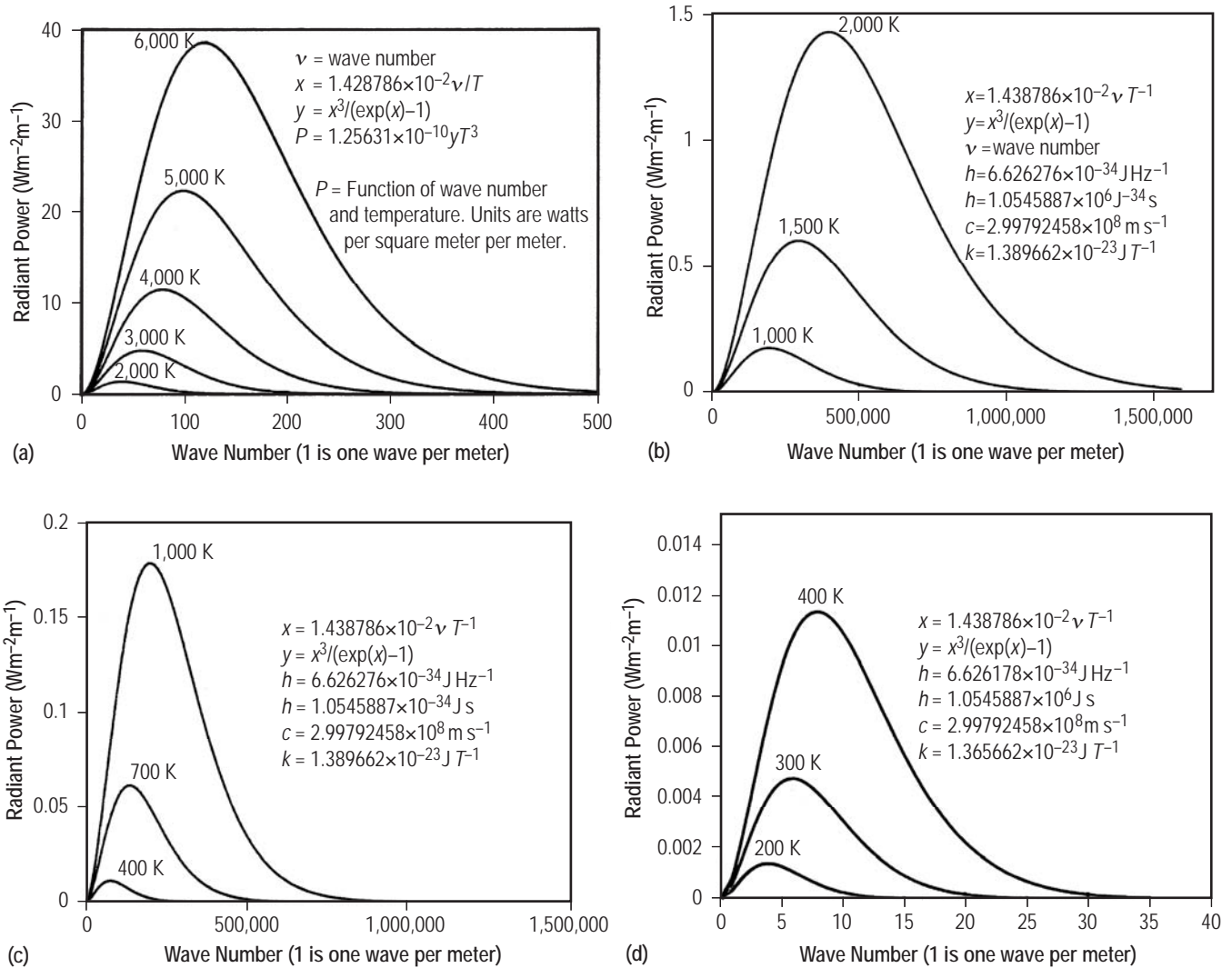


Figure 4-2. Radiant power function ( $\text{Wm}^{-2}\text{m}^{-1}$ ) for blackbody sources of (a) 6,000, 5,000, 4,000, 3,000, and 2,000 K temperature; (b) 2,000, 1,500, and 1,000 K temperature; (c) 1,000, 700, and 400 K temperature; and (d) 400, 300, and 200 K temperature (modified after Chantry (1984)). The constants and variables follow:  $x = (h\tilde{\nu})/kT$ ;  $y = x^3 / (\exp(x) - 1)$ ;  $\tilde{\nu}$  = wave number in  $\text{m}^{-1}$ ;  $c = 2.997924580 (10^8) \text{ ms}^{-1}$ ;  $h = 6.626176 (10^{-34}) \text{ JHz}^{-1}$  or  $1.0545887 (10^{-34}) \text{ Js}$ ;  $k = 1.380662 (10^{-23}) \text{ JT}^{-1}$ ; and  $F(\tilde{\nu}, T) = 1.25631 (10^{-10}) y T^3$ .

The value of the constant is 0.2897 cm per degree if the wavelength ( $\lambda$ ) is in centimeters. Mathematically, this may be solved by setting the first derivative of the equations above to zero. The hyperbola describes the position of the maxima. The wave number ( $\text{cm}^{-1}$ ) corresponding to  $\lambda_{\text{max}}$  is  $3.451 T$ . See Chantry (1984), p. 94. Visually, in the above figures, the shift of the maxima to the right with increasing temperature is seen.

The wave number  $\text{m}^{-1}$  is 1, where 1 is one wave per meter. The spectral intensities for wave number is  $\text{Wm}^{-2}\text{Hz}^{-1}$  and for wavelength is  $\text{Wm}^{-2}\text{m}^{-1}$ ; i.e., watts per square meter per Hertz and watts per square meter per meter.

Chantry (1984) provides a good discussion as well as tabular data that may be used to produce such theoretical blackbody radiation curves if one wants to use a small electronic calculator or computer. Such was done to produce the above curves.

Further discussion of radiation defers to the important section—section 11. There, the subject is the atmospheric gases, especially the trace gases.

### 4.3 Atmospheric Heat Budget

Housekeeping or bookkeeping on the radiation received from the Sun and the small amount emitted from the Earth itself is necessary. Only with such techniques can the budget of the Earth's radiational energy be determined. Here, the input from the interstellar regions is not accounted for. Not that it may be unimportant in the long run but because it is, though variable, small and really unknown. There are facets within the Earth's atmosphere that are also unknown and not accounted.

There are many models. London (1957) provides an excellent study of the atmospheric heat budget. This, of course, was not the first, nor will a later one be the last.

Books and journals on climate generally include discussions on radiation, both extraterrestrial (solar) and terrestrial (Earth). There are many; therefore, the discussion here is not too detailed. Forsythe (ed. (1937)) provides good discussions on the measurement of radiant energy. Deacon (1969) also discusses in some detail the radiation budget in his section on "Physical Processes Near the Surface of the Earth." Flach (1981) details many of the aspects in his "Human Bioclimatology." His figure 2 (after Trendelenburg (1961)) presents the well-known electromagnetic spectrum of oscillations. His figure 3 provides the spectral distribution of the energy of extraterrestrial (solar) radiation in  $\text{Wm}^{-2}$  and the relative brightness  $V$  of the human eye in relative units after Schulze (1970). Flach (1981) gives in table 2 (after Schulze (1970)) radiation amounts for extra terrestrial (solar) radiation. His figure 8 (after Landsberg (1963)) depicts generalized isolines of global radiation at the surface in  $\text{kcal cm}^{-2}\text{y}^{-1}$ . On a specific location, Hamburg, Germany (1955–1960), after Schulze (1970), and Flach (1981) show the mean annual variation of daily amounts of the radiation balance and its components.

Major et al. (1981) present world maps of relative global radiation. The World Meteorological Organization (WMO) Technical Note publication 177-WMO-557 presents the appropriate tables and maps for the annual and monthly values. Table 4-1—taken from that publication with permission—gives the annual and monthly values of the astronomical global radiation (AGR) in  $\text{MJm}^{-2}$ . Their table 2 provides spot comparison locations. One such spot is Wrangel. Figure 4-3(a) and (b)—from Technical Note 177 with permission (figs. 4.2.1 and 4.2.7, respectively)—illustrate the January and July relative global radiation derived from tabular data. The chart data are in terms of percentages of the actual to the possible (table 4-1 data); i.e., reflected global radiation. Satellite measurements were used to aid the analysis of data. The three assumptions were that the brightness values are strongly correlated with cloudiness, that cloudiness affects the global radiation that reaches the Earth, and that satellite brightness can be transformed into meaningful radiation parameters. See Miller (1971) referenced in section 9, clouds.

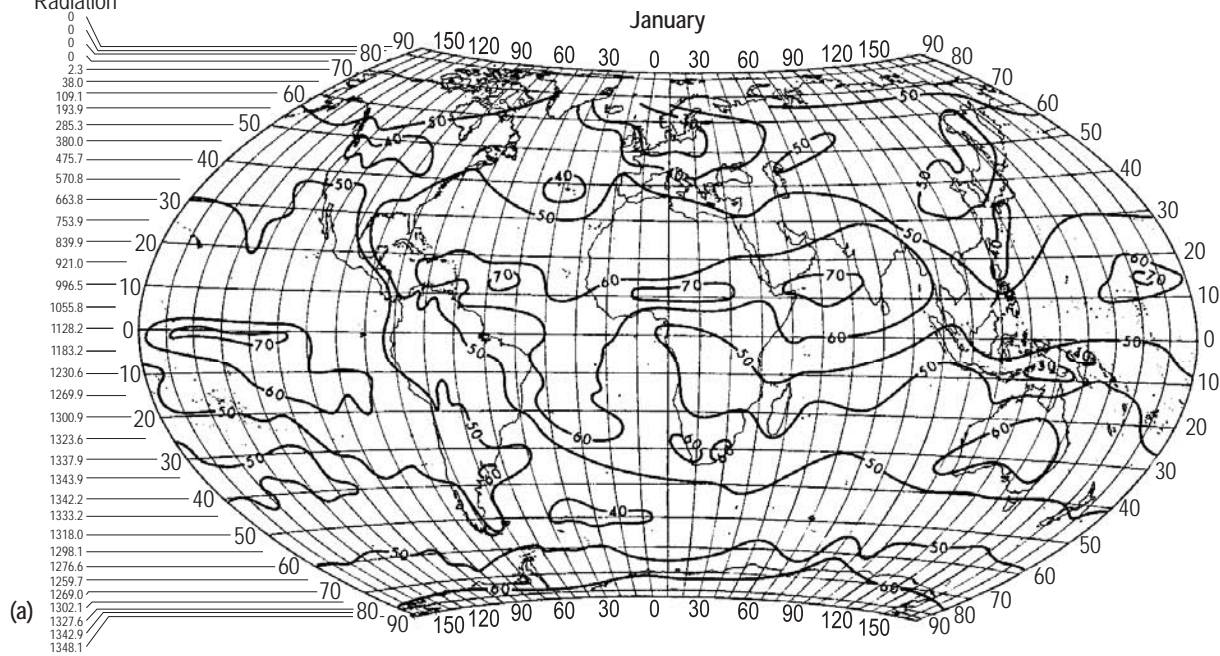
The AGR data range from about  $5,500 \text{ MJm}^{-2}$  in the polar regions to  $13,000$  in  $\text{MJm}^{-2}$  in the tropics annually. In January, the range is from about zero at the North Pole to  $1,300 \text{ MJm}^{-2}$  at the South Pole. In July, the range reverses. December data show a slightly larger range.

Kessler (1985) in his "Heat Balance Climatology," vol. 1A of this series, brings the reader up to date. His historical remarks are well worth reviewing by the reader. He discusses in detail the heat and radiation budget of the Earth-atmosphere system. As mentioned previously, this is a prime—if not the prime—element of climate. He then discusses in sequence the (1) net radiation at the Earth's surface, (2) latent heat flux on the Earth's surface, evaporation, evapotranspiration, and condensation, (3) sensible heat flux on the Earth's surface, and (4) heat flux into the

Table 4-1. Astronomical global radiation ( $\text{MJm}^{-2}$ ) (after Major et al. (1981)).

Latitude	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Year
90° N.	0	0	43.5	584.0	1,149.2	1,346.9	1,287.2	854.4	208.4	0	0	0	5,473.5
85° N.	0	0	76.1	582.0	1,144.8	1,341.8	1,282.3	851.2	238.2	2.4	0	0	5,518.7
80° N.	0	1.1	156.5	593.4	1,131.7	1,326.4	1,267.6	841.8	307.3	30.6	0	0	5,656.5
75° N.	0	23.3	251.7	634.7	1,110.0	1,301.0	1,243.3	843.5	392.8	93.7	0.2	0	5,894.4
70° N.	2.3	80.8	348.3	698.5	1,092.9	1,265.7	1,210.4	874.8	479.4	180.0	17.0	0	6,250.1
65° N.	38.0	157.4	443.5	766.0	1,106.9	1,231.3	1,196.6	924.1	563.7	272.5	73.3	12.5	6,785.8
60° N.	109.1	240.4	536.0	831.8	1,135.6	1,231.4	1,209.6	975.7	644.6	366.4	150.7	73.0	7,504.3
55° N.	193.9	325.6	624.7	893.6	1,165.9	1,240.0	1,227.7	1,024.9	721.0	459.6	236.5	152.2	8,265.6
50° N.	285.3	411.1	709.0	950.1	1,193.3	1,248.7	1,244.4	1,069.4	792.2	550.5	326.3	240.8	9,021.2
45° N.	380.0	495.2	788.0	1,000.4	1,215.6	1,254.1	1,257.1	1,108.0	857.5	638.1	417.5	334.3	9,745.9
40° N.	475.7	576.8	861.2	1,043.8	1,231.7	1,254.4	1,263.9	1,139.6	916.5	721.6	508.4	430.1	10,423.7
35° N.	570.8	655.1	927.9	1,079.9	1,240.5	1,248.5	1,264.1	1,163.9	968.7	800.1	597.5	526.2	11,043.0
30° N.	663.8	729.3	987.6	1,108.3	1,241.8	1,235.7	1,256.9	1,180.2	1,013.6	872.9	683.8	621.2	11,595.0
25° N.	753.9	798.6	1,039.9	1,128.6	1,235.1	1,215.7	1,242.1	1,188.5	1,050.8	939.4	766.3	714.0	12,072.8
20° N.	839.9	862.4	1,084.3	1,140.8	1,220.3	1,188.4	1,219.5	1,188.4	1,080.1	999.1	844.3	803.4	12,470.8
15° N.	921.0	920.2	1,120.6	1,144.5	1,197.4	1,153.8	1,189.2	1,179.9	1,101.3	1,051.5	917.0	888.5	12,784.6
10° N.	996.5	971.5	1,148.3	1,139.8	1,166.4	1,111.9	1,151.1	1,163.0	1,114.1	1,096.1	983.7	968.6	13,011.0
5° N.	1,065.8	1,015.1	1,167.4	1,126.8	1,127.6	1,063.0	1,105.6	1,137.8	1,118.5	1,132.6	1,043.9	1,042.9	13,147.7
0°	1,128.2	1,053.0	1,177.6	1,105.4	1,081.2	1,007.4	1,052.9	1,104.5	1,114.5	1,160.7	1,097.2	1,110.8	13,193.3
5° S.	1,183.2	1,082.5	1,178.9	1,075.9	1,027.5	945.6	993.4	1,063.3	1,102.0	1,180.2	1,142.9	1,171.8	13,147.3
10° S.	1,230.6	1,104.3	1,171.3	1,038.4	966.9	878.0	927.6	1,014.6	1,081.2	1,191.0	1,180.9	1,225.4	13,010.2
15° S.	1,269.9	1,118.1	1,154.8	993.4	900.0	805.2	856.0	958.7	1,052.2	1,193.0	1,210.9	1,271.2	12,783.4
20° S.	1,300.9	1,123.9	1,129.6	941.0	827.3	727.7	779.3	896.1	1,015.3	1,186.1	1,232.7	1,309.1	12,469.1
25° S.	1,323.6	1,121.7	1,095.8	881.8	749.4	646.5	698.1	827.4	970.7	1,170.5	1,246.3	1,338.9	12,070.7
30° S.	1,337.9	1,111.6	1,053.8	816.3	667.2	562.2	613.3	753.0	918.8	1,146.2	1,251.6	1,360.6	11,592.6
35° S.	1,343.9	1,093.7	1,003.8	745.0	581.4	475.9	525.8	673.8	860.0	1,113.6	1,248.9	1,374.4	11,040.2
40° S.	1,342.2	1,068.3	946.2	668.5	493.0	388.6	436.5	590.4	794.7	1,073.0	1,238.4	1,380.6	10,420.5
45° S.	1,133.2	1,035.8	881.6	587.5	403.1	301.7	346.9	503.8	723.5	1,024.7	1,220.6	1,380.0	9,742.4
50° S.	1,318.0	996.8	810.4	502.7	313.0	217.0	258.4	414.9	647.0	969.3	1,196.3	1,373.6	9,017.4
55° S.	1,298.1	952.0	733.1	415.3	224.6	136.7	173.3	325.0	565.7	907.4	1,166.8	1,363.6	8,261.6
60° S.	1,276.6	902.5	650.6	326.1	140.4	65.0	94.9	235.7	480.5	839.9	1,134.2	1,353.7	7,500.0
65° S.	1,259.7	850.4	563.5	236.8	65.4	10.6	30.0	149.7	392.0	768.0	1,102.6	1,352.8	6,781.3
70° S.	1,269.0	799.3	472.7	149.8	13.1	0	0.8	71.9	301.3	693.7	1,084.2	1,389.6	6,245.4
75° S.	1,302.1	761.9	379.6	70.6	0	0	0	18.2	209.8	621.8	1,097.2	1,428.4	5,889.7
80° S.	1,327.6	754.1	286.9	18.3	0	0	0	0.4	120.7	569.0	1,118.4	1,456.3	5,651.7
85° S.	1,342.9	761.7	208.0	0.2	0	0	0	0	49.4	547.0	1,131.3	1,473.2	5,513.8
90° S.	1,348.1	764.6	175.8	0	0	0	0	0	18.8	546.7	1,135.7	1,478.8	5,468.5

Astronomical Global Radiation



Astronomical Global Radiation

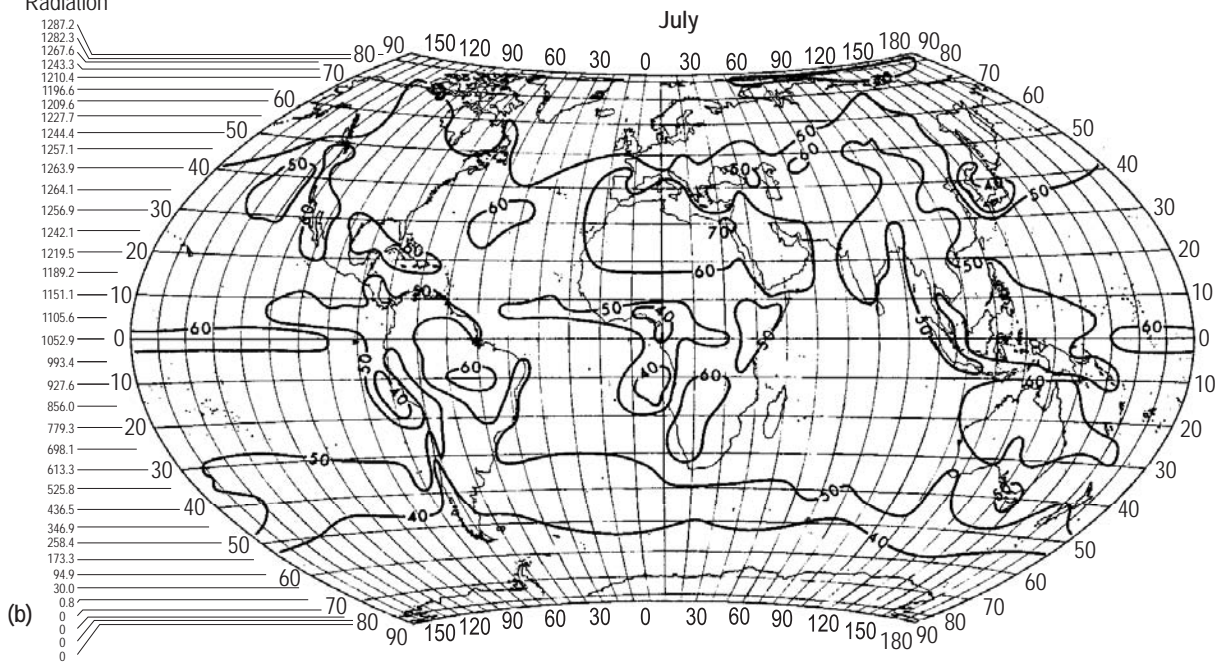


Figure 4-3. Relative global radiation ( $\text{MJm}^{-2}$ ) for (a) January and (b) July. Percentages are actual with reference to possible (adapted with permission of the WMO from TN-177-WMO and courtesy of Major et al. (1981)).

ground and water. Net radiation maps are provided for the hemispheres, oceans, continents, and the polar regions. Tables and graphs illustrate much of the information. Substantial reference bibliographies are presented in the references cited above for those who wish to study the subject in more detail and to obtain ancillary information.

#### 4.4 Albedo

Albedo is that part of the solar radiation falling on the Earth, its land, its water, its air, cryosphere, and its clouds, which is reflected and is lost. The reflections vary for each of the surfaces and the atmospheric constituents. All estimates of the Earth's albedo fall between 25 and 45 percent with the majority falling between 30 and 40 percent, and of these, most fall between 32 and 38 percent. References are Petterssen (1940), Haurwitz (1941), Berry, Bollay, and Beers (1945), Fritz (1951), Trewartha (1954), Byers (1959), Lettau and Haugen (1960a), Sellers (1965), Winston (1969), Barrett (1974), Gringorten et al. (1985), Kessler (1985), and Goody and Yung (1989). Both Winston (op. cit.) and Kessler (op. cit.) provide good discussion of the radiation and albedo characteristics. Barrett (op. cit.) reveals some of the potential in developing a climatology from satellite sensing.

As has been indicated previously, most models of climatic change at the present time (1992), deal only with the projected warmings associated with the increasing amounts of the "greenhouse" gases. These deal in only the most rudimentary and limited sense with the effects of increasing evaporation and transport of water in vapor and cloud form. There is no total system analysis. The establishment of a lunar observatory would do much to provide a good record of the Earth's albedo on a continuous basis. Thus, from a climate point of view, the development of a climatology of the Earth's albedo would do much to help track climate. Such an observatory potentially could serve many purposes—Earth's climate measurement among them. Regional albedos will differ with the type of surface or material upon which solar radiation falls. Instrumental sensitives would differentiate, among other things, clouds, types of clouds, lack of clouds, cloud adulterating pollutants, the increase and translocation of cloudiness, and the desertification changes, for whatever reasons. Albedo would come into its own as a climatic element, a summation of the many effects of energy exchange. Temperature is the measurable effect of energy and is often considered a prime climatic element. Presumably, this is so, because it is one of the easier measures of energy available and is a descriptor of the basic climatic element, energy. With this statement goes the statement that such a lunar observatory would serve as a basis for the measurement of solar radiation output, which output is now partially obscured from the Earth's surface by the intervening atmosphere. Thus, the measurement of both the incident and the reflected energies on the Earth will help to provide a climatology more basic than is available today.

#### 4.5 Absorption, Conversion, and Outgoing Longwave Radiation

##### 4.5.1 Solar Radiation Attenuation

The Earth receives a small measure of the Sun's energy output. That received consists of energy in wave and particulate form where the particulates are the material protons. The generally assumed transmitted radiant energy form is that shown in figure 4-2(a) for 6,000 K. This is not a constant. For most arguments, it is so considered. But the slight variability that is associated with different energy and particule levels is a part of or one of the forcing functions of Earth's climate. Another element of Earth's climate is the loss of energy. Albedo, discussed just above, is a manifestation of such loss. It is usually associated with viewing and within the visible (to human eyes) portion of the spectrum.

The wave number rather than wavelength is often used, as the absorption is proportional to the areas under the curves. Figure 4-4 (fig. 16-10, p. 16-15, Gast (1960)) illustrates the energy curve for blackbody radiation at 6,000 K along with the solar irradiances for the outside atmosphere and at sea level. Here, the more familiar, perhaps, wavelength form is used. In addition, there are the spectral absorbances by ozone (O<sub>3</sub>), oxygen (O<sub>2</sub>), water (H<sub>2</sub>O), and carbon dioxide (CO<sub>2</sub>). The wavelengths extend from zero to 3.2 μ. These are laboratory measurements and not actual measurements made in the atmospheric mixture. Thus, one is able to illustrate contribution of each

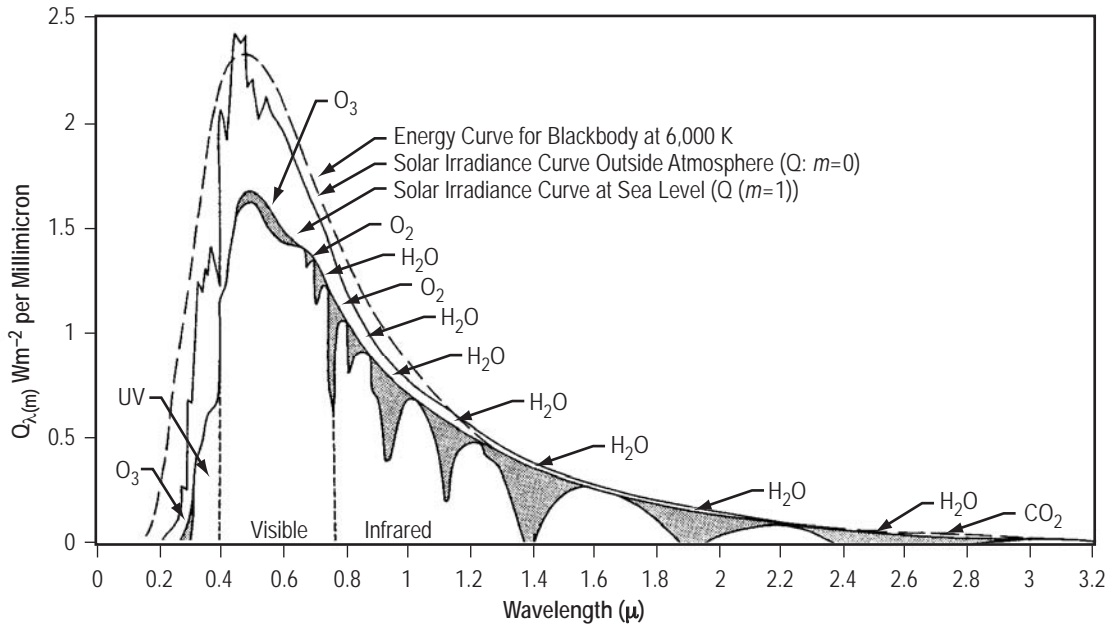


Figure 4-4. Blackbody radiation energy curve at 6,000 K with solar irradiances for the outside atmosphere and at sea level. The axes are wavelength of zero to 3.2  $\mu$  and power zero to 25  $\text{Wm}^{-2}\text{nm}^{-1}$ . Absorption by selected gases is shown (with permission of Air Force Cambridge Research Laboratories (Gast (1960))).

gas to the transmittance and the absorption of radiation. In a complementary sense, the remaining regions indicate energy available for further absorption by other gases or available to strike the Earth or its clouds. This does not show the increased absorption by other gases in the absorbing region for ozone.

Quite clear in figure 4-4 as presented by Gast (op. cit.) is the effect of absorption and transmission of solar radiation through the Earth's atmosphere. Figure 4-5 indicates the theoretical blackbody radiation at 6,000 K from the Sun as does the dashed line in figure 4-4. As Gast (op. cit.) indicates, ozone ( $\text{O}_3$ ) completely absorbs the solar radiation below 0.29- $\mu$  wavelength ( $\approx 4,000 \text{ cm}^{-1}$ ), partially between 0.29, the far ultraviolet, and 0.35- $\mu$  wavelength numbers, and to a lesser extent, in the visible portion of the spectrum below 0.8  $\mu$ . The regions of the infrared affected by  $\text{O}_2$ ,  $\text{CO}_2$ , and the broad range affected by  $\text{H}_2\text{O}$  are clearly evident in this depiction from zero to  $\approx 3 \mu$ . Luther and Ellingson (1985), with editors MacCracken and Luther (1985), present a figure consisting of two parts. Figure 4-5(a) (reproduced with permission), in line with the arguments on figures 4-1(a) and (b), shows the normalization of the curves for blackbody radiation for 6,000 and 255 K. Figure 4-5(b) contains the normalized absorption zero to 100 percent on a logarithmic wavelength scale. Please note the additional absorption lines for  $\text{CH}_4$  and two of the halocarbons,  $\text{CFCl}_3$  and  $\text{CF}_2\text{Cl}_2$ . These are in the vicinity of  $850 \text{ cm}^{-1}$ . Other halocarbons are expected to also be sensitive in this part of the microwave region. Chloroform ( $\text{CHCl}_3$ ) is receptive and active near  $750 \text{ cm}^{-1}$  (Fessenden and Fessenden (1986)).

Also, note the absorption region for  $\text{N}_2\text{O}$  near 16  $\mu$  and the almost total absorption by water vapor beyond 14  $\mu$  and certainly beyond 25  $\mu$ . This region influences the molecular rotation. Figure 4-5(a) is also shown by Goody and Yung (1989).

#### 4.5.2 Outgoing Longwave Radiation

In the 1950s, the advent of satellites, as indicated previously, ushered in an age of, among other things, instrumental platforms. New measurement tools installed on these platforms—fixed or moving, with respect to the

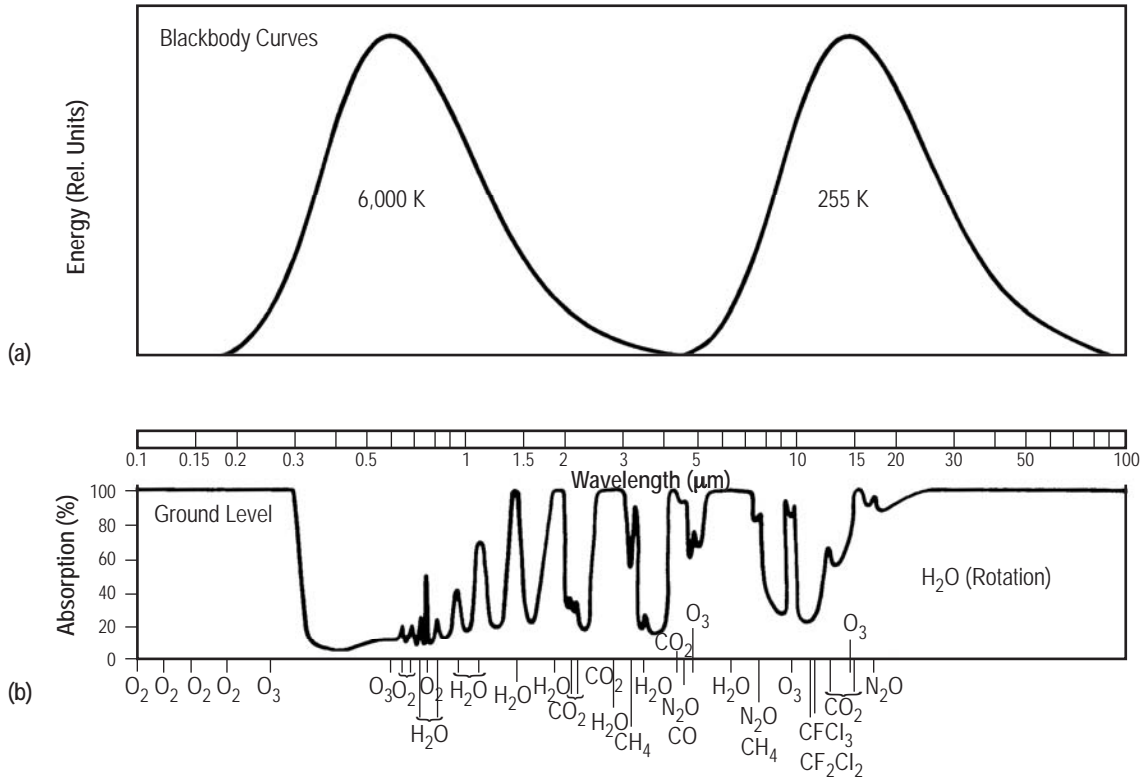


Figure 4-5. Radiation curves (solar): (a) Blackbody curves for 6,000 and 255 K, and (b) normalized absorption curves for the atmosphere,  $0 < \% \leq 100$ , with indicated regions (points) for selected gases (with permission, University of California Livermore National Laboratory and Department of Energy (DOE/ER-0237); MacCracken and Luther (1985) and Luther and Ellingson (1985)).

Sun, the Earth, or any other body—are beginning to provide information useful in many disciplines. Specialty tools can and are being devised. One type of tool deals with the measurement of outgoing, longwave radiation (OLR) from the Earth. This loss is a part of the Earth's energy or heat loss. Good measurements are useful in estimating the extent of such losses. Beginning in the 1970s, among the various international groups working on these problems and among the various satellites in use, the Nimbus-6 and Nimbus-7 satellites also have provided OLR data. Workers have reported on various aspects of the observing program. Along with such platform satellite development, the tools and techniques to measure, to transmit, to process, to record, to archive, and to service the instrumental output has been necessary.

Bess and Smith (1987a,b) and Bess, Smith, and Charlock (1990) placed a set of measurements in the hands of the climatologist. These measurements provide a global database for the terrestrial radiation climatologist. These data, derived from Nimbus-6 and Nimbus-7 transmissions, are in tabular form and are spherical harmonic coefficients and global contour maps for each month. Comparison may be made with previous data and will be made to future data sets. The reports mentioned above cover the approximate decade 1975–1985. By the time you read this, another decade of data will be available for comparison.

Bess, Smith, and Charlock (1990) discuss the OLR data for the decade 1975–1985. They point out the occurrence of two El Niño episodes during the period. One of these was exceptionally strong. Therefore, the reader is reminded that relatively short periods of record should not be used to establish a fixed norm or model. In a sense,



this period is a sample of no more than 10, and effectively, perhaps, a sample of only two or three at most. Extrapolation is not recommended. The occurrence of the two El Niño episodes indicates lack of stationarity in the statistical sense.

Here is the abstract of the Bess, Smith, and Charlock (1990) article entitled, “A ten-year monthly data set of outgoing longwave radiation from Nimbus-6 and Nimbus-7 satellites”:

“Monthly mean outgoing longwave radiation (OLR) measurements in the form of global contour maps and coefficients of spherical-harmonic functions for each month of the 10-year period July 1975 through October 1985 have recently been completed. One data set contains three years (July 1975 to June 1978) of ‘continuous’ data from the wide field-of-view sensor of the Earth Radiation Budget (ERB) experiment aboard the Nimbus-6 satellite. The other data set contains seven years (November 1978 to October 1985) of ‘continuous’ data from the ERB experiment aboard the Nimbus-7 satellite. The OLR broadband time series could be used, for example, to study the inter-annual variability of OLR. An example is given of two El Niños that occurred in the 10-year timeframe.” NASA publications, Bess and Smith (1987a,b) document the data sets that are available on a floppy diskette, that can be read by any IBM-compatible desktop computer. The foregoing two publications and the Bess, Smith, and Charlock (1989) article document the satellite programs, the instruments used, their characteristics, and their performances. Where degradation was detected, the procedures to appropriately modify the instrumental, transmission, and reception information is described. There are problems as in any climatological observational program. Reliability, quality assurance, and quality control techniques are necessary and continuing as with any other program. The reader is referred to the publications noted above.

The reader can obtain the floppy diskette. See Bess, Smith, and Charlock (1990). Design and output of the OLR data can then be formatted by the user as needed. The following figures are provided courtesy of NASA (Bess, Smith, and Charlock (1989)). Presentations of only few of the many possible are shown here. The units are  $\text{W}\cdot\text{m}^{-2}$ . The period of record is 1975–1985. The sample is therefore a sample of 10. The standard deviation values are based on this 10. The geographic coverage ranges from  $60^\circ$  S. to  $60^\circ$  N. latitude and from  $180^\circ$  W. to  $180^\circ$  E. longitude. The methods used to compute, average, and process the information are described by Bess, Smith, and Charlock (op. cit.). The color bars on the color presentations provided the guide for the assessment of the OLR in  $\text{W}\cdot\text{m}^{-2}$ . In the isoline presentations, in general, the OLR  $<240 \text{ W}\cdot\text{m}^{-2}$  is indicated by the dashed isolines.

Figure 4-6 shows mean OLR in false arbitrary color for (a) January and (b) July; figure 4-7 shows mean OLR in isolines for (a) January and (b) July; figure 4-8 shows standard deviations of average monthly OLR in false arbitrary color for (a) January and (b) July; and figure 4-9 shows standard deviations of average monthly OLR in isolines for (a) January and (b) July—all for the years 1975–1985. The standard deviation map of change in inter-annual OLR ( $\text{W}\cdot\text{m}^{-2}$ ) for 10 summers and 10 winters is shown in figure 4-10.

There are many things to note in these figures. Regions of minimum and maximum OLR may be determined in each figure. Only the summer-winter seasons and the midmonths of these seasons are given. For the other months and seasons, please refer to Bess and Smith (1987a,b). The standard deviation charts show the regions of minimum and maximum variation. For example, in the charts shown here, minimum mean long radiation occurs in the equatorial regions of the rain forests during December-January-February; South American, Africa, and the East Indies and extreme western and eastern Pacific near the International Date Line. Near maximum variability of this loss occurs in small areas in the East Indies, about  $20 \text{ W}\cdot\text{m}^{-2}$  and maximum variability from  $180^\circ$  W. eastward through  $120^\circ$  W., peaking near  $25 \text{ W}\cdot\text{m}^{-2}$ . Variability over the rainforests of South America and Africa are low, ranging from 12 to  $3 \text{ W}\cdot\text{m}^{-2}$ . Due to the inherent correlation of these data, the effective degrees of freedom are probably near 3 and not 9. Therefore, a better sense of the variance for the next 10 yr ought to be near twice ( $3^{1/2}$ ) that given here. This does not imply an error but simply an application mode. See Brooks and Carruthers (1953).

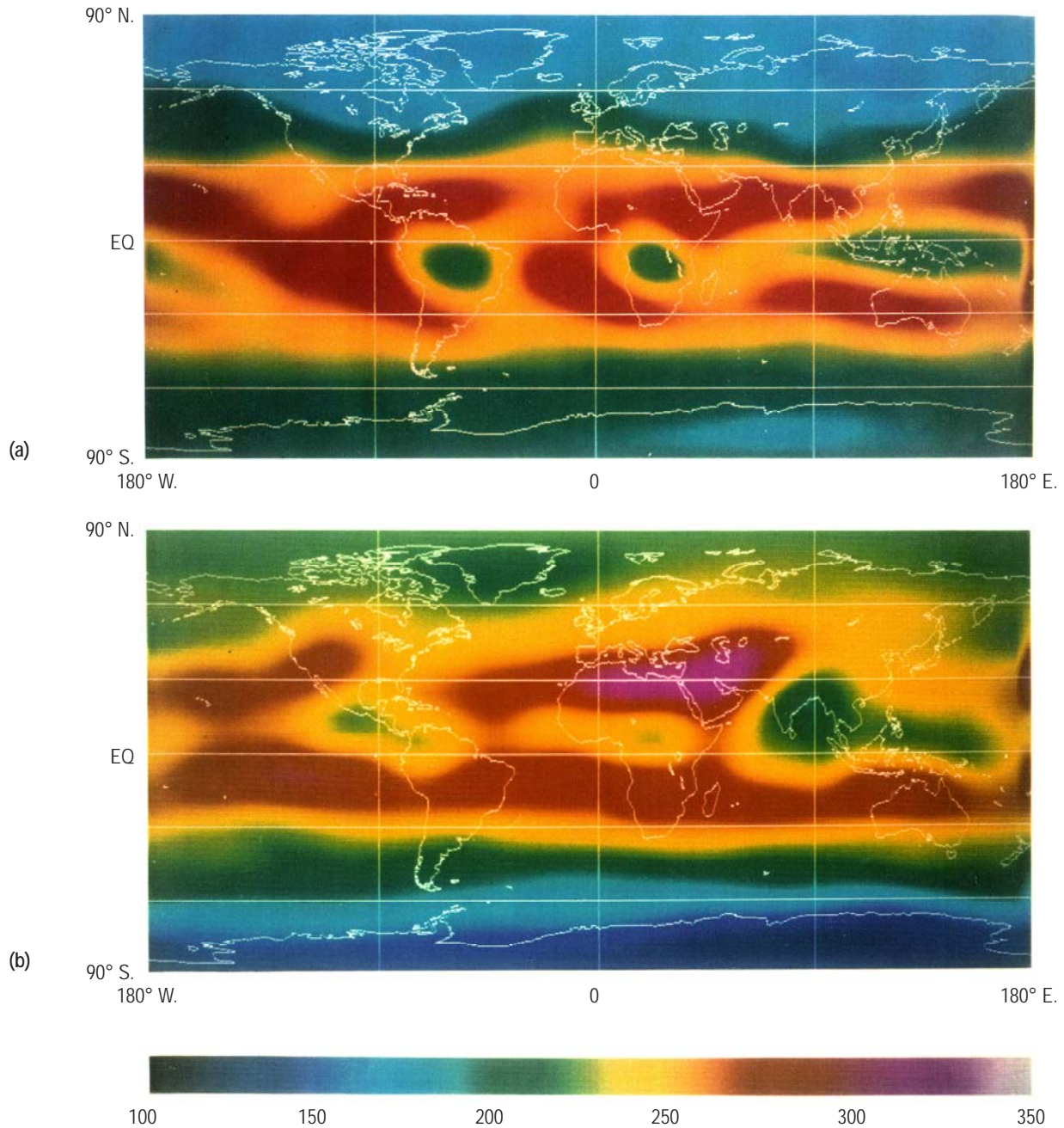


Figure 4-6. Mean OLR in false arbitrary color ( $W \cdot m^{-2}$ ) for 1975–1985 for (a) January and (b) July (with permission, American Meteorological Society, courtesy of NASA Langley Research Center, Bess, Smith, and Charlock (1989)).

Figure 4-11 provides a look at some changes with time over the 10-yr period. The OLR over the equatorial band 7.5° S. to 7.5° N. from the Greenwich meridian eastward around the globe. Chronology is provided in years on the vertical scale—July 1975 to July 1985. Four months of missing data create the blank horizontal strip. Note the negative anomalies from the mean interannual records as indicated by the blue regions. These are strong in the years 1976–1978 and in 1982–1983. Equally strong positive anomalies to the west of the negative anomalies

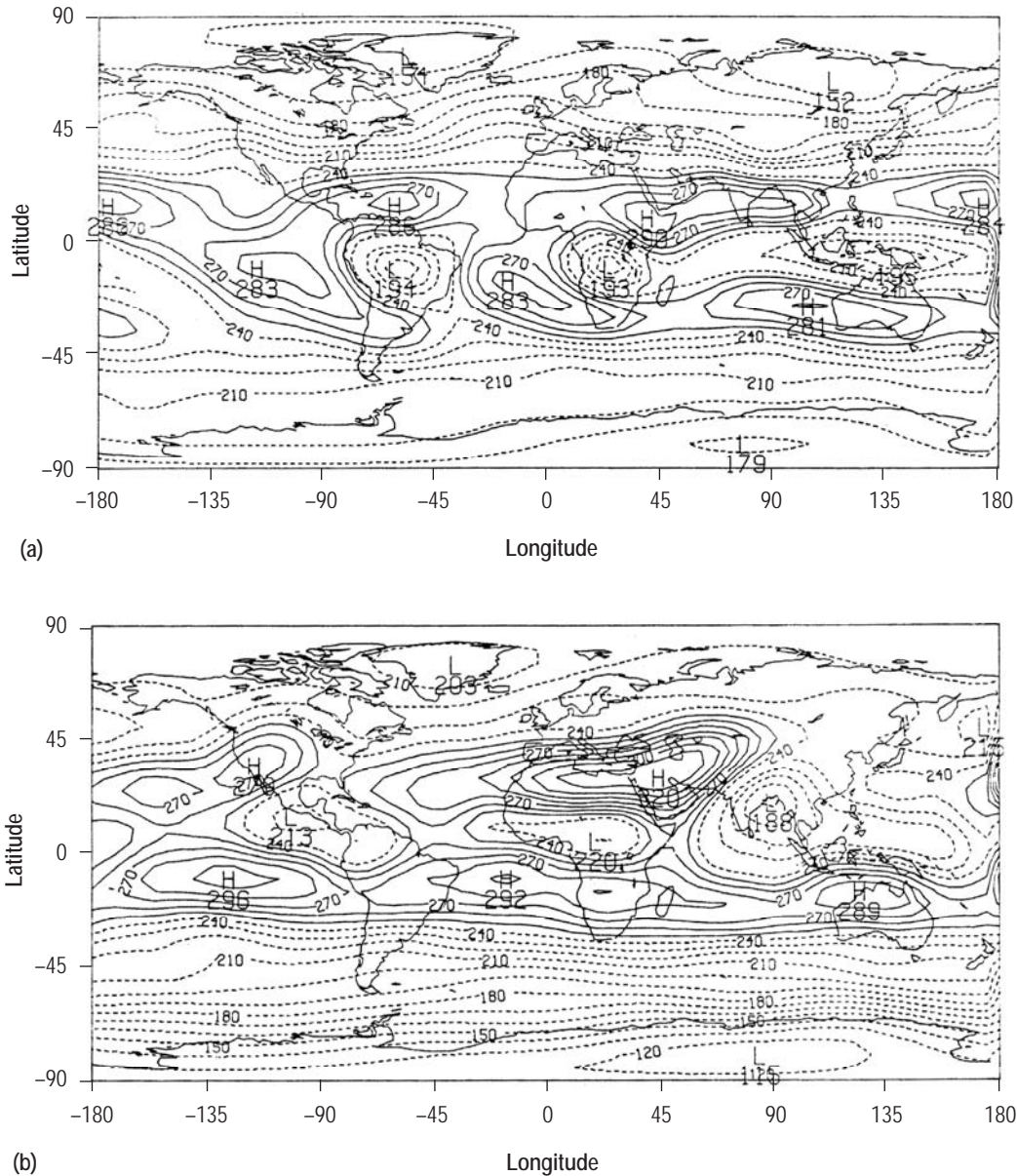


Figure 4-7. Mean OLR in isolines ( $W \cdot m^{-2}$ ) for 1975–1985 for (a) January and (b) July (with permission, American Meteorological Society, courtesy of NASA Langley Research Center, Bess, Smith, and Charlock (1989)).

occur in 1982–1983 and moderate positive anomalies occur near the International Date Line in 1975–1976 and in 1983–1984. These are the years associated with the two El Niño periods. Note the general tendency of the patterns to shift to the east with time. Discussions by Bess, Smith, and Charlock (1990) provide considerable more information. As pointed out by Bess, Smith, and Charlock (op. cit.), the anomalies range from  $-70 W \cdot m^{-2}$  near Tahiti to  $50 W \cdot m^{-2}$  at Darwin.

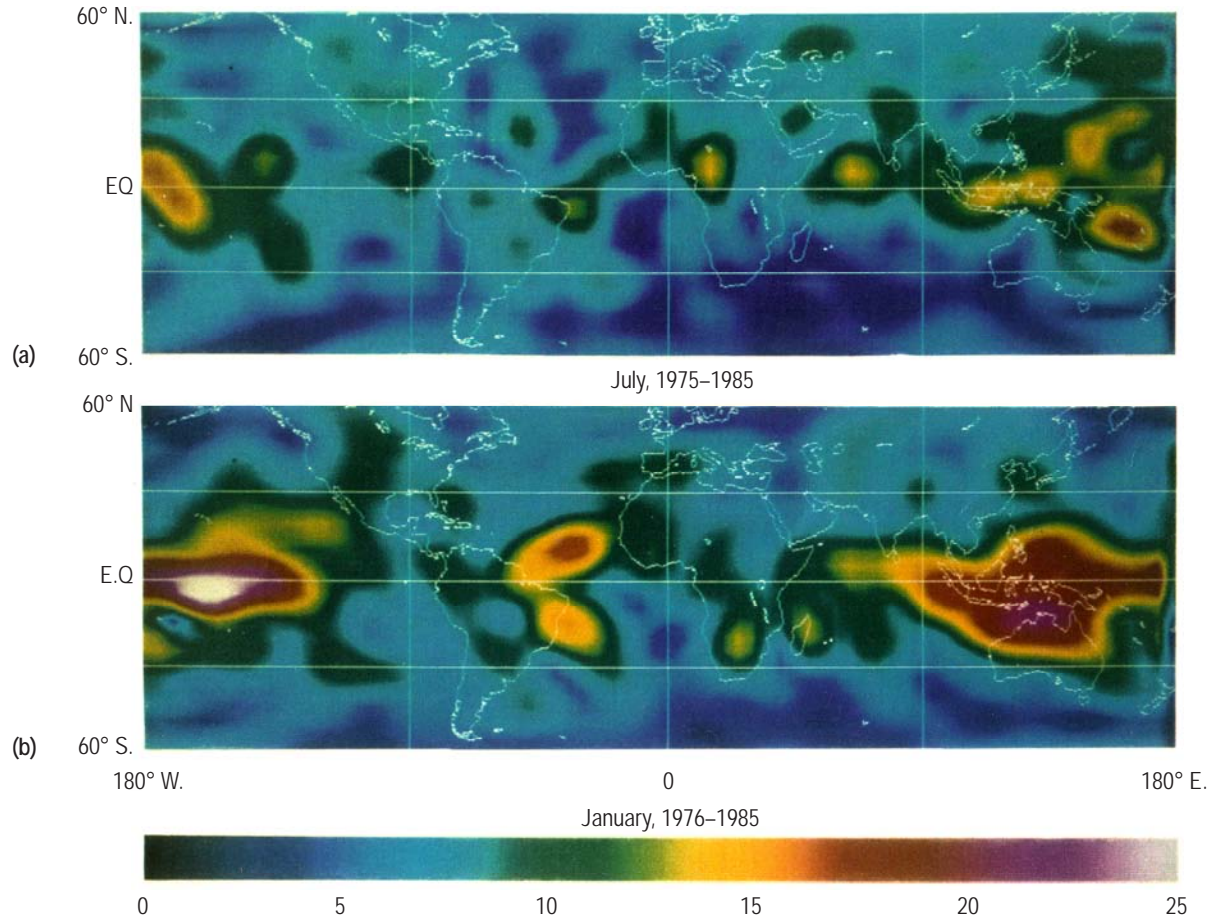


Figure 4-8. Standard deviations of average monthly OLR in false arbitrary color ( $W \cdot m^{-2}$ ) for 1975–1985 for (a) January and (b) July (courtesy of NASA Langley Research Center, Bess, Smith, and Charlock (1989)).

#### 4.6 Radiation Forcing of Climate

Without question, radiation influences climate. In a work by the name of “Radiative Forcing of Climate,” lead authors Shine, Derwent, Wuebbles, and Morcrette (1990) consider this problem. As their executive summary indicates, the climate of the Earth is affected by radiative forcing due to several sources known as radiative forcing agents. These sources include the concentrations of the radiatively active (greenhouse) gases, solar radiation, and albedo. Many gases produce both direct and indirect effects. The major gas involved is  $CO_2$  (61 percent), with substantial contributions from  $CH_4$  (17 percent), nitrous oxide ( $NO_2$ ) (4 percent), and chlorofluorocarbons (CFCs) (12 percent). The contribution of  $H_2O$  vapor, particularly in the stratosphere, is  $\approx 6$  percent.

The above are expected to provide a positive warming. Stratospheric aerosols injected by volcanic eruptions and those resulting from manmade emissions of sulphur will have a cooling effect. These, along with water cloud effects, speculatively may be of equal magnitude but opposite in sign to the greenhouse forcing. This article by Shine, Derwent, Wuebbles, and Morcrette (op. cit.) is recommended reading and study.

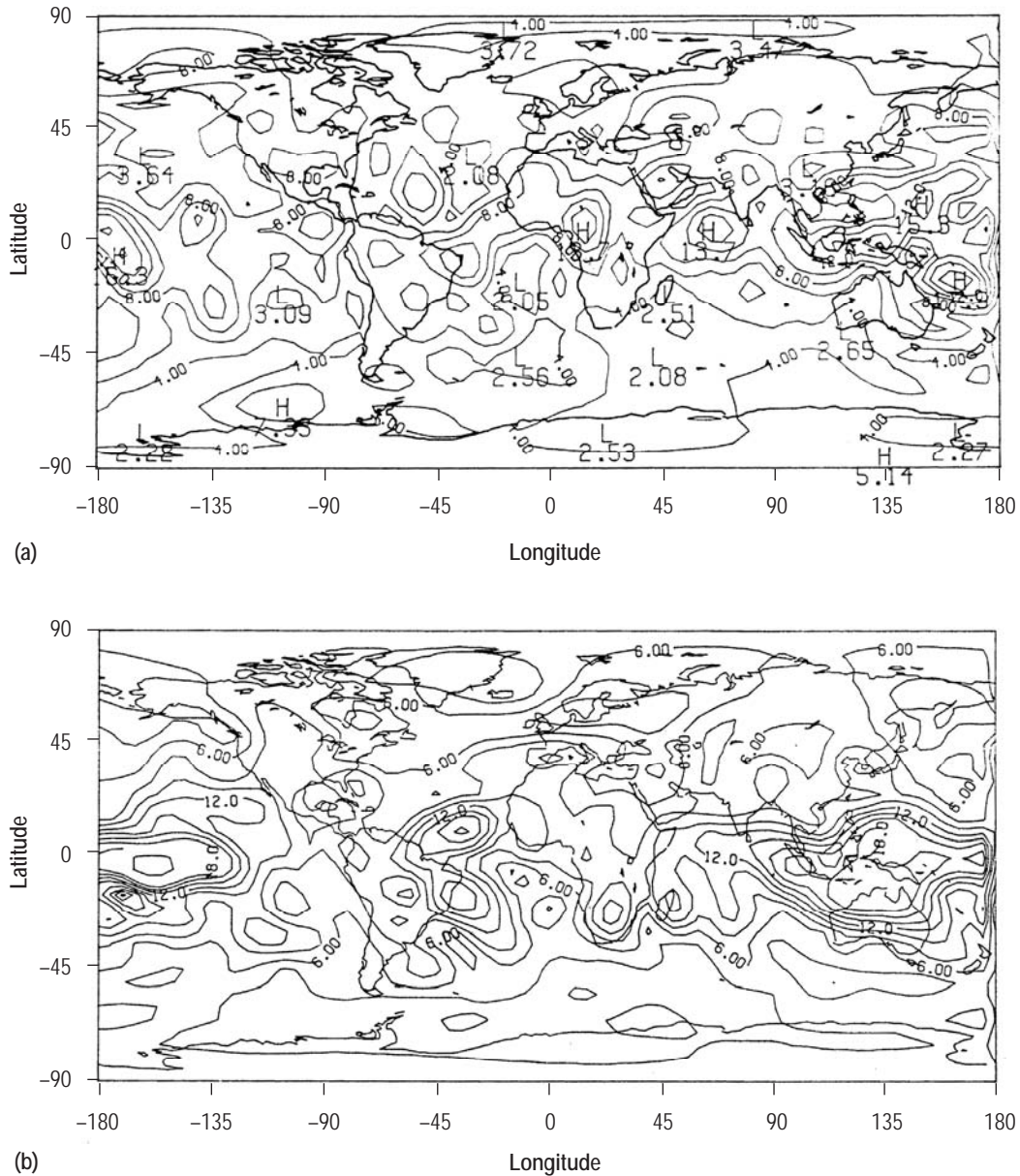


Figure 4-9. Standard deviations of average monthly OLR in isolines ( $\text{W}\cdot\text{m}^{-2}$ ) for 1975–1985 for (a) January and (b) July (courtesy of NASA Langley Research Center, Bess, Smith, and Charlock (1989)).

#### 4.7 Solar Variability

Solar variability, as with the end products of planetary climates, is complex indeed. Earthian climate is no exception, though it appears to be a unique ensemble. Zirin, Moore, and Walters (1976) edit the proceedings of a workshop on the solar constant and the Earth's atmosphere. A year later, White (1977) edits symposium results on ideas as to the solar output and its variation. Donnelly, Frederick, and Chameides (1987) collect and edit a series of papers on solar variability and its effects on the Earthian spheres, the stratosphere, the mesosphere, and the thermosphere. Goody and Yung (1989) discuss atmospheric radiation. This includes the absorption, reflectance, and

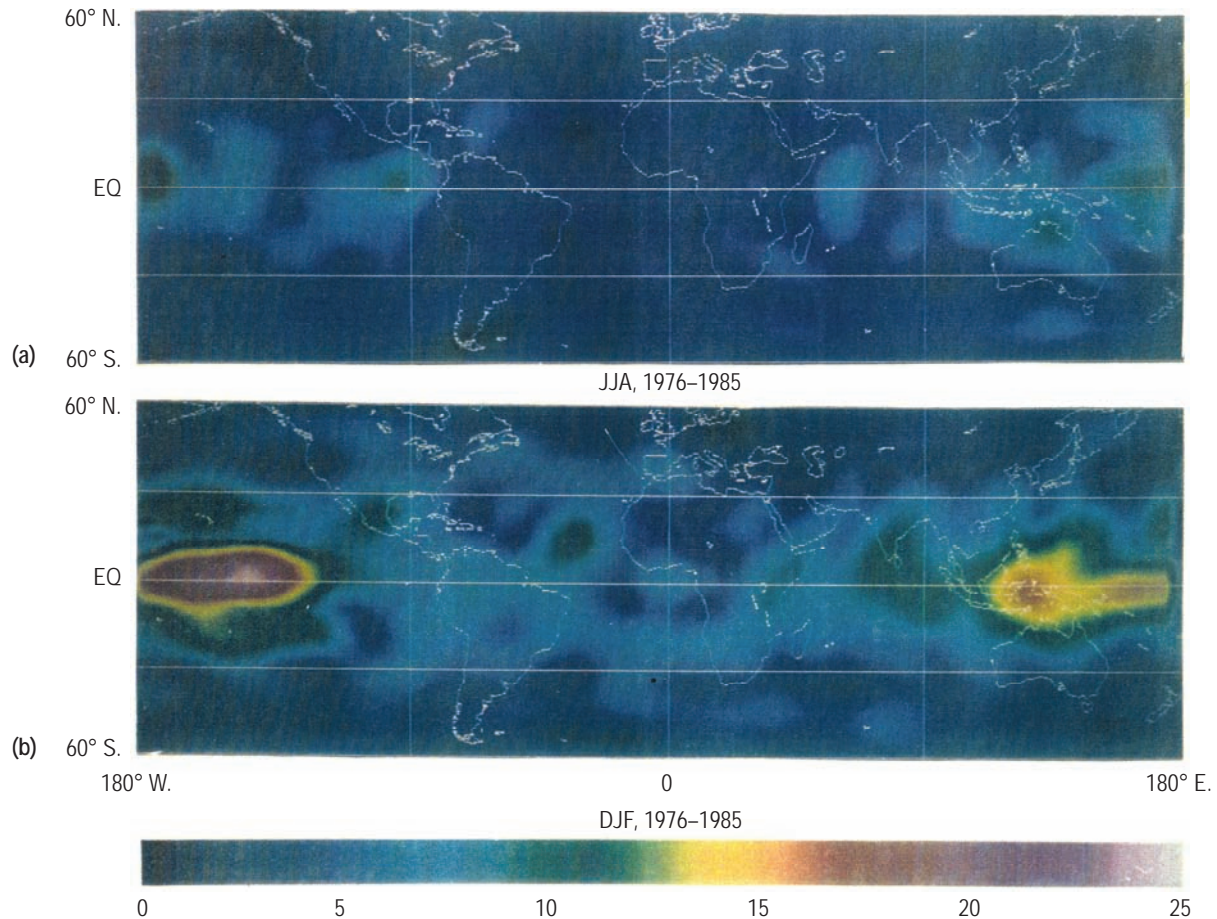


Figure 4-10. Standard deviation map of change in interannual OLR ( $W \cdot m^{-2}$ ) for 10 summers and 10 winters (1975–1985) for (a) June, July, and August and (b) December, January, and February (with permission, American Meteorological Society, courtesy of NASA Langley Research Center, Bess, Smith, and Charlock (1989)).

international radiation exchange. The lifework and ambitions of many people are involved in these publications and many others are not mentioned.

#### 4.7.1 Constancy or Variability

Presumably, there is nothing that is constant in the universe or in any of its parts, including the solar system and its planetary system. There is some variation; attempts are made to obtain some idea(s) as to the bounds of the variation.

Consensus and estimates of the age of the universe ranges from 10 to 20 billion years and of this particular galaxy, 5 to 15 billion years, and of the solar system, 4.5 to 5 billion years. Mitchell (1977) places some bounds on Earthian climate. He indicates that in the last 3 billion years, there is no evidence that the entire temperature climate has exceeded the bounds of the liquid phase of water. That is, the planet has not been totally ice covered nor has it been totally immersed in water at the boiling point of water. Present-day consensus of orbital configurations of the planets and their attitudes over time create a changing distribution of the intercepted solar energy. See Milankovitch (1957) and Vernekar (1932). Vernekar (op. cit.) provides a history of Earth's orbital variations with respect to the

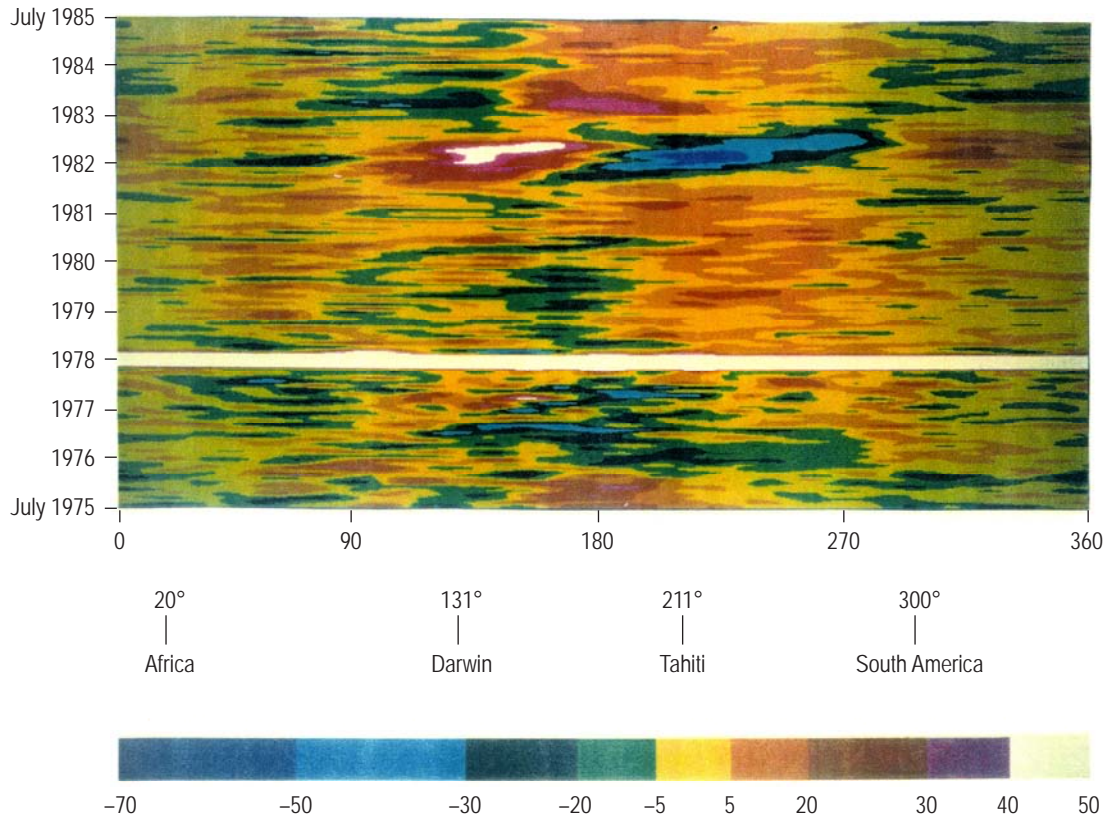


Figure 4-11. Time longitude plot of OLR ( $W \cdot m^{-2}$ ) in false arbitrary color (with permission, American Meteorological Society, courtesy of NASA Langley Research Center, Bess, Smith, and Charlock (1989)).

orbital eccentricity, obliquity of the ecliptic, and precession of the Earth's axis over the past million years. Thus, even if the solar output were constant in terms of its spectral energy output, the energy receipt at some Earth points would vary by as much as 10 percent. Mitchell (op. cit.) provides a table showing the nature of the quasi-periodic variation of Earthian climate, the characteristic wavelengths in time, and their most plausible origins. An inference drawn from Mitchell's (1977) remarks is that Earthian climate has not even closely approached the solid and/or totally gaseous water phases. A secondary inference is that the Earthian system may be self-regulating and that within these bounds, life itself may be a variable and interactive part of that mechanism. White (1977) indicates in a summary chapter that the goal of that study is to define uncertainties in the solar output and its variations. The bounds discussed above are one step. Further, as White and Newkirk (1977) indicate, the total solar radiant flux establishes important boundary conditions for climate aspects. This includes matter, radiation, and the magnetic fields. Information is sought on these. At this juncture, it is important to indicate that the spectral output varies with time throughout the spectrum. It is important to try to track these variations.

#### 4.7.2 Sunspots

Sunspots in themselves can only indicate solar processes that will affect Earth's climate. These are a part of the solar flare system that produces the solar winds and the sometimes visible aurorae. These are only indicators of the activities of our active nuclear star. These mark regions of coalescence or reentry of energies back into the Sun.

The marked quasi-periodicity of the observations of solar sunspots is well documented over the past 150 yr, less so in the prior 150 yr, and incompletely in the prior historical records.

From time to time, historical accounts reveal the occurrence of large sunspots. Only the largest spots can be seen by the unaided eye, but these do not necessarily occur at the cycle maxima. Presumably, those watching had learned how to protect their vision by using intervening clouds or screens or by other indirect means. But even these accounts are few and far between. Only with telescopic aids and filters has sunspot observation and recording come into its own. Many have been observed and studied. Arguments and definition have developed. The cycle of solar activity is easily seen in a plot of annual means—smoothed or unsmoothed—of the observed sunspots. Waldemeier (1961) shows such a plot. Eddy (1976) updates and shows Waldemeier's presentation. The period covered is A.D. 1610 to 1975 with consistent consecutive data showing the quasi-periodic cycle beginning after the Maunder minimum near A.D. 1700. Goody and Yung (1989) show this same presentation. McKinnon (1987) and McKinnon (1991—to be published) updates these figures. Figure 4-12—courtesy of McKinnon—presents the modified 1991 rendition. Prior illustrations as well as those of Waldemeier (1961), Eddy (1976), and others show the mean waveform evident in geophysical data. See also figure 13-9 on ocean wave heights. After the maxima, inertia seems to prolong builddown. The quasi-periodic oscillations are asymmetrical. In the case of sunspot numbers as shown here, the buildup or rise to maximum periods range from 2.9 to 9 yr with an average of 4.8<sup>+</sup> yr. The builddown or fall to minimum periods range from 3.5 to 10.2 yr with an average of 6.2<sup>+</sup> yr. The cycle lengths in years range from 8.2 to 15 yr with an average period of 11.1 yr. The respective ranges and midpoint averages are 6.1, 5.95, and 4.8<sup>+</sup>; 6.7, 6.85, and 6.2; and 6.8, 11.6, and 11.1 yr. The asymmetry visually noted in figure 4-12 is indicated also by the fact that the averages are less than the respective range midpoints. If a statistical model were to be selected to represent these forms, the normal distribution presumably would not be selected. Essenwanger (1986) discusses a variety of models that could be examined. There may be a modulation envelope to these data. This appears to be so with a low count number near zero. Sporer (1887) and Maunder (1890) and minima the wave shape of the maxima. But this is not certain any more than the premise that these comparable cycles extend back in time and will extend into the future (Eddy (1977) and White (1977)). In the case of the prolonged minima, Eddy (op. cit.) believes, based on 14C dendrochronological studies, that minima similar to the Maunder minimum have occurred. An inference is that such minima will occur again.

### 4.7.3 Sunspot Variability

**4.7.3.1 Daily Sunspot Numbers.** The above discussion concerns only the mean annual numbers. These are composed of the cumulations of the daily (or monthly) cumulations of data. Figure 4-13 depicts the swarm of daily data with time from 1818 through 1988. The rendition indicates some values near to or equal to zero. A review of the numbers provided in McKinnon (1987, 1991) indicate some periods of zero counts. Figure 4-13 (McKinnon (1991)) is presented so that the reader can assess the variability regions qualitatively.

**4.7.3.2 Variation With Solar Latitude.** After a fall to a minimum in spot number count, a new cycle is indicated by incipient sunspots in the solar midlatitudes. They do show motion with respect to the Sun's rotation. As time goes on, the development of flares and ensuing spots move closer to the solar equator. An inference is made that as they drift close to the solar equator, these solar flares direct more energy toward the Earth.

**4.7.3.3 Variation of Magnetic Polarity.** The magnetic polarity of the Sun changes from one sunspot cycle to the next succeeding cycle. This cycling of the magnetic polarity is called the Hale sunspot cycle. It is the subject of intense investigation. The period averages slightly more than 22 yr.



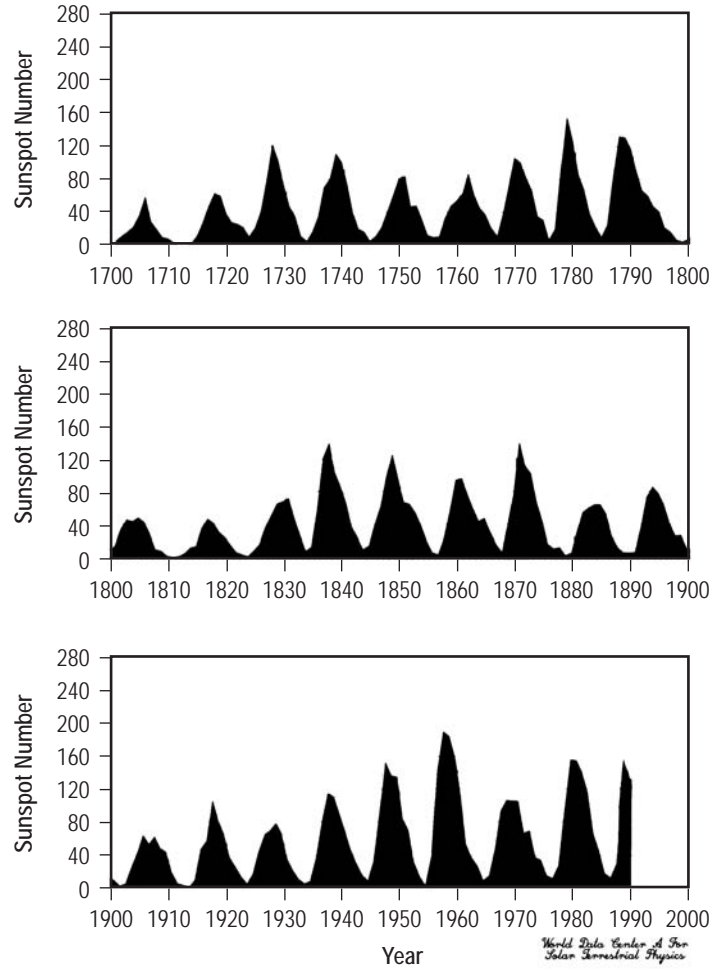


Figure 4-12. Annual mean sunspot numbers 1700–1988 (McKinnon (1991) with permission).

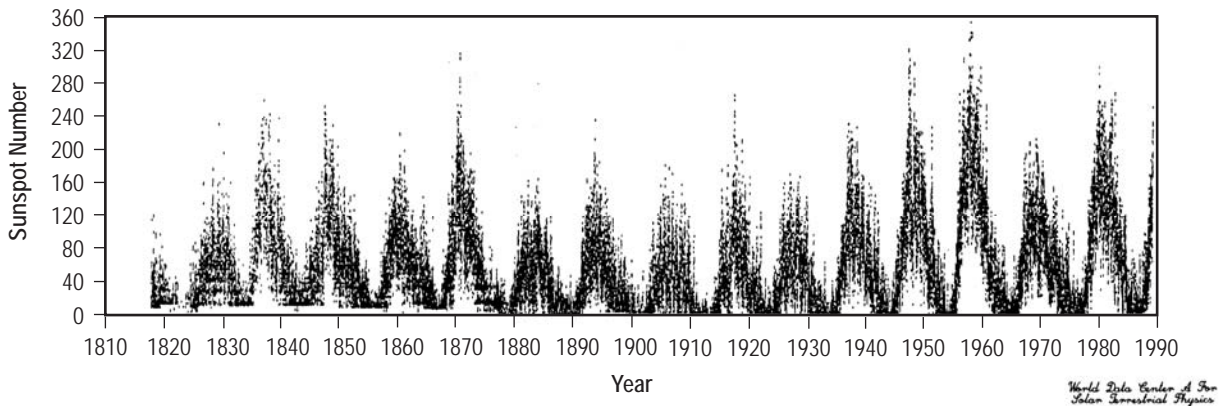


Figure 4-13. Daily course of sunspot numbers from January 8, 1818, to December 31, 1988 (from McKinnon (1991) with permission).

#### 4.7.4 Spectral Variability

Just as sunspots, flares, and magnetic fields vary, so do the various parts of the solar spectrum. The entire spectrum may not vary as one entity but the various portions may vary in seeming independence. The figures showing the solar irradiance (figs. 4-4 and 4-5) are steady curves only because a constant temperature is assumed for each. This is not precisely the case with our active Sun. The nuclear physical and chemical processes create turbulent energies that are influenced by the Sun's motion and rotation. The output for any wave number or wave number ensemble varies. The higher wave numbers with their greater intensities and energies penetrate more deeply and actively through space, the atmospheres of the planets, and onto the planetary surfaces. Recent work is involved with investigating these variable intensities within the solar spectrum all the way from the highest to the lowest wave numbers, from the x-ray regions to the radio waves and beyond. Donnelly and White (1977), two of the many contributors of White (1972), discuss the solar spectrum and provide the wave numbers of the eight spectral regions reported. As they indicate, the progress in understanding over the then past 15 yr has been possible only by the development of space technology. The period has now doubled to 30 yr and technology has increased correspondingly. But much more funding work and personnel will be needed. Donnelly, Frederick, and Chameides (1987) edit a series of papers (1985) in solar variability and stratospheric, mesospheric, and thermospheric effects of solar variability. The subjects are quite important to an understanding of our climate. But here only a short treatment is possible. Donnelly (1989) presents in his figure 2 several curves of solar activity. These are the time series of the (1) Ottawa F10 Solar Radio Flux and (2) the Lyman- $\alpha$  production by Rottman (1988) and Barth, Tobiska, and Rottman (1988), and the Mg II Core-to-Wing Ratio of Heath and Schlesinger (1986). See figure 4-14, courtesy of Donnelly (1989), personal contribution and communication. This figure shows the above series through the last fall from maximum to minimum sunspot activity and the rise toward the maximum of solar cycle 22. With respect to solar activity and output, the higher the radiation wave number, the greater the potential penetration of the atmospheric shells. Subsequently, the physical and ensuring chemical structure of the atmosphere is modified.

The irradiance curves show the minimum of the end of solar cycle 21 in 1985–1986. This presentation closely parallels, in general, the sunspot cycle shown in figure 4-12. The reader is referred to Donnelly (1989) for a discussion concerning the peaking of the flux of ultraviolet and other wave number groups during the 1979 maximum. Some led and others followed the peaking of the sunspot numbers. Whether this will be the same picture obtained in the 1989–1990 peaking will not be known until about 1993.

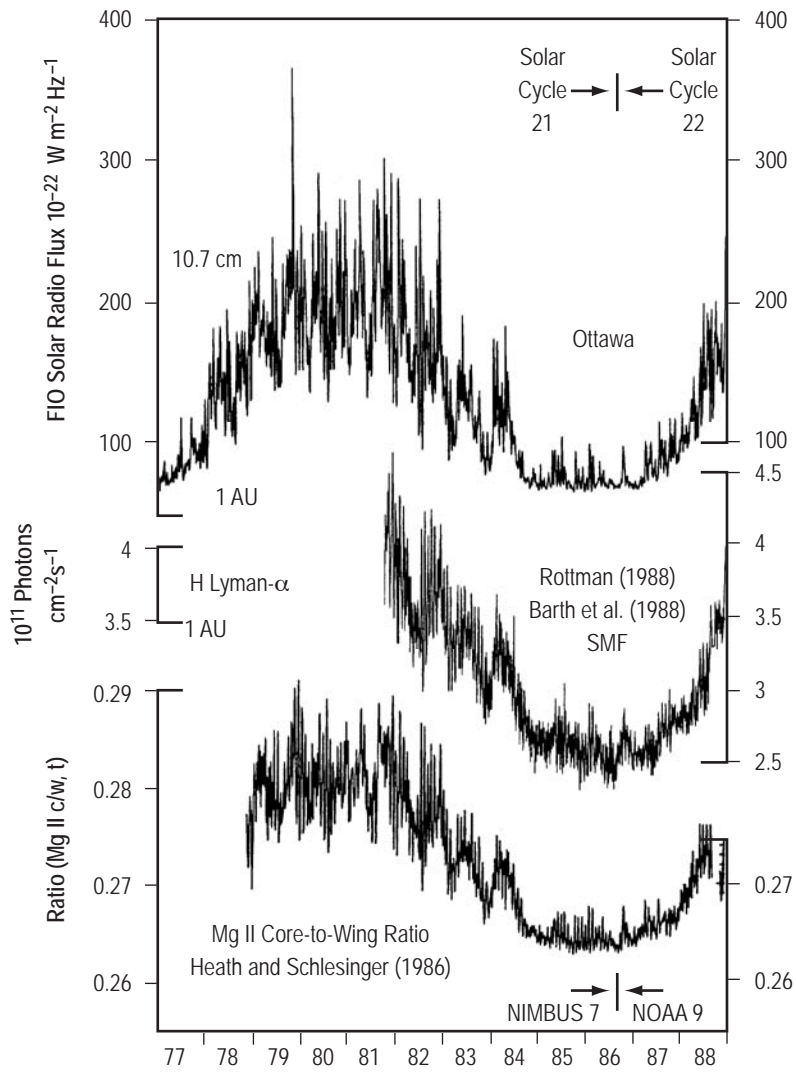


Figure 4-14. Selected wave numbers solar output (1977–1989) solar cycle 21 and part of solar cycle 2 (from Donnelly (1989) with permission).



## 5. TEMPERATURE

### 5.1 Definition and Scale

Temperature may be defined in several ways, though basically, it is a measure of molecular or atomic motion (energy). One temperature definition may be described as the condition of a body which determines the transfer of heat—to or from that body—by molecular motion. According to Hodgman (1952, p. 2630), “The standard scale of temperature adopted by the International Committee of Weights and Measures in 1887 is based on the variations of hydrogen at constant volume. The hydrogen is taken at an initial pressure at the temperature of melting ice, of one meter of mercury (0 °C, sea level, latitude 45°). The scale is defined by taking the temperature of the melting ice as 0° and that of condensing steam under 760 mm pressure as 100°.” Based on the decimal system, this is the centigrade system, and the temperatures so measured are Celsius temperatures though Celsius used an inverted scale. In 1927, the Seventh General Conference of Weights and Measures, representing 31 nations, unanimously adopted a temperature standard.

Hydrogen (molecular) becomes a liquid and solid at lower points on the temperature scale than any other gas. Within the range of temperatures experienced naturally on Earth, there would be no interference from a hydrogen phase change. The effect of the hydrogen isotopes, deuterium, and tritium is expected to be small as their mass contribution to the total hydrogen is small. Presumably, this was one of the reasons it was originally chosen as the model gas. The changes of state for all other chemical elements, compounds, or mixtures—eutectic or not—exist at higher energy levels.

Hydrogen, in its atomic form, exists with at least three different energy levels. There are three acknowledged isotopes. These exist and are maintained only in regions of intense radiation (energy fields) whether in outer space, near ionizing radioactive material, or in the laboratory. With a lack of energy absorption, the highest isotopes will eventually degrade to the lowest form. The same is true for oxygen and other elements though the number of isotopes may differ. With time, the more unstable forms—the higher energy forms—become more stable. In regions protected from ionizing radiation, the stabler forms predominate. Considering three isotopes of hydrogen and three isotopes of oxygen, the water molecule has at least 18 configurations. But, of these, the stablest form composed of the stablest hydrogen and oxygen atoms predominate. The predominance of the more stable elements in any molecular configuration may be expected.

Water is abundant and forms the hydrosphere. It serves as a standard reference base. Its sensible and latent energy capacity exerts great control on the temperature regimes on Earth.

The following are some pertinent excerpts from the report by Burgess (1928) on the decisions reached by the conference (Berry, Bollay, and Beers (1945)).

#### 5.1.1 The Thermodynamic Centigrade Scale

“The thermodynamic centigrade scale,” from Berry, Bollay, and Beers (1945), “on whether the temperature of melting ice, and the temperature of condensing water vapor, both under the pressure of 1 standard atmosphere, are numbered 0 degrees and 100 degrees, respectively, now is recognized as the fundamental scale to which all temperature measurements should ultimately be referable.”

### 5.1.2 The Temperature of Equilibrium Between Ice and Air-saturated Water at Normal Atmospheric Pressure (Ice Point), 0.000 °C

### 5.1.3 The Temperature of Equilibrium Between Liquid Water and Its Vapor at a Pressure of 1 Standard Atmosphere (Steam Point), 100.000 °C

#### 5.1.4 Other Points

“Other points on the temperature scale at the liquid-vapor equilibrium phases of oxygen and of sulphur and the solid-liquid equilibrium phases of silver and gold were assigned. Respectively, these are  $-182.97$ ,  $444.6$ ,  $960.5$ , and  $1,063$  °C. The standard atmosphere was defined as the pressure due to a column of mercury 760 mm high having a mass of  $13.5951 \text{ gm cm}^{-3}$ , subject to a gravitational acceleration of  $980.665 \text{ cm sec}^{-2}$ , and equal to  $1,013,250 \text{ dynes cm}^{-2}$ ” (Berry, Bollay, and Beers (1945)).

Defined in another way and based on the average kinetic energy per molecule of a perfect gas, Lord Kelvin proposed the absolute or thermodynamic temperature scale. Referred to as the Kelvin temperature scale, the melting point of ice under the above conditions is  $273.16 \text{ K}$  in terms of the centigrade scaling, and the boiling point of water is  $373.16 \text{ K}$ . Through the years, as experimental and theoretical work progressed, these values have changed slightly in the hundredths place. For most climatological work, the values of  $273$  and  $373$  could be used.

#### 5.1.5 Another Version

The first sentence of this subsection implied other definitions. For those who want to view the definitions of temperature from another aspect, Mandelbrot (1962, 1989) provides interesting reading. Several references are provided. Mandelbrot (op. cit.) asserts that for closed thermodynamical systems, the notion of temperature is imperfectly defined. Easier to define is the temperature fluctuation. As Mandelbrot (1989) indicates, the idea of an ill-defined temperature with a well-defined temperature fluctuation may seem odd. However, he believes that with some thought, this idea will be generally accepted. For large systems, the practical difference is small; so, for climate understanding, there should be few problems.

#### 5.1.6 The International Temperature Scale

Noted earlier were the 1887 and 1927 meetings of the International Committee on Weights and Measures. Now the 18th meeting of this committee in 1989 promulgates the ITS-90, the International Temperature Scale of 1990 (Preston-Thomas (1992)). See also NIST Technical Note 1265 (Mangum and Furukawa (1990)). Here, as before, the unit of the fundamental quantity, the thermodynamic temperature, symbol  $T$ , is the kelvin, symbol  $\text{K}$ . It is defined as the fraction  $(1/273.16)$  of the thermodynamic temperature of the triple point of water. Various texts will provide  $273.15$  or a number to three decimals. With long, long time, the number  $273.16$  will change due to changes in the physical bases of the Earth and solar system. A subscript 90 of  $T$  represents temperatures determined in accord with the definitions of ITS-90. Temperature ranges are separated: (1)  $0.65$  to  $5 \text{ K}$ , (2)  $3$  to  $24.5561 \text{ K}$ , the latter being the triple point of neon, (3)  $13.8033$ , the triple point of equilibrium hydrogen, and  $961.78 \text{ °C}$ , the freezing point of silver, and (4) above the freezing point of silver, the Planck radiation law and a defining fixed point is invoked.

The first range is defined in terms of the vapor-pressure relations of  $^3\text{He}$  and  $^4\text{He}$ . The second range is defined by means of a helium gas thermometer. Calibration is affected at three experimentally realizable temperatures. In the third range,  $T_{90}$  is defined by means of platinum-resistance thermometers calibrated at specific sets of defining fixed points. Specified interpolation procedures are used.

The reader will realize that some of these ranges overlap and that calculation equations will produce different values. However, these differences are judged to be not significant. Mangum (1990a,b) to the readers of Preston-Thomas (op. cit.) points out some tabular errors of which the reader should be aware. Preston-Thomas (op. cit.) provides descriptions of techniques over each of the ranges. In an appendix the ITS-27, ITS-48, ITS-68, ITS-76, and amendments to these are described briefly by Preston-Thomas. In all respects, these definitions tie back to the thermodynamic temperature arguments previously discussed.

As Mangum (op. cit.) points out, the Consultative Committee on Thermometry is only one of the committees of the International Committee of Weights and Measures. Mangum's (op. cit.) article summarizes the results of the 17th Session of the Thermometry Committee. Mangum's (op. cit.) article goes into more detail in the subranges of temperature of more immediate interest to the climatologist. See also Mangum and Furukawa (1990) for guidelines to realize the 1990 international temperature scale.

At this point, a digression is made. No matter how good the definitions are and no matter how good the instrumentation may be, instrument exposure should not be changed if the results are to be valid in the climate sense. Again, the establishment of good "benchmark stations" is mandatory.

## 5.2 Measurements

There are infinite ways to measure temperature and scales. The instrumentation varies. Some use the volumetric change of liquids, gases, solids, or combinations of these. Some use the resistance of liquids, gases, or solids to the passage of an electric current. Some use color changes, frequency changes, or energy absorption (interferometry). There are others, and others will be devised. All must in some way transform their output to the scales mentioned above. This can be done because of a corollary to the second law of thermodynamics which Keenan (1941) presents, "A temperature scale may be defined which is independent of the nature of the thermodynamic substance."

There could be an infinite number of scales, but for most purposes, there is the Rankine scale which is the absolute system using the Fahrenheit scaling degree interval. Another absolute scale is the Kelvin scale which utilizes the centigrade scaling. There are also the Celsius temperature scale and the Fahrenheit scale which are used in most meteorological and climatological work. There is a shift to the proposed use of the Kelvin and Celsius systems. All temperature scales are linear, but they in effect measure an equivalent average kinetic energy of molecules in a volumetric sense.

There are many factors involved in the measurement of temperatures involved in the determination of supposedly precise and accurate numbers to quantify climate. Only consistent work to properly train the observers, to manufacture and calibrate the measuring instruments and recorders, the development of effective auditing techniques, and the installation of equipment can help to produce reliable information. The tendency for all meteorological services to change equipment, to change location exposures, and the natural change of exposure all work against representative data sets. Trends, jumps, and oscillations that are not part of the climate often are induced. Reading of Mitchell's (1953) work reveals many of the problems. Phillipov (1968) discusses quality control of data-gathering techniques.

Water temperature measurements are made of oceans, seas, lakes, and rivers, and of temperatures at various soil depths. Some effort goes into measuring soil temperatures in various types of soils; the database is small indeed. Temperature measurements are made in the boundary layer of the atmosphere in the land-air and sea-air interfaces and in the free atmosphere. Various types of probes—both direct and indirect—seek to obtain temperature information in the various layers or spherical shells above the troposphere. In the outermost spheres, the dissociation of the molecular to the atomic and ionic forms require redefinition and different measurement modes.

Recent advances in satellite technology permit assessment of the vertical structure of the atmosphere including that of temperature.

There are many aspects of the temperature regimes in climates. There is at least one aspect for each of man's endeavors. As man's activities increase and diversify, so will the requirement for specialized temperature measurements. For some purposes, the average temperature of the Earth's air boundary layer would be helpful if it could be obtained. This, of course, presumes that some period of time is stated.

In a survey of temperatures alluding to climate, one will find, among many items, average temperatures, maximum temperatures, minimum temperatures, temperature ranges, durations of temperatures, and oscillations of temperatures from time periods of a few seconds to days, months, years, decades, centuries, and millennia. There are many others, including dewpoint temperatures, potential temperatures, etc. For any contingency, there will be a newly defined temperature. From a phenologic point of view, the hours of sunlight, the hours of darkness, and the diurnal oscillations of temperature, pressure, and other weather elements are driving forces in both the animate and inanimate worlds. Therefore, diurnal characteristics or changes averaged over 2 wk or more constitute two important items in any climatic study. Annual variability characteristics are also important. These are quite different in the tropic, subtropic, temperate, and polar zones. Information is sought on periodic and aperiodic phenomena and characteristics, but the period of record is so short that few, if any, mathematical or statistical tools are available to extract pertinent and cogent information kernels if these do exist for prediction purposes. Thus, climate knowledge remains largely descriptive; i.e., where data are available, models of what has gone before can be developed. Inferences can be made within this framework. Extrapolation beyond is precarious. Until more is understood about the dynamics of the input, little can be said about the dynamics of the output.

The dynamic processes of the Earth and interactions of the three primary spheres—the lithosphere, the hydrosphere, and the atmosphere—create dynamic climatic regimes. Being dynamic, these regimes must change as their input reservoir capacity and output change. Those who examine the fluctuations of temperature on a point, regional, or global scale realize that the values obtained simply reflect the measurement of the system at some point in time.

It is reasonable to assume that over geologic time, continental drift (tectonic plate movements), mountain building, trench development, and changing ocean currents, erosion, and injection of volcanic and meteoric dust into the atmosphere will produce slow as well as abrupt changes in climate.

A study of temperatures in a multispace sense is required if one wishes to really understand what is actually happening. Thus, temperatures in the three variable frame of  $x$ ,  $y$ ,  $z$  and the fourth variable, time, are required for the simple temperature measurement. To these, add the various types of temperature changes, directions, and extremes. Present mathematical, statistical, and computer capabilities cannot handle these complex interactions. Therefore, the simpler presentations of means, ranges, extremes of temperatures over arbitrary periods of time, through the year or through the days or for specified times of the year or day are sought.

Riehl (1969), Deacon (1969), Geiger (1969), Flohn (1969), and Lamb (1969) discuss heat and temperature in Volume 2 of the *World Survey of Climatology*.

The aspects of the poleward flux of sensible and latent heat in the atmosphere are discussed along with the vertical distribution of these energies and their loss through radiational cooling. The daily courses of temperatures and heat balances, gradients, and changes are studied within the boundary layer and in the soil at selected diverse sites or regions, including prairies and downland. Daily ranges of sea surface temperatures by summer, winter, and year over various oceanic areas are also presented.



Temperature is one of the basic and pervasive climate elements. For that reason, it is discussed in nearly all reports and texts on climate. The series of the *World Survey of Climatology* is no different. It receives some treatment in each and every volume; in some, it is extensive. Essenwanger (1986) provides extensive discussions and provides statistical models to treat the data.

### 5.3 Temperatures and Variability

A basic publication information source is the World Weather Records. Pressure, temperature, and precipitation data are presented when available for selected stations. The first three sets of data were published by the Smithsonian Institution. The first set contains data up through 1920. Subsequent volume sets exist for each decade, with a volume for each region of the world. Publication dates are 1927, 1934, 1947, 1959, 1965, and 1987. The average time for publication after the end of a decade is  $\approx 7$  yr. Hopefully, with improvement in communication, media, and funding, this 7-yr lag can be shortened. At present, these data are available in book form, microform (microfilm or microfiche), magnetic tapes, flexible (floppy) magnetic disks, and Compact Disk–Read Only Memory (CD–ROM) form. For the tapes, disks, and CD–ROMs, electronic computers are required which can be programmed to utilize the information. For information, the reader may contact the National Climatic Data Center in Asheville, NC. Other national centers may also be contacted. In most cases, there are charges, depending upon the medium requested and handling or mailing (shipping).

Tables A-5-1 and A-5-2 provide worldwide selected temperatures and precipitation data, respectively. The temperature data are January, April, July, and October, maximum and minimum average daily temperatures in  $^{\circ}\text{C}$ . The precipitation data are monthly averages in millimeters. These data have been converted from data contained in *Climates of the World* (op. cit.). These are in the same format. The data are from the period prior to 1970. Comparison may be made to publications of more recent data. For example, there is the continual update provided by the publication of World Weather Records. As a basic period is a decade, these publications are always published 10 yr or more after the completion of a decade. See also Willmott, Mather, and Rowe (1981) for temperature and precipitation data for the Eastern and Western Hemispheres.

Boden, Kanciruk, and Farrell (1990) provide considerable detail with relation of temperature data anomalies, globally and regionally. In general, the annual and seasonal anomalies are given in respect to the time period 1958–1977 on a U.S. national basis, long-term averages for the period 1901–1987. Again, there is a regional presentation. Numeric data packages (NDPs) are available from the Carbon Dioxide Information Analysis Center (CDIAC). If you have any questions about the availability of these NDPs, you may contact CDIAC by phone or fax or any of the telecommunication networks listed below:

Carbon Dioxide Information Analysis Center  
Building 1000, MS-6335  
Oak Ridge National Laboratory  
P.O. Box 2008  
Oak Ridge, TN 37831–6335, USA  
(615) 574–0390  
(615) 624–0390 FTS  
(615) 574–2232 Fax

BITNET: CDP@ORNLSTC  
OMNET: CDIAC  
INTERNET: CDP@STC10.CTD.ORNL.GOV.

Figure 5-1(a) and (b) present approximate average values of January and July surface temperatures ( $^{\circ}\text{C}$ ), respectively, for the world. The scale does not permit great detail. Equally lacking and uncertain are the temperatures in the mountainous regions. In fact, isotherms in the mountainous regions either have been briefly treated or omitted. Temperature of the free atmosphere is sensitive to altitude decreasing approximately  $6.5^{\circ}\text{C}$  per km increase in altitude. These presentations have been constructed in part with reference to the 30-yr normal period 1931–1960,

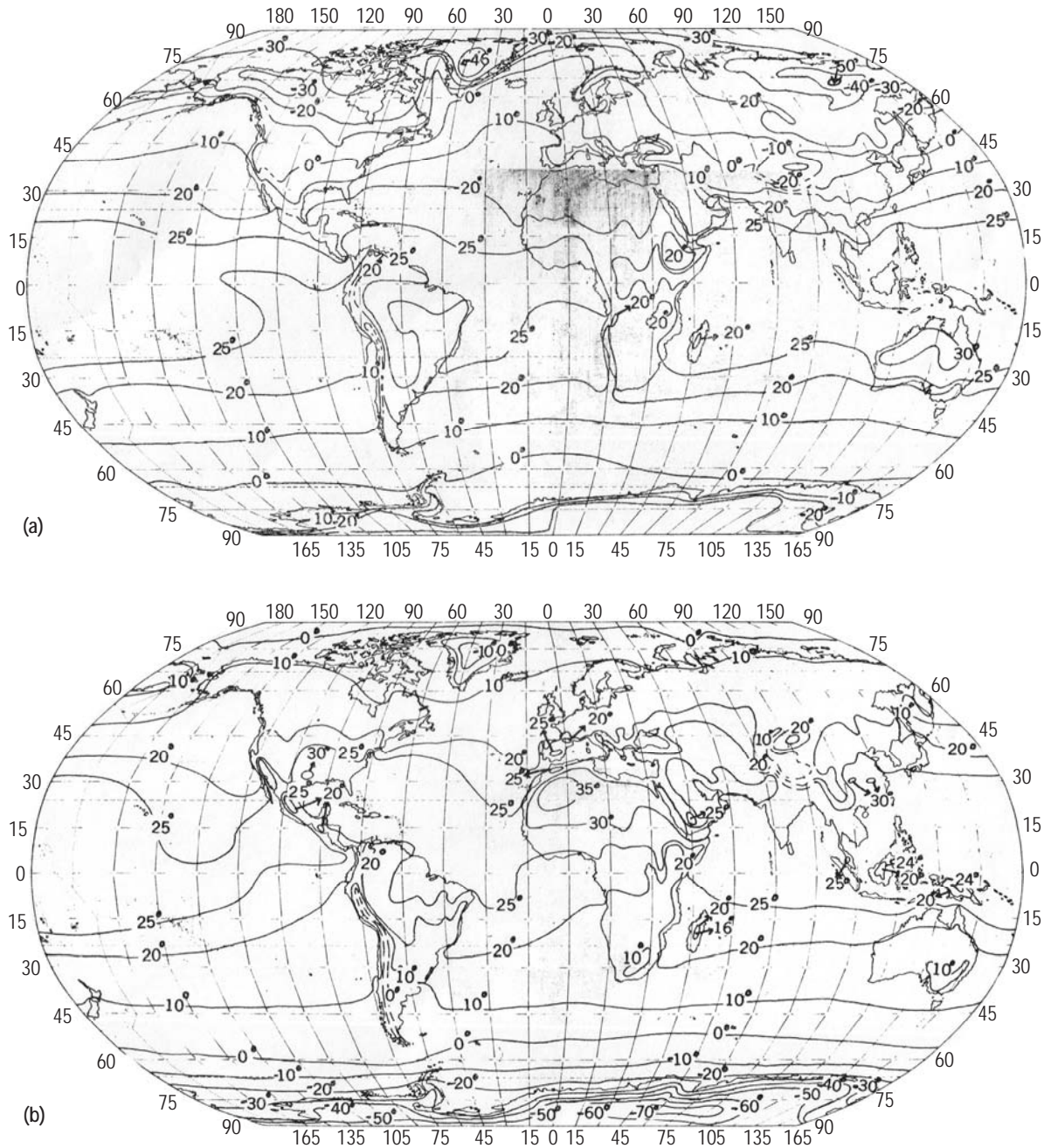


Figure 5-1. Approximate average surface temperatures ( $^{\circ}\text{C}$ ) for the world for (a) January and (b) July.

with reference to the U.S. Navy and Russian (Morskoi) marine climatic atlases previously discussed. Comparison has been made also with the U.S. Department of Commerce publication, *Climates of the World* (1969).

Several atlases contain information on temperatures on regional, hemispheric, and global scales. These also contain information on other elements. Perhaps the most extensive of these is the U.S. Navy Marine Climate series. Beginning in 1955, nine regional volumes were issued at about one per year. Then this atlas series was updated, in some cases with a revised format. One drawback, on the global scale, was the presentation of only marine area data for the surface. See Crutcher (1969b) for the free atmosphere. See also the series Taljaard et al. (1968), Taljaard et al. (1969), van Loon et al. (1971), and Crutcher et al. (1971), who present the first atlas on the Southern Hemisphere which contains surface as well as upper air information, including temperatures. All of the above atlases used point (station) observed data as the basis for analysis.

The 1989 atlas issue of the DoD, U.S. Navy/U.S. Air Force uses the daily output of global analyses as the base for a global upper air climatology. The period of data is 1980–1985, 6 yr from a solar maximum to a solar minimum. There may be trends in the data which do not appear in these analyses. Also, no prior atlases or this series provide the necessary variance-covariance matrix measures by which real and/or statistical differences between the atlases can be estimated for significance. A decided improvement in these series of atlases is the provision of histograms or standard deviations to assess some measure of variability. A further step for improvement and use and in assessment of climatic change would be the provision of the multivariate mean variance-covariance matrices. It is realized that, in printed form, these would be voluminous. However, data reduction techniques are available in statistical, scale, and physical form. Today, there exist the now commonplace digital magnetic tapes and the CD-ROM storage and retrieval potential.

The data to produce the U.S. DoD, U.S. Navy/U.S. Air Force (1989) atlases were the 2.5° latitude-longitude grid point analyses of the European Center for Medium Range Forecasts (ECMWF). Informal comparison between selected grid point data of prior atlases and these atlases indicated no extreme differences. Without doubt, the procedures used to produce this series of atlases are forward progress in terms of costs, time, and personnel requirements. The reader is cautioned that all analyses are made by computer algorithms and that considerable differences may occur between one model and another. Differences detected between atlases may well be created, in part, by the differences in model concepts. Also, much smoothing usually is incorporated in the analyses. This smoothing may damp the ridges and trough properties. There also is the problem of geostrophic smoothing. In some cases, gradient adjustments are made. However, in general, at least in the past, the tendency has been to force a balance in circulation. If there is a balance, there can be no net transport of climate identities.

The U.S. Navy/U.S. Air Force atlases (op. cit.) provides by month, for 13 pressure levels (1,000 to 30 mb), means and standard deviations for temperatures (°C), dewpoints (°C), heights (dkm), winds (kt), and densities ( $\text{kg m}^{-3}$ ). Polar stereographic and latitudinal-longitudinal strips present the Northern and Southern Hemisphere information. In addition, there is information on jet streams and wind roses. The wind rose presentation is extensive and regional. In some respects, these wind rose presentations may be considered to be polar histograms.

Cayan, Ropelewski, and Karl (1985) present an atlas of United States monthly and seasonal temperature anomalies for the period December 1930 through November 1984. They present (1) seasonal long-term means and standard deviations, (2) monthly long-term means and standard deviations, (3) seasonal standardized anomaly time series and monthly standardized anomaly frequency distributions for selected divisions, and (4) monthly and seasonal standardized temperature anomalies.

The analyses of temperatures at 337 climate divisions in the contiguous United States serve as the base. Standardization implies the division of the temperature anomaly by the standard deviation. The seasons are the

traditional Northern Hemisphere season, December through February, etc. For selected divisions, time series of seasonal standardized anomalies and frequencies of the standardized values are shown. The data shown include some of the corrections for bias in a paragraph below.

Figures 5-2(a) and (b) (after Cayan, Ropelewski, and Karl (1986)) illustrate seasonal grand mean temperature ( $^{\circ}\text{C}$ ) and standard deviation individual charts for the contiguous United States. The isopleth values of the standard deviations need to be multiplied by 0.1.

There is a need indicated in the above paper and in the experience of the writer for quality editing (not quality control) and the methods to make adjustments for (1) change of observation time, (2) change of observer, (3) change of station location, (4) change of instrumentation of the same or different type, (5) degradation of instrumentation as indicated by inspection records or by comparison with regional norms, and (6) change of exposure, such as grass and irrigation in arid regions; drainage of nearby bog type; change of nearby trees and/or shrubs; and heavy nearby construction, such as great highways, great buildings, or paving, such as concrete and/or macadam at airports or dock areas. For all of these reasons, it is important that, wherever possible, benchmark stations with considerable terrain be set aside where the major portion of the above problems can be alleviated. Control limits are established in the design of a system. Editing can only determine whether data obtained are within the specified limits. Quality cannot be built into the data. The above comments apply to all climatological/meteorological services in all states.

Figure 5-3 provides a time series and frequency distribution of the climatological division, 4103, North Central Texas, USA, of the standardized seasonal temperature anomalies, 1931–1984. The “Z” values, the usual statistical notation for standardized normal distribution values, must be multiplied by the appropriate standard deviation. The product should then be added algebraically to the mean-value as an approximation to a value that may have been used in derivation of the mean and the standard deviation. Closely approximate values only can be obtained. These are due not only to rounding errors always inherent in such presentations but to the fact that the value so obtained is theoretical and highly probable. A glance at this information does not portray a period cooling or warming. The histograms contain an overlay normal distribution curve.

The WMO has indicated that, wherever possible, some measure of variability always be provided. The usual measure provided is the standard deviation. At this point, it is urgent to state that the mean and the variance (standard deviation) are arithmetic artifacts. These can be derived empirically for any set of data no matter what the fundamental distribution model may be. The standard deviation is very useful whatever the underlying distribution may be. But the user must have some idea as to what that distribution model may be. For example, in the above data, the implied distribution is the normal distribution. The probable occurrence of any value or less can be given. Where precipitation is involved, the implied distribution may be the gamma or perhaps the log-normal. Here, also, the standard deviation is useful in arriving at similar statements of expected values equal to or less than a given value. The treatment, of course, is not the same as in the normal distribution. In these and other distributions, the standard deviation is an extremely useful statistical parameter. See Essenwanger (1976, 1986) for more details.

In a time sequence from about 1890 to 1983, figure 5-4(a) and (b) show the course of annual maximum, minimum, and average temperatures ( $^{\circ}\text{C}$ ) for before and after processing at the NCDC, at Corpus Christi, TX. The original data, though still retained as the original record, now show in the adjusted record the application of some of adjustments for bias indicated above. These are unpublished. See Karl and Williams (1987) for details. The viewer might say that the adjusted record implies a warming trend. However, this slight warming trend is not noted at all for the other stations in the United States. In fact, the stations in the southeastern United States show a slight cooling trend. This feature will also be noted later in the discussion on sea surface temperatures.

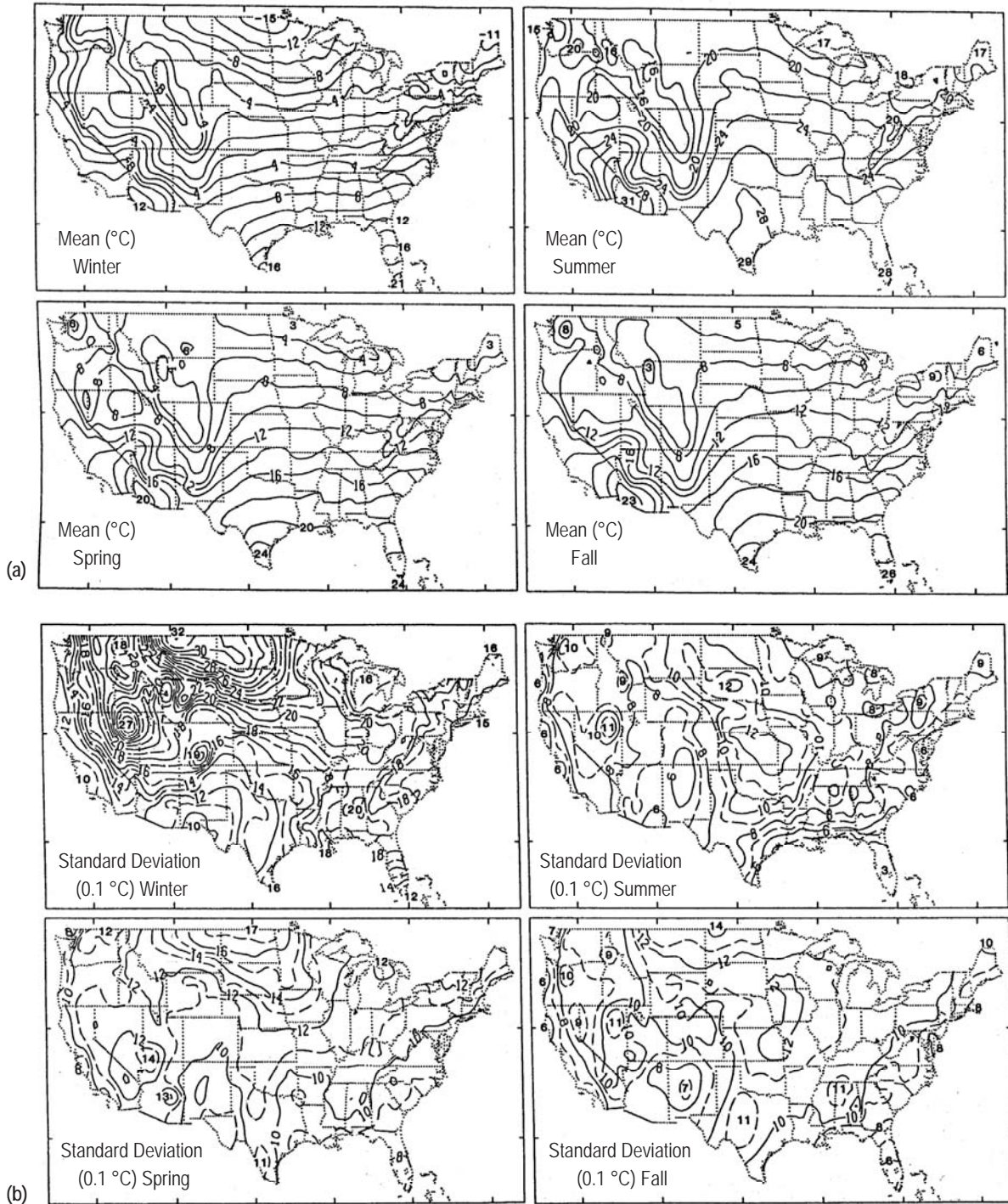


Figure 5-2. Seasonal (a) grand mean temperatures (°C) and (b) standard deviations of temperatures (°C) for the contiguous United States (courtesy of Cayan, Ropelewski, and Karl (1986)).

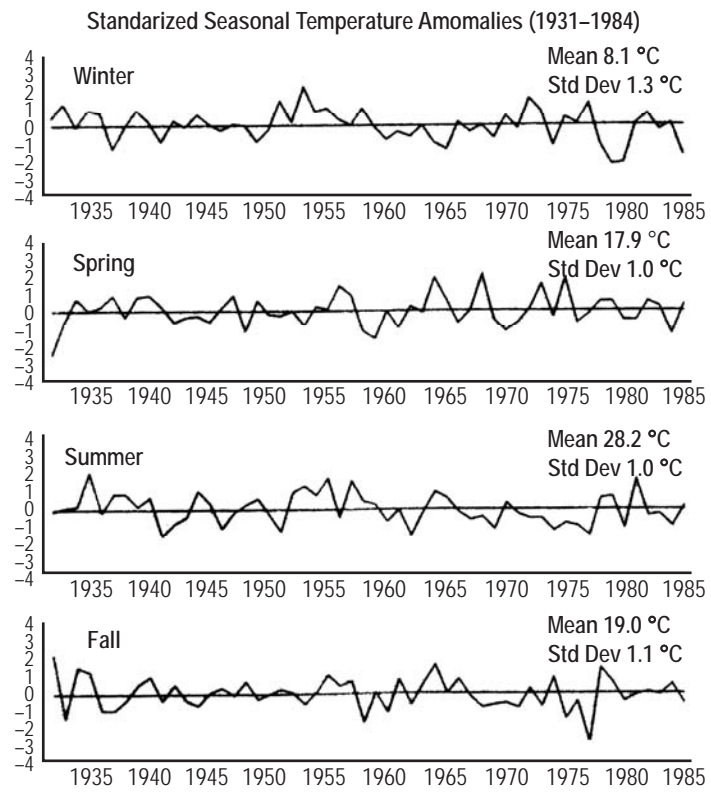
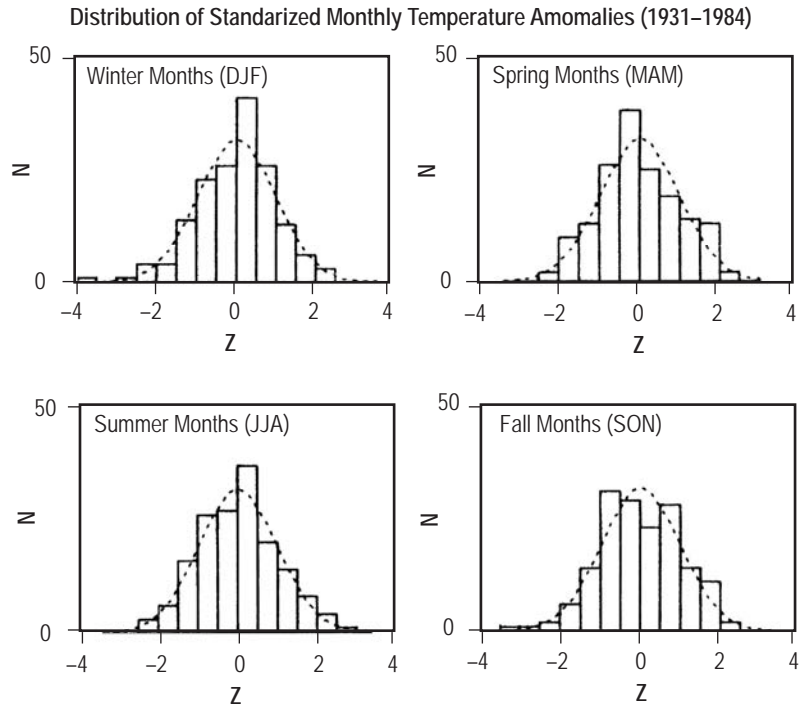


Figure 5-3. Time series and frequency distribution of standardized seasonal temperature anomalies (°C), 1931–1984, of the Climatological Division, 4103, North Central Texas, USA (courtesy of NOAA, NCDC).

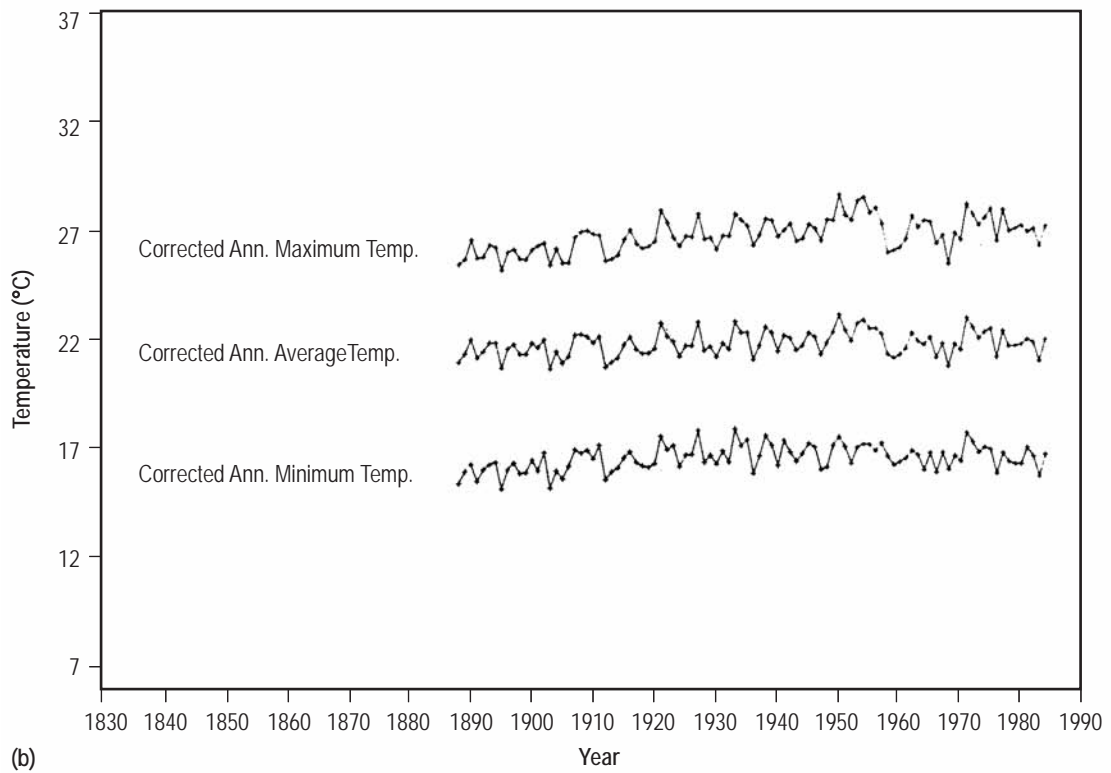
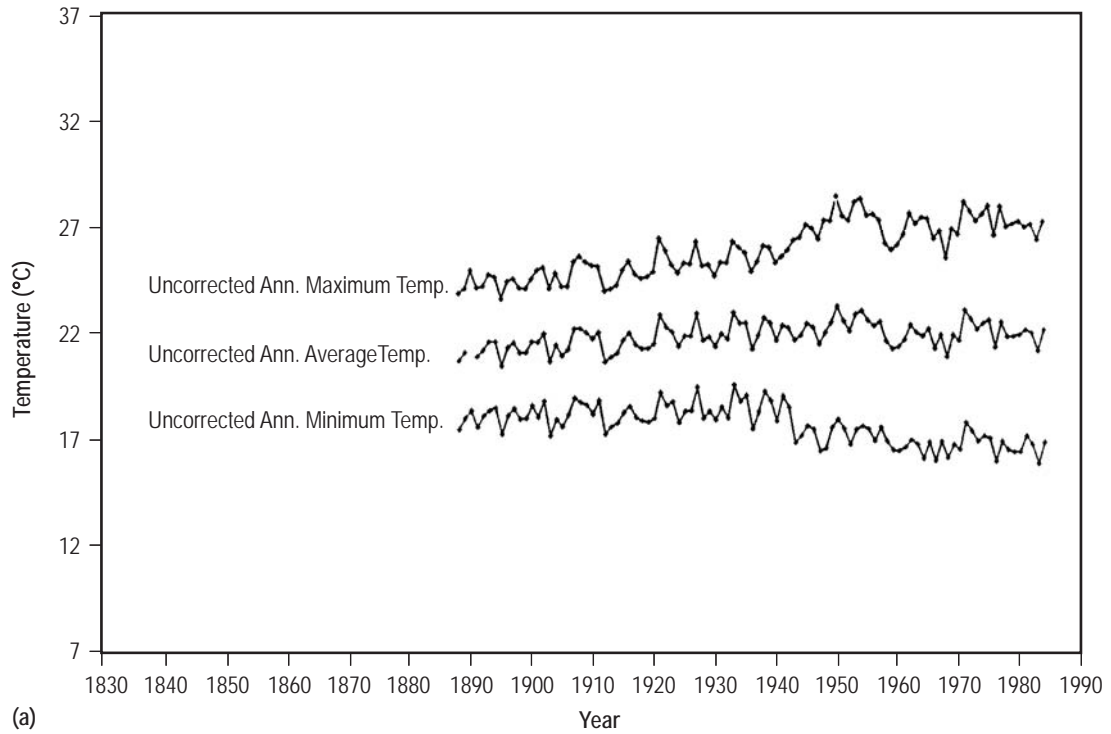


Figure 5-4. Course of annual maximum, minimum, and average temperatures (°C) for (a) original temperatures before editing and processing and (b) adjusted temperatures after editing and processing at station No. 412015, Corpus Christi, WSO AP, TX, at the NOAA, National Climatic Data Center (unpublished) (courtesy of NOAA, NCDC).

Figure 5-5(a)–(c) (1895–1985), modified after Karl and Koss (1984), show the results of temperature data processing at the U.S. National Climatic Data Center. The data are really weighted. These figures, respectively, show the national (USA) annual mean temperatures for the period 1895 to 1983 and the southwestern and southeastern portions of the United States. The general view of these figures and others in the same publication does not support a general warming for this period. Instead, these permit an inference of a slight warming trend in the early part of the period, reaching a maximum in the 1930–1940s with a subsequent return to cooler periods. This characteristic is noted for the other sections of the United States. The period 1986–1988 (not shown here) has been warmer.

The effect of urbanization on the observed temperatures has long been a factor considered by climatologists. Such assessment is difficult. Mitchell (1961), Landsberg (1981), Kukla, Gavin, and Karl (1986), and Karl, Diaz, and Kukla (1988), among many others, provide information on the problem of urban effects. In particular, much care needs to be used to establish any definitive statements on temperature trends. Long-term trends are especially sensitive to urbanization and to the other problems discussed above.

Figures 5-6a through 5-6c show original summer temperatures and the results of adjustments for changes in observation times and location changes, 1885–1983, Setauket, NY. See Karl et al. (1986), Karl and Williams (1987), Karl, Baldwin, and Burgin (1988), Karl, Williams, Quinlan, and Boden (1990), and Kukla et al. (1986). Figure 5-6a provides traces of the mean maximum, mean minimum, mean temperature, and the temperature range. In this case, the only observation time change occurred with a station location change in 1960. Figure 5-6b shows the curves after adjustment for the observation time change for each of the foregoing measures. Included is an indication of the variance and the 16 to 84 percent confidence interval. Figure 5-6c shows the curves after adjustments for both the observation time and location changes. Again, a measure of the variability is indicated by the confidence intervals on the horizontal line drawn across the top of the chart. As no good estimate of urban warming is yet available, no corrections for that feature are made here. Figures 5-6a through 5-6c should be viewed as if urban warming is nil, though it is considered to be a serious factor.

The heavier curves are third-order or 9-point binomial smoothing procedure. The reader should not attempt to deduce any forecasting capability from these particular curves. All that these curves attempt to portray is general trends. As such, they seem to portray fairly well the central portion of each data set. Do not attempt to read too much from the first quarter nor the last quarter.

Figure 5-7(a) and (b) also show an indication of temperature trends in Alaskan seasonal temperatures (Diaz (1980)). Figure 5-7(a) is for the season October–March while figure 5-7(b) is for the season April–September for the period 1930–1979. The heavily starred curve is a third-order polynomial fit to the data. The winter season appears to have about twice the amplitude of the summer season with a mean temperature of about  $-12.8^{\circ}\text{C}$  versus  $6.2^{\circ}\text{C}$ .

Figure 5-8(a) and (b) represents the winter time means, respectively, for the surface air temperature at Asheville, NC, and Philadelphia, PA, for the period 1888–1976. Figure 5-9 represents the winter surface air temperatures' departure from the long-term mean (1895–1979) for Illinois. The trend lines are a third-order polynomial fit. Quite clear in all these records is the maximum of the temperature occurring somewhere between 1940 and 1950, the exact time being a function of location. Also, this feature was noted during the preparation of the pilot volume, Volume 1, North Atlantic Marine Climatic Atlas of the U.S. Navy. Optimum periods for the determination of climate means were being sought. Since the end of the 1970s there has been a tendency for some regional temperatures to rise, but even this is not evident across the entire United States nor the world. There are those who do not agree with the last statement and will present their evidence. Perhaps the United States and the northern oceanic regions are too parochial a view.



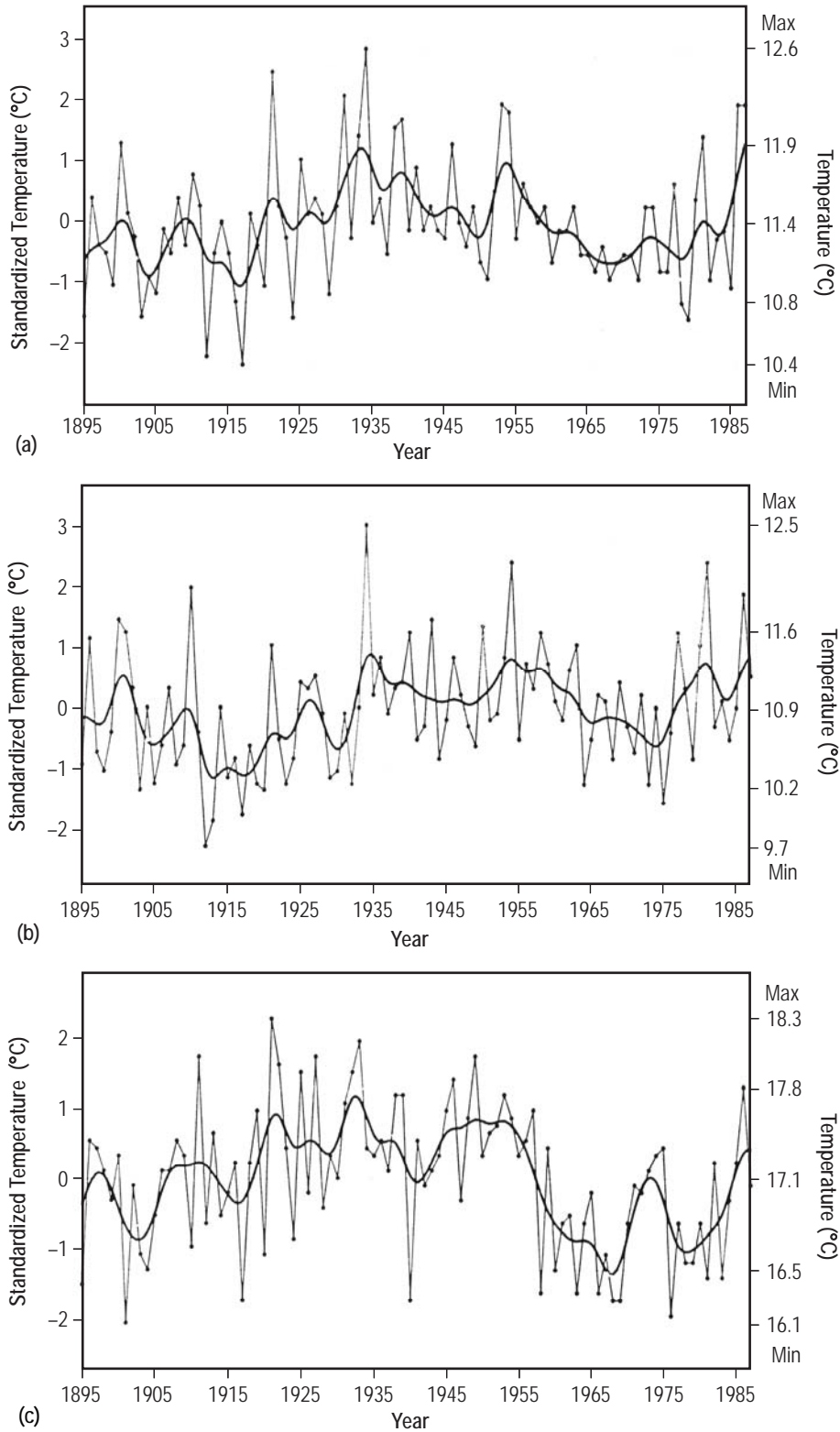


Figure 5-5. Annual areally averaged, weighted, processed mean temperature (1895–1985) data for the United States for (a) national temperature, (b) southwestern temperature, and (c) southeastern temperature (modified after Karl and Koss (1984)).

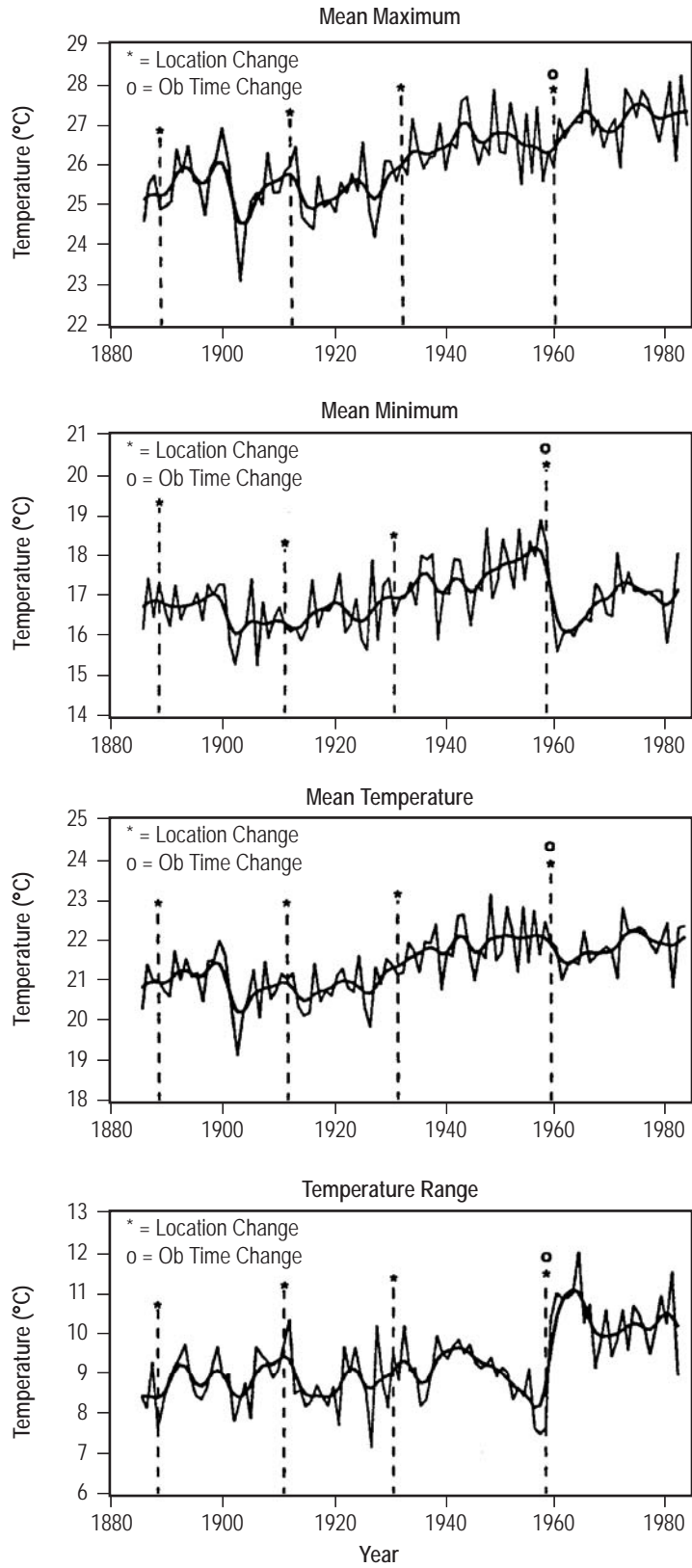


Figure 5-6a. Setauket, NY, original summer temperature traces for the 1885–1983 period of the mean maximum, mean minimum, mean temperature, and temperature range. The open circles denote an observation time change and the asterisks denote a station location change (courtesy of NOAA, NCDC).

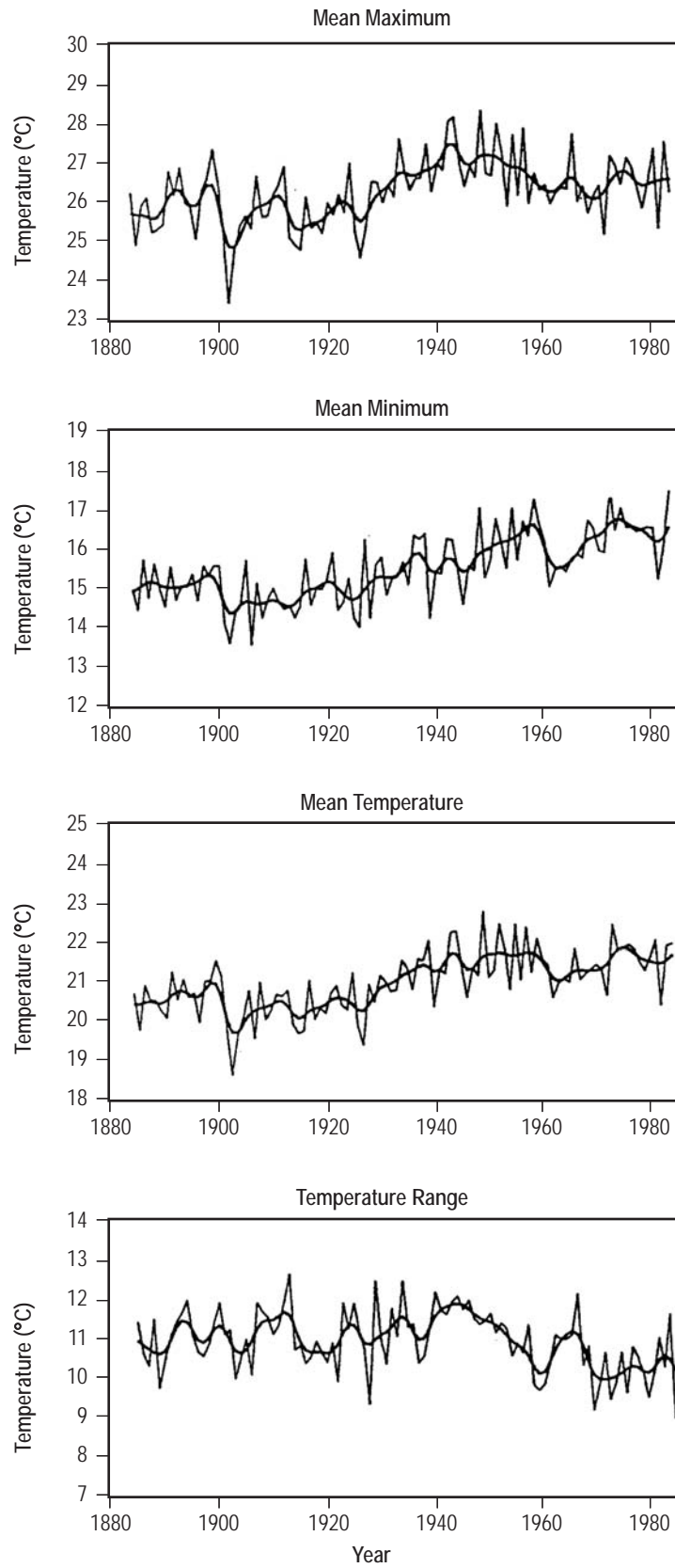


Figure 5-6b. Setauket, NY, location change adjusted summer temperatures for the 1885–1983 period of the mean maximum, mean minimum, mean temperature, and temperature range (courtesy of NOAA, NCDC).

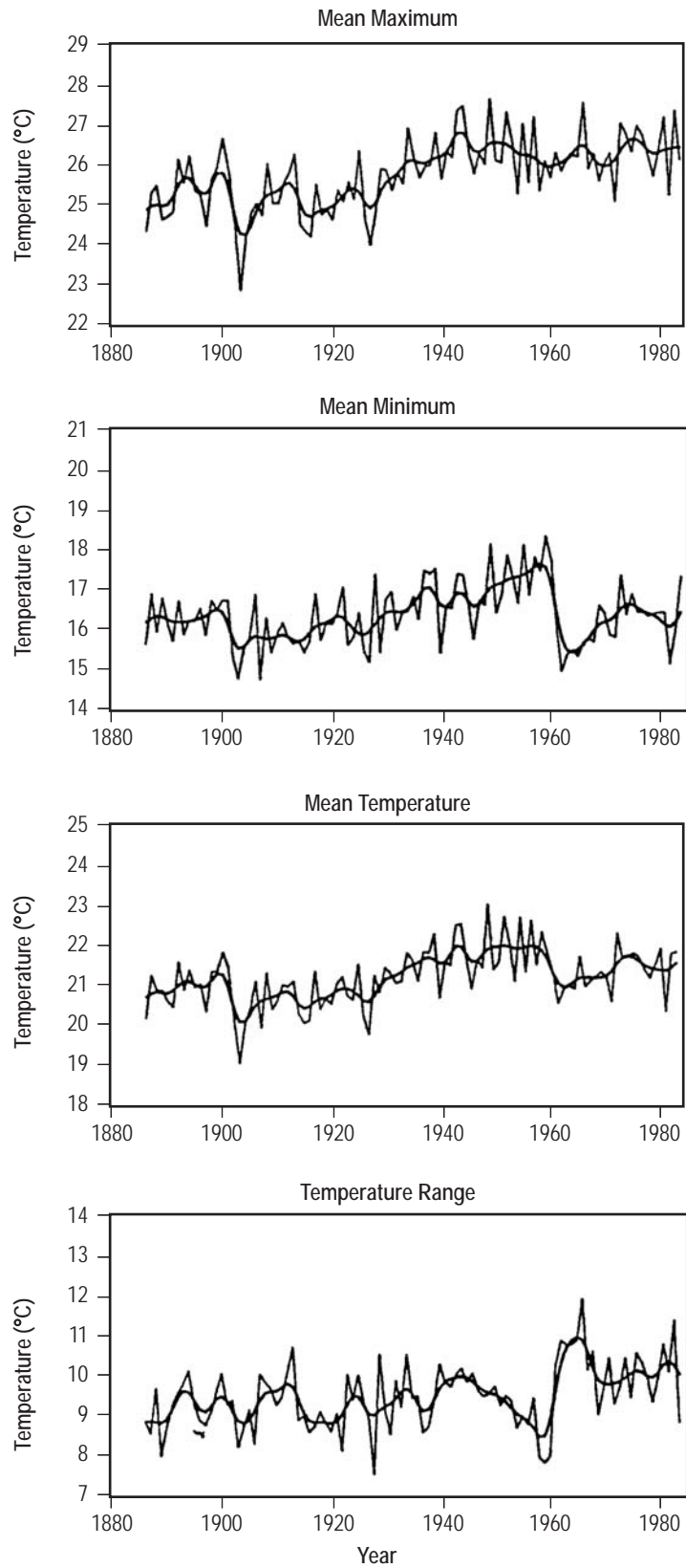


Figure 5-6c. Setauket, NY, summer temperatures for the 1885–1983 period of the mean maximum, mean minimum, mean temperature, and temperature range. Changes have been made with respect to both observation time change and station location change (courtesy of NOAA, NCDC).

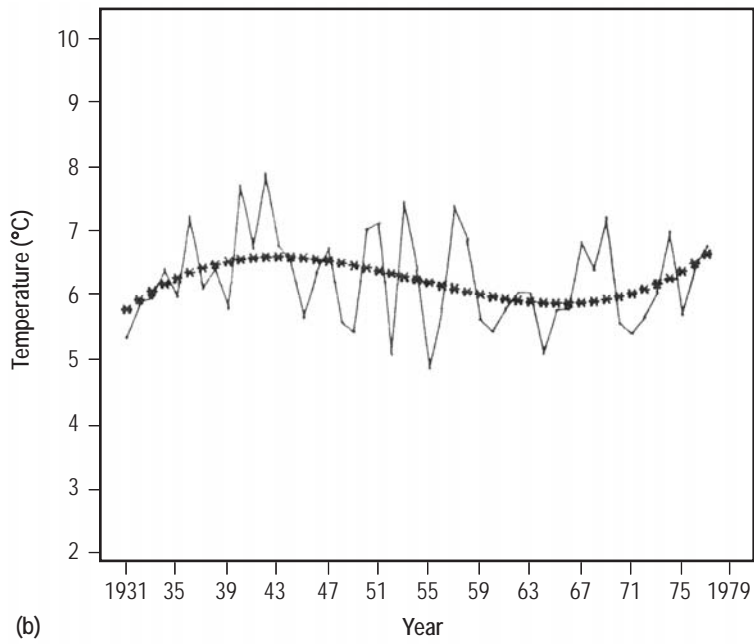
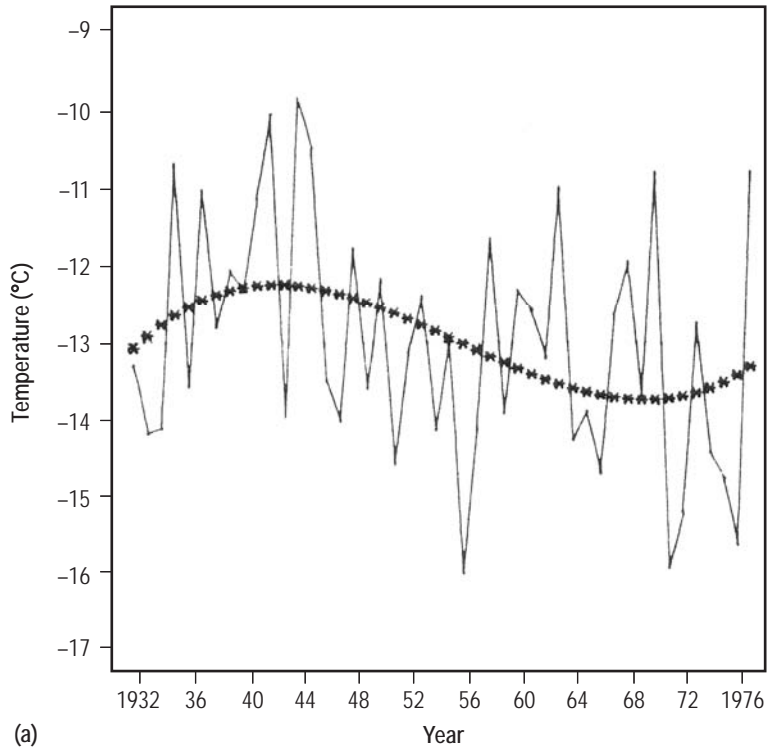
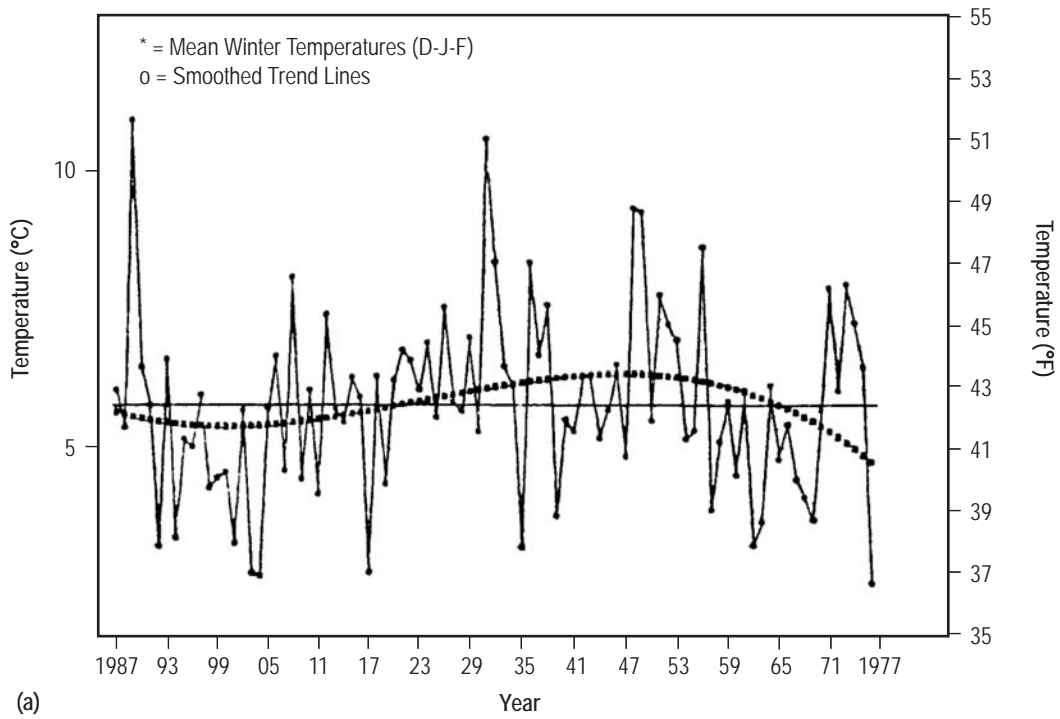
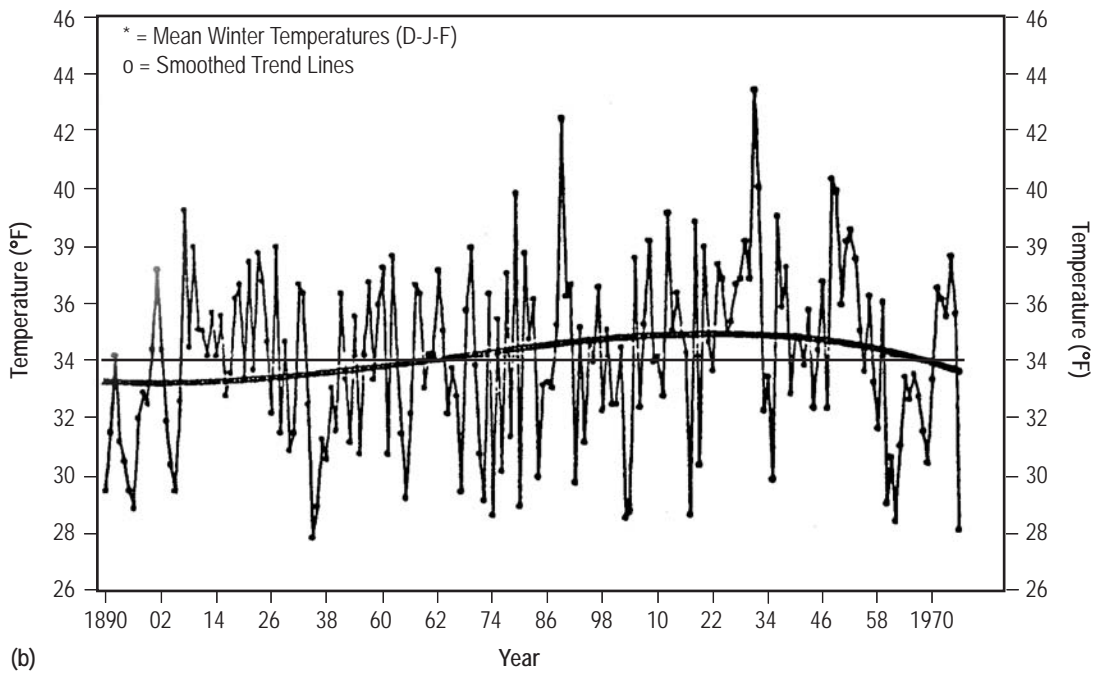


Figure 5-7. Alaskan seasonal temperature for (a) October–March and (b) April–September, 1930–1979. The heavily starred curve is a third-order polynomial fit (courtesy of Diaz (1980)).



(a)



(b)

Figure 5-8. Mean winter temperatures for 1888–1976 for (a) Asheville, NC, and (b) Philadelphia, PA (courtesy of NCDC).

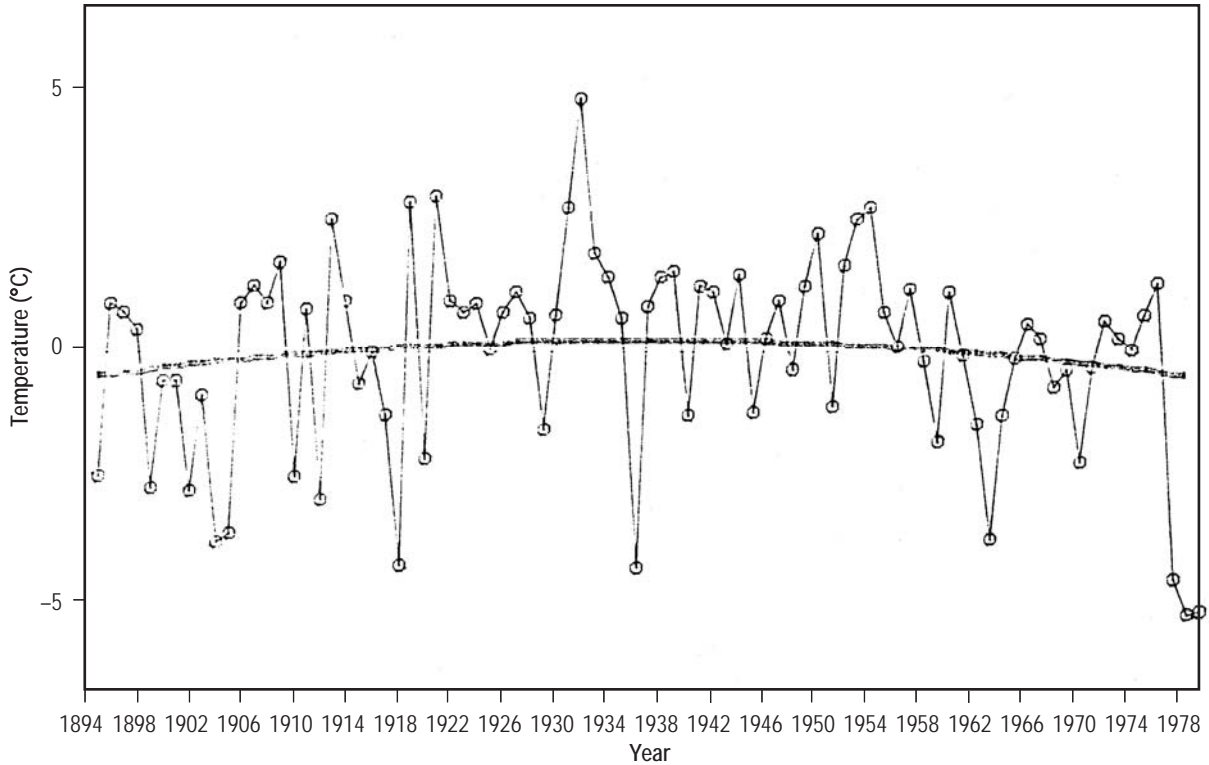


Figure 5-9. Illinois winter (D-J-F) surface temperature departure from the long-term mean (1895–1979) with suggested trend line (courtesy of NCDC).

#### 5.4 Temperature Relationships

Figures 5-10 and 5-11 present another aspect of the temperature variability. These appear in *Climate and Food*, a National Academy of Science publication (Crutcher (1976)). Figure 5-10 portrays the progression of 20-yr annual averages of temperature in the United States with periods overlapping every decade from 1931 to 1950 and 1951 to 1970. With the exception of the extreme west-southwest, the temperature indicates a cooling expansion or a southward progression. Figure 5-11 was prepared in 1975 to compare the 5-yr period 1969–1974 with the 1951–1970 isotherms of figure 5-10. The arrows imply that the cooling trend exhibited in figure 5-10 may have slowed. These data have been updated by comparing the U.S. 1951–1970 and 1961–1980 data. With the exception of the southernmost part of Florida and extreme northwestern portion, cooling continues. It is noted here that this technique of comparing overlapping 20-yr means would be the same as comparing every other decade beginning in 1931.

The selection of 20-yr periods is completely arbitrary. Ten-year comparisons were made as well as 30-yr comparisons. Understandably, the 10-yr presentations show a considerably more variable position of the isotherms while the 30-yr average temperatures for the periods are, in general, not as variable. This is simply a manifestation of the central limit theorem in statistics.

Another aspect of variability is shown in figure 5-12(a) and (b) taken from figures 1 and 8 of van Loon and Williams (1976). Also see Crutcher (1978). Respectively, these figures show the slopes of the regression lines, or equivalently, a measure of the temperature correlation coefficients for the periods 1900–1941 and 1942–1972. The important point is that the figures display a change of slopes of the trends with time. The shorter the time interval, the more rapid the slope may change. As time goes on, the correlations are expected to change (vary) at a point or

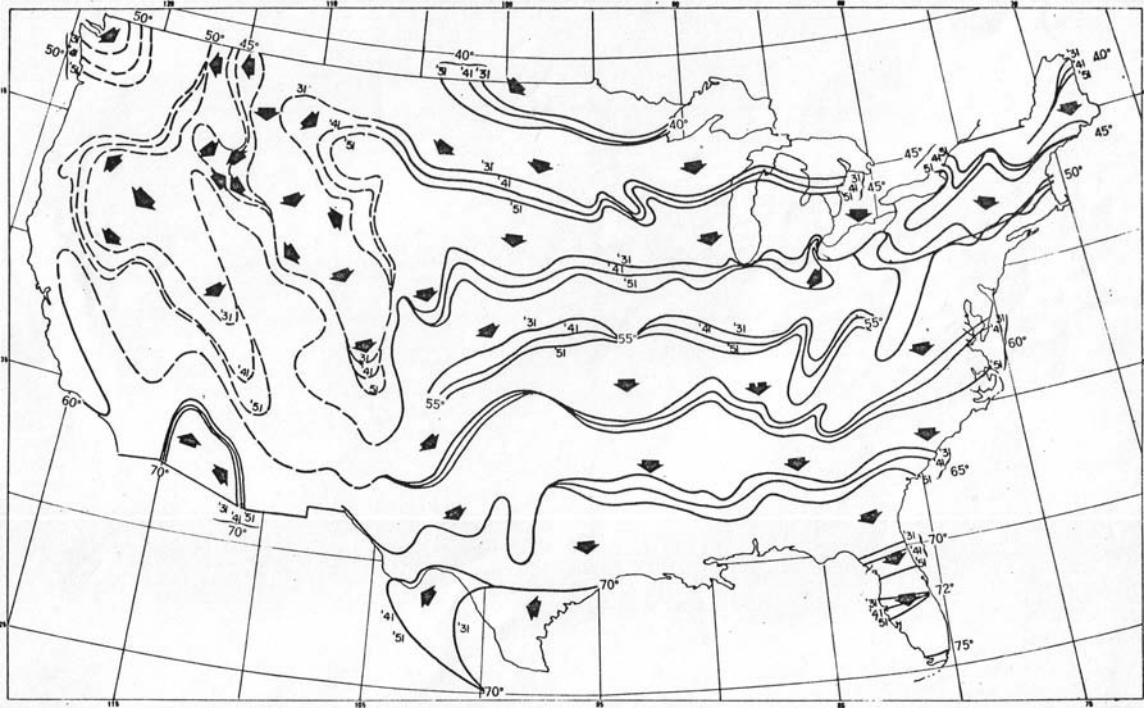


Figure 5-10. Twenty-year isopleth progression temperature changes for the United States for the periods 1931-1950, 1941-1960, and 1951-1970 (after Crutcher (1976)).

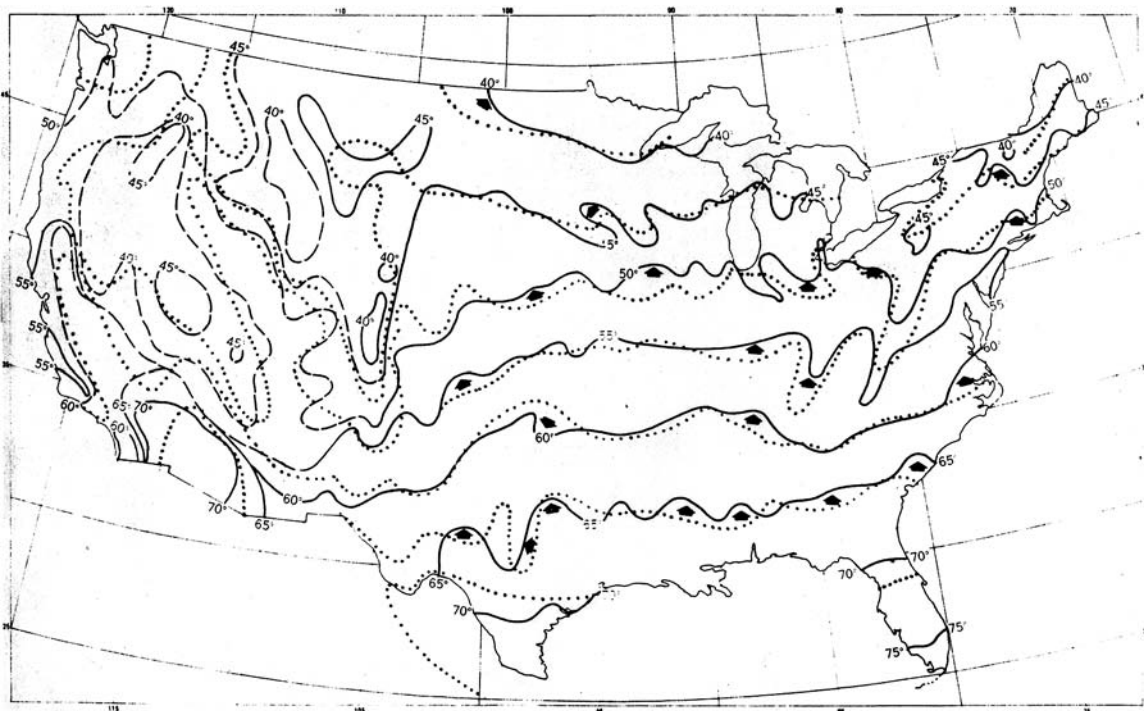


Figure 5-11. Comparison of the isopleths of the United States pentad, 1969-1974, temperatures with the 20-yr period, 1951-1970 (after Crutcher (1976)).



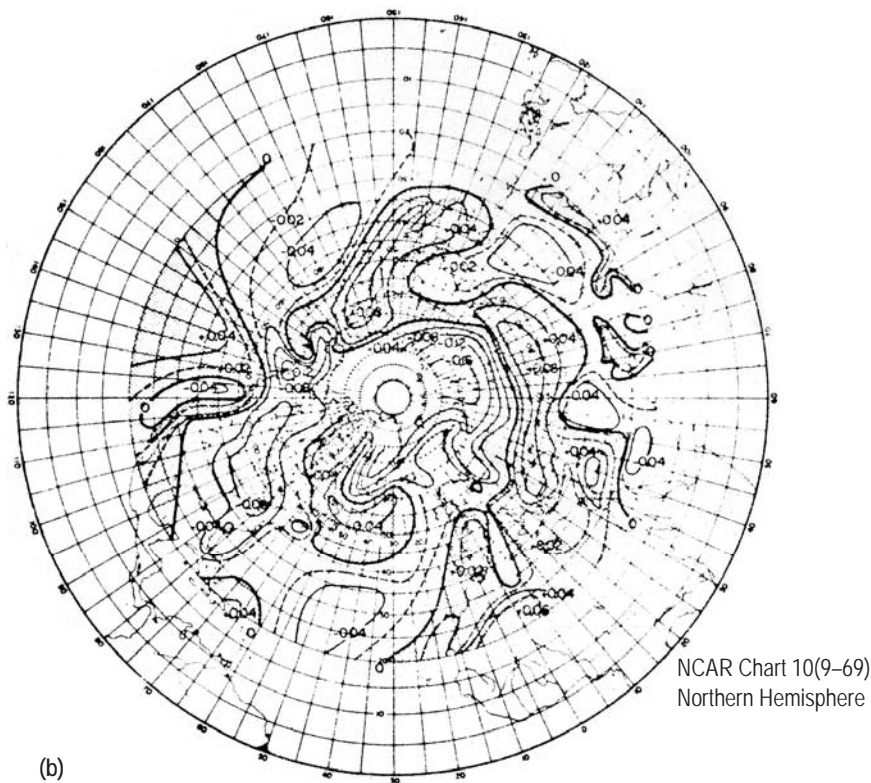
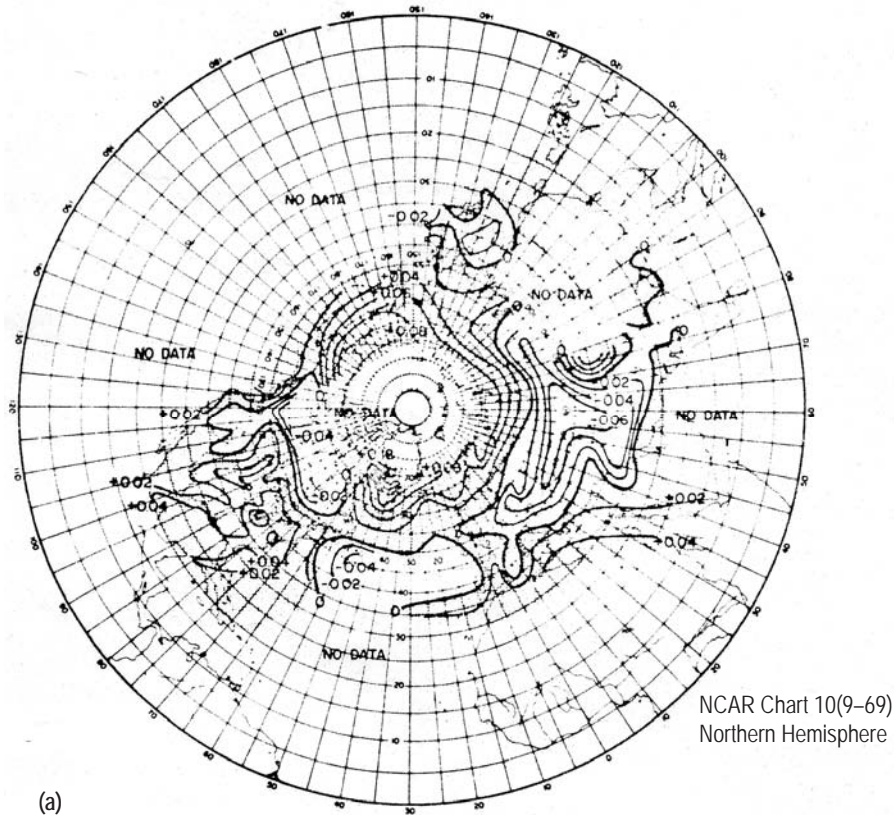


Figure 5-12. Isopleths of the slope of the regression line for winter mean temperature for (a) 1900–1941 and (b) 1942–1972 (with permission, after van Loon and Williams (1976), American Meteorological Society).

in an area or region within the weather and climate complex. Still another facet is shown by Crutcher (1960) who provides tabular and map presentation means and variances of temperature and precipitation for 43 stations in North America (1906–1943). A procedural statistical description of temperature, precipitation, and combined temperature-precipitation climates is proposed. The data in that study are limited to monthly mean data through the years and only to temperatures and precipitation. This objective procedure reproduced, at least within the contiguous United States, the Koppen classification, Koppen (1931, 1936) described by Trewartha (1954). The temperature-precipitation matrices used were  $6 \times 6$  composed of the first three harmonic coefficients of the monthly means of the temperature and precipitation at 43 stations. The use of these coefficients reduced the primary matrices from  $24 \times 24$  to  $6 \times 6$ . At the time this study was done, the inversion of  $24 \times 24$  matrices was not a viable option on a electric or manual desk calculator. That is not true today but other restrictions exist. The procedure is unrestricted except for the computer capacity and costs involved in processing large data banks. The user, as in all other cases, must consider effort, time, and cost. Clusters of relatively homogeneous locations are suggested through the use of pattern recognition clustering and discriminant function applications.

The statistical concepts employed in that study and based on Fisher (1936) have been expanded and improved in Wolfe (1971), Crutcher and Joiner (1977), Rhodes (1980), and Crutcher et al. (1986). The computer programs are provided in the last three. NORMIX is the computer program acronym for normal mixtures program (Wolfe (1971)). Basically, the data sets are normalized, if necessary, and then standardized. The first transforms data sets such that the normal distribution may be used to describe each marginal data set. The standardization; i.e., the division of the data by the standard deviations of the transformed sets produces dimensionless data in the sense, for example, that if the data were originally in degrees, these are now just pure numbers. Due to the formation of these dimensionless standardized data, the applications are universal over any or all disciplines. The data may be multivariate; i.e., temperature, precipitation, etc. In the case of winds, the directions and speeds will have been transformed to orthogonal components. These multivariate vectors are then compared one by one and grouped into clusters which are in themselves more alike than those in neighboring clusters. Discriminant function equations are then formed to allow the classification of each individual datum into an appropriate cluster. Additionally, new data may be classified into those clusters. Of course, if the original data were trivariate—say temperature and wind components—the new data must be in the same form. As an example of the output, see figure 7.6.1 from Crutcher and Joiner (1977) which will be shown in that later section.

## 5.5 Dewpoint

In the first section, the change of state was mentioned briefly. In the atmosphere and on oceans and land, there are important changes of state associated with water or the moisture in the air. These are the evaporative-condensation (sublimation) and the fusion (ice)-melting (water) boundaries. Energy and moisture are the basic ingredients. The changes of state involve considerable exchanges of energy; see the introduction. Energy—within a state, in part, measured by temperature—exerts the main control. Much energy absorption is involved in the transformation of solid water (ice) to water vapor. There is no change of temperature at the transformation points—melting and vaporization. The energy held in the state as latent energy will be released in the condensation and fusion process. As mentioned previously, the energy for the total transformation of solid to gas or back to solid is the greatest of any chemical component. Two of the several temperature arguments are important here. These are the dry-bulb temperatures and the dewpoint temperatures. The first was discussed in the foregoing paragraphs simply as temperature. The second is a variable control on latent energy release. At a constant pressure, the amount of moisture that the atmosphere can hold is a function of temperature. Further importance of the dewpoint lies in its information, as to the amount of moisture available, for it is the saturation temperature of the air being sampled. Starting at the dewpoint, any reduction of temperature will result in a change of state under ordinary atmospheric conditions with production of water and release of the latent heat in a sensible form. These temperatures are useful in other ways—one of which is to permit the assessment of precipitable water in the atmosphere above the measurement locale. See Linsley, Kohler, and Paulhus (1949). Thus, some idea as to the potential precipitation is obtained. The dewpoint can be used to help identify boundaries of an air mass.

Figure 5-13(a) and (b) illustrate mean dewpoint temperatures on a global scale for January and July. These are for liquid conditions; i.e., over water, and not over ice. There is a difference because the vapor pressure of water vapor over ice is different than over liquid water—ice and liquid water being two different states of water. Because the relationship is not linear, the use of mean dry-bulb and mean wet-bulb temperatures to obtain mean dewpoint temperature or a mean humidity will not obtain the same value as the averaging of the individual dewpoints

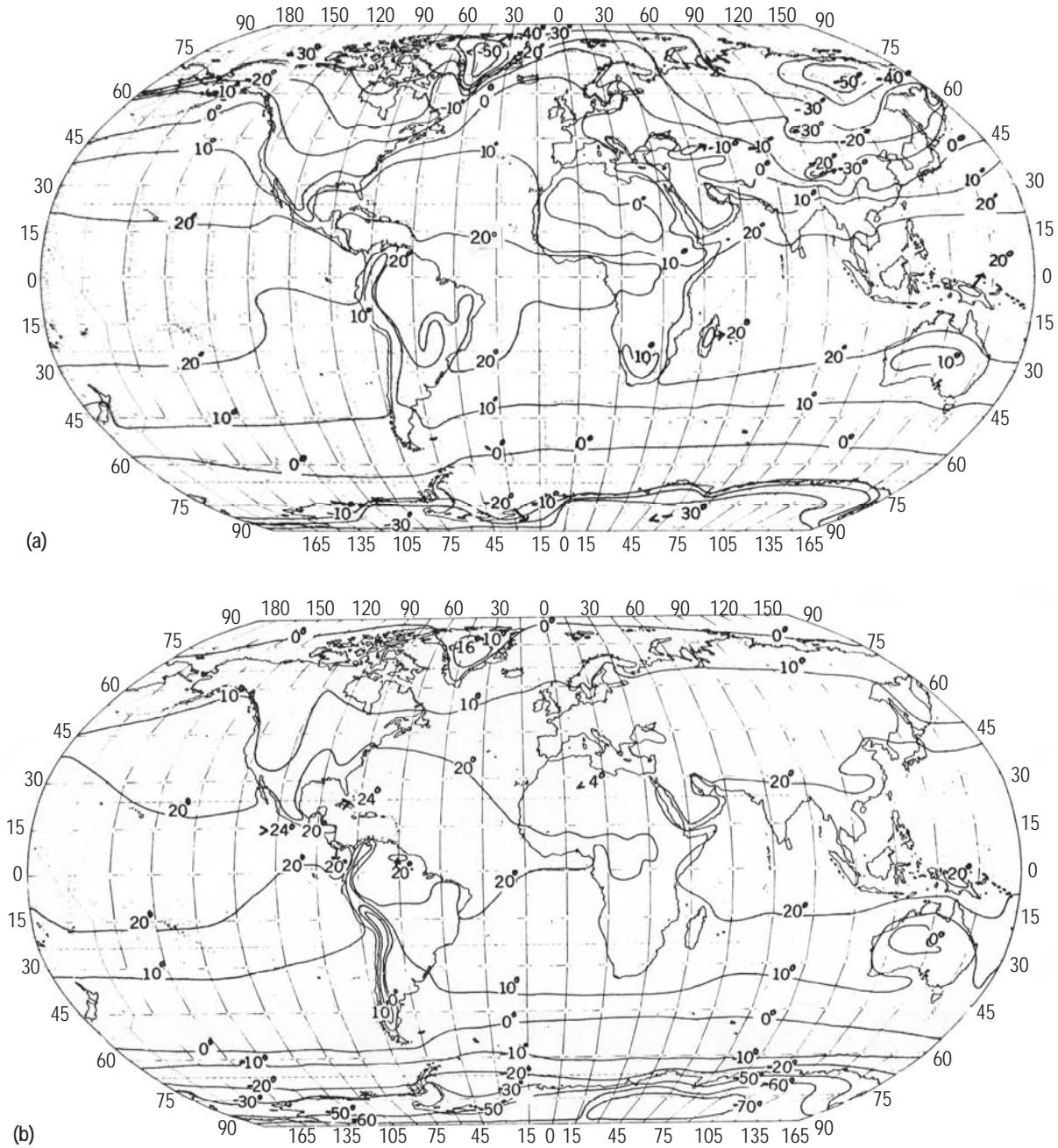


Figure 5-13. Global mean dewpoint temperatures (°C) for (a) January and (b) July.

or humidities. Generally, the values will be close. Comparison with the dry-bulb temperature charts of figure 5-1(a) and (b) will provide a very rough idea as to the relative humidity, the wetness or dryness of the area being examined. The greater the difference, the drier the air. There are several measures usually associated with atmospheric moisture. These are vapor pressure, dry-bulb, wet-bulb, and dewpoint temperatures as well as humidity. Humidity may at times be given in specific, absolute, or in relative terms. Absolute humidities are often used in volumetric problems, such as breathing, or in motors involving combustion. Given any two of the first four measures, the remaining two can be determined. Tables are available in Berry, Bollay, and Beers (1945), List (1958), Marvin (1900), and Environment Canada (1976). In the United States, slide rules are now used and recourse to tables is minimized (U.S. Government, Department of Commerce, 1979). Computer and associated software programs may be used with appropriate and equivalent algorithms to derive moisture relationships when two of the above variates are provided.

See Crutcher (1969b) for humidity (dewpoints) of the upper air, 850 mb through 500 mb. The DoD, U.S. Air Force Handbook of Geophysics (1985) extensively and excellently treat the closely related subjects of water vapor, precipitation, clouds, and fog. Fourteen colleagues contribute that chapter, Chapter 6. See also Gringorten et al. (1966) who present a Northern Hemisphere Atmosphere Humidity Atlas. See the Traveler's Research Center report (1966) which discusses the inadequacy of the solutions to the global classical equations. The same problem remains today. Again, it is urged that considerable attention be made to the provision and maintenance of adequate sensors, recording devices, and archival. Crutcher, Cadavid, and Villegas (1979) support Wiesner's (1970) consideration of the association of 27.5–28 °C water temperatures with land surface dewpoints of 25.3–25.8 °C in 12-hr storms. The inference is made from accompanying figures (not shown here) that these values are indeed valid for the southwestern Colombian coast but that the available moisture is greater in the remaining coastal areas. The suggested water temperatures (dewpoint) for these areas is 28.5 °C. This is equivalent to a maximum of ≈6 mm of precipitable water between the surface and 200 mb above the amount associated with the temperatures considered by Wiesner (op. cit.), for a total of ≈106 mm.

A review of maximum dewpoints for the Amazon River Basin, particularly the southern Venezuelan, the southeastern Colombian, the northeastern Peruvian, and the northern Brazilian regions maxima of 22 to 24 °C. This may be due to the daily early convection process and to the porous soil percolation of excess rainfall. In the interior of the continent, the maxima decreases to 22 to 23 °C. Apparently, the atmosphere cannot maintain the 24 °C in the day-to-day evaporation, precipitation, and reevaporation processes as the air moves inland. The percolation and runoff are sufficient to progressively damp the water availability. Dry regimes occur. These are seasonal in character and vary with the geographic region. The arid regions attest to the predominance of low dewpoints.

In comparing the dewpoint charts with dry-bulb temperature charts, and in comparing the distributions derived through use of the variances of the standard deviations, this concept should be kept in mind. The dewpoints are limited by the dry-bulb temperatures; i.e., the dewpoint should not exceed the dry-bulb temperature. Because of this and nonlinearly of the relationship, care should be exercised in interpreting the relationships when the difference is small.

The freezing (frost) point of water is important to all life and inanimate forms. Some life forms are not affected but the remainder and the inanimate eventually submit to the freezing and thawing cycles of water. For many plants, only one cycle is required. Unprotected tissue of animals is subject to rupture. Solid material is subjected to cleavage. Surface is destroyed, particle by particle, and on a larger scale, rocks and the ground are sundered. On a much larger scale, the ratcheting action of the freeze and thaw cycle along rivers, lakes, and ocean shores can physically move and/or destroy large structures—natural or man made. There are other effects. Thus, the measurement of and the recording of the important phase change temperature of water is helpful for guidance principles. It is seen that some plants can survive the occurrence of 0 °C, the freezing temperature of pure water at atmospheric pressure. But the fluids within the cells do lower the freezing point temperature. There is the feature of

frost (freeze) and the hard frost or hard freeze. Many plants can survive the first light or moderate freeze, some can survive the second, but cannot survive the third, also known as the killing frost or freeze. This last stage temperature is in the neighborhood of  $-4.5\text{ }^{\circ}\text{C}$ .

Due to the importance of the phase change, freezing temperatures, individuals, organizations, and National Meteorological Services do keep records of freeze and frost data. Koss, Owenbey, Steurer, and Ezell (1988) present freeze/frost data in *Climatography of the U.S.*, No. 20, Supplement No. 1. They present freeze/frost occurrence data by state for threshold values of  $2.2\text{ }^{\circ}\text{C}$ ,  $0\text{ }^{\circ}\text{C}$ , and  $-2.2\text{ }^{\circ}\text{C}$  for spring and fall dates for the probability levels of 0.9, 0.5, and 0.1. For 3,108 locations, they present the days of frost-free periods and the probability of a freeze/frost day in the yearly period for the same probability levels. As the freeze/frost phenomena closely control the growing degree season and as the radiation energy received and used by the plants depends on the first and last freeze/frost dates, figure 5-14 is of interest. Figure 5-14 is an example of a growing degree units graph from microfiche for Andalusia, AL.

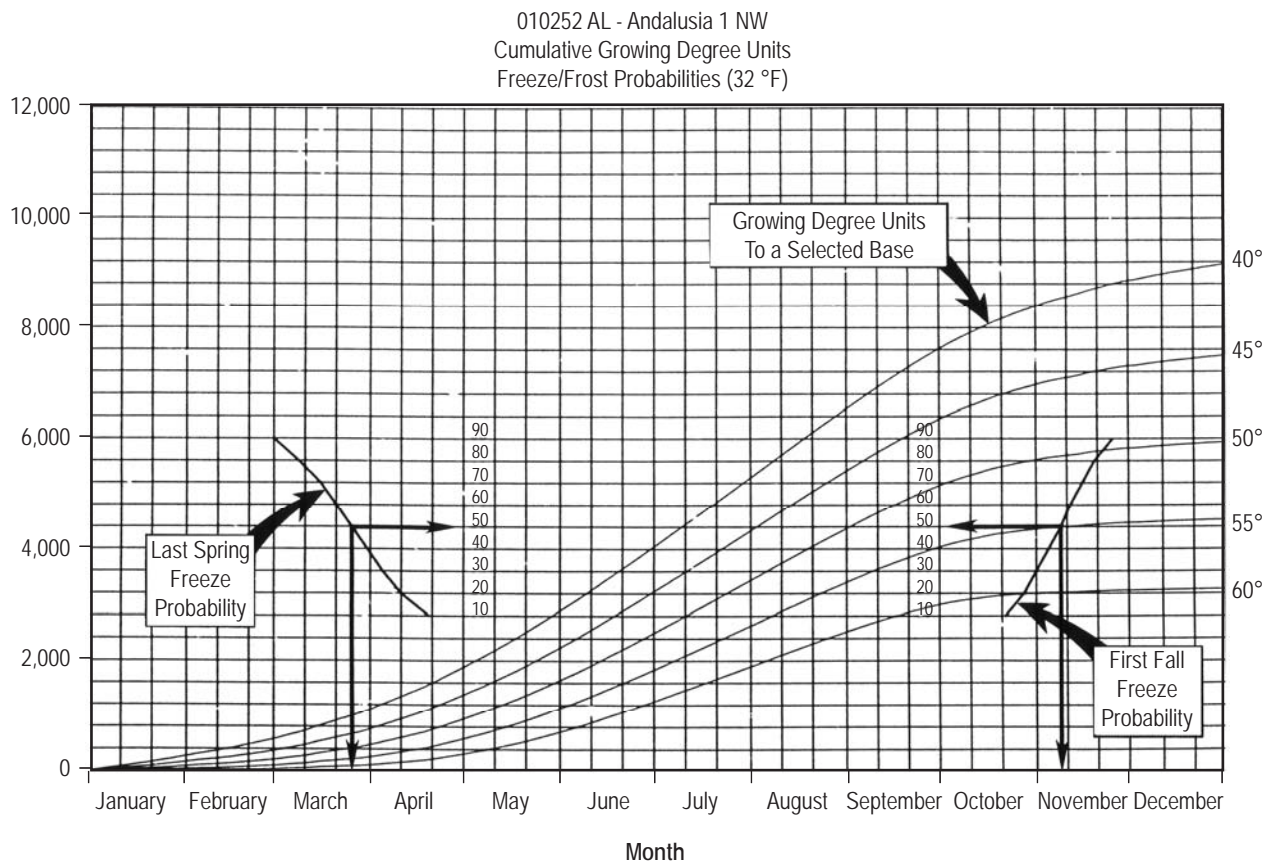


Figure 5-14. Growing degree units for Andalusia, AL (courtesy of Koss et al. (1988)).

Figure 5-15 from the same publication above presents a chart of the freeze-free period at a 0.9 probability level of a longer duration in days with temperatures above  $32\text{ }^{\circ}\text{F}$  ( $0\text{ }^{\circ}\text{C}$ ). It must be understood by the reader that there are certain uncertainties in the temperature thresholds present. The temperatures used are the temperatures in shelters usually at 2 m above the ground surface. The radiation, cloudiness, and wind will influence the ground temperature. Consequently, expect—on a microscale basis—some small variance from the tables and charts of this and other publications of the same phenomenon.

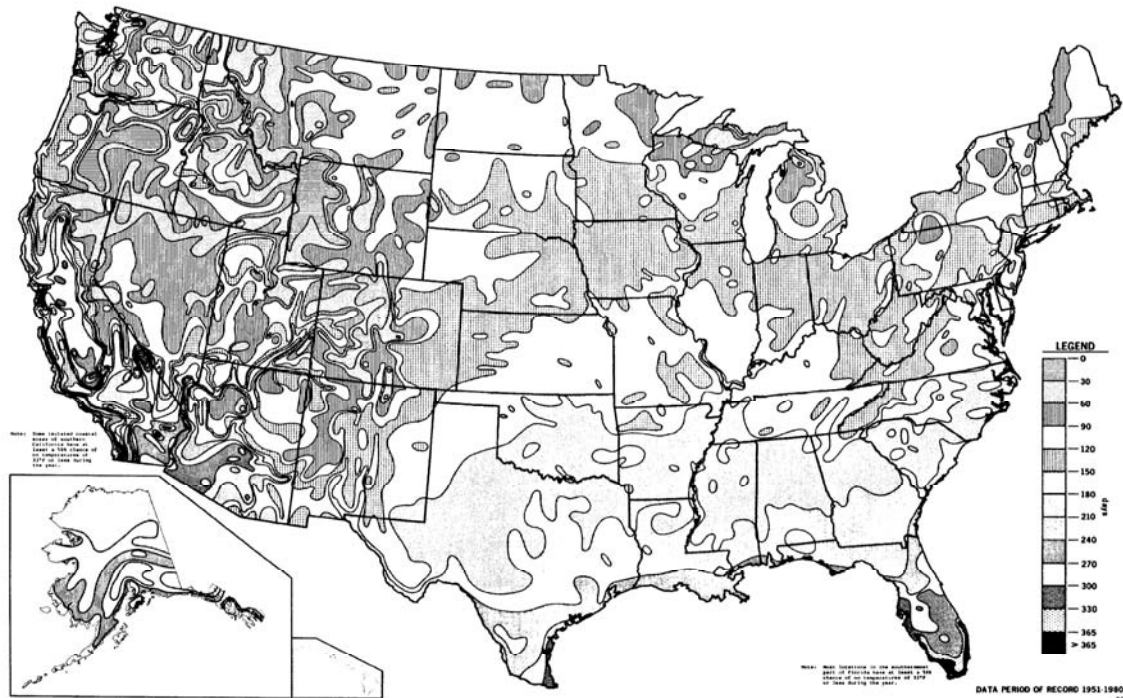


Figure 5-15. Freeze-free period at the 90-percent probability level of a longer duration (days) with temperatures above 32 °F for the United States (courtesy of Koss et al. (1988)).

## 5.5 Temperature Oscillations

In the long term, discussions continue on the importance and the effect of the planetary system and the Earth's orbital geometry on Earth's climates, including that of temperature. With the passage of time, opinions noted in the literature seem to be more responsive to and in accord with those of Milankovitch (1957). See Vernekar (1972) and Kukla et al. (1981).

The daily temperature is perhaps the one climatic element in which people are primarily interested. The importance of the other elements is recognized but the primal need is for an equable temperature. Given that an equable temperature is assured, an equable moisture allotment is sought. Extremely moist or dry conditions are uncomfortable. Suitable clothing and food are sought. Migration may be an only recourse. As the annual course of temperature in a sequential representation of the daily temperature runs, it is interesting to consider some aspects of daily and annual temperature regimes or characteristics. The literature is replete with examples. A few references of the many available follow.

Haurwitz (1941), Haurwitz and Austin (1944), Conrad and Pollak (1950), Brunt (1952), Court (1949, 1953), Trewartha (1954), and Geiger (1965) discuss and provide illustrations of the daily and annual course of surface air temperatures. Some of these also discuss the temperature regimes during the course of the day. Harmonic dials are often used to illustrate periodic phenomena such as daily and annual courses of climatic elements, including temperature. One of the earliest classic examples of the interest in temperature variation with height—outside of comparison of valley and mountain surface air temperatures—is the comparison of daily runs of temperature at the Eiffel Tower (Schmidt (1917, 1921) and Haurwitz (1941)). The amplitude and times of maximum and minimum are evident in any study of the surface air layer as well as at the surface itself. It is the writer's experience from studies

for California that the daily oscillation of temperature generally is evident in radiosonde soundings to a height of 3 to 4 km above msl before it damps out. There is the lag in time. Soil temperatures also play an important part in climatology as do the water temperatures of the oceans, seas, lakes, and rivers. For subsurface temperatures, the oscillations also damp out at some depth. Oscillations on a greater time scale are evident in these annual progressions, extending through the decades and over longer periods. Many of these will have been viewed in previous figures and will be seen in figures to follow.

In general, the diurnal surface air temperature has a maximum of  $\approx 2$  hr after local noon and a minimum about one-half hour after local sunrise. These occur where there is a general balancing point of outgoing and incoming radiation. These times are variable, being dependent upon local physical configurations and synoptic conditions. With the formation of or the advent of cloud cover, the diurnal temperature oscillations are damped—the maximum is less and the minimum is greater. Damping is also noted in ocean water temperatures. In the illustration and excellent discussion provided by Roll (1965, p. 238), based on the work of Kuhlbrodt and Reger (1938) reporting on the cruise of the “Meteor,” in the equatorial and subtropical regions of the Atlantic Ocean, a minimum and maximum in the ocean water temperatures occur at 0400 and 1500 local time. It is stressed that this is only for one region of the Earth and other regions may and do exhibit other magnitudes and phases (times of day). Quite clear in all representations is the damping effect of water on air temperature whether the water is warmer or colder than the air.

It is emphasized here that the annual variation of the temperature in the tropics is generally so small that it is not often used as a climatic marker. However, the marked departure in terms of variance should be viewed as important changes. Regionally and worldwide, these may be even more important. For example, see the phenomenon of the El Niño and La Niña. The first goes along with the warming westerly equatorial winds and the second goes along with the cooling easterly winds of the tropical Pacific Ocean. Kerr (1988) attributes the name La Niña to Philander (1985), Ropelewski and Halpert (1987), and Bradley and colleagues as supporting the reality of the phenomenon now called La Niña. El Niño and La Niña are associated with dryness and wetness, depending upon the stages of development and the regions of the world.

Wunsch (1990) reviews Philander (1989) with respect to El Niño, La Niña, and the Southern oscillation (ENSO). The worldwide climate effects, such as long periods of drought, of rainfall, and their shifts are features associated with ENSO. Whether one can be called the producer of the other is not known. However, surely this phenomenon is an ever-present varying mode of atmospheric-oceanographic circulation. This simply suggests that more and better instrumentation be dedicated to the worldwide problems associated with the observation and documentation of worldwide climate and weather.

Landsberg (1958) shows a mean temperature and range in the tropics, respectively, as 26.2 and 0.8 °C. At 80° N. and S., the means and ranges are given as  $-16.7$  and  $-19.8$ , and 35.3 and 25 °C, respectively. Sellers (1965) also provides a tabular latitudinal distribution of physical and climatological data including temperature. For a good review and update of tropical meteorology, see Riehl (1979). For a good record of selected English data, see Manley (1953, 1974).

In the tropics and the subtropics, the twice-a-year overhead passage of the Sun and the concomitant inter-tropical convergence zone movement often produces a marked bimodal precipitation annual distribution; i.e., two precipitation maxima. This is true also for temperature, cloudiness, and other regimes. There is some lag so overhead position of the equatorward moving Sun meets the poleward moving zone. At that point, there is only one maximum. The time of maxima diverges towards the equatorial time positions. Due to the very slight changes in temperature, as Snow (1975) indicates, though it is difficult or even impossible to detect this phenomena at the surface, it is sufficiently pronounced in the higher altitudes that climatic differentiation is available in the northern Andes in the montane and paramont regions, both in the precipitation and temperature regimes.

Haurwitz (1941), as indicated previously, indicates that the usual time lag for surface air temperatures is roughly 2 hr. Roll (op. cit.) indicates a lag of  $\approx 3$  hr for the maximum in equatorial water temperatures. With respect to change of temperature in the vertical, Haurwitz (op. cit.) and Schmidt (1921) discuss the effect of a variable coefficient of turbulent mass exchange ( $A$ ) on the amplitude and phase retardation distribution.

Deacon (1969) shows the variation air temperature and windspeed with height, high Sun, and a clear day. There is a general decrease of the air temperature and an increase of the wind speed.

## 5.6 Soil Temperatures

Soil temperature plays an important part in climate just as the subsurface waters of the oceans, seas, lakes and rivers do. Though soil does not have the heat capacitance of water, it does have heat capacitance greater than air. Therefore, it can and does, as do the oceans, through its gain and loss of energy from and to the air, act as a surge tank. In electronic analogy, it acts as a capacitor coupled with a bleed resistor to ground.

When radiation is absorbed at any point in any medium, it may be later reradiated in all directions in the same or a different part of the electromagnetic spectrum. If there is an excess of energy being received from one direction, the reradiation will effectively increase the energy received in the deficit region. The reradiation effect is not immediate so there develops a significant delay or retardation commonly called a lag. During the day and during the year, therefore, there is a tendency for an increase of energy moving to deeper parts of the soil. When the Sun has passed the daily zenith and the seasonal equatorward overhead position of the Sun begins to lower, there is no longer an excess driving the energy deeper and deeper. In fact, the process is reversed. When the outgoing (incoming) radiation equals and then exceeds the incoming (outgoing) radiations, a minimum (maximum) in the measured temperature develops. The time difference between the maximum (minimum) of the incoming radiation and the maximum (minimum) described above is the lag.

In the study of soil temperatures and to the air temperatures very close to the soil, there are many ways to depict or describe the temperature distributions. No one description can fit all cases as the soils are different, and there are many ways to stratify data by time, location, and altitude or depth. It is understood that the soil surface is the real region of activity in the sense that it is this surface that first receives, absorbs, and emits energy. Therefore, it will show the greatest temperature increase with insolation and decrease with terrestrial radiation. The air temperature to some height above the surface and the soil temperature will lag behind the energy absorption and emission of the surface itself. There is only a finite amount of time in any day or year in which the surface receives an increasing amount of radiation. For this reason, during this time, the penetration of energy into the soil is not steady but appears as a pulsating wave front. In the allotted time available, this wave can penetrate just so far and no more. Below that depth, the temperature of the soil is essentially constant.

Geiger (op. cit.) presents the penetration of the daily heat wave into the ground on an undisturbed summer day from observation by T. Homen in Finland (1897). A similar presentation is provided by Carson (1961, 1963) for the Argonne, IL, area. Johnson (1954) also discusses heat flux in the soil.

Leyst (1890) provides illustrations of a daily sequence of temperature in May, from 10-yr averages at Pavlovsk in sandy soil. At 1, 2, 5, 10, 20, and 40 cm, the minima, respectively, occur at about 3, 4, 5, 6 hr, and noon local time. At 80 and 160 cm, the temperature is constant. The maxima, respectively, occurs at 13, 14, 15, 16, 19 hr, and midnight. Note the 12-hr or one-half day lag at the lowest depth.

At Potsdam, Germany, 1894–1948, Hausman (1950) shows as Geiger (op. cit.) indicates for annual average temperature fluctuations at 100, 200, 400, 600, and 1,200 cm depth, respectively, of 19.6, 13.6, 7.3, 4.2, and 0.7 °C. The respective minima occurs at February 11, March 4, April 3, May 4, and August 10, while the maxima occurs



at July 30, August 15, September 22, October 30, and February 10. The respective average annual temperatures are 20.7, 17.2, 13.7, 11.9, and 10 °C. Note the 8-mo lag at the lowest depth.

At Konigsberg, Schmidt (1891), the annual sequence at 3, 31, 63, 125, 251, 502, and 753 cm, at 2° less on the average at Potsdam, shows minima at January, February, February, February, March, mid-April, and mid-June. The maxima occur, respectively, during July, mid-July, mid-July, August, September, October, and December. Note here the 6-mo lag at the lower depths.

Amplitudes and phase of retardation of the temperature waves through the day and year are a function of soil type, soil condition—dry, wet or frozen, cover, and depth. Chang (1958), according to Carson (1961), indicates that soil temperature averages approach stable—nonvarying climatological averages—much faster than surface air temperature averages. At the latitude of Argonne, IL, and with the soil types involved, Chang (op. cit.) suggests that stable averages in the soil are reached in  $\approx 15$  yr of record at and above 10 cm, in 12 yr at 30 cm, and in only 8 yr at 60 and 120 cm and below. In contrast, the World Meteorological Organization (1958) suggests 30 yr for climatic normal averages. Thus, the careful observation, reduction of data, and study of subsoil and subsurface waters may be a more stable, consistent, and less noisy monitor of climate, climate normals, and climate change.

Carson (1963) and Carson and Moses (1963) analyze and discuss the diurnal and annual heat exchange cycles in the upper layers of the soil at the Argonne National Laboratories near Chicago, IL. The soil type is identified. The period of record is short (1953–1955) and can only be considered to be representative of that period. In fact, Carson (op. cit.) notes that the period is anomalous and warm. The temperatures at depths are warmer than the average of the normal temperature of  $\approx 9.5$  °C at 1.9 m above the surface. However, the general characteristics or patterns should hold. It is hoped that further work can be done with data which should now cover a 40-yr period.

Carson (op. cit.) shows that, respectively, at 1, 10, 20, 50, 100, 200, 250, and 740 cm below the surface, the average departure above the norm of 9.5 °C for the years 1953, 1954, and 1955 were about 2.2, 1.9, 1.8, 1.7, 1.6, and 1.4 °C. Graphs of the annual course of the air temperature and the subsoil temperatures at each of the levels mentioned quite clearly show the increasing lag with depth. Even at a depth of 7.8 m, the oscillation has not damped out and the maximum and minimum occur at 7 to 8 mo after the respective summer and winter solstices; i.e., they occur in the January-February and July-August periods, one-half year after the actual surface maximum and minimum. As the amplitude of the oscillation has not been completely damped at the 740-cm depth, it is assumed without any data that this will occur at  $\approx 8$  m. Potter (1956) computes a constant temperature depth of  $\approx 7.9$  m.

Deacon (1969) discusses heat conduction into the ground. Deacon's (1969) figure 8 (after West (1952)) shows the diurnal course of temperatures at three depths—5, 15, and 30 cm—in a sandy loam in New South Wales. The soil surface is bare and uncultivated. The decrease in amplitude and increase in lag with depth is evident. The same feature is noted in the annual run of data at depths of 2.5 cm and 2.43 m. The lag for the latter is  $\approx 2$  mo. His figure 10 provides a diagram of the change of amplitude and phase with depth at the same location.

Kessler (1985) also discusses this phenomenon, the heat flux, and its variability into the ground. He also discusses the heat flux with respect to the oceans. Along with these he discusses the latent heat fluxes associated with evaporation and condensation.

## 5.7 Summaries

There are many summaries of data. For the users of PCs, and in particular, the IBM-compatible PC, and the compact disc, the CD-ROM represents a relatively new technique in information supply, at the present time (1990) from the National Climatic Data Center, Asheville, NC. The U.S. Navy has reduced a multitude of summaries from single-page summaries. This includes temperature as well as many other measures of climatic elements. The

physical stack of summaries would be near 5 m in height. The present cost is near \$61 U.S. including handling and mailing. One disk contains all of this series of surface observation summaries. This CD-ROM was discussed also in section 8 on Data.

### **5.8 Upper Air Temperatures and Dewpoints**

Crutcher (1969b) presents global upper air temperature and associated elements. Since that time the U.S. Navy has continued to issue atlases. The latest atlas is the U.S. DoD joint U.S. Navy/U.S. Air Force climatic study of the upper atmosphere. This is a 12-volume series, January–December. This series contains information on a global scale, by Northern and Southern Hemispheres. The pressure charts range from 1,000 to 30 mb for 13 pressure levels. The charts contain information on pressure-height, wind roses, jet streams, temperatures, dewpoint densities, and standard deviation of these. Excepted are the wind roses and jet stream presentations. This study is based on the 1980–1985 twice-daily gridded analyses produced by the European Center for Medium Range Forecasts. Dewpoints appear on only charts 1,000 through 300 mb. The wind roses appear at 5° latitude-longitude grid points. The presentations are by polar, stereographic, and latitude-longitude configurations. The units of height (geopotential) are dkm; of temperature, °C; and of wind, kt. Selected for presentation here are only the charts for the 500 mb, Northern and Southern Hemispheres, and for January and July.

A forward step in the production of these atlases is the inclusion of variance assessment through the provision of the standard deviations, the square root of the variance. Additional help and information would have been the covariances. This would allow a better assessment of change in any set of data from one period to another. Also, the number of data per chart element is not provided. On the assumption of two data per day over a period of 6 yr, an approximation may be obtained. In lieu of these, summary magnetic tapes developed in the project may be obtained from the National Climatic Data Center at a cost of reproduction and mailing. These contain the number of data used and histogram information in digital form.

## 6. PRESSURE

### 6.1 Definition and Perspective

In thermodynamic systems, there may be many variables or so-called coordinates. In the atmospheric thermodynamic system, temperature is one such variable while pressure is another. These are directly measurable variables. Such thermodynamic systems were briefly alluded to in the first section. The thermodynamic formula,  $PV=nRT$ , expresses the relationship amongst the three variables—pressure, temperature, volume—and a proportionality constant, the constant  $R$  for a particular gas. The number of moles of gas is  $n$ . The same relationship holds for a mixture of perfect gases but the value of  $R$  now is a weighted average of the constants for each gas in the mixture. Thus, for dry air, which is a mixture, there is a gas constant, usually denoted as  $R_a$ , while for water vapor, the gas constant is usually denoted as  $R_v$ . The composition of the air mixture does change as the amount of water vapor (gas) increases or decreases. Therefore, the gas constant does change for the changing mixture. The constant will change as more of certain gases are added to or deleted from the atmosphere.

There are several physical laws involved here. These are found in many texts such as Barton (1935), Berry, Bollay, and Beers (1945), Guggenheim (1950), Routh, Eyman, and Burton (1969), and Chang (1986). These are as follows:

- (1) Avogadro's Law (1811)—states that at constant pressure and temperature, the volume of a gas is directly proportional to the number of moles of gas present. This may be written as  $V \propto n$  or  $V = Cn$  where  $C$  represents a proportionality constant.
- (2) Boyle's Law (1662)— $V \propto P^{-1}$  (at constant  $n$  and  $T$  (K)).
- (3) Charles Law (1787)— $V \propto T$  (K) at constant  $n$ , which was demonstrated in 1801 by GayLussac.

These laws may be combined to provide  $PV=nRT$ . Here  $R$ , the proportionality constant, is called the gas constant and  $n$  is the number of moles of gas present. Avogadro's number is the number of molecules present. At standard temperature and pressure (STP) and 1 mole of any specific gas, there are 22,414 molecules.

$$\begin{aligned}R^* &= 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \text{ for an ideal gas.} \\R_J &= 2.8704 \times 10^6 \text{ erg g}^{-1} \text{ K}^{-1} \text{ for 1 g of dry air.} \\R_v &= 4.6150 \times 10^6 \text{ erg g}^{-1} \text{ K}^{-1} \text{ for 1 g of water vapor.} \\R_d &= 6.8557 \times 10^{-2} \text{ IT cal g}^{-1} \text{ K}^{-1} \text{ for 1 g of dry air.} \\R_v &= 1.10226 \times 10^{-1} \text{ IT cal g}^{-1} \text{ K}^{-1} \text{ for 1 g of water vapor.}\end{aligned}$$

Where virtual temperature is used in lieu of temperature per se, the moisture amount is considered and the gas constant for dry air is used; i.e.,  $2.8704 \times 10^6 \text{ erg g}^{-1} \text{ K}^{-1}$ . See List (1958) and table A-2-12. In general, this is the formula used for the hydrostatic equation for the atmosphere.

Pressure may be defined as force per unit area. If there are no stresses, it can be shown that pressure in a fluid (gas) is the same in all directions if it is further defined as the limit of the ratio of the forces normal to an area, as the area decreases in size without limit. The atmosphere is not a perfect gas though it closely approximates one. The static pressure may be measured.

Piezoelectric materials, torsion equipment, or balances may be used. Mercurial barometers balance the weight of a column of mercury against the weight (or mass) of the atmosphere above it. The length of the mercury column is a transform of the pressure. The aneroid barometer balances the weight (or mass) of the atmosphere above it by means of the resistance to deformation by an evacuated cell or cluster of cells. In both cases, the vacuum in the tube of mercury and in the aneroid cell are used as end points. The vacua are not total in either case. In any case, the measuring instruments are calibrated to the system used. Measurements may be made visually and hand recorded.

Other recording mechanisms are mechanical, some are electronic, and some use digital readouts for visual observation or for data storage. Reference to Grossman (1960) may be made for a good discussion of air pressure-measuring instrumentation. Many types are treated.

Units of pressure which are often used are atmosphere (atm), bar, dynes  $\text{cm}^{-2}$ , N (newtons)  $\text{N}^{-2}$  in (inches), mm, etc. Others are used and undoubtedly many have been used and forgotten. Here are some equivalencies: 1 bar =  $10^3 \text{mb} = 10^6 \text{dynes cm}^{-2} = 10^5 \text{Pa}$  or  $10^2 \text{kPa}$ , and 1 torr = 1 mm Hg. A dyne as a unit of force is defined as the force necessary to give an acceleration of 1 cm per second per second to 1 g of mass (Weast (1988)). A newton is the force necessary to give an acceleration of 1 m per second per second to 1 kg of mass (Weast (1988)). One pascal (Pa) is 1 newton (N)  $\text{M}^{-2}$ . The term bar implies pressure and presumably is of Greek origin as the barometer in an instrument to measure pressure.

Standards are always sought. Generally, the Earth is used as a base. Pressures as measured will be subject to the mass distributions and gravitational forces of the geoid and will vary regionally as to latitude, longitude, and altitude.

One atmosphere (atm) of pressure at sea level is equivalent to:

$$\begin{aligned} 1.01325 \text{ bar} &= 1.01325 \times 10^3 \text{ mb} = 1.01325 \times 10^5 \text{ Pa} \\ &= 1.01325 \times 10^2 \text{ kPa} = 1.01325 \times 10^6 \text{ dynes cm}^{-2} \\ &= 760 \text{ torr (mm mercury (Hg))} \\ &= 14.6960 \text{ lb in}^{-2}. \end{aligned}$$

For most purposes, the variances indicated by latitude, longitude, and altitude are ignored but are particularly important in upper air studies and in satellite operations. Sea level itself varies and the assumption of 1013.25 mb as a mean against which anomalies may be measured is a logical assumption. The highs and lows on the weather chart are such anomalies.

The atmosphere is not static. It is constantly in motion in response to differential heating and to the Earth's rotational forces as well as to friction with the Earth's surfaces and other atmospheric motions. These motions create, in a more or less quasi-balanced form, the general circulation with its great semipermanent centers and bands of high and low pressure. These permanent and semipermanent centers, their slow modification, and, at times, their imperceptible movement are part of the Earth's climate systems.

The great high pressure areas or anticyclones of the north and south Pacific, Atlantic and Indian Oceans, the Icelandic and Aleutian low pressure areas, and the continental high pressures which wax and wane, respectively, in winter and in summer, are all well known. In the context of continental drift, tectonic plate shifting, mountain and trench building, and ice cap formation and decay, the areas of maximum and minimum pressure regions must change in relative position, strength, and effect. The monsoon phenomena associated with the seasonal development and decay of the great centers of action and the interaction among these centers have great effects in the regions they dominate. When the adjustment is too fast or too slow, the disruptions in man's industries and food-producing efforts may be disastrous. Man's planning depends upon some constancy in the timing of the seasonal changes.

Although winds are generated in part by pressure differences, which may be initiated in part by thermal differences, pressure differences can be created by the winds. On the windward side of ridges, the pressures will be increased. On or above the plateau regions, this creates problems in attempting to deduce the height above sea level of a pressure-measuring instrument—the barometer—whether it is mercurial or aneroid. On the lee side, the pressure is reduced. Large errors are created in the altimeters on board aircraft when these are based on an aneroid barometer mechanism. On the windward side, the pilot will think the aircraft is lower than it actually is. On the leeward side, the pilot will believe that the aircraft is higher than it actually is. Many fatal accidents have been induced. By the same token, those who deal with climatic data must realize and, if necessary, adjust for pressures on the windward and leeward side of ridges. During seasons when the large-scale winds have a large perpendicular component to the long, high mountain ridges, the lee valley pressures will be low. Reduction of pressures to sea level will be anomalous. For this reason, troughs of low pressure with corresponding wind adjustments occur in the lee of mountain ranges. The same phenomenon plagues those who utilize undersea craft along trenches, escarpments, and ridges. Of course, radar, acoustic, and other techniques are designed and used to help alleviate these problems but these may not be supported redundantly and may fail.

Prior to 1945, pressures in the upper air often were presented at constant height levels. With the advent of isentropic analysis and then the assumption that temperature isoline on constant pressure charts was equivalent to isolines of density, constant pressure charts replaced, in practice, the constant height charts. This reasoning follows from a consideration of the  $PV=nRT$  expression, where the reciprocal of the volume ( $V$ ) is the density. Many atlases and tabulations of upper air-related data are referenced to specific constant pressure surfaces. The foregoing expression may be arranged as follows:  $T(K) = n^{-1}R^{-1}P^{-1}$  where  $(n^{-1}R^{-1}P^{-1})$  is a constant on a constant pressure chart. In sections 5, 6, and 7, as examples, the 500-mb level is used. These charts are taken from the climatic upper air atlases of the U.S. Department of Defense (DoD)/U.S. Navy/U.S. Air Force (1989). The reciprocal of density is constant along a temperature isoline. Therefore, density is also constant along such a line.

## 6.2 Surface Maps

Flohn (1969) provides an excellent discussion of surface atmospheric pressures and the general circulation studies from about 1750 to the present. Also, he presents both a written and a pictorial history of the pressure observational networks. Comparative examination provides a good background in the relationships with other climatological element data. The following figures can only bring the reader a little more up to date. Some idea of variability may be obtained through perusal of the standard deviation charts.

Figure 6-1(a) and (b) (Crutcher 1979, unpublished) illustrates the location of the surface pressure systems for the winter and summer months of January and July or of July and January, depending upon the hemisphere under consideration. The isoline units are millibars. The numbers 96, 00, and 04, respectively, represent 996, 1,000, and 1,004 mbs.

Given in tables A-6-1 through A-6-3 (National Climatic Data Center) are the U.S. standard atmospheric mean pressures and the other associated mean thermodynamic parameters from zero through 1,000-km altitude.

## 6.3 Upper Air Charts

On upper air charts, the pressure levels are generally fixed. Here, in section 5 and 7, the selected pressures discussed are 500, 300, or 30 mb. As on these charts, the pressure is constant. No pressure charts are presented. In other publications and in some summaries, heights are held constant. On these, pressures do vary but here constant height charts are not discussed further. None are presented.

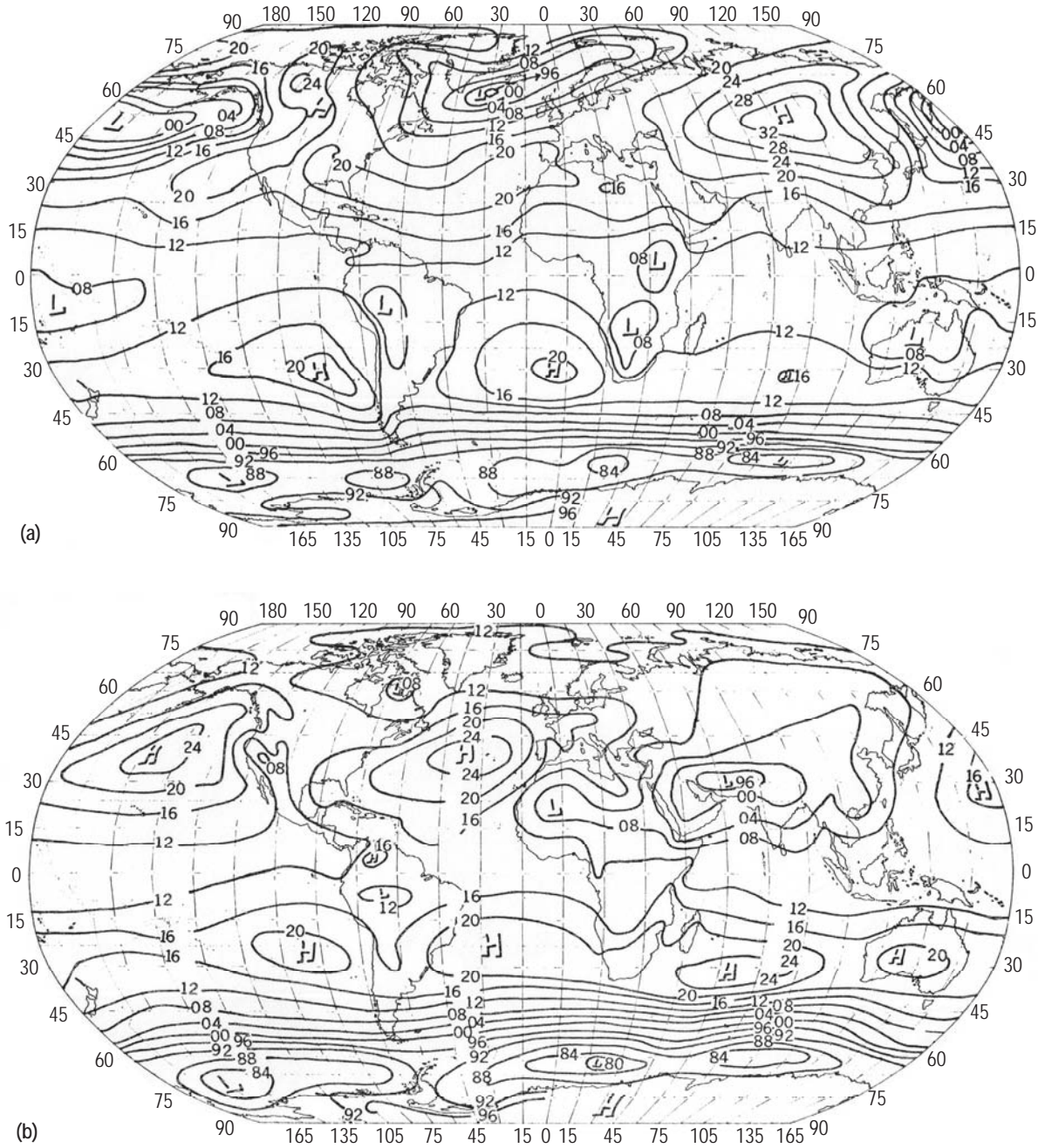


Figure 6-1. Global atmospheric surface pressure charts (isoline units are mb) for (a) January and (b) July. The base pressure is 1,000 m (Crutcher (1979), unpublished).

Appendix A, tables A-6-1 through A-6-3 provide selected values of the U.S. Standard Atmosphere from the surface to 1,000 km. The data shown for the selected altitude levels are temperature (K), pressure (mb), density of  $\text{gcm}^{-3}$ , pressure scale height (km), number density ( $\text{cm}^{-3}$ ), and molecular weight (amu).

The U.S. Standard Atmosphere also provides tabular data where the prime argument is pressure rather than altitude; these data are not shown here. See the short discussion in section 3 of this publication.

All these are data assumed to represent the vertical structure of the atmosphere based on general mean considerations. Other publications present standard atmospheres by latitude and season for those who need more detail.





## 7. WINDS

### 7.1 Introduction

Just as with temperature, it is difficult to write text or a survey on climatology without references to pressure and/or to winds. For good discussions on these and more, see each of the 15 volumes of this series, the *World Survey of Climatology*. The discussion here on winds provides supplementary material although some basic considerations are made. In addition, reference may be made to Shaw (1933), Court (1948), Brunt (1952), Conrad and Pollak (1950), Trewartha (1954), Lettau and Haugen (1960b), Panofsky and Dutton (1984), and United States Department of Defense (DoD), AFCRL (1985).

To compensate for pressure and force differences, air tends to flow out from the high-pressure areas, spiraling into low-pressure centers. In the Northern (Southern) Hemisphere, the air tends to move in a clockwise (counterclockwise) sense out of high-pressure areas. The situation is reversed in the case of low-pressure areas as the air turns from the high into the low. See texts such as Haurwitz (1941), Holmboe, Forsythe, and Gustin (1945), Berry, Bollay, and Beers (1945), Namias and Clapp (1951), and Petterssen (1969). The coriolis force is a factor as the air (and water), driven by the pressure gradients, move over the globe. This important factor is not discussed further here. The reader is referred to standard meteorological and physics texts.

Wind is a three-dimensional vector (velocity) composed of a direction (from which it comes) and a magnitude. In some texts and papers, the word velocity may be used incorrectly in applying the word only to the magnitude such as the speed. The reader is urged to determine in which sense the word velocity is being used by any author. The author of any study ought to stipulate, and the user ought to determine, whether the wind being considered is one-, two-, or three-dimensional measurements or representations. Winds are the atmospheric motions produced to equalize the pressure differences induced by solar heating, radiational cooling, and the shearing action of the Earth's rotation. At the Earth's surface, due to different densities and velocities, momentum is added to or subtracted from the atmosphere. A wind generally is measured relative to some fixed point at the Earth's surface. For surface winds, the usual height above ground is 10 m. For the upper air, these may be measured at any level. These are known as Eulerian winds, the winds discussed here. Wind, however, may be measured as a flow from point to point along a path. These are known as Lagrangian winds. There are inherent difficulties associated with these winds but they are most important in turbulence research. The change of wind from point to point is known as the shear. See Panofsky and Dutton (1984). See also the discussion in the first section and the comments of Lorenz quoted.

Names applied to winds in various parts of the world characterize some important feature. In general, these describe some global, regional, or local quality or peculiarity. Some of these are (1) the easterlies, the westerlies, and the jet streams (Namias (1952) and Riehl (1979)); (2) monsoon (Ramage (1971)), roaring forties, northerlies, southerlies, doldrums; and (3) backing, veering, mountain, valley, land, sea, sirocco, harmattan, chinook, foehn, santa ana, and mistral.

There are indirect modes of measuring winds such as doppler radar and satellite probing. Wind directions and speeds also can be inferred from time lapse photographs (actually maps of the received electromagnetic spectrum). The levels of the winds are inferred from the type of cloud, which in turn is inferred from an appropriate portion of the spectrum. In a sense, perhaps the best of both, the Eulerian and the Lagrangian techniques are a part of these particular techniques. Atkinson and Sadler (1970) provide a gradient wind climatology for the 30° S. to 30° N. latitude band as well as a cloud climatology. Sadler (1969, 1972) discusses, respectively, cloudiness and

winds in the tropics and the eastern Pacific. Gray, Irwin, Kreuger, and Varnadore (1976) provide a wind climatology derived from interpretation of satellite information. The eyes of hurricanes may be tracked inferentially assuming that a certain cloud mass configuration surrounds and helps to locate the eye of the hurricane. If the eye is not discernible, at least the hurricane mass can be tracked. The large thunderstorms that spawn tornadoes can be tracked night and day.

Generally, the wind direction is given in degrees from north. North is designated as zero or  $360^\circ$ . Moving in a clockwise fashion, east is  $90^\circ$ , south is  $180^\circ$ , and west is  $270^\circ$ . Magnitudes of the wind may be in terms of measurement, speeds such as  $\text{m sec}^{-1}$  ( $\text{ms}^{-1}$ ),  $\text{km hr}^{-1}$ ,  $\text{mi hr}^{-1}$ , or in distance of travel. This system is used in both hemispheres. The presentation of wind information is often the bivariate form of wind directions versus wind speeds and a category for calms. The categories of directions and of speeds can be of any size within the constraints of the system. The statement that the winds are from all directions and all speeds, though a viable one, is not very useful from an informational point of view for the sum of the probabilities is 1. See discussions on the informational theory by Billingsley (1965) and others. The user generally wants to know more about the makeup of this informational packet; i.e., some of the details. The visual bivariate form for winds may be in rectangular or in polar form. The latter is the basis for the terms “wind rose” or also as “windstar” (Shaw (1933) and Conrad and Pollak (1950)). The latter is a composite type employing speed distributions for each direction. The term “wind rose” is used here, even if the polar form is not used. The scaling of the wind speeds may be linear, logarithmic, or a power form.

Winds, directions, and speeds, as vectors, can be broken down into components. Generally, these components are orthogonal; i.e., they are at right angles to each other. The user must ascertain that this is or is not the case. Treatment of vectors except through the treatment of their decomposition into components is essentially intractable with present-day mathematics. The user of any climatological (meteorological) wind data in component form must check the wind component formats used prior to about 1965. Consensus is now that wind components are positive if the directions are from the south and/or west and negative if from the north and/or east (Huschke (1959)). They are positive in upward motion and downward in negative motion. Publication of a consensus standard cannot assure automatically immediate conformance. That is, it is reasonable for the user to check the component value signs in any publication carrying a publication date prior to 1965. Even others may not have gotten the word. Some wind roses have been produced and still are produced where the components form the bivariate axes. In these cases, it is crucial to determine whether these were or are arranged in Cartesian or meteorological convention. This problem will be discussed in some detail later.

Some applications require components along other prescribed orthogonal (right-angled) components, such as along and across (1) the mean wind, (2) a prescribed route, or (3) along axes where the components are not correlated. Again, the sign of the components must be checked. In pollutant studies, the dispersion patterns of the pollutants are related closely to wind patterns; the winds do create them.

Some confusion exists in application when only the component form is provided. Data provided in the usual cartesian coordinate form may be misinterpreted. Only partial information is available in component form presentation. Component information should be supplemented by vector information. This often occurs with computer programmers required to manipulate and process data. The user should verify the system. The system recommended—and in general use for surface winds and winds of the troposphere and stratosphere—is the meteorological convention system. Thus, a wind component directed from west to east, from south to north, along the mean wind, or in the general direction towards which the wind blows, is designed to be positive. Wind components from the opposing sectors are then considered to be negative.

Presentation modes generally are developed in response to immediate or perceived needs. Thus, as time goes on, new depiction types become available. However, there are other features to wind data ensembles that are important and useful. Presentation may be in the form of wind roses computed on the data ensembles. Crutcher

(1957, 1958, 1959) and Crutcher and Baer (1962) illustrate several wind roses commonly used and propose a new form, the standard vector deviation wind. Preferably, this could be called the vector standard deviation wind rose. This specific model is unimodal in form and is most applicable to winds in the free atmosphere; i.e., the atmosphere above the planetary boundary layer, the friction layer. This will not be as representative for multimodal distributions. This wind rose should be accompanied by its progenitor—the ordinary and customary wind rose. In fact, these should be considered as one and will be so presented. This wind rose is based on the mathematical-statistical procedures developed by Bravais (1846) and Bertrand (1888). Bartels (1932) and Chapman (1951), and later Haurwitz (1964), applied the limiting unimodal form of this bivariate normal elliptical distribution, the circular normal, to tides and wind currents of the ionosphere.

Heterogeneity of surface wind distributions limited depiction of winds. There was no adequate mathematics to treat the data, except the direction-speed wind roses. The increased development of statistics beginning in the 1920s provided a sufficient base for the increasing developments of the 1940s in climatology (meteorology). The extraordinary and prolific work of Brooks et al. (1946) led to rapid exploitation of wind information. Coupled with this development was the minimum heterogeneity of winds in the middle troposphere. Homogeneity was assumed in the use of the limiting circular normal (isotropic) unimodal bivariate distribution of winds. They indicated that this assumption was tenable in about two-thirds of the cases. For developments with respect to the increased statistical treatment and exploitation of winds, the reader may refer to, among many others, Brooks, Durst, and Carruthers (1946), Brooks, Durst, Carruthers, Dewar and Sawyer (1950), Sawyer (1950), Mintz and Dean (1952), Hull and Godson (1954), Henry (1957), Graystone (1958), Court (1956), Crutcher (1956b, 1957, 1959, 1961, 1975), USAF (1959), Heastie and Stephenson (1960), Crutcher and Baer (1962), Maher and McRae (1964), Crutcher and Quayle (1974), Essenwanger (1959, 1967, 1986), Crutcher, Wagner, and Arnett (1966), Guterman (1967, 1970), Crutcher and Joiner (1977a), and U.S. DoD, AFCRL (1960, 1985). A fruitful exploitation of models for wind distributions followed. For the wind speeds alone, the mixed gamma, the mixed Weibull, the mixed log Pearson, or the mixed Rayleigh may be used for description.

In most of the above references, the assumption is made that the wind vectors are bivariate normal in their distribution. The earlier works are limited to the use of the simplest form, the one mode circular form. For example, it is now well known that neither wind directions nor wind speeds may be described in total by the normal distribution; subsets may be. This is often done but the subsets are usually limited to a sector of  $<1$  radian.

Exceptional is the case where the directions are univariate normal or where the speeds are univariate normal. The probability that direction is normally distributed at the same time that the speeds are normally distributed is minuscule indeed. However, simultaneously the vectors of wind direction and speed or their orthogonal components form a distribution that may be adequately described by the multimodal multivariate distribution. Additionally, the marginal components distribution may be described by the normal model. The marginal bivariate distributions may be elliptical or circular in the unimodal sense or multimodal.

The premise that the single-mode bivariate normal distribution serves to describe the free tropospheric winds (Brooks, Durst, and Carruthers (1946), Brooks and Carruthers (1953), and Crutcher (1959)) is still a viable assumption and option in about two-thirds of the cases for the upper air. This decision to use the circular normal distribution was to be expected. It is a reflection of the use of the Pareto principle, so useful in quality assurance and control. Choose that item or element which covers the majority of cases. In the case of a histogram, choose the highest to exploit. See Essenwanger (1986) for a fuller description of the Pareto distribution.

Crutcher and Joiner (1977b) show that coastal winds, such as at San Juan, Puerto Rico, may be represented by two or more principal modes, each in itself bivariate normal. There, three principal modes are the land breeze, the sea breeze, and the northeast trades.

The multimodal bivariate normal distribution is a tenable model for all atmospheric levels. If vertical motion winds are available, the distributions may be modal trivariate (Crutcher and Moses (1963)). These also may be multimodal trivariate.

Gray, Irwin, Kreuger, and Varnadore (1976) present, in terms of computer-derived geostrophic winds, the average circulation in the tropical troposphere. Atkinson and Sadler (1970) present gradient winds and average cloudiness in the tropics. Geostrophic winds are presented and discussed by van Loon et al. (1971) for the Southern Hemisphere and by Oort and Rasmusson (1971) for the globe.

## 7.2 Examples and Applications

Table 7-1 depicts the correspondences among the terms (1) Beaufort Force, (2) knots, (3) m hr<sup>-1</sup>, (4) effects at sea, and (5) symbols, which often are used to depict wind speeds. Use of symbols requires that the arrow flag or pennant shaft indicate the direction from which the wind is blowing. The shaft will indicate the station position (Crutcher and Quayle (1974) after Kotsch (1970)). In similar descriptions for land-based stations, the sea effects are replaced by effects on soils, grasses, trees, etc.

Table 7-1. Correspondence among the terms (1) Beaufort force, (2) knots (kt), (3) mi hr<sup>-1</sup>, (4) effects at sea, and other symbols used to depict wind speed.



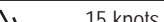


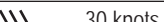
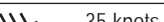




Required Number	Knots	Miles Per Hour	Description	Effects at Sea	Wind Symbols on Weather Maps
0	0-0.9	0-0.9	Calm	Sea like a mirror.	☉ Calm
1	1-3	1-3	Light air	Scale-like ripples form, but without foam crests.	☉ Almost calm
2	4-6	4-7	Light breeze	Small wavelets, short but more pronounced. Crests have a glassy appearance and do not break.	 5 knots
3	7-10	8-12	Gentle breeze	Large wavelets. Crests begin to break. Foam has glassy appearance. Perhaps scattered white horses.	 10 knots
4	11-16	13-18	Moderate breeze	Small waves, becoming longer. Fairly frequent white horses.	 15 knots
5	17-21	19-24	Fresh breeze	Moderate waves, taking a more pronounced long form. Many white horses are formed. Chance of some spray.	 20 knots
6	22-27	25-31	Strong breeze	Large waves begin to form. White foam crests are more extensive everywhere. Some spray.	 25 knots
7	28-33	32-38	Moderate gale	Sea heaps up and white foam from breaking waves begins to be blown in streaks along the direction of the wind. Spindrift begins.	 30 knots
8	34-40	39-46	Fresh gale	Moderately high waves of greater length. Edges of crests break into spindrift. Foam is blown in well-marked streaks along the direction of the wind.	 35 knots
9	41-47	47-54	Strong gale	High waves. Dense streaks of foam along the direction of the wind. Sea begins to roll. Spray may affect visibility.	 45 knots
10	48-55	55-63	Whole gale and/or storm	Very high waves with long overhanging crests. The resulting foam in great patches is blown in dense white streaks along the direction of the wind. On the whole, the surface of the sea takes a white appearance. The rolling of the sea becomes heavy and shocklike. Visibility is affected.	 50 knots
11	56-63	64-73	Storm and/or violent storm	Exceptionally high waves. Small- and medium-sized vessels might for a long time be lost to view behind the waves. The sea is completely covered with long white patches of foam lying along the direction of the wind. Everywhere, the edges of the wave crests are blown into froth. Visibility seriously affected.	 60 knots
12	64 or higher	74 or higher	Hurricane and typhoon	The air is filled with foam and spray. Sea is completely white with driving spray. Visibility is very seriously affected.	 75 knots

Figure 7-1 (Crutcher (1957)) illustrates five of the many wind rose types. The data from the rectangular wind rose at the top are used to construct the other four. The data are not symmetrical as recorded. This may be a good representation of the winds in the Western Caribbean Marsden Square or it may be an artifact either of observing practices or the lack of sufficient direction categories. Comparison with other data sets might illuminate the problem. Now presentation types often are developed in response to immediate or perceived needs.

Bowditch (1958) and Crutcher and Quayle (1974), modifying Bowditch's work, present yet another aspect—this time for the global surface air motion in terms of direction, constancy, and force. Direction has been defined previously. Constancy is the ratio of the vector mean wind to the scalar mean wind. The width of the arrow is a measure of speed while the length of the arrow indicates a generalized degree of wind direction constancy. The vector mean wind is the average of the winds added vectorially, while the scalar mean wind is the average of only the magnitudes (speeds) of the winds. Zero and one bound the constancy. Force is used in terms of Beaufort force (Kinsman (1969) and Crutcher (1975)). January-February and July-August charts are presented. Figure 7-2 (Crutcher and Quayle (1974)) presents the above same charts. These include the average positions of the arctic, antarctic, polar, and intertropical fronts or boundaries of the air masses. Court (1988) (personal communication) indicates that the Beaufort scale was not original with Beaufort, who was not an admiral at the time the system was promulgated.

In monsoon circulation regions, on an annual basis, the vector wind may be near zero as the summer monsoon may balance the winter monsoon. The vector wind in the summer or winter generally will not be zero. Therefore, this attribute must be carefully interpreted on the basis of region and of season.

Various features of winds are used in climatological publications. Though not necessarily the same in all cases, generally, the prevailing wind is the point of the compass showing the highest frequency of occurrence. The dominant wind is judged in relation with the quarter showing the most wind. Sometimes the presentations show the travel of the wind past an observation point; sometimes only the wind speed is presented.

McDonald (1938), for the marine (oceanic) areas by month, gives the predominant direction, constancy, and force of the winds. Mean resultant winds, usually called resultant winds, are provided. The Morskoi Atlas (1952), an extensive atlas covering many disciplines, including climatology, provides the same information. The Pilot Chart series of the U.S. Navy (1977), for example, and the Morskoi Atlas present wind rose data in essentially the same format. Sixteen points of the compass show histograms of the speeds while the resultant direction is indicated by a radius arrow with barbs and/or pennants. Attention will be drawn to the bias in these presentations later in this section.

Figure 7-3(a) and (b) are global representations of surface vector mean winds and speeds in  $\text{m sec}^{-1}$  (isopleths) for January and July, respectively.

## 7.3 Wind Variability

### 7.3.1 Wind Variability

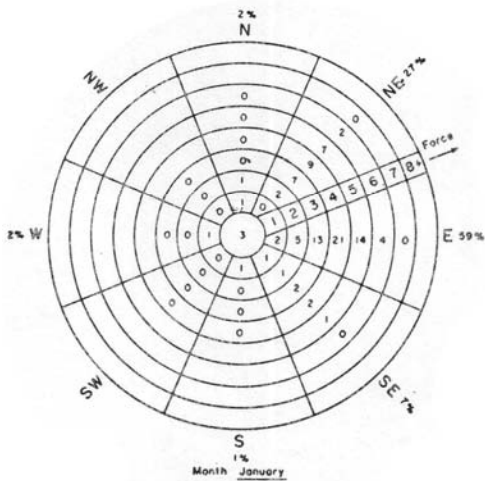
Figure 7-4 presents the usual wind direction versus wind speed type of distribution. In addition, at the bottom of the figure are the symbols and the definition of the estimates of the statistics of a potential bivariate normal distribution.

### 7.3.2 Bias

Bias seemingly exists in all modes of measurement and recording. It is not restricted to just wind measurements.

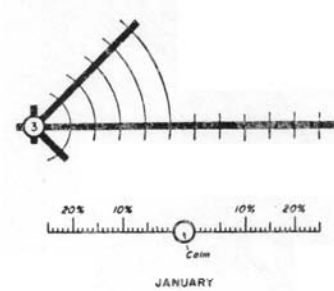
OCEAN AREA		MARSDEN SQUARE		Month JANUARY						
10°-044		5°-50								
Latitude 010-020 N		The numbers "0" indicates								
Longitude 070-080 W		observed but less than 1%								
664 observations.										
PERCENTAGE OF OCCURRENCE OF WIND FORCES										
Beaufort Force	0	1	2	3	4	5	6	7	8	Total
Direction										
Calm	3									2
N		1	1	0	0	0	0			2
NE		0	2	7	9	7	2	0		27
E		2	5	13	21	14	4	0		59
SE		1	1	2	2	1	0			7
S		1	0	0	0					1
SW		0	0	0	0					0
W		1	0	0						2
NW		0	0	0						0

(a) Contingency Table



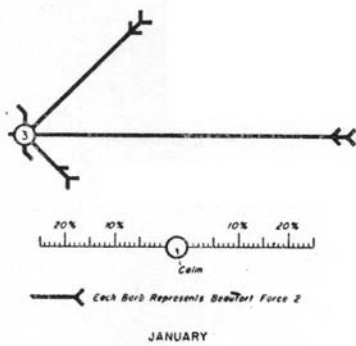
Percentage Occurrence of Wind Forces  
The Number "0" Indicates Observed but Less Than 1%

(b) Contingency Wind Rose



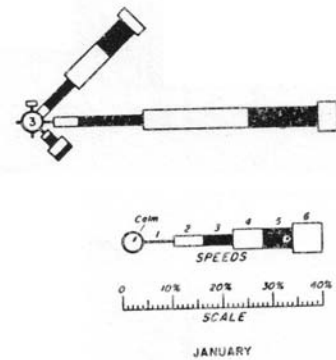
Percentage Occurrence of Wind

(c) Wind Rose (Direction Only)



Percentage Occurrence of Wind Forces

(d) Wind Rose (in Beaufort Forces)



Percentage Occurrence of Wind Forces

(e) Wind Rose (Bailey Type)

Figure 7-1. Wind distributions and roses which illustrate various methods of wind data presentation: (a) Contingency table, (b) contingency wind rose, (c) wind rose (direction only), (d) wind rose (in Beaufort forces), and (e) wind rose (Bailey type). Data are for Marsden Square area in the Caribbean at 10° to 20° N. and 70° to 80° W. Number of observations is 664 and time ranges from 1880 to 1930 (courtesy of American Meteorological Society, Crutcher (1957)).

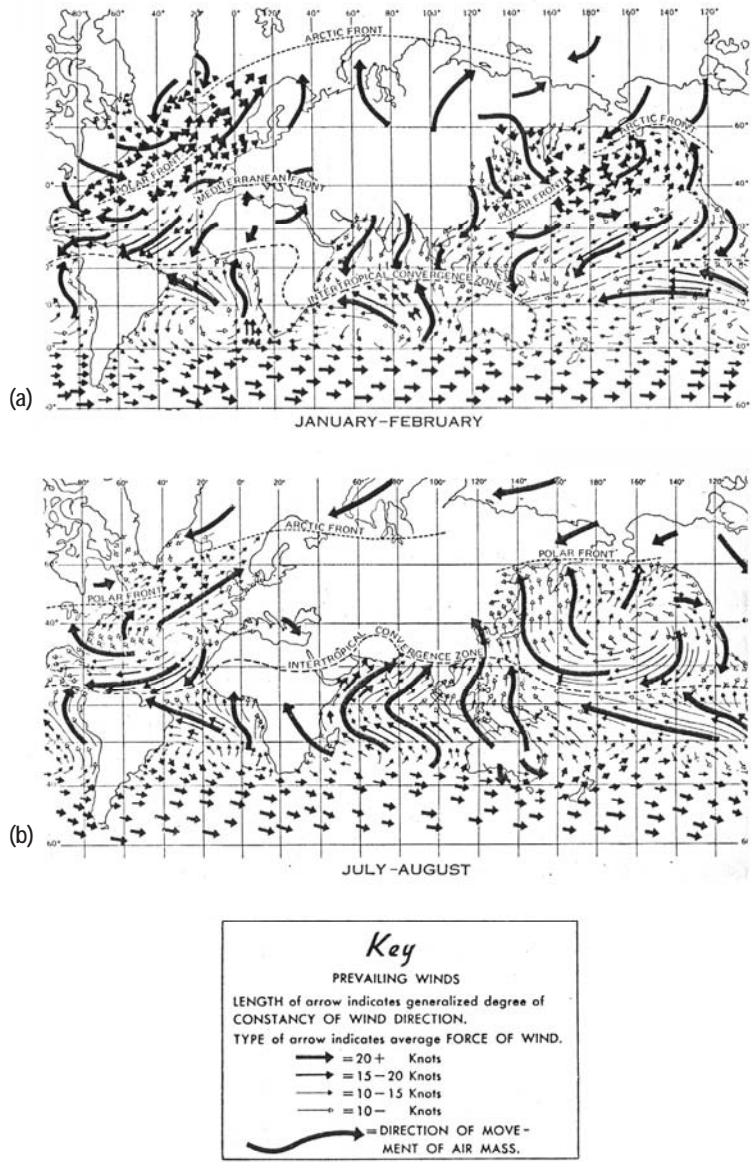


Figure 7-2. Global surface for (a) January-February and (b) July-August charts of air motion in terms of direction constancy and force (after Bowditch (1958) and Crutcher and Quayle (1974)).

Figure 7-5a illustrates the wind distribution at 850 mb, February, all hours 01/56-12/60 and 01/65-12/67 at Cape Town, South Africa, station 68816. The wind rose is of the type designed by Crutcher and Horton during 1957-1958, at the now National Climatic Data Center for use by the three services—the U.S. Navy, the U.S. Air Force, and the (then) U.S. Weather Bureau. The wind rose consists of two parts: (1) The oft-used rectangular wind rose form consisting of the matrix of wind directions versus speed, and (2) the estimates of the unimodal bivariate statistical parameters derived from the data.

This Cape Town wind rose was chosen at random. It has two salient features. Bias is the first salient point and the second point is that possible bi- or multi-modality may be indicated. These two points noted here are characteristic of nearly all wind data distributions, notably in the surface boundary layer and the friction layer data ensembles.

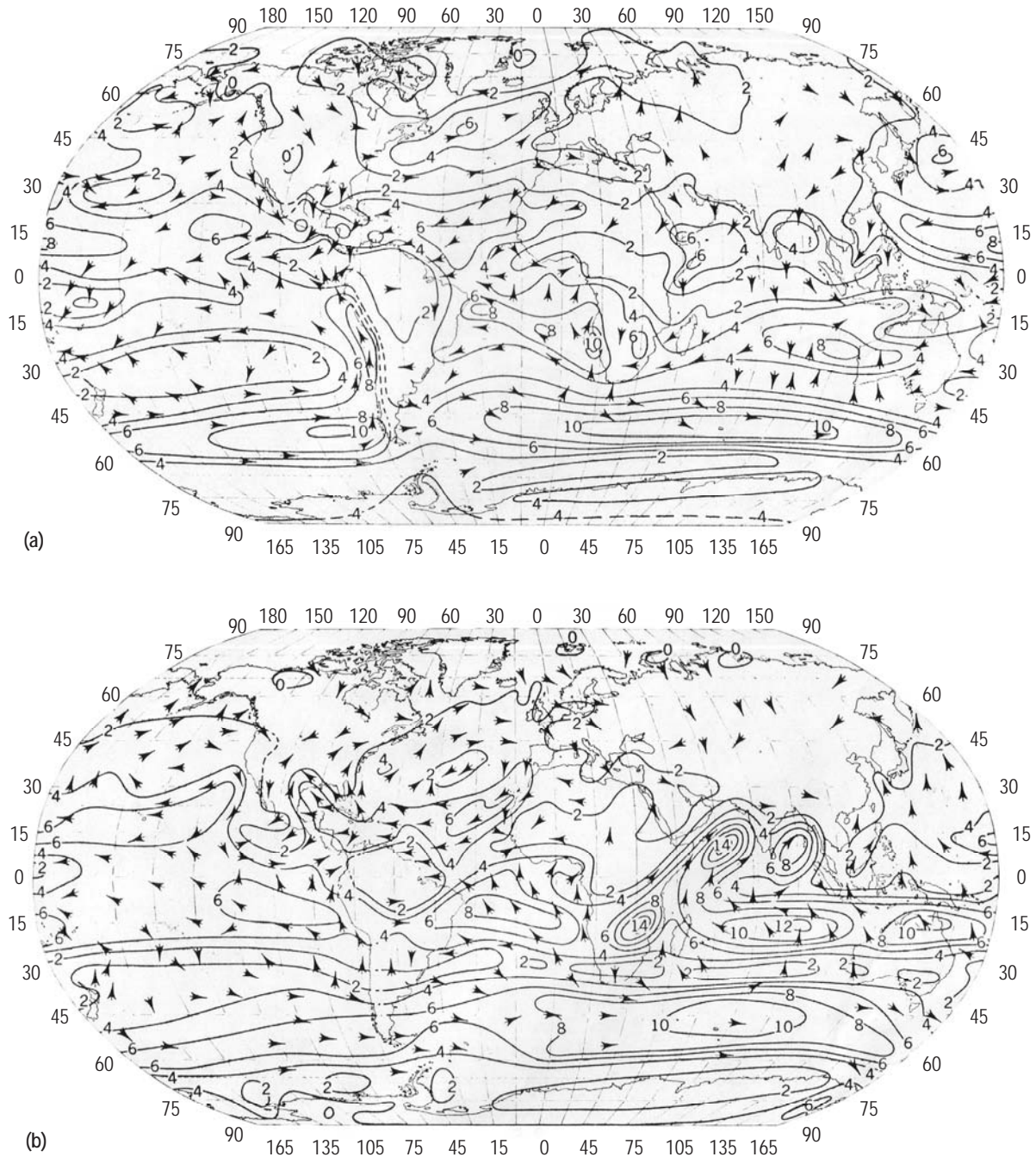


Figure 7-3. Global representations (isopleths) of surface vector mean winds and speeds in  $\text{ms}^{-1}$  for (a) January and (b) July.

Ratner (1950) discusses the biases and indicates how these can be attenuated in some cases in the data sets. Later in this section, the author proposes an alternative procedure. Please note the bias here in the frequency counts by direction. The human observer is programmed by eye and by the number system to most readily observe and record data to the most prominent features. Thus, where ship's magnetic compass roses were used as background design as the cardinal directions, the  $45^\circ$  angles and then the intermediate angles received prominence in the area and the color dominating the compass rose face. These prominences unknowingly are transferred in observation and



{ PERCENTAGE }  
OF DIRECTIONS  
FREQUENCY }  
BY SPEED GROUPS

WINDS ALOFT SUMMARY  
USCOMM-NOAA-NCC

STATION	STATION NAME	YEARS	MO. OR SEASON												TYPE OF OBSERVATION	LEVEL					
			1-4		5-10		11-15		16-20		21-25		26-30				31-38		39-51		52-77
SPEED		M/S	1-4	5-10	11-15	16-20	21-25	26-30	31-38	39-51	52-77	78-102	≥ 103	TOTAL ALL OBS.		SPEED (KNOTS)					
KNOTS		1-9	10-19	20-29	30-39	40-49	50-59	60-74	75-99	100-149	150-199	≥ 200	OBS.		SUM						
M.P.H.		1-10	11-22	23-33	34-45	46-56	57-68	69-85	86-114	115-172	173-229	≥ 230	%		MEAN						
DIR.	N																				
	NE																				
	E																				
	SE																				
	S																				
	SSW																				
	SW																				
	WSW																				
	W																				
	WNW																				
	NW																				
	NNW																				
	CALM																				
	TOTALS																				
	PERCENT																				
	MEAN SPEED (KNOTS) BY GROUP																				
	$\theta$		$V_r$	$\sigma_y$	$\Sigma XY$	$\Sigma Y^2$	$n\sigma_y/\Sigma X$	$\sigma_y/\sqrt{r}$	$\sigma_a$	$\sigma_b$	$\sigma_a$	$\sigma_b$	$\sigma_a$	$\sigma_b$	$\sigma_a$	$\sigma_b$	$\sigma_a$				
	$n$		$\Sigma X/n$	$\sigma_x$	SUM. OF E. COMPONENTS ( $\Sigma X$ )	$\Sigma X^2$	$n\sigma_x/\Sigma X$	$\sigma_x/\sigma_a$	$r$	$\theta$	$\psi$	$V_r$	$\Sigma V$	$\sigma_a$	$\sigma_b$	$\sigma_a$	$\sigma_b$				
	$\psi$		$\Sigma Y/n$	$\sigma_y$	SUM. OF N. COMPONENTS ( $\Sigma Y$ )	$\Sigma Y^2$	$n\sigma_y/\Sigma Y$	$V_r/\psi$	$\Sigma V$	$\psi$	$\psi$	$\psi$	$\psi$	$\psi$	$\psi$	$\psi$	$\psi$				

$\sigma_x$  Standard deviation of east components  
 $\sigma_y$  Standard deviation of north components  
 $\sigma_r$  Standard vector deviation of wind velocity  
 $r$  Correlation coefficient of north and east components  
 $\bar{V}$  Average wind speed  
 $V$  Scalar Wind Speed  
 $\sigma_a$  Standard deviation of wind components along the major axis of the distribution  
 $\sigma_b$  Standard deviation of wind components perpendicular to the major axis of the distribution  
 $\psi$  Angle of rotation of the major axis of the wind distribution counter-clockwise from E-W direction  
 $\theta$  Resultant wind direction  
 $V_r$  Resultant wind speed  
 $\sigma_a$  Standard deviation of wind speeds  
 $\sigma_b$   $\sigma_a/\sigma_b$

Figure 7-4. Blank wind distribution form for direction-speed categories and statistical estimates for a bivariate normal distribution.

NAVAL WEATHER SERVICE COMMAND  
Environmental Detachment  
Asheville, N. C.

PERCENTAGE OF DIRECTIONS  
FREQUENCY

WINDS ALOFT SUMMARY

68816 STATION CAPE TOWN, S. AFR. TYPE OF OBSERVATION RA08 850 MB LEVEL  
NO. OR SEASON JANUARY

ALL HOURS 01/56-12/60 01/65-12/67 YEARS

SPEED # DIR	PERCENTAGE OF DIRECTIONS FREQUENCY												TOTAL ALL OBS. OBS. %	SPEED (KNOTS)				
	1-4	5-10	11-15	16-20	21-25	26-30	31-38	39-51	52-77	78-102	103	≥ 200		SUM	MEAN			
N	19	13	1	1									34	9.4	334	9.8		
NNE	5	2	1										8	2.2	78	9.7		
NE	7	3											10	2.8	89	8.9		
ENE	6	4											10	2.8	87	8.7		
E	13	4											17	4.7	128	7.5		
ESE	6	6	3										15	4.2	192	12.0		
SE	6	8	2	1									17	4.7	253	14.9		
SSE	9	8	4										21	5.8	274	13.0		
S	10	25	2										37	10.3	472	12.8		
SSW	6	4											10	2.8	82	8.2		
SW	6	12	3										23	6.4	266	11.6		
WSW	9	8											17	4.7	146	8.6		
W	18	19	4										41	11.4	431	10.5		
WNW	12	10	4	4	1								31	8.6	490	15.8		
NW	8	12	6	3									29	8.1	470	16.2		
NNW	12	16	5	2									35	9.7	458	13.1		
CALM													5	1.4				
TOTALS	154	154	35	11	1								360		4250	11.0		
PER CENT	42.8	42.8	9.7	3.1	0.3								100.0					
MEAN SPEED (KNOTS) BY DIR	5.9	13.4	24.4	34.8	40.8													
$\theta$	279	$V_r$	2.840	$\sigma_v$	13.817	$\Sigma XY$	$\Sigma V^2$	$\Sigma X^2$	$\Sigma Y^2$	$\Sigma V \sigma_v$	$\Sigma X \sigma_x$	$\Sigma Y \sigma_y$	$\Sigma V \sigma_v$	$\Sigma X \sigma_x$	$\Sigma Y \sigma_y$	$\Sigma V \sigma_v$	$\Sigma X \sigma_x$	$\Sigma Y \sigma_y$
N	360	$\Sigma X/N$	2.808	$\sigma_x$	9.320	1010.759	71438.312	34023.555	37414.801	3.633	3.320	1.80	4.87	4.87	1.80	4.87	4.87	1.80
$\psi$	129	$\Sigma Y/N$	-0.425	$\sigma_y$	10.200	-152.884	37414.801	34023.555	37414.801	3.320	3.320	1.80	4.87	4.87	1.80	4.87	4.87	1.80
		$\Sigma V/N$	-0.425	$\sigma_v$	10.200	-152.884	37414.801	34023.555	37414.801	3.320	3.320	1.80	4.87	4.87	1.80	4.87	4.87	1.80

$\sigma_x$  Standard deviation of east components  
 $\sigma_y$  Standard deviation of north components  
 $\sigma_v$  Standard vector deviation of wind velocity  
 $r$  Correlation coefficient of north and east components  
 $\bar{v}$  Average wind speed  
 $V$  Scalar wind speed  
 $\bullet$  Ratio of standard deviations =  $\sigma_y/\sigma_x$   
 NAVWEASERVCOM SMOR

$\sigma_x$  Standard deviation of wind components along the major axis of the distribution  
 $\sigma_y$  Standard deviation of wind components perpendicular to the major axis of the distribution  
 $\psi$  Angle of rotation of the major axis of the wind distribution counter-clockwise from E-W direction  
 $\theta$  Resultant wind direction  
 $V_r$  Resultant wind speed  
 $\sigma_v$  Standard deviation of wind speeds  
 $\bullet$  Wherever ratio  $\geq 1000.000$  printed 999.999  
 $\bullet\bullet$  Wherever ratio  $\geq 100.00$  printed 99.99

SUMMARY OF METEOROLOGICAL OBSERVATIONS  
 RAWIN/RADIOSONDE

Figure 7-5a. February bivariate wind distribution at 850 mb for all hours 01/56-12/60 and 01/65-12/67 at Cape Town, South Africa. The lower portion provides the bivariate statistics (courtesy of the NCDC).

recording. Note the prominences, if any, in the field display and in the total frequency count or percent frequency columns. North, east, south, and west receive higher counts at the expense of the intermediate directions. A redesign of the dial faces to degrees with heavier markings at multiples of 5° and still heavier markings at 10° did lessen and spread the bias. But even here the dial face will be reflected in the data ensembles.

The bias is extended to multiples of two except in the vicinity of multiples of five. The use of recording equipment does not completely eliminate this bias for the lines on the recorder records vary as to width. Electronic digital recording is somewhat better but reflects the computing algorithms.

Modality is the second feature of bias. Several modes or clusters of data may be inferred. These are better seen if the wind rose is in a polar form. But these may well be the result of the biases in the directions. There does not seem to be a bias in the speeds. The Rayleigh distribution is a good model here. A chi-square test indicates that it does provide a good fit to the speeds. Other models may do as well, such as the Weibull distribution (Weibull (1951), Hahn and Shapiro (1967), Mann, Schafer, and Singpurwalla (1974), Essenwanger (1976), Justus (1978), and Panofsky and Dutton (1984)). These items, biases, and modality will be discussed in more detail later in this section.

Figure 7-5b similarly illustrates the 500 mb January Rawin data for San Nicolas Island, CA, station 93116. Here, the directional bias, though seemingly existent, is not so evident. Please note that the mean speed is quite different from zero. The noncentral Rayleigh distribution would be needed here for a better model fit rather than the central Rayleigh for figure 7-5a. There appears to be two modes—one in the northwest and one in the south-southeast.

The lower portions of figures 7-5a and 7-5b provide the five estimates of the statistical parameters for a unimodal bivariate distribution of the respective wind data sets. These are the two estimated component means, their standard deviations, and their correlation, one with the other. Additionally, there are estimates of other derived parameters. The statistical estimate tabulation should always be accompanied by the wind rose in the upper part. If there is a pronounced bimodality or multimodality in the upper wind rose, then the model below will not be a good fit. The user should be aware of this and know that the single-mode representation is only an approximation. The case of the multiple modes will be discussed later. Also the definitions of the estimates will be treated later.

Please note that the format of these wind roses provide for speed measured in  $\text{m sec}^{-1}$ , knots, or  $\text{m hr}^{-1}$ . If other than knots, an asterisk in the upper left identifies the units used.

In many atlases where surface wind roses are displayed in the polar coordinate form with arrows and pennants, the bias described above is quite evident. See any atlas and charts, such as the present pilot charts used by all maritime interests.

To attenuate the obvious bias in wind presentations, such as seen in wind roses, and particularly those displayed on pilot charts, the following may be done:

- (1) Compute the statistics, under the assumption of distribution normality, of the wind data and display in tables such as shown at the bottom of figures 7-5a and 7-5b for perusal of the investigator.

- (2) Step 1, a quality edit may be by-passed if prior experience and prior checks imply that such is not mandatory.

- (3) By integration of the noncentral elliptical bivariate normal distribution, compute new percentage frequencies for each wind rose. The use of the isotropic form, the circular normal, is not recommended.

- (4) Prepare new wind roses.

# WINDS ALOFT SUMMARY

PERCENTAGE OF DIRECTIONS  
FREQUENCY

BY SPEED GROUPS

93116 SAN NICOLAS IS, CALIFORNIA STATION NAME RAWINS TYPE OF OBSERVATION 500 MB LEVEL

JANUARY NO. OR SEASON

64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 YEARS

SPEED DIR	M/S		KNOTS		M.P.H.		16-20		21-25		26-30		31-38		39-51		52-77		78-102		TOTAL ALL OBS.		SPEED (KNOTS)	
	1-4	5-10	11-15	20-29	30-39	40-49	50-59	60-74	65-85	86-114	100-149	150-199	≥ 200	OBS.	%	SUM	MEAN							
N	.4	2.1	2.6	1.6	1.2	.4	.4	.4	.1					66	8.7	1930	29.2							
NNE		1.2	1.1	.5	.8	.1								29	3.8	842	29.0							
NE	.1	.8	.3	.4										12	1.6	243	20.2							
ENE	.4	.4	.4	.1										10	1.3	169	16.9							
E	.5	.7	.1	.4										13	1.7	210	16.1							
ESE	.8	.8	.1	.1										8	1.1	144	18.0							
SE	.1	.1	.3	.1										5	.7	134	26.8							
SSE	.4	.3	.3	.3										7	.9	95	13.6							
S		.4	.3	.1	.1									7	.9	171	24.4							
SSW	.3	.4	.7	.4	.3									16	2.1	445	27.8							
SW	.1	.7	1.2	1.1	1.1	.7	.7	.1						42	5.5	1606	38.2							
WSW	.8	1.4	2.8	2.6	1.8	1.8	1.8	.3						102	13.4	3915	38.4							
W	1.2	2.4	5.7	4.2	2.5	2.5	2.1	.1						157	20.7	5587	35.6							
WNW	.4	3.0	3.8	4.2	1.4	1.6	.7							115	15.2	3699	32.2							
NW	.9	1.7	3.3	3.6	2.0	1.3	.8	.3						105	13.8	3594	34.2							
NNW	.9	1.8	1.6	1.1	1.1	1.2	.5	.1						64	8.4	2111	33.0							
CALM														1	.1									
TOTALS	50	138	183	157	94	74	54	7	1					759		24895	32.8							
PER CENT	6.5	18.1	24.1	20.6	12.3	9.7	7.1	.9	.1					100.0										
MEAN SPEED (KNOTS) BY DIR	5.6	14.9	25.6	35.0	44.7	54.3	64.8	79.4	106.9															
$\theta$	288	22.5554	29.346		40359.280-		1038911.506							$\frac{\sum \sigma_x}{\sum X}$	$\frac{\sum \sigma_y}{\sum Y}$	$\frac{\sigma_x}{V_r}$	$\frac{\sigma_y}{V_r}$							
N	759	21.435	20.942		16269.131		681172.507							$\frac{\sum \sigma_x}{\sum X}$	$\frac{\sum \sigma_y}{\sum Y}$	r	$\frac{\sigma}{V_r}$							
$\psi$	43	7.021-	20.557		5328.647-		357733.075							$\frac{\sum \sigma_x}{\sum X}$	$\frac{\sum \sigma_y}{\sum Y}$	$\frac{\sigma}{V_r}$	$\frac{\sigma}{V_r}$							

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$\sigma_x$  Standard deviation of east components  
 $\sigma_y$  Standard deviation of north components  
 $\psi$  Standard vector deviation of wind velocity  
 $r$  Correlation coefficient of north and east components  
 $V_r$  Average wind speed  
 $V$  Scalar wind speed  
 $\sigma$  Ratio of standard deviations =  $\sigma_x/\sigma_y$

$\sigma_x$  Standard deviation of wind components along the major axis of the distribution  
 $\sigma_y$  Standard deviation of wind components perpendicular to the major axis of the distribution  
 $\psi$  Angle of rotation of the major axis of the wind distribution counter-clockwise from E-W direction  
 $\theta$  Resultant wind direction  
 $V_r$  Resultant wind speed  
 $\sigma$  Standard deviation of wind speeds  
 $\bullet$  Wherever ratio  $\geq 1000.000$  printed 999.999  
 $\bullet\bullet$  Wherever ratio  $\geq 100.00$  printed 99.99

Figure 7-5b. January bivariate wind distribution at 500 mb San Nicolas Island, CA. The lower portion provides the bivariate statistics (courtesy of the NCDC).

Figure 7-6(a) (Crutcher (1957)) is a standard vector deviation wind rose for Charleston, SC, for the winter season, 1948–1953 at 300 mb. Concentric circles provide magnitude of winds in increments of 20 kt. Distribution and circles are 25-, 50- and 75-percent central distributions (within the circles) plus the percent that may be attributed to each respective cone. Overlaid on the standard vector deviation presentation is a rendition of the polar wind rose for the data distribution used to compute the appropriate bivariate statistics from which the standard vector deviation wind rose was constructed. The numbers are percentages of the total count; i.e., their sum should be near 100. These may be summed and compared with the appropriate probability ellipse.

Figure 7-6(b) shows a similar rose comparison but this time for another level and an elliptical distribution format. The period is 1948–1953 at 300 mb, December–February, at Omaha, NE. There were 480 data. The format is the same as for figure 7-6(a). Again, appropriate integration of the bivariate function and computation of percentages for the same annular sector areas will produce better agreement between the data and the visual rose, as they should. This is one option to remove or at least attenuate the bias in observational and recording procedures discussed previously.

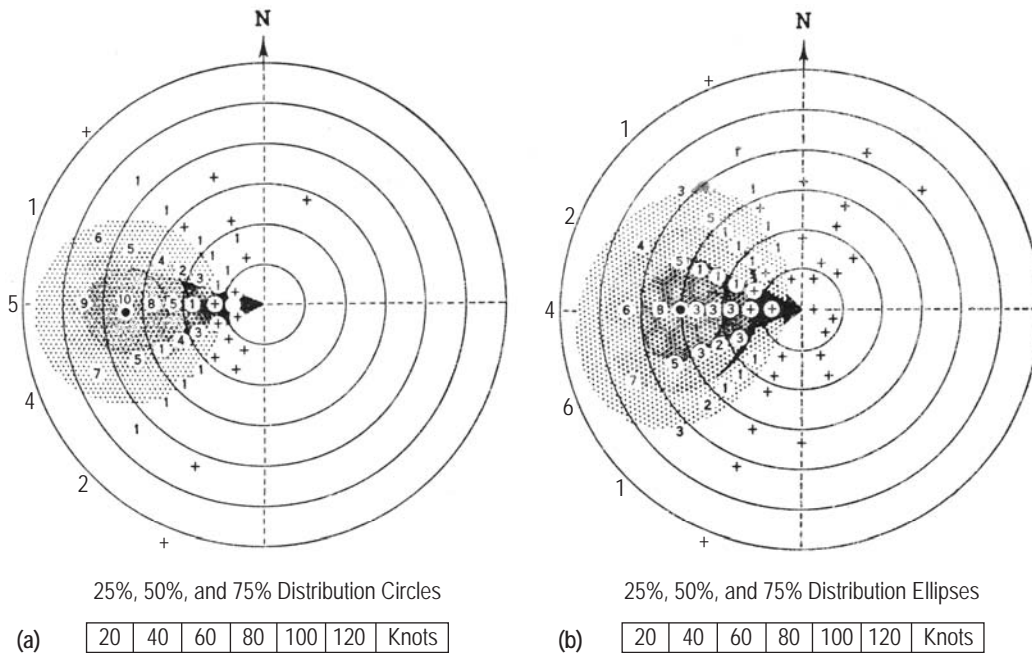


Figure 7-6. Standard vector deviation wind rose for (a) Charleston, SC, and (b) Omaha, NE, winter season, 1948–1953 at 300 mb (courtesy of the American Meteorological Society (Crutcher (1957))).

The major axis of the Omaha, NE, wind rose lies parallel to the general long-wave axis troughing region of the general circulation in that region. This orientation is characteristic of the lee regions of the important high mountain ranges. As such, it and the associated statistics is a measure of the meridional transport of momentum (Riehl (1969)). See the discussion in Holton (1979), p. 265; if the correlation is positive, the troughs and ridges will have southwest to northeast tilt in the Northern Hemisphere.  $A < u 'v' > > 0$  implies a poleward momentum transport.

In this case, the transport is poleward. Of course, the tilting of the axes for poleward transport in the Southern Hemisphere is from the northwest to the southeast. Comparison of figures 7-6(a) and (b) indicate that, at Charleston, SC, (a) is essentially isotropic at the 300-mb level, in which case there is no net poleward flux nor equatorward flux of momentum at that level. This assumes that there is isotropic distribution of density. The net flux

at the point of observation from the surface to some designated level will be the summation over all altitude levels in the vertical. Additionally, the point statistics of turbulence and the transport of momentum are provided in the standard deviation wind rose as shown at the bottom of figures 7-5a and 7-5b. These are, in part, the ratios of the component standard deviations to the appropriate means; not all possible are given here.

### 7.3.3 Bias in Ocean Wave and Current Observations

The same problems and solutions occur in databases of ocean wave and swell observations and in ocean current data. In fact, wherever velocity data observations; i.e., simultaneous directions and speeds, are available, similar biases exist. These biases or their effects should be removed as much as possible.

### 7.3.4 Vector Standard Deviation Wind Rose

Examples of the vector standard deviation wind rose have been presented above. Though it was developed 40 years ago, there are at least two reasons why it has not been used much. Few people understand unimodal bivariate statistics and their applications. Fewer yet appreciate the multimodal, multivariate situation. But then there have not been many expository articles or papers. The one atlas is that of U.S. Navy, NAVAER-50-IC-535 (Crutcher (1959)) for the Northern Hemisphere. There the symbols, equations, arithmetic, the geometry, and some helpful monograms and tables are shown. The monograms and tables refer to the limiting circular normal bivariate distributions of the horizontal winds. Appropriate attributions to colleagues, particularly Henry of Canada and Vitalis of the U.S., are made there. The component wind variances are equal and their correlation is zero. Vertical motions to produce the trivariate distribution are not considered. In any case, if component wind variances are unequal and/or the correlation is zero, the more general form is suggested. See Court (1956), Solot, Cole, Endlich, and Darling (1960), and Gringorten and Tattelman (1985). For the more general case of the elliptical distributions, see the tabular presentations of Groenewoud, Hoaglin, and Vitalis (1967) and Crutcher (1967b).

Computer programs are now available to perform the necessary integration under the unimodal bivariate normal surface of the bivariate distributions and within the surface spheres of the trivariate normal distribution (DiDonato (1982, 1988), DiDonato and Hageman (1980), and DiDonato, Jarnagin, and Hageman (1978)). Thus, probability statements concerning winds coming from selected intervals of component speed regions or sectors can be given. In addition, one of the computer algorithms will produce such probability statements for any polygon, regular or irregular, or such as appear in figures 7-5a, 7-5b, and 7-6(a) and (b).

These procedures are applicable to any set of bivariate vectors, some of which are described in Crutcher (1967) and Crutcher, Neumann, and Pelissier (1982) for tropical cyclones. For other multimodal, multivariate statistics, the reader is referred to Crutcher, Rhodes, Graves, Fairbairn, and Nelson (1986). Figure 7-7 described in a following section presents aspects of a multimodal bivariate distribution.

Crutcher (1959) provides upper wind statistics of the Northern Hemisphere. Fifteen seasonal estimates are provided for each pressure level 850, 700, 500, 300, 200, 100, and 50 mb. The estimates are those of the zonal and meridional means, their respective standard deviations and their correlation, the angle of rotation of the major axis from the zonal axis (east-west), the major and minor axis means and their standard deviations, the vector and scalar means and their respective standard deviations, and the constancy of the wind. The last is the ratio of the vector mean to the scalar mean. Explanatory text precedes the charts.

Transparent overlays are provided in Crutcher (1959). With transparent overlays, visual comparison may be made with reference to height (pressure) or season. One of the advantages of this type of presentation is that if

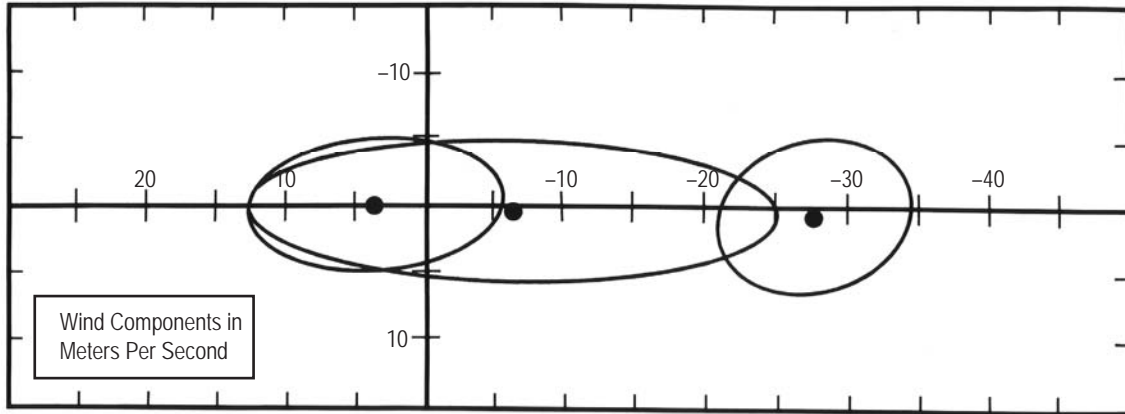
wind distributions are needed at a specific point where data do not exist in tabulated form, the statistical estimates required to construct a wind rose may be interpolated from charts in such an atlas. The basic assumption here is that there is one mode. The user may decide whether to use the general or limiting forms; i.e., the elliptical or the circular. The use of the circular implies that the component variances are not significantly different and that the component correlations are essentially zero. Other atlases do provide additional information on the correlations between levels. A single-mode bivariate wind rose may be computed and additional output in graphical form, such as in figures 7-5a or 7-6 may be made.

Application of Hotellings- $T^2$  test (Hald (1952)), using these statistics and the statistics at any other points or group of points, may be made. An inference may be made as to whether the distributions are significantly different. As indicated previously, there are no other atlases available to enable such tests outside the time or space domain of the Crutcher (1959) atlas. Only internal comparisons can be made until such time that other period statistics are available. Of course, the user might wish to prepare such a set of statistics for any point and any other period to make such a test.

### 7.3.5 Heterogeneous Distributions

Surface winds are influenced by topography and by contrasting surfaces, such as land and sea. Heterogeneity is induced. Wind distributions up to  $\approx 2$  km above the surface also show similar heterogeneity. Crutcher and Joiner (1977) through cluster analysis show that heterogeneous, multivariate, multimodal ellipsoidal sets of data may be separated into their homogeneous, multivariate unimodal ellipsoidal data subsets. Thus, from a surface set of a bivariate bimodal land-sea breeze set of data, the statistical parameters of the land set and the sea set could be easily ascertained. There are no atlases, small or large, which yet treat these mixed distributions. Thus, all general presentations are of the combined heterogeneous populations. In the subtropics, for example, San Juan, Puerto Rico, the distribution is multimodal. The clusters are (1) land breeze, (2) sea breeze, (3) tradewinds, and (4) along-shore winds.

The usual concept of the average or mean is that it is a value to be expected in the future. In the case of a bimodal or mixed distribution where the modes are distinctly separated and, in fact, the grand mean is the mean of two different normal distributions (or other type distributions), each of the two modal values has a higher expectation than the grand mean; i.e., the probability of occurrences is greater. Thus, in some instances, values near the mean value of the total set may occur infrequently. For example, figure 7-7 (Crutcher and Joiner (1977)) illustrates this feature with statistics at the 30-mb (pressure) surface at Canton Island. Upper air observation at Canton Island ceased over two decades ago. The midseason months of January, April, July, and October, 1953–1967, are used. Directions are north at the top and east at the right of each small figure. The central elongated 50-percent probability ellipse depicted in each mid-season month is the analytical solution under the assumption of a single-mode, elliptical bivariate distribution. The centroid of this ellipse is the vector mean of all winds; i.e., the grand mean. This characteristic presumably added credence to the previous idea that the stratosphere is essentially quiescent. However, under the assumption of a mixed distribution, with two modes—westerly and easterly—the decomposition is marked. The ellipses represent the central 50-percent probabilities of winds for that mode. Equally interesting is the tendency for the easterlies to be stronger, less variable, colder, and occur at lower altitudes than the westerlies. For July, the easterly group—winds from the east—constitute 47 percent of the total set while the westerly groups constitutes 53 percent of the total set. For the October and January periods, the westerlies occur  $\approx 70$  percent of the time. The westerlies means are  $\approx 10$  m sec<sup>-1</sup> while the easterlies are  $\approx 30$  m sec<sup>-1</sup>. This feature is closely related to the now well-known quasi-biennial oscillation (QBO) in the tropical stratosphere but it is a treatment of the total set of data without respect to the dynamics or the existence of the QBO phenomenon.



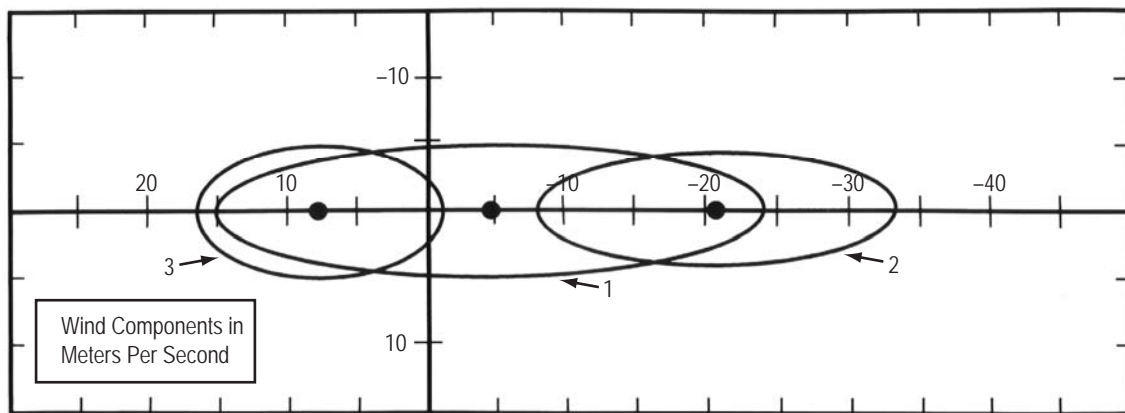
Canton Island, 30 mb (January 1953-1967)

(a)

Group No.	% Obs Within
1 Total Ensemble	100
2 Easterly	31
3 Westerly	69

Group No.	Height (m)	Temperature (°C)
1	23,765	-57
2	23,720	-57.4
3	23,785	-56.9

Prob. Level (Ellipsis)
0.50



Canton Island, 30 mb (April 1953-1967)

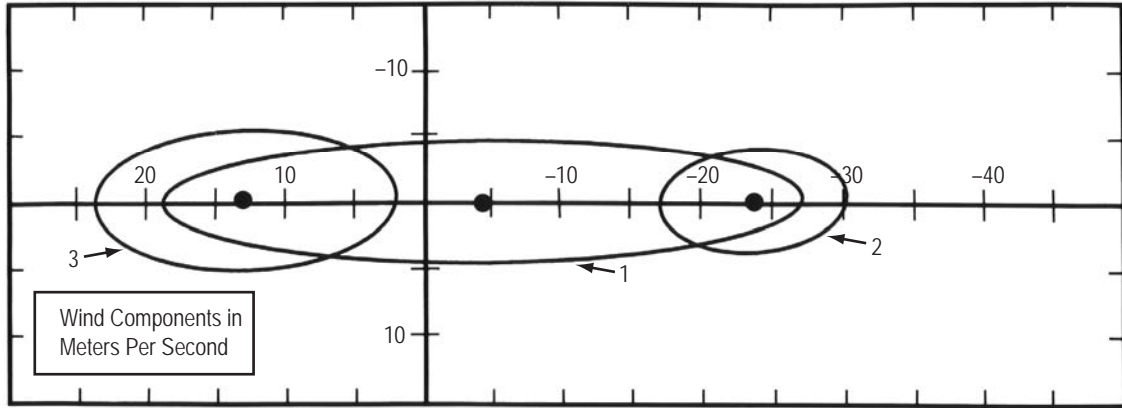
(b)

Group No.	% Obs Within
1 Total Ensemble	100
2 Easterly	42.7
3 Westerly	57.3

Group No.	Height (m)	Temperature (°C)
1	23,801	-54.9
2	23,774	-56.1
3	23,821	-54

Prob. Level (Ellipsis)
0.50

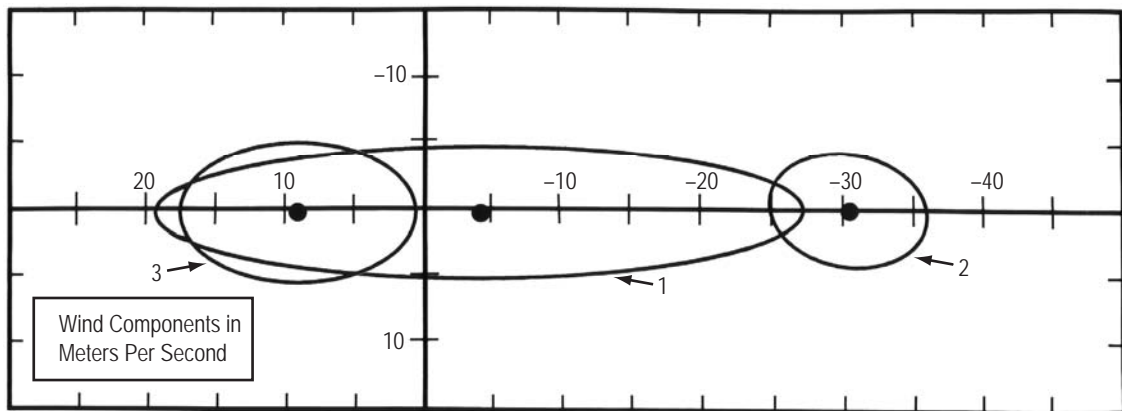




Canton Island, 30 mb (July 1953-1967)

Group No.	% Obs Within	Prob. Level (Ellipsis)	Group No.	Height (m)	Temperature (°C)
1 Total Ensemble	100	0.50	1	23,938	-53.6
2 Easterly	47		2	23,880	-55.4
3 Westerly	53		3	23,990	-52.1

(c)



Canton Island, 30 mb (October 1953-1967)

Group No.	% Obs Within	Prob. Level (Ellipsis)	Group No.	Height (m)	Temperature (°C)
1 Total Ensemble	100	0.50	1	23,887	-55.1
2 Easterly	33		2	23,829	-55.9
3 Westerly	67		3	23,915	-54.7

(d)

Figure 7-7. Multimodal bivariate distributions at the 30-mb surface at Canton Island. Variates are wind components ( $\text{ms}^{-1}$ ), temperatures ( $^{\circ}\text{C}$ ), and heights (gdm) for (a) January, (b) April, (c) July, and (d) October 1953-1967 (courtesy of American Meteorology Society, Crutcher and Joiner (1977)).

Reed and Rogers (1962) discuss the circulation of the tropical atmosphere in the years 1954–1960. They reference the works of Viezie (1958) and Graystone (1958) who discuss the marked reversal of stratospheric winds in 1956 and 1957. Reed (1959) and McCreary (1959) discussed the features of these reversals at symposia. McCreary (1959) noted that the reversal first occurred at the high levels and worked downward. Reed and Rogers (1962) point out that Ebdon (1960), Reed (1960), Reed et al. (1961), and Ebdon and Veryard (1961) discuss this feature of the atmospheric circulation. See also the presentations of McCreary (1960, 1961) on winds and circulation of the equatorial Pacific stratosphere.

As pointed out by the above authors, the timing of the reversal is not exactly 1 yr. Apparently the period is a variable one, running from 18 to 36 mo with a mode at  $\approx 26$  mo, hence the name quasi-biennial oscillation. Also, the amplitudes vary. Neither a consensus nor an agreed-to formulation of the dynamics involved exist. Of course, there are several theories that have been published, each one purporting to be the solution. The reader is urged to keep up with the research on this phenomenon.

Labitzke (1982, 1987), Labitzke and Van Loon (1988), and Van Loon and Labitzke (1988) deduce a most interesting picture of the relationship between the approximate (average) 11-yr solar cycle, the QBO, and the atmosphere. They show a probable association of sea level pressure, surface air temperature, and 700-mb temperature and geopotential height with the 11-yr solar cycle only if the data are clustered according to the phase of the QBO.

Landsberg, Mitchell, and Crutcher (1959) study the power spectra of the temperature and precipitation data of the Woodstock College data. This station was, at that time, considered to be a “benchmark” station. Figure 7-8 indicates a significant rise in the spectrum of the temperatures at Woodstock College near the period between 1.8 and 2.7 yr and at periods longer than  $\approx 50$  yr. The first would appear to be a reflection or a feedthrough of the same forces that control the QBO. However, this same period is not indicated by the precipitation data. These points will be discussed slightly more in section 10.

The QBO is not restricted to the tropical stratosphere nor only to winds. The user of any set of charts for climate values which present means only usually has no way to know whether the mean value should be the expected value. With no contradictory information, the inference, correct or not, is understandably made that the grand mean value is the expected value. The figures presented in section 7 up to this point show the grand means without regard to whether a mixed distribution exists.

Ebdon (1970), using a slightly different technique than Crutcher (1957), provides estimates of elliptical bivariate normal wind distributions for the midseason months over the Northern Hemisphere at 50 mb, 1957–1961. The difference in treatment is in the use of or nonuse of the angle of rotation. Ebdon (1970) deduces that at the 50-mb level, it is not necessary to use the angle of rotation. Thus, all representative ellipses are either parallel to or perpendicular to the zonal axis. Ebdon (1970) also treats the bimodal distribution of winds at Canton Island differently than Crutcher and Joiner (1977b). Ebdon first categorizes the months as being predominantly easterly or westerly in direction at the 50-mb level. The statistics are estimated separately for each of the categories. Crutcher and Joiner (1972) use clustering techniques, utilizing all data as the initial set. The angle of rotation is obtained in the derivation of the elliptical axes and the variances along these axes. The results are quite similar, as one expects for this region of the well-marked QBO. Ebdon (1970) also furnishes in chart form the means and standard deviations of temperature, geopotential heights, zonal and meridional components, the average winds (isotachs), and streamlines for the Northern Hemisphere 50-mb level, mid-season months, 1957–1961. If one is interested in the circular normal distribution application, the vector variance is the sum of the two component variances.

The QBO and the El Niño (La Niña) Southern Oscillation (ENSO) phenomena are well established in recent, and to some extent, in past, history. The decadal patterns seem also to be dominant. These together, according to Rasmusson (1990) (personal communication), may be considered a systematic climatic fluctuation and a semipermanent,

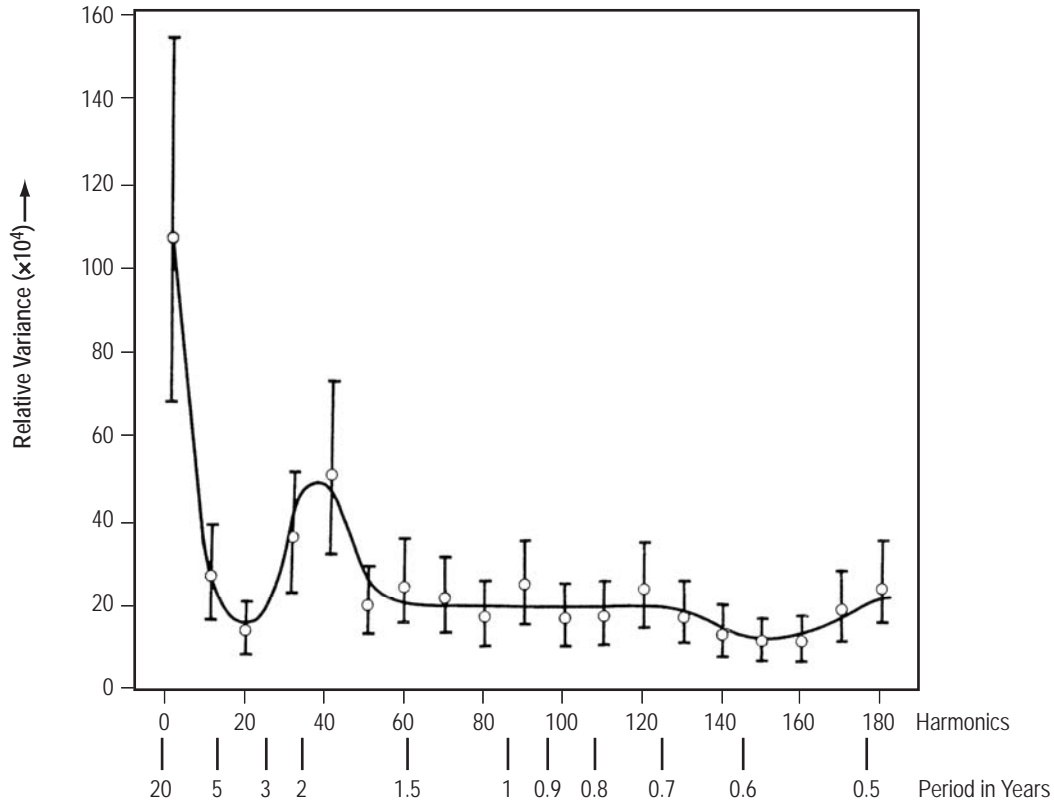


Figure 7-8. Residual normalized power spectrum analysis of monthly average temperatures, Woodstock, MA, 1,032 mo, 1870–1956. Harmonics averaged by consecutive groups of ten. Open circles show averages. Vertical lines show the 5 and 95 percent chi-square limits (courtesy of the American Meteorological Society, after Landsberg, Mitchell, and Crutcher (1959)).

if not a permanent, feature of Earth’s global circulation. This combined phenomenon may be considered to be an integral part of the circulation contributing to variability in all climatic element distributions discussed in section 7: radiation, temperatures, dewpoints, densities, winds, clouds, drouth, etc.

### 7.3.6 Variability

Attempts are made to present features of wind variability as indicated in the foregoing sections. Wind roses do this. Prior to 1940, few publications provided any other measure of variability except through measures of range or differences between extremes. The range does provide a measure of variability, the variance, and its square root, the standard deviation.

If the underlying distribution is known, the mean and the variance provide considerable information. Ideas on variability were and are present in any time-ordered presentations. Two- and three-way presentations are also available, such as upper air, temperature-wind speed, temperature-wind direction, etc. In the case of multimodal, multivariate distributions (mixed distributions), the marginal means and variances and the internal covariance matrices contain and display the information of the total data set.

Standard deviations of climatological data in chart form for wind data as well as for other elements are presented in the U.S. Navy Marine Climatic Atlases for the Northern Hemisphere (Crutcher (1959) and Crutcher and Meserve (1967)) and for the surface (Crutcher, Wagner, and Arnett (1966)). These data are presented by month at each 5° latitude and longitude in tabular form and in isopleth form on the charts.

For the Southern Hemisphere, standard deviations are provided at station locations at all mandatory levels by Taljaard et al. (1969) and by Guterman (1970).

The publication of variability measures, such as the standard deviation, is increasing slowly. See new global atlases of upper air data of the U.S. Navy and U.S. Air Force (1989). This is a good step forward for climatology as well as for operational meteorology.

Few, if any, publish measures of variability, especially of winds and, in particular, the measures shown in figures 7-7, the sharp, distinct difference between the two modes shown. Additionally, as indicated previously, the wind, temperature, and height data of the Canton Island 30-mb data are broken out into four distinct groups. The westerlies decompose into three groups, two of them indicating flows from the west-northwest and from the west-southwest.

In the case of winds, most of the authors mentioned above do provide the useful estimates of the mean and the standard deviation, yet there are many who do not. Sawyer (1950) and Graystone (1958) furnish statistical estimates along and across air routes, not necessarily oriented to the four cardinal compass points. Brooks et al. (1946, 1950) present statistical estimates for the upper air using the vector mean and the vector standard deviation. For the Northern Hemisphere upper winds, Crutcher (1959) discloses estimates of 14 statistics (or combinations) for the assumed unimodal elliptical bivariate normal distribution. The above atlas is partially supplemented in time by more recent atlases. For the Northern Hemisphere, Crutcher and Meserve (1967) give monthly means and standard deviations in chart and tabular form for stations for upper air temperatures, dewpoints, and heights of pressure surfaces. They present analyzed mean charts for selected standard levels in the troposphere, including the surface. Mean winds are overprinted on the height charts. For the Southern Hemisphere, Taljaard et al. (1969) present similar information except that no analyzed charts of the standard deviation are included. The tabular information is given in grid-point value form rather than station data form but does not contain a measure of the variance (the standard deviation). However, though the station location data, means, and standard deviations by month are shown, no annual means or standard deviations are included.

The basic assumption here is that there is one mode. The user may decide whether to use the general or limiting forms; i.e., the elliptical or the circular form. The use of the circular implies that the component variances are not significantly different and that the component correlations are essentially zero. Other atlases do provide some additional information on the correlations between levels.

A second advantage is the ease of graphical extraction of equivalent head and tail winds (wind aid and retard) over any path (Crutcher (1956a,b)). See also Binden and Thorne (1950) and Sawyer (1950). For upper winds, the works generally of the Northern Hemisphere, see Henry (1957) and Crutcher (1959), U.S. Air Force (1959), Heastie and Stephenson (1960), Tucker (1960), Maher and McRae (1964), Crutcher and Meserve (1967), Taljaard et al. (1969), and Ebdon (1970).

Van Loon et al. (1971) depict the components of the geostrophic wind in the Southern Hemisphere at standard levels and in cross-section form. In addition, derived geostrophic winds are computed and included for each month. Geostrophic wind computations use the sine of the latitude in the denominator. Thus, geostrophic winds closer than 15° latitude to the equator must be considered to be invalid. As the geostrophic winds were computed

from the mean fields of height (or pressure), no standard deviations are available. The winds presented then are geostrophic mean winds, which are not necessarily the same as mean geostrophic winds.

For the Southern Hemisphere, Guterman (1967, 1970) presents upper air analyzed charts of means similar to the above work. In addition, nine of the statistics of the model unimodal elliptical bivariate normal distributions for specific station locations are computed and displayed at the sides of the charts.

Crutcher, Wagner, and Arnett (1966) provide Northern Hemisphere 1,000-mb (or surface) wind components and their respective standard deviations. No correlations are presented. These data are presented in analyzed form and in grid-point values extracted by eye from the analyzed charts. The grid points are those used by the U.S. Weather Service National Meteorological Center by its numerical analysis and prediction groups. These data are available on magnetic tape at the now National Climatic Data Center, Asheville, NC, at the cost of reproduction and handling.

The series of U.S. Navy marine climatic atlases of the world was designed to supplement and augment the work by McDonald (1938). This series consists of volumes for the North Atlantic, North Pacific, Indian Ocean, South Atlantic, South Pacific, Arctic, and Antarctic. Volume I was issued in 1957, followed at regular intervals by the other volumes. Revision of this series began in 1975 and has been completed except for the Arctic and Antarctic volumes, which will not be revised. Hastenrath and Lamb (1977) provide considerable information on the climates of the eastern Pacific and the tropical Atlantic. Variability information for wind and other elements is supplied by cumulative distributions, generally truncated at the 0.05 and 0.95 empirical probability (5 and 95 percent) levels.

These atlases contain considerable information on winds and their empirical distributions by direction (roses) and in conjunction with one or two more variables. Data are included for selected oceanic areas. The wind roses depict directions with speeds (or forces) as well as cumulative percentage frequencies by Beaufort Forces. Included are isolines of speeds by categories equal to or less than Beaufort force 3 (about  $5 \text{ m sec}^{-1}$ ) and those equal to or greater than gales (force 8—about  $18 \text{ m sec}^{-1}$ ). The series revision provides the direction and magnitude of the vector mean wind as well as the scalar measures.

It is pertinent here to state that wind roses for U.S. data are available or can be produced at the National Climatic Data Center. Presumably, other National Centers can do the same. These may be designed for special purposes, such as wind roses, for different types or degrees of weather, such as cloudiness, precipitation, or temperature. In addition, a special wind rose is available which contains the usual breakdown by direction and speed and supplemented by statistics using the assumption of a unimodal bivariate elliptical normal distribution, based on work by Crutcher (1957).

The recent upper air atlas series, U.S. Navy/U.S. Air Force (1989), has been mentioned in section 5 on temperatures and dewpoints. Here, section 7 provides figures for the hemispheric January and July 500 vector mean winds and their standard deviations and heights. Heights and winds are presented together for one can be used as an aid to estimate the other.

## 7.4 Examples

Wind data presentation can take many forms, particularly in wind rose formats. Figure 7-2 with its accompanying legend is almost self-explanatory. The reader's attention is drawn to the rather strong position change in eastern Africa of the intertropical convergence zone. Comments concerning figure 7-3 applies to figure 7-2 also. Figure 7-3 already shown illustrates estimates of the global vector mean resultant wind directions (only)

during January and July, respectively. The isopleths indicate the speeds. On the scale of these particular charts, only approximations can be indicated. Due to monsoon effects in some regions, the annual mean resultant vector could be zero. With a separation of 6 mo, considerable differences might be noted. From both resultant wind and dominant wind patterns (McDonald (1938)), cross-equatorial flow is noted. In figure 7-3(b), the July northward flow,  $m\ sec^{-1}$ , across the equator east of Africa is marked. In January, figure 7-3(a), the flow is southward but not as strong as in July. The patterns generally associated with the cyclone and anticyclone circulation are evident in these figures. It is stressed here that the equatorward moving air on the east side of the anticyclones kept relatively dry by subsidence produce and maintain the continental and marine deserts. McDonald (1938) and the U.S. Navy (1955–1980) supply surface maps by month and season for selected wind characteristics.

## 7.5 Applications

Wind aid and retard (equivalent head and tail winds) statistics have been developed for aircraft and for surface transport. Winds play an important part in the diffusion or concentration of atmospheric pollutants. These pollutants are effective agents in health and material degradation. Increase in intensity and spread of the degenerative diseases of old age are often attributed to pollutants. These conditions are created in part through the production of energy (power) through the use of fossil and radioactive fuels and the necessary dissipation of by-product effluents, some deleterious and corrosive. For this reason, as do the other climatic elements, winds and studies of winds play an ever-greater part in life. The U.S. Environmental Protection Agency (1978) (USEPA), from its Office of Air Quality and Planning and Standards, provides a workbook for comparison of air quality models. Crutcher et al. (1986) discuss the separation of wind and pollutant heterogeneous distributions into coherent homogeneous groups. Details, examples, and computer programs are given in Rhodes et al. (1980).

The insistent search for energy (power) sources underlies the exploitation of presently available and future supplies. Some of these sources are the tides, the winds, the Sun (solar), hydroelectric, ocean currents, coal, petroleum, fission of the radioactive materials, fusion of the lighter chemical elements (notably, hydrogen), geothermal, ocean currents, and the wind currents (the winds).

Wind, as a climatic element, is once again gaining importance in the field of power generation and its application. Fossil fuel availability is of concern. Formerly and still used to pump water, grind grain, and to drive or propel ships, its use as an available power form to provide electric energy is under intense investigation. Therefore, its observation and recording increasingly become more important. The literature worldwide is expanding rapidly. The reader may refer to the current literature. A few items of the many available follow.

Moses and Bogner (1967) present a specialized climatology of the Argonne National Laboratories site that includes a detailed study of 15 yr of tower wind data. Included are shorter periods of solar radiation, temperature, dry-bulb and dewpoint, precipitation, pressure, relative humidity, and soil temperatures.

Reed (1974) provides some charts showing electric power generation potential regions from the winds. Changery (1975) gives information on wind data availability and instrumental exposures at many U.S. locations. Cermak (1975) edits the proceedings of a meeting devoted to wind engineering and research. Eaton (1975) edits the proceedings of the Fourth International Conference on "Wind Effects on Buildings and Structures." Changery, Hodge, and Ramsdell (1977) present a list of summarized wind data compilations. Frost, Long, and Turner (1978) develop an engineering handbook for use in wind turbine generator development. Simiu and Scanlan (1978) discuss the wind effects on structures as an introduction to wind engineering. The State of California (1978) describes the wind and wind power potential in California. Exploitation of the electrical wind energy potential shows slow but consistent development throughout the world. Much research and development remains to be done. In some areas, as in the Los Angeles area of California, the casual visitor may see some so-called windmill farms. These, at close range, appear to be a veritable small forest of trees (tall windmills of various types). Spera and Richards (1979)

discuss modified power law equations for vertical wind profiles. Mehta (1979) edits the proceedings of the workshop on wind climate held in Asheville, NC, at the present National Climatic Data Center. Calvert (1979) discusses the application of windpower principles on a small scale. Ramsdell, Houston, and Wegley (1980) develop measurement strategies for estimating long-term average wind speeds. Doran, Buck, and Heflick (1982) present basic concepts and power law extrapolations of wind speed. Sandusky, Renne, and Hadley (1982) present candidate wind generator site summarized meteorological data for the period December 1976 through December 1981.

Gebhardt (1984) details tests on small wind turbines in the Weber Basin area near Ogden, UT. The conclusion drawn from this test was that, if a site met the site requirements, small power production from wind energy is both feasible and economically sound.

Elliott et al. (1986) provide an extensive wind energy resource atlas of the United States. Charts for monthly, seasonal, and annual average wind power are indicated by states and/or regions.

Simiu, Changery, and Filliben (1979) cover the aspect of wind extremes. Studies such as these are useful to the industries, such as architecture, construction, frost prevention, shipping, agriculture, forestry, and lake control.

In fact, wind plays a salient part in all aspects of life on this planet. The measurement, recording, and transmission of information on wind, its effects, and uses have always been important. With respect to marine interests, Crutcher (1975) describes briefly some of the relationships associated with the connotation Beaufort wind force and its scaling. The scale of Beaufort force essentially linearizes the wind representation where the usual nonlinear representation is in speeds. It provides a better measure of the available energy (or power) than does the speed representation. Coding and signaling is essentially binary. Some codes and signals to shipping interests are excluded so as to reduce confusion.





## 8. PRECIPITATION

### 8.1 Historical

Climate is an ongoing interaction product of many dynamic elements. Excess or deficiency of any essential element is sufficient to change expected conditions or the “status quo” of climate. Moisture, in the form of vapor, fog, clouds, or precipitation and evaporation effects is an extraordinary and fantastic ingredient in the climate mix. The presence of or the lack of water vapor in the atmosphere is the main control of precipitation potential. The temperature climate controls the occurrence and type of precipitation. Spatially, the temperature is more responsive to altitude than to latitude. Pressure and condensation nuclei do play a part. Snow-capped peaks and glaciers exist near the Equator in South America, Africa, and in the East Indies. The action of the dewpoints as a variable control dependent upon the existing temperature and moisture variables has been discussed previously.

The atmospheric circulation is a distributive system for the evaporation and precipitation processes yet is influenced itself in a feedback loop sense by the precipitation, condensation, and evaporation processes. In the troposphere, the rising and cooling of air in convective processes and displacement in the poleward movement and the falling and warming of the air towards the surface and in the equatorward movement are part of the process. Coupled with interaction with topographic land features, with the oceans and with air masses with their distinguishing boundaries or fronts, the process becomes more complex. Regions of wetness and dryness are created. Those wax and wane. Droughts and deserts develop as do swamps and wetlands. Man’s activities play their part and, in turn, are affected.

Moist air (dry air mixed with the water vapor) may rise to high altitudes through local convection as in thunderstorms, particularly in the equatorial regions and in frontal zones. These often reach the temperature inversion capping the tropopause. If energetic enough, these may even penetrate the inversion to some distance. Also, moist air may be forced up and over topographical barriers such as high mountain ranges. On the upslope cooling windward sides of the mountains, moist conditions will prevail, while in the lee downside warming sides, arid conditions exist. In some surface arid regions there may be sufficient upper air water vapor for precipitation but the temperatures cannot cool to the dew point. No clouds form and no precipitation falls. At the surface though, radiational cooling may be sufficient to produce dew. This dew is collectable. Even some small microclimate areas may develop which are quite different from the neighboring environments.

### 8.2 Surface Maps

Figure 8-1 portrays the relative magnitudes of precipitation over the globe on an annual basis. Heavy rainfall occurs in the equatorial regions of South America, Africa, the East Indies, and the Indian subcontinent. In particular, the rainfall is heavy on the ramparts of the northwestern-western Cordillera flank of the Andes in Colombia. Over 5,000 mm of precipitation occurs there on an annual basis, fairly well distributed over all months. Heavy rainfall also occurs in the Indian area against the southern and eastern Himalayan escarpments during the moist monsoon season. The Rocky Mountain slopes facing the North Pacific in southeastern Alaska, British Columbia, and northwestern United States are quite moist. Locally, island configurations also produce small areas of excessive or deficient rainfall. Locally, in the subtropical regions, hurricanes (typhoons, cyclones) may produce extremely heavy rains.

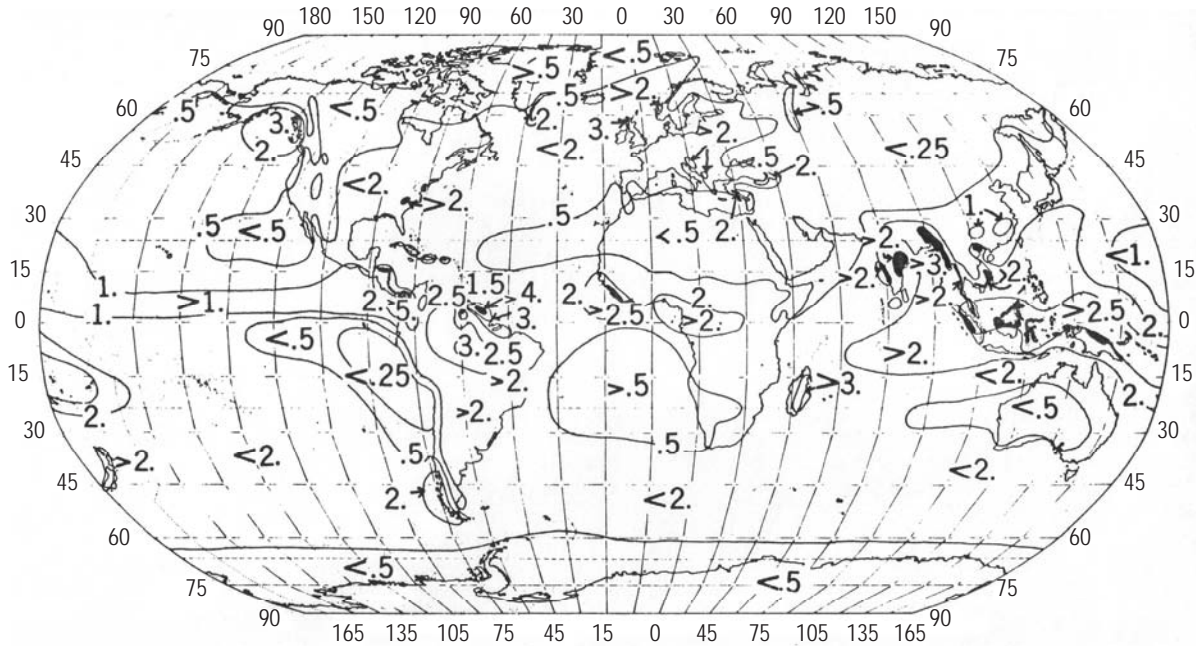


Figure 8-1. Global relative magnitudes of annual precipitation (m).

At the other end of the moisture spectrum are the dry, arid desert regions. These exist in the polar regions as well as oceanic and continental regions. The polar desert conditions exist in regions of low evaporation and low temperatures which limit the maximum vapor content of the air. This dryness is made more severe by the dry subsiding air from aloft which, though warmed by subsidence, is quickly cooled by terrestrial radiation through the essentially radiationally transparent atmosphere. This air is often already desiccated by condensation processes before it reaches the polar regions. Oceanic desert regions or bands are also created by the subsiding warming air in the anticyclone (high pressure) areas. Even more pronounced are the continental west coast desert regions which lie approximately between  $15^{\circ}$  and  $45^{\circ}$  latitude. These are exemplified by the Californian and Sonoran deserts of North America, the southwestern United States, the Kalahari region of southwest Africa, the Peruvian and Chilean deserts in South America, and the Australian desert regions. Supplementing these are the additional continental or inland deserts of the Sahara, the Gobi, the Arabian, and Pakistan regions. In Asia, the high Himalayan ramparts effectively keep moisture from entering the interior of Asia. When this effect is coupled with the subsiding drying air of Asia's great winter cyclone, the great interior deserts of Asia are produced. With the continuation of this circulation in the southward lee of the Himalayas, the stage is set for the generation of the deserts of India, Pakistan, and Arabia.

Among the many presentation modes, the movement of patterns or lines of equal precipitation measures is often used. For the United States, figure 8-2 shows the decadal movement of the 500- and 1,250-mm isohyets for the Great Plains, and the central and southeastern areas of the United States. In figure 8-3, attention is drawn to the 500-mm isohyets located farthest east during the drought period of the 1930s era. It moves westward during 1941–1950, then slowly moves eastward, becoming more or less stationary between the 1931–1940 and the 1941–1950 position. For the period of 1921–1980 (not shown in this figure), the lower portion of the curve shifts westward slightly and shifts eastward in the upper portion.

Spatially, the 10-yr periods of precipitation are quite variable. Confidence in the exact position of these lines is low but there is the indication that these lines are indicative of the drought variation. No decadal line lies entirely east of the 1931–1940 decadal line, the years of considerable drought. However, it must be emphasized here—and will be indicated again later—that drought is not measured simply by precipitation amounts. Winds, incoming and

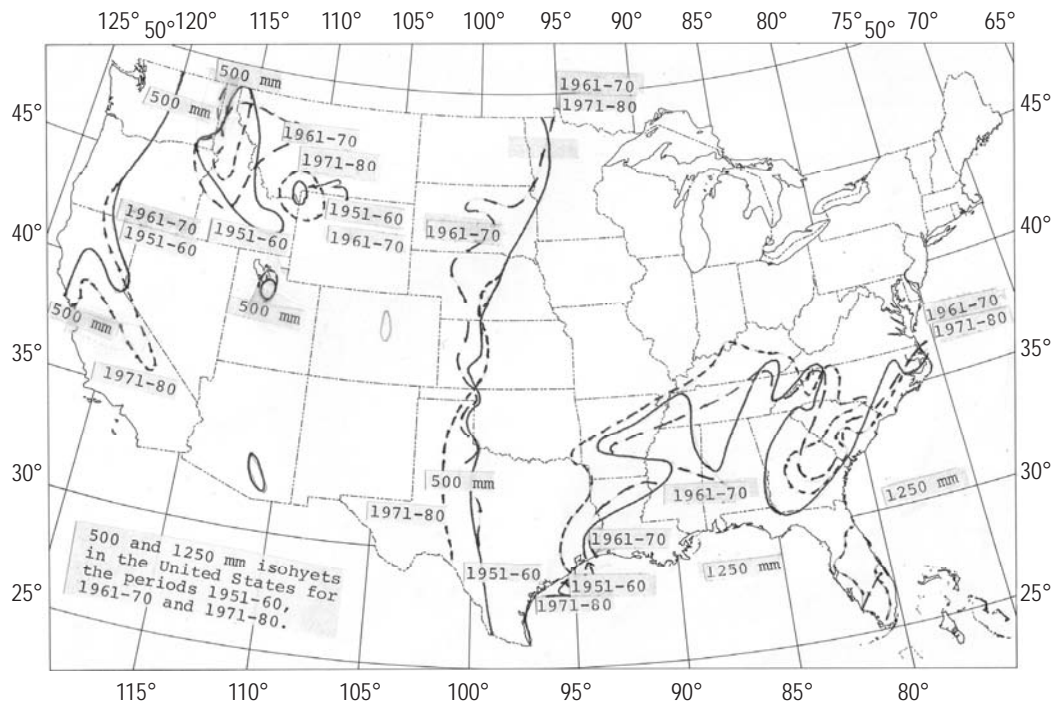


Figure 8-2. Decadal positions of the United States 500- and 1,250-mm isohyets. The decades shown are 1951–1960, 1961–1970, and 1971–1980.

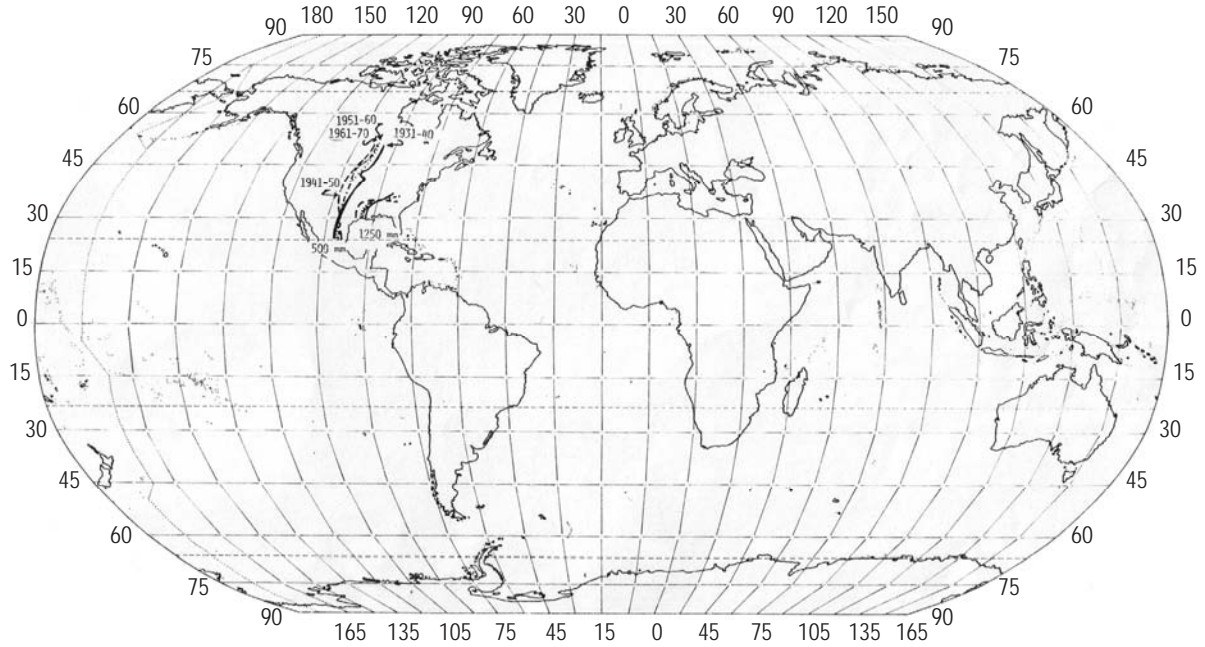


Figure 8-3. Decadal positions of the United States 500- and 1,250-mm isohyets. Shown are 1931–1940, 1941–1950, 1951–1960, and 1961–1970.

outgoing radiation and soil moisture storage are involved. Garcia et al. (1977) provide information on precipitation distributions for the Mexican states of Queretaro and Hidalgo. They, using the incomplete gamma distribution, prepare monthly cumulative graphs overlaid with the actual cumulative precipitation amounts. In sectional chart (map) form, they present for individual stations mean precipitation and the probability of precipitation equal to or greater than the mean. Fifteen or more years of data were available at all stations. The reader is referred to the later discussion on models.

Hershfield (1961) provides a rainfall frequency atlas of the United States. The durations are for 30 min to 24 hr with return periods from 1 to 100 yr. Salmela, Sissenwine, and Lenhard (1971) provide a preliminary atlas of 1-, 0.5-, and 0.1-percent precipitation intensities for Eurasia.

Yao, Barger, and Crutcher (1971) author a precipitation probability atlas for eastern Asia. The gamma distribution model is used.

Miller, Frederick, and Tracy (1973) provide a series of precipitation atlases for the western United States, one for each state of the United States.

Taylor's (1973) atlas is for the rainfall of the Pacific Islands.

Among the many problems associated with precipitation measurement, there is one problem which apparently has not been studied. Precipitation on one day may depend on precipitation that falls in a prior period and has been partially evaporated. Thus, although portions of the rainfall may be utilized by plants and other portions may contribute to runoff, the amounts recorded though free of observing and recording errors in each instance may, in cumulation, provide an overestimate. This process, of course, represents a type of "memory" in these processes. The use of antecedent precipitation is a tool in forecasting techniques. See later discussions in the section on drought. In statistical or mathematical modeling, this may be reflected, in part, in Markov processes of several orders, generally ranging from zero to three. Persistence is another facet of the process. As far as is known, this problem, over cumulations, has not been resolved. A double-blind study using radioactive or fluorescent tracers might be developed.

Precipitation is also estimated from satellite photographs. So far, considerable success has been obtained in the U.S. area by the NOAA groups involved in the day-to-day forecasting and those involved in research. Most success has been obtained with the convective storm types. The reasoning goes like this. The higher the convective cloud, the lower the cloud top temperature with the resultant production of more rain. In the temperate zones there are the orographic storms, the frontal storms, and the air mass storms, in which, at times, the convective storm is found to be involved, more so in the air mass storms. Follansbee and Oliver (1975), Griffith, Woodley, and Martin (1976), Oliver and Scofield (1976), Scofield and Oliver (1977), Woodley, Sancho, and Miller (1972), Woodley and Sax (1976), and Sickler and Thompson (1979) provide excellent background material.

Barrett and Martin (1981) discuss rather extensively the monitoring of rainfall by use of satellite information. Ingraham, Amarocho, Guilarte, and Escalone (1977) and Cadavid, Mejia, and Crutcher (1979) discuss the application of satellite imagery interpretation to tropical areas, specifically Venezuela and Colombia. The results for the temperate zones are excellent and preliminary results for the tropics are extremely promising but need further comparison against ground truth data.

Meitin, Woodley, and Flueck (1984) report on the second phase of the Florida Area Cumulus (FAC-2) experiment. They investigate the possibility that cloud seeding may have affected the rainfall outside the intended target area. Rainfall was estimated over one  $3.5 \times 10^5$  km<sup>2</sup> area centered on the target using geosynchronous infrared imagery and the Griffiths-Woodley rain estimation technique. The results show more rainfall (in the mean) on "seed" than "no seed" days both in and downwind of the target but lesser rain upwind.

Griffith and Fedor (1985) examine the precipitation from tropical cyclones. First, they explore the limitations. As they indicate, the estimation of convective rainfall from satellite data is a controversial topic. The inherent problems from the beginning concern the ability to remotely sense, at nonoptimal wavelengths visible or infrared, a quantity of rainfall which is known to exhibit high variability in both space and time. The authors discuss these and the two additionally major sources of error in the estimation of rates and quantities. As SeaSat data were available for some of the storms studied, they present the use of the SeaSat data as well as the other sources. The procedural output will allow estimates of hurricane rainfall output prior to landfall. Future correlations with actual rainfall and the estimated rainfalls will develop the understructure for these promising techniques.

Two important questions now need to be asked. The first question is, "How representative of the rainfall at a point is the catch at a gauge from only one storm?" The second question is, "How representative of the geographic point directly below the cloud top point is the estimate of rain production of the rain that falls into the gauge?" This applies to all regions.

In the case of point rainfall, the developed techniques so far as is known now do not as yet serve very well. The interpretation must be for areas where more than one gauge is available. On a daily basis, the results are poor, but over a large area and over a period of time, the results are encouraging. However, see the following comments.

The problems are many. First of all, it is the rate of convective processes that best show the rainfall production rate in the tops of the clouds. Generally, the wind structure is not easily determined beneath the cirrus shield. The rain will take from 20 to 30 min to fall from the high altitudes and pass through varying wind fields before falling into a small rain gauge which may be 5 or 25 cm in diameter at a spot on the ground. This brings to our attention the fact that the rain gauge itself may not be a good measuring device under all conditions. Topographic and surrounding features contribute to the effectiveness of the gauge. The ability and the training of observers has its effect. Gauge types vary. The catch at any gauge underestimates the actual rainfall by anywhere from 5 to 20 percent, depending on the wind speeds. To partially answer the second question posed above, Griffith (1987) compares gauge and satellite rain estimates for the central United States during August 1978. Rainfall estimates, inferred from the thermal infrared channel of the Geostationary Operational Environmental Satellite-East for August 1979 were compared with gauge rainfalls over hourly and daily timeframes for area averaged amounts and for point values. Over the month, the satellite rainfall estimates tend to be 20–40 percent smaller than the gauge amounts but are less variable.

### 8.3 Interrelationships

Previously, it was indicated that there seems to be a long-term change in correlation patterns of temperature from 1900–1940 to 1941–1970 (van Loon and Williams (1976)). Crutcher (1978) shows that the temperature-precipitation correlations within the same month; i.e., zero lag, change from the period 1906–1948 to 1949–1970. Figures 8-4 and 8-5 (Crutcher (1978, figs. 2b and 5b)) for July show the changes that took place for that month. For example, the correlation of 0.2 (not significantly different from zero in the usual statistical sense of independent data) for the 1906–1948 period in south-central Nevada moved to central Idaho in 1949–1970, while the significant negative correlation of southeastern Washington state became more significant (–0.6) but moved to northwestern Washington, being replaced in the southeast by insignificant positive correlations associated with the central Idaho correlations. The May, June, and August correlations are included in the figures for comparison.

All of the above do not indicate climate change in the long run. These do indicate features of the long-term variability. Changes must be expected. There is no "status quo." Short-term changes, however, may be important but none of those carry any indication of permanent change. This, in turn, requires constant vigilance in order to assess the import of the received signals.

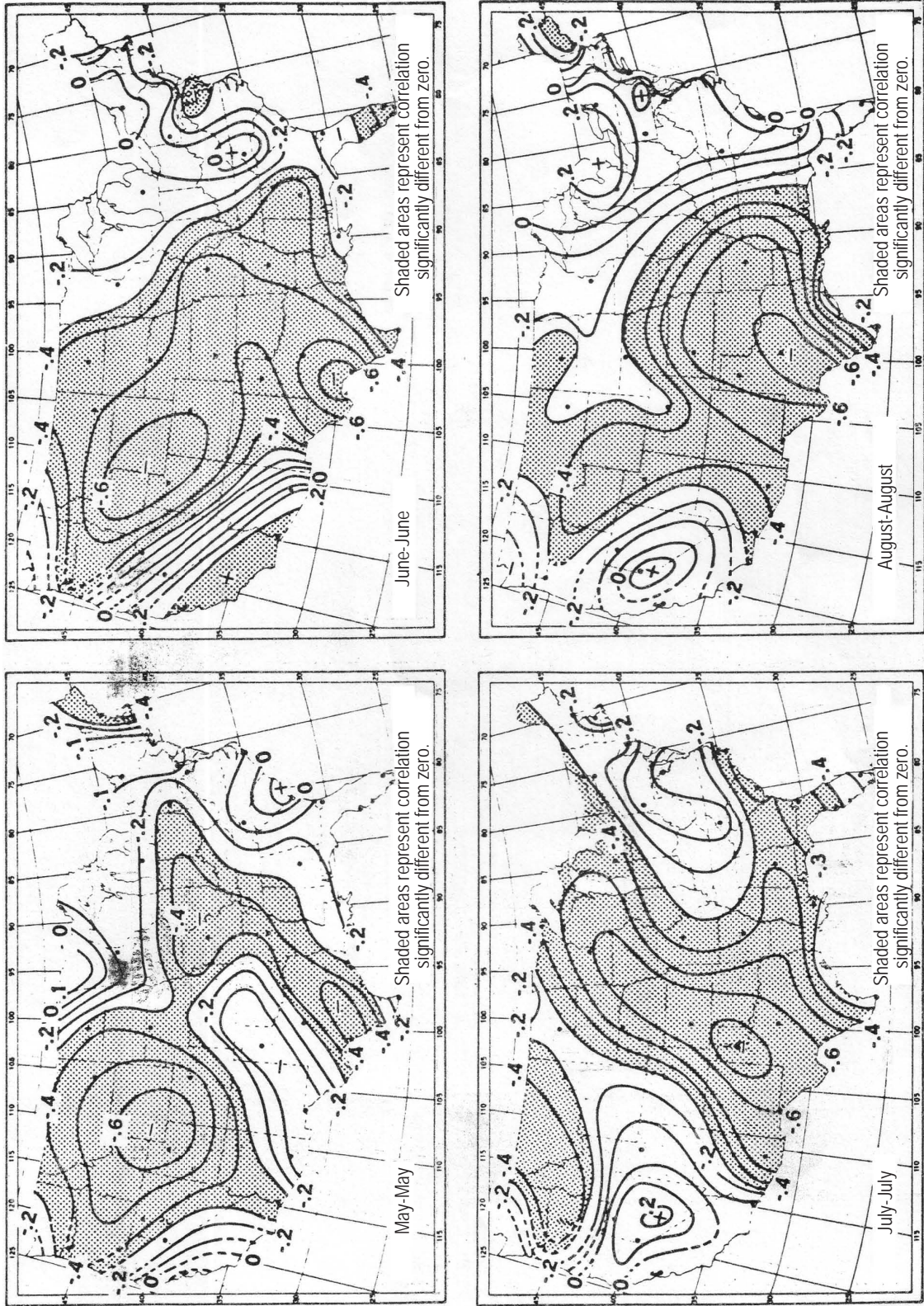


Figure 8-4a. Isopleths of correlations, LAG 0, between monthly average temperature ( $^{\circ}\text{F}$ ) and monthly total precipitation (inches) $^{1/3}$  at 42 selected North American stations, 1906–1948 (Crutcher (1978)).

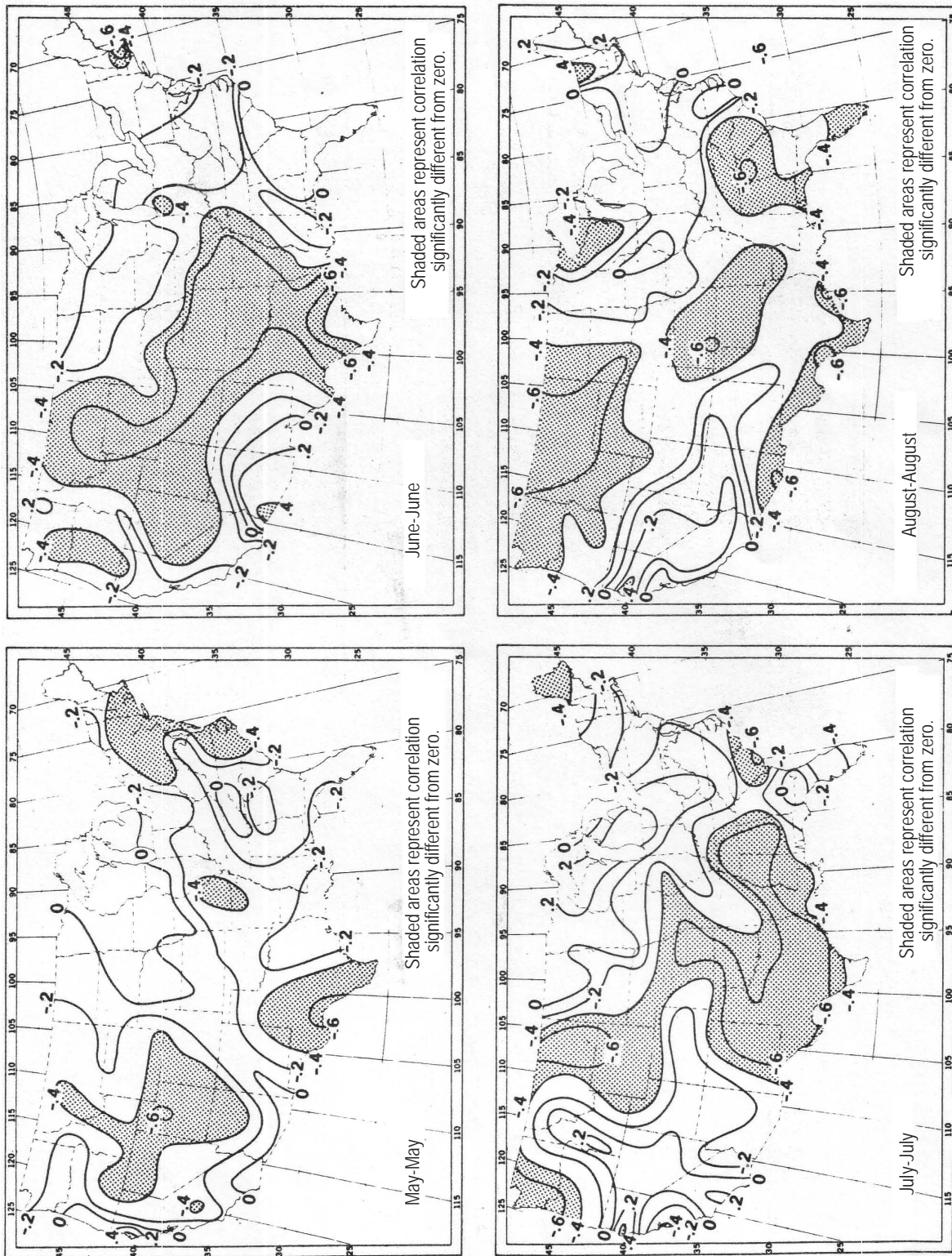


Figure 8-4b. Isopeleths of correlations, LAG 0, between monthly average temperature (°F) and monthly total precipitation (inches)<sup>1/3</sup> at 102 selected North American stations, 1949–1970 (Crutcher (1978)).

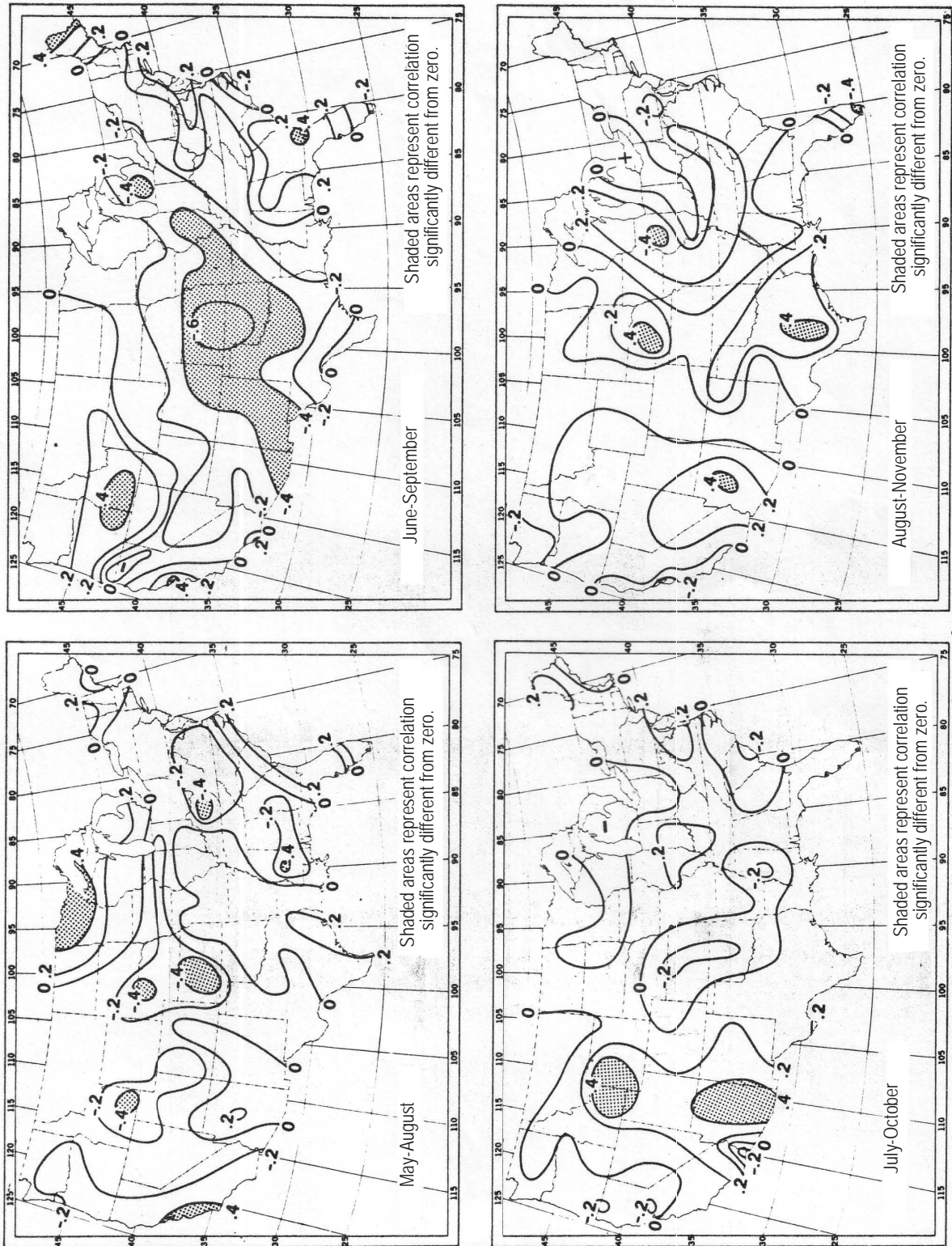


Figure 8-4c. Isopleths of correlations, LAG 3, between monthly average temperature (°F) and monthly total precipitation (inches)<sup>1/3</sup> at 102 selected North American stations, 1949–1970 (Crutcher (1978)).



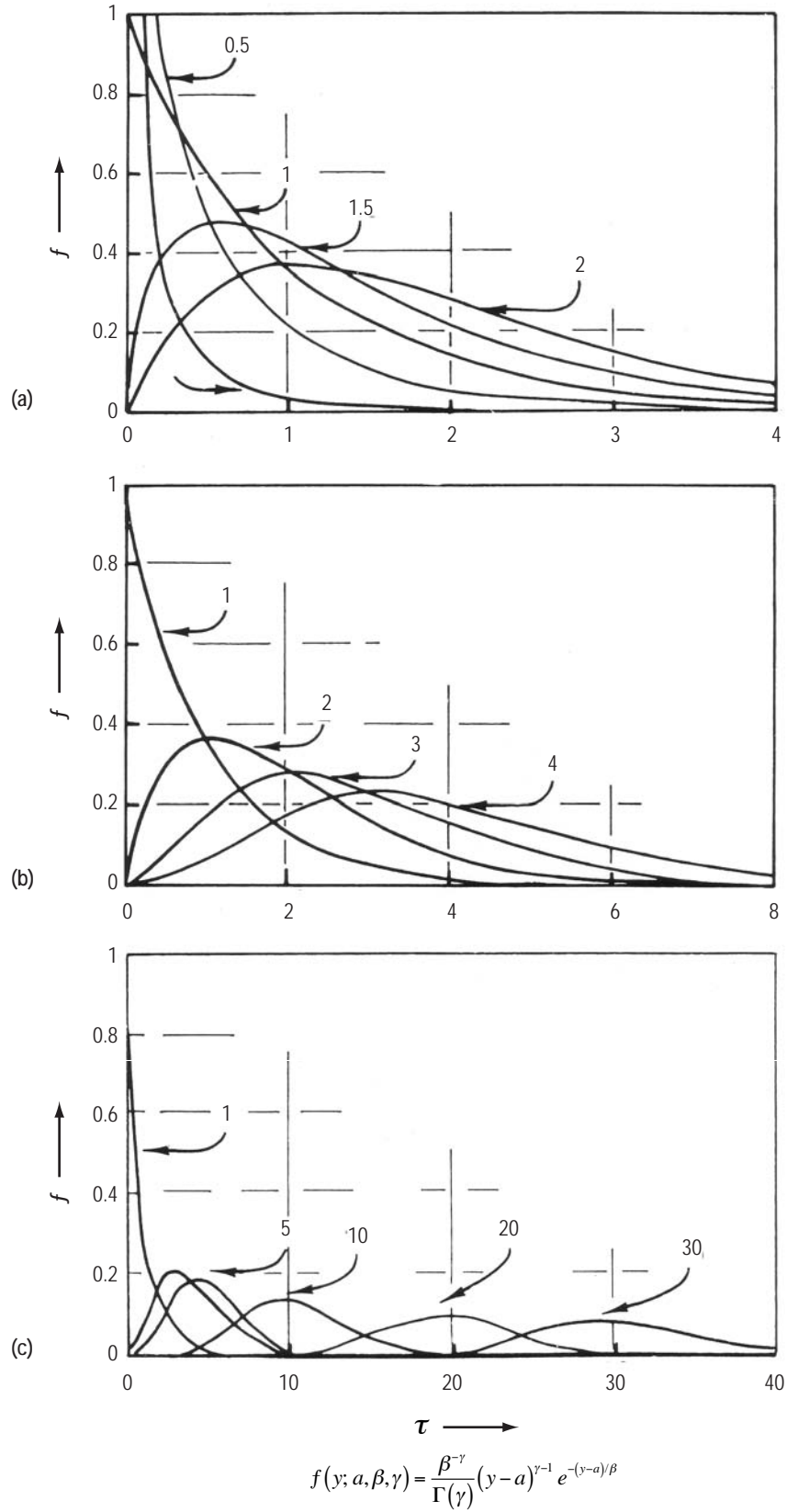


Figure 8-5. Selected gamma distribution curves where  $a$  and  $\beta$ , the origin and scale parameters, respectively, are set equal to zero and 1 (Crutcher and Joiner (1982)).

Crutcher (1978) also presents temperature-precipitation linear correlations with a lag of 3 mo (fig. 8-6) in addition to the zero lag mentioned above. As indicated by Crutcher (1978), the relationship noted by Blair (1931) and Madden and Williams (1977) hold. In the strip running from Texas to New England, wet summers are cool, dry summers are hot, wet winters are warm, and dry winters are cold. Among the reasons for this are (1) the moisture in summer limits the sensible heat by permitting earlier overturning and replacement of the surface air layer and producing cloudiness and storms. In winter the precipitation-producing clouds limit radiation loss and freezing releases the latent heat of fusion which keeps the temperature from dropping even though there is a loss of energy and (2) the lack of moisture which limits cloudiness permits solar radiation and terrestrial radiation to create the hot, dry summers and cold, dry winters.

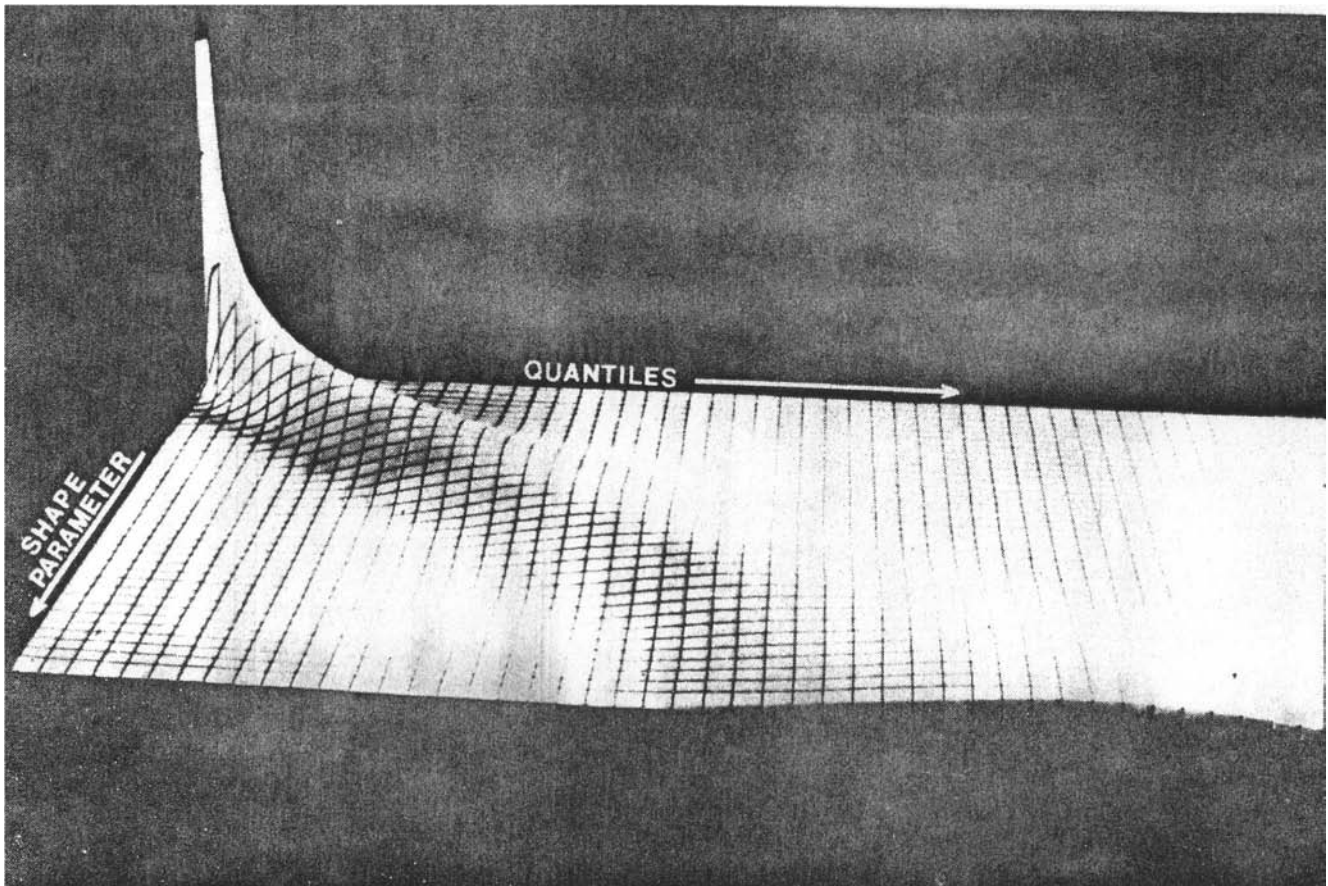


Figure 8-6. Physical model illustration of the General Gamma Distribution (Crutcher and Joiner (1978), courtesy of Water International).

The best lag U.S. linear correlation, 1949–1970, noted was the June average temperatures related to the September precipitation. A negatively correlated area extends from southern Arizona to Michigan with a maximum of  $-0.6$  in Kansas-Oklahoma. This is still not very good, for, at best, given the June average temperature, this simple correlation explains only  $\approx 40$  percent of the variance of the September precipitation. Figure 8-6 (reproduced from fig. 8b, Crutcher (1978)) shows the above relationship. An important point is that the correlations and their interactive patterns do not remain constant. That is, the serious investigator must always be updating his climate information matrices.

In addition, the investigation of the nonlinear correlations should be made to determine whether improvement in inferences may be made.

### 8.4 Distribution Models

Climatic risk assessment is a necessary course of action. Some do it well, others do not. The information base is crucial but so are the models which may be used to extract the salient informational message wanted. Some of these may be heuristic and the investigator may arrive at assessments derived through interactive background experiences. Others may need to use sophisticated statistical techniques and models. In the hydrologic and hydraulic fields, the reader may refer to the following publications which are just a few of the many available: Linsley, Kohler, and Paulhus (1949), Gumbel (1958), Chow (1964), Kite (1978), and Shen (1979). The Pearson Type III (Elderton (1953)) statistical model with all its variant forms is used by many investigators.

Essenwanger (1976) neatly compiles detailed discussions of many models of statistical distributions. Only the gamma distribution function is discussed here. The discussion is brief. For precipitation, the log normal, the log Pearson, and the gamma models are often used. Most of the procedures used for estimation have a bias, and the shape parameter estimates are too great. This has received some attention in work since 1948. See Barger and Thom (1949), Thom (1958, 1968), Bowman and Shenton (1968, 1988), Shenton and Bowman (1970a,b), Crutcher and McKay (1978), and Crutcher and Joiner (1982). Bowman and Shenton (1988) represent the culmination of more than two decades of excellent work on their part with respect to the gamma distribution function. Various algorithms to reduce the bias are discussed and referenced in works since 1968. One algorithm, the jackknife technique of estimation, effectively removes all bias but has an unfortunate flaw in that it sometimes produces an extremely erroneous estimate in small samples.

The gamma distribution function is an extremely useful one. It serves many disciplines. Among the many applications are those often made to life tests, other quality control and assurance problems, reliability, maintenance, and precipitation. Wherever a distribution is bounded at one end and unlimited at the other, the gamma distribution is one candidate among many that might be used to describe that distribution.

The general gamma distribution with origin parameter  $\alpha(-\infty < \alpha < +\infty)$ , scale parameter  $\beta(\beta > 0)$ , and shape parameter  $\gamma(\gamma > 0)$  has the probability density function shown in

$$f(y; \alpha, \beta, \gamma) = \beta^{-\gamma} (\Gamma(\gamma))^{-1} (y - \alpha)^{\gamma-1} e^{-(y-\alpha)/\beta}; y > \alpha; -\infty < y, \alpha < +\infty \quad (8.1)$$

and

$$f(y; \alpha, \beta, \gamma) = 0, y \leq \alpha \quad (8.2)$$

The distribution function given by

$$F(y; \alpha, \beta, \gamma) = \int_{\alpha}^y f(t; \alpha, \beta, \gamma) dt \quad (8.3)$$

is for all  $y > \alpha$ .

With the origin obtained, the following expression is pertinent:

$$x = y - \alpha \quad (8.4)$$

Then, equations (8.1) and (8.2) become

$$f(x; 0, \beta, \gamma) = \beta^{-\gamma} (\Gamma(\gamma))^{-1} x^{\gamma-1} e^{-x/\beta}; 0 < x < \infty \quad (8.5)$$

and

$$f(x; 0, \beta, \gamma) = 0, x \leq 0 \quad (8.6)$$

Thom (1968 and in his earlier papers) utilizes this form. As shown by Thom (1958) and Wilk, Gnanadesikan, and Huyett (1962), if the variate  $x$  assumes a transform by division of the scale parameter  $\beta$ , the distribution function develops as

$$F(x'; 0, 1, \gamma) = (\Gamma(\gamma))^{-1} \int_0^{x'} \tau^{\gamma-1} e^{-\tau} d\tau; x' > 0 \quad (8.7)$$

and

$$F(x'; 0, 1, \gamma) = 0; x' \leq 0; \quad (8.8)$$

that is a standard form with  $\alpha = 0$  and  $\beta = 1$  and is positive when  $x' > 0$ .

The distribution of precipitation amounts, including zero amounts, is a mixed distribution of two or more groups. Zero amounts are one group. This same model is used for wind speed distributions, U.S. Department of Defense, AFCRL (1985). The actual rainfall amounts may be characterized by data which seems to cluster as air mass precipitation, frontal precipitation, and tropical storm precipitation. These include a further breakdown into snow, hail, and rain clusters, but the usual procedure is to change the snow and hail to water equivalents. Periods of record are usually so short that the errors of estimation become rather large. For example, in the usual likelihood estimation procedure with sample numbers of 100, 30, and 10, on average, the estimates are too large by 3, 10, and 30 percent, respectively. See Crutcher and Joiner (1982). This plays havoc with the probability estimation for 90 percent or larger. The errors also are related to the size of the shape parameter itself; the smaller the shape parameter, the greater the error. See Crutcher and Joiner (1982). Shape parameters tend to become smaller with decreasing area covered, interval of time, and as known arid regions are approached. On the other hand, as indicated by Barger and Thom (1949) the models also are useful in drought conditions. The zero precipitation probabilities are easily identified. Also, the number of days with precipitation and the number of days without precipitation can be handled by this model.

Figure 8-5 from Crutcher and Joiner (1982) illustrates various forms of the gamma distribution. The origin and scale parameters are set to zero while the shape parameter ranges from 0.1 to 30. Note that as the shape parameter increases, it approaches the normal form. At zero, the form would be the single-line spike for the zero amounts; in this case, the events of no precipitation. The model for the amounts other than zero does not allow for zeros. Thus, the distribution is always a mixed distribution of zeros and nonzeros. In completely arid regions, even for annual rainfall, the distribution may be almost all zeros. For example, at Iquiqui, Chile, rain falls perhaps once in 11 yr. The author in 1949( $\pm 1$ ) forecast rain. A very strong, deep, cold front had passed eastward over southern Chile (and the Andes), had entered Argentina, had then penetrated northward in Argentina approaching Brazil and Bolivia. The southern end front was strong and deep enough to curve westward up and over the Andes over northern Chile and southern Peru to the Pacific. A trace of rain was observed and recorded falling from a high layer of alto cumulus-alto stratus. Such intense lows and troughs are exceptional indeed. The theory of fronts had not yet been accepted by the old-line forecasters and forecasting was done on the basis of movements of high, low, ridge, and trough pressure position and the cloudiness regimes. Their forecasting was as good as those who used the frontal analysis for they had developed the necessary expertise for their region. The author at that time was serving with the

U.S. State Department, Federal Aviation Administration, Department of Commerce, Weather Bureau as a member of the U.S. Civil Aviation Missions.

With respect to the always mixed distribution of precipitation (two or more groups with one group being zeros), the following statement holds (Thom (1951) and Crutcher, Fulbright, and McKay (1977)):

$$H(x) = q + \sum p_i (G_i(x)) , \tag{8.9}$$

where  $q$  is the probability of zeros or of origin values or less,  $p_i$  is the probability contributed by the  $i$ th subset ( $G_i(x)$ ), and  $\sum p_i = 1$ . Generally, only the sets of zeros and nonzeros (precipitation amounts) are used. It is known that the nonzeros contain several distributions but little work has been done on this model as has been done for the normal (Crutcher et al. (1982, 1986) and Rhodes et al. (1980)).

The gamma distribution is a very useful model not only with precipitation but generally with any distribution bounded below and unbounded above. See Bowman and Shenton (1988).

Figures 8-6 and 8-7, published in Water International, show physical models of the gamma distribution (after Crutcher and McKay (1978)). The approach to normality is evident along the abscissa of quantiles and the shape parameter increase. Figure 8-7 illustrates the physical model of the gamma distribution sliced into pieces. Here, the slices—each representing one shape parameter, or in an equivalent sense, an increasing interval of time (or area)—again may be seen to approach a normal distribution as the time and/or area increased.

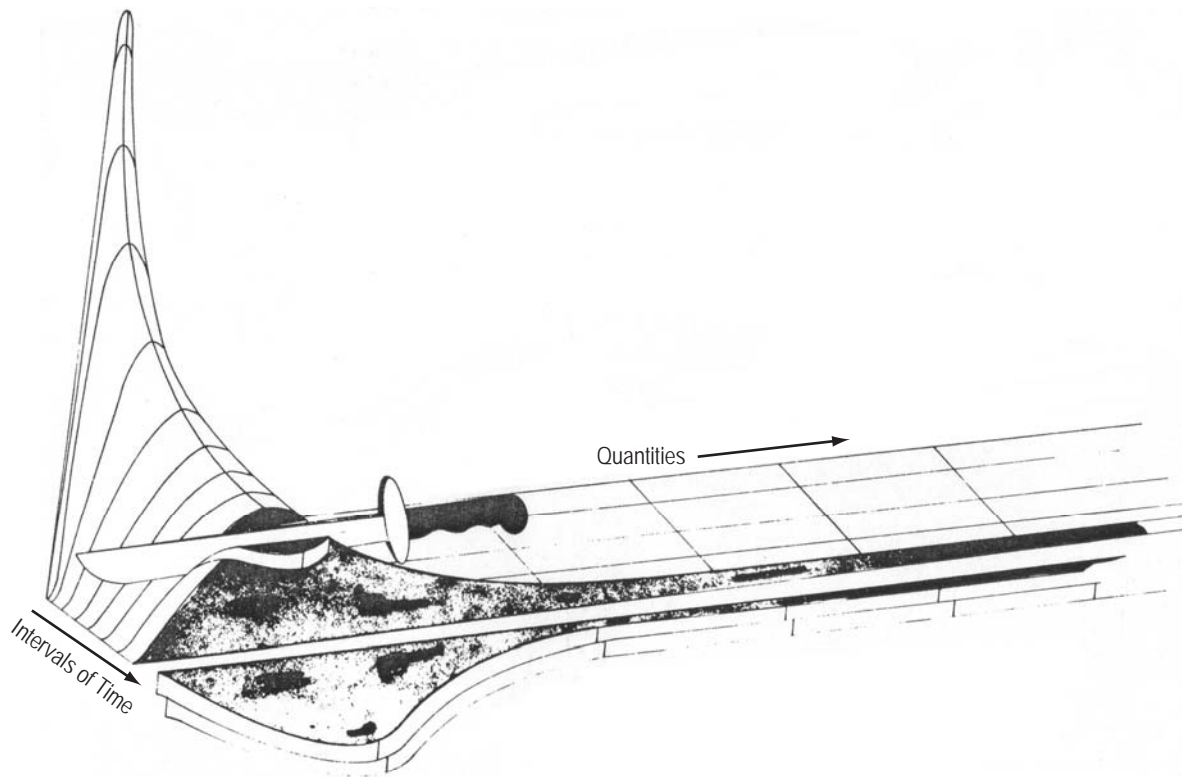


Figure 8-7. Physical model illustration of the General Gamma Distribution (Crutcher and Joiner (1978), courtesy of Water International).



## 9. CLOUDS

### 9.1 General

The geochemical process involved in the aeons of the production of water and the development of the oceans and seas are outside the purview of this discussion. A start is made with the present global system of seas and continents.

### 9.2 Cloud Development

Water, evaporated from oceans, seas, rivers, lakes, the cryogenic sphere (the icefields and icecaps), and the land, changes from the solid and liquid phases to the gaseous form. It is then lifted and transported to other regions, some very near and some very far. Dependent upon the availability of condensation nuclei on pressure and temperatures, it changes state from the vapor state to liquid or crystalline form. Swarms of the fine liquid droplets and/or the solid crystals compose the clouds. Clouds reflect, block, absorb, and reradiate energy. In layered form, clouds keep surface temperatures from rising rapidly during the day or falling rapidly during the night. In convective form or from mechanical lifting over rising terrain, cloud droplets coalesce and fall as precipitation—rain, snow, or hail.

Clouds and cloudiness are important climatic elements. Discussions appear in all basic climatological and meteorological texts such as Haurwitz and Austin (1944), Trewartha (1954), Landsberg (1958), Byers (1959), Riehl (1979), and Rudloff (1981). Good coverage exists in climatic form by atlases such as McDonald (1938), Atkinson and Sadler (1970), and the U.S. Department of Defense (DoD), U.S. Navy (1955–1980). In volume 4 of this series, Conover, Lanterman, and Shaefer (1969), in Rex (1969), discuss major cloud systems. See also the cloud atlas of Bleeker (1966). This atlas describes the various cloud forms, gives definitions, and provides a picture of each type, some in color, some not. Bean and Somerville (1981) discuss some worldwide cloud cover models. All national meteorological and climatological services provide descriptive and objective material and instructions to observe, record, and report clouds. Therefore, further discussion is generally limited to a newer form of observation.

Clouds are a product of the interaction of various physical and chemical atmospheric constituents including solids. The solids act as nucleating agents for gases. The solids may be dust particles or crystals of water or other gases. In the far reaches of the atmosphere, there are clouds composed of the atmospheric constituents themselves. Even ozone seems to move as clumps or clouds. As a byproduct and an ever physically changing one, clouds, particularly those composed of water, are a prime modifier and change agent of climate. Further references in this section, unless otherwise specified, refer to water clouds.

### 9.3 Cloud Irradiances

It is difficult to change old ways of doing things. Bridges of comprehension and understanding need to be developed. New ways of remote sensing of clouds usually are of immediate benefit, yet are building the foundation of a completely new climatology. There may be no good transfer function available between the two cloud observation modes or techniques. It will take a generation or two to see full development. An initial step may be seen in the Global Atlas of Relative Cloud Cover (1967–1970) (Miller (1971)). A better title might be a Global Atlas of Cloud Irradiances. Early satellite sensors and resolution could not adequately detect the irradiances from cirrus and fairweather cumulus. Therefore, differences in cloud irradiances from one decade to another, as yet, cannot be attributed entirely to a change of climate.

The illustrations presented in the Atlas (Miller (1971)), have been placed on magnetic tape and 35-mm film and archived by the National Climatic Data Center at Asheville, NC, USA. (Individuals or organizations requesting copies of the relative cloud cover brightness charts or wanting information on the format and cost of the available data should write to Director, National Climatic Data Center, Federal Building, Asheville, NC, USA 28801. The above atlas is a joint production of the U.S. Department of Commerce and the U.S. DoD.)

The output of the National Environmental Satellite Service (NESS) satellites and the NESS electronic computer were used. A publication of the U.S. Department of Commerce keeps this type of output current with perhaps a 1-yr lag. This is in the Key to Meteorological Records Documentation entitled “Environmental Satellite Imagery.”

Several figures now follow which represent only a few types of output available. The availability of processed signals on magnetic tape permit specialized output for smaller areas but in greater detail than is seen in the following figures. Figure 9-1 shows in mean oktas, relative satellite cloud cover at 1400 local standard time (LST) for September 1967–1970. Two strips in a graytone scale cover the region from 40° S. to 40° N. Thus, a new type of climatology began to develop. This will be quite different from the usual idea of a climatology.

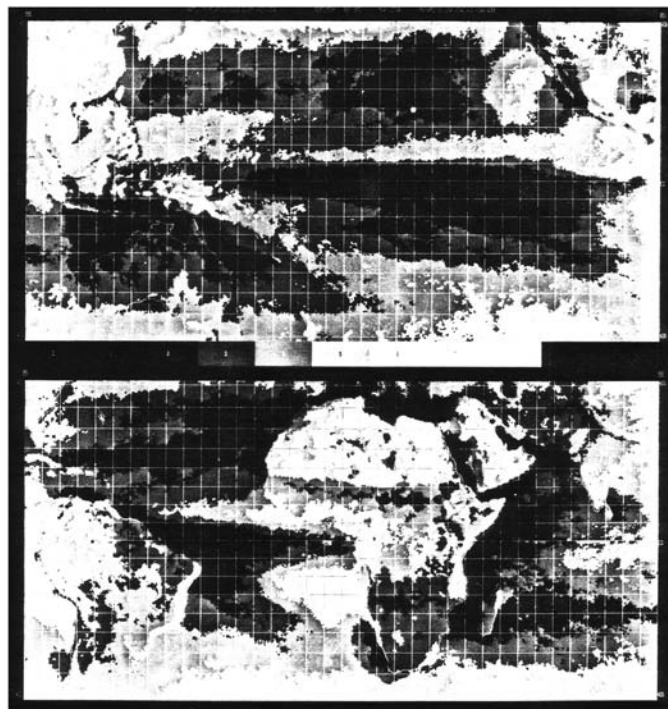


Figure 9-1. Global relative satellite cloud cover, mean oktas at 1400 LST, September 1967–1970 (Miller (1971)).

See Hadfield, Wiegman, Vieze, and Serebreny (1964) on initial studies on interpretation of satellite cloud photographs. See also Garcia (1985), an atlas of highly reflective clouds for the global tropics.

Barrett (1974) in *Climatology From Satellites* underwrites the new climatology. But as with all books, parts are out of date at the time of publication, or if not out of date, can be augmented by new data. By the time this volume is read by the interested student, two decades will have passed. Barrett (op. cit.) discusses the dynamics of the cloud-producing systems. Discussed are both the linear and nonlinear dynamics. The brief discussion in the introduction of Lorenz’s works might be reread with respect to the nonlinear features.



Figure 9-2(a) presents a polar aspect of cloud systems from the North Pole to the equator for October 18–19, 1974. Frontal characteristic and tropical vortices are clearly evident. Figure 9-2(b) depicts the polar view of cloud irradiances from the South Pole aspect to the equator for the same period. The essentially simultaneous view permits

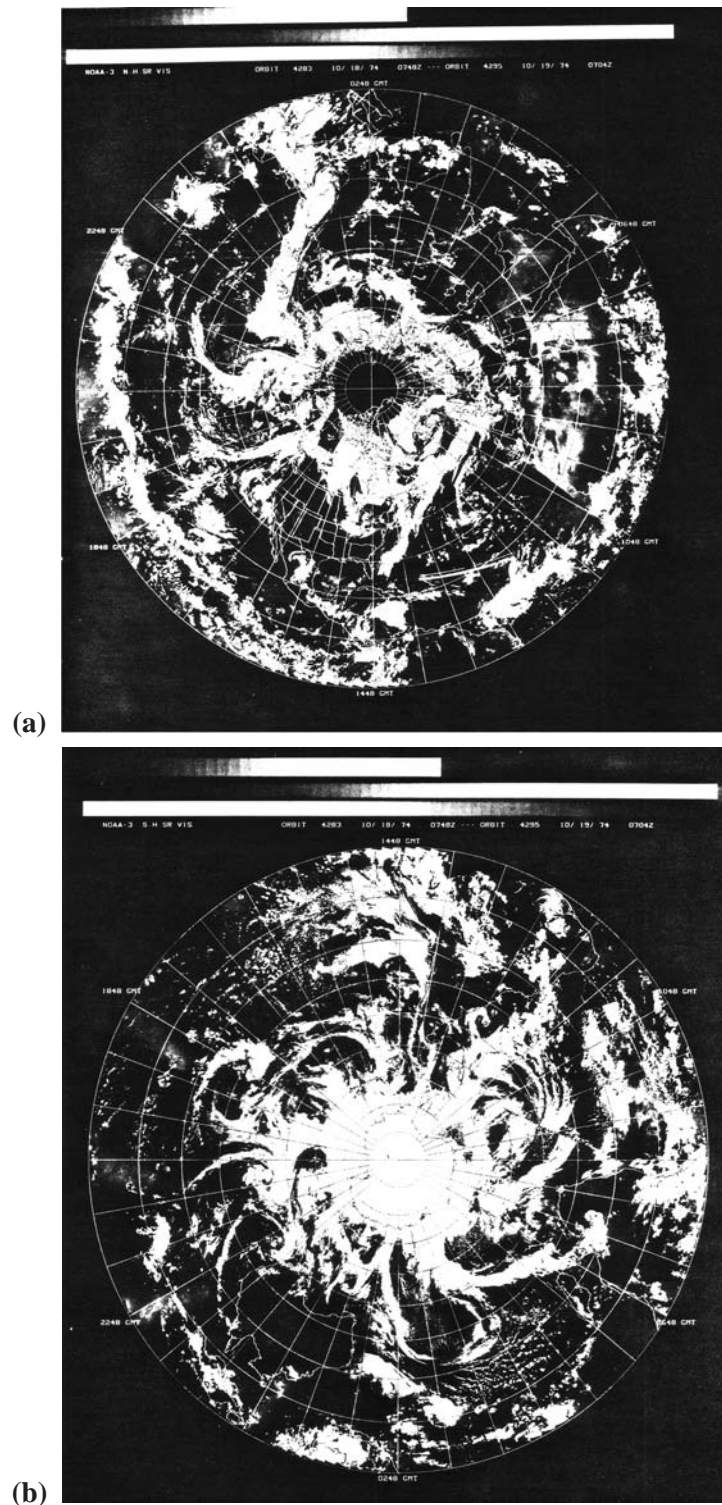


Figure 9-2. Polar aspect of cloud systems (satellite irradiance observations), October 18–19, 1974, for the (a) Northern Hemisphere and (b) Southern Hemisphere (courtesy of NOAA).

the assessment of large-scale circulation systems for the same time. These are mosaics prepared from stripviews sensed by polar orbiting satellites, which passing over the equator at local noon require 24 orbits to complete one day's soundings. Differences in time creates some discontinuities at some stripedges of the mosaic, particularly between the first and last orbit strips. The times of equatorial fly-over are shown on the circumference.

Figure 9-3 portrays full disc photos from a vantage point above the equator at 2145 on August 23, 1977. Clearly seen at the top is the vortex of the Aleutian low in the northeast Pacific. Equally evident is the south Pacific line of clouds running from west-northwest to east-southeast and the circular wave patterns originating in the anti-cyclone just west of the southern tip of South America. This seems to be a permanent feature. See McDonald (1938). The position of the clouds of the Intertropical Convergence Zone (ITCZ) is evident. Each of these are near their mean positions as shown in figure 9-1.

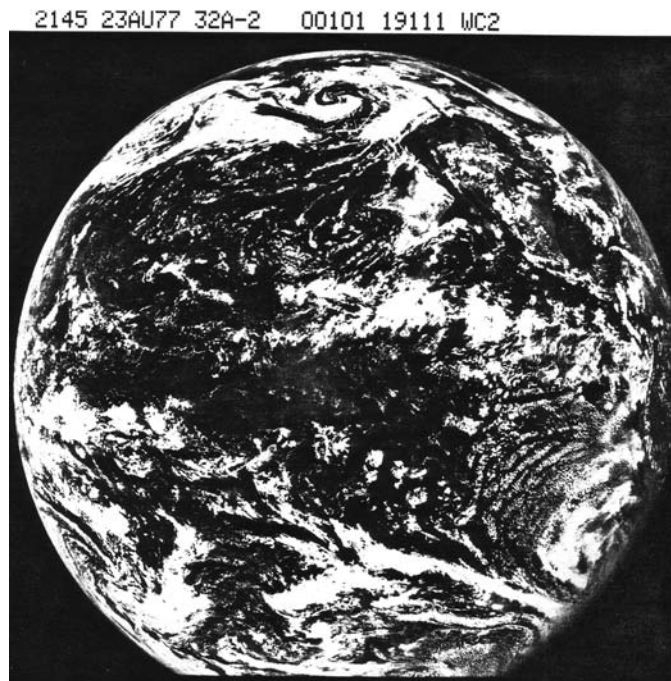


Figure 9-3. Full disc cloud photo above the equator at 2145, August 23, 1977 (courtesy of NOAA).

Figure 9-4 presents another view of the full disc type from a viewpoint over northern South America at 1700 on April 13, 1978. Within the equatorial regions there develops lines of clouds more or less parallel to the equator. Sometimes these are evident and sometimes they are not. Considerable controversy exists as to why and no name has been fully accepted as descriptive and definitive for this feature of the atmosphere. With sufficient moisture, the position of these cloudy bands of the ITCZ again is clearly seen and the position of western traveling vortices within the zone are evident. It should be remembered that, in the general average, the surface atmosphere at all points lags behind the more eastward-moving lithosphere and hydrosphere. Thus, the apparent, but for us the effective, westward motion of the vortices is caused, especially in the tropical and subtropical regions. The cloud development over the tropical areas and the Icelandic low circulation are clearly evident.

The reader's attention is drawn to another feature of the general circulation. The Icelandic low is noted in the right upper portion of figure 9-4.



Figure 9-4. Full disc cloud photo from a viewpoint over South America at 1700, April 13, 1978 (courtesy of NOAA).

On a smaller area, figure 9-5 presents a satellite picture of Anita, a fully developed hurricane in the north-west Gulf of Mexico at 1630, September 1, 1977. The eye of this hurricane (Anita) is quite evident. Figure 9-6 is a photograph of hurricane David as it begins to enter the eastern Caribbean area from the east at 1403, August 29, 1979. Later, it devastated the island of Hispaniola, especially the eastern part, the Dominican Republic. This hurricane of August and September 1977 was followed a few days later by hurricane Frederick. Figure 9-7 shows fully developed hurricane Frederick at 2018, September 12, 1979, in the northern Gulf of Mexico before it passed onto land near Mobile, Alabama.

From a climatological point of view, hurricanes are phenomena in themselves. Climatologies of hurricanes have been developed. From the global perspective, Crutcher and Quayle (1974) present the statistics of hurricanes by regions, these including the preferred tracks. William Gray has been active in the development of physical models and the forecast of hurricane development on a seasonal basis. Gray (1989) critiques the 1989 forecast. Work still needs to be done to advance Gray's important contribution. From other perspectives, extreme winds, extreme rainfalls, and dangerous storm surges are associated with hurricanes. These features are often associated with tornadoes embedded in the hurricanes.

#### 9.4 Image Enhancement

One of the capabilities of the numerical processing of the satellite signals is that signals may be categorized and produced in bands of color or grayscale. Thus, cloud structure by 10 °C increments could be distinguished. Any increment can be selected and the increments need not be the same. This technique is called image enhancement. Where previously only the continuous gray tones were available in the visual and in the infrared (IR) portions of the spectrum of irradiances, now enhancement is available. Early use of this enhancement procedure produced considerable success in correlation of certain cloud top temperatures, their development, and changes, with precipitation. However, the enhancement intervals have been changed to produce different increments and to permit assessment

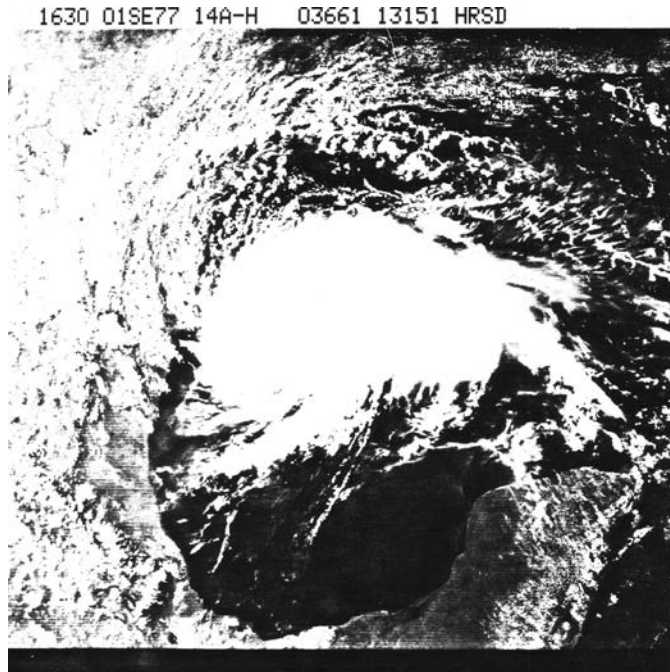


Figure 9-5. Anita, fully developed hurricane in northwestern Gulf of Mexico at 1630, September 1, 1977 (courtesy of NOAA).

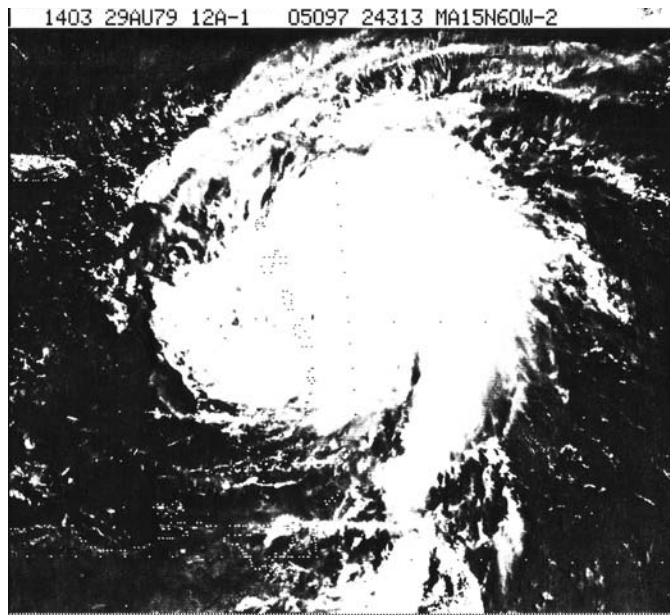


Figure 9-6. David, entering the Caribbean from the east at 1403, August 29, 1979 (courtesy NOAA).

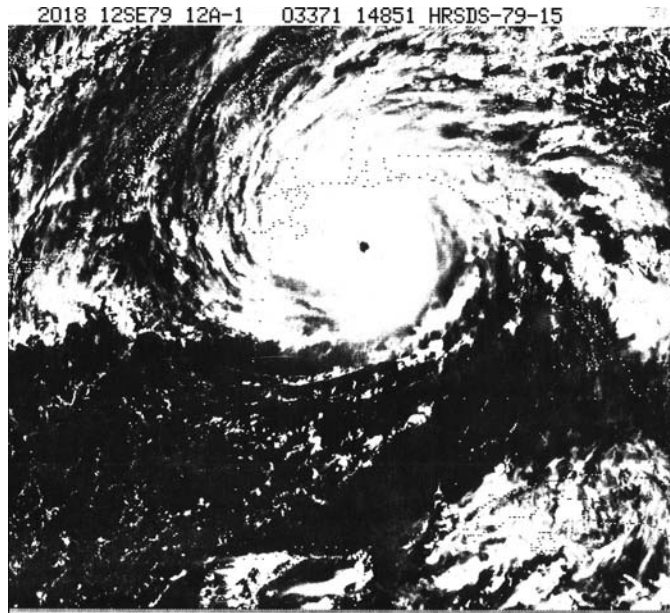
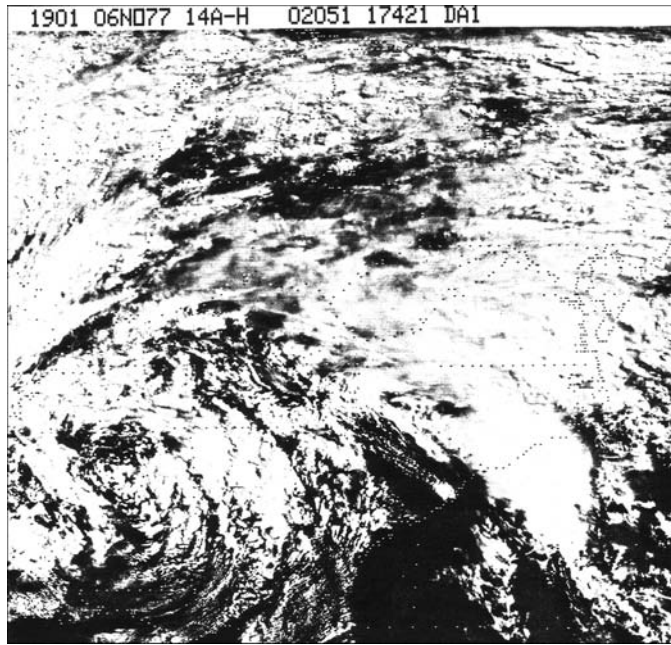


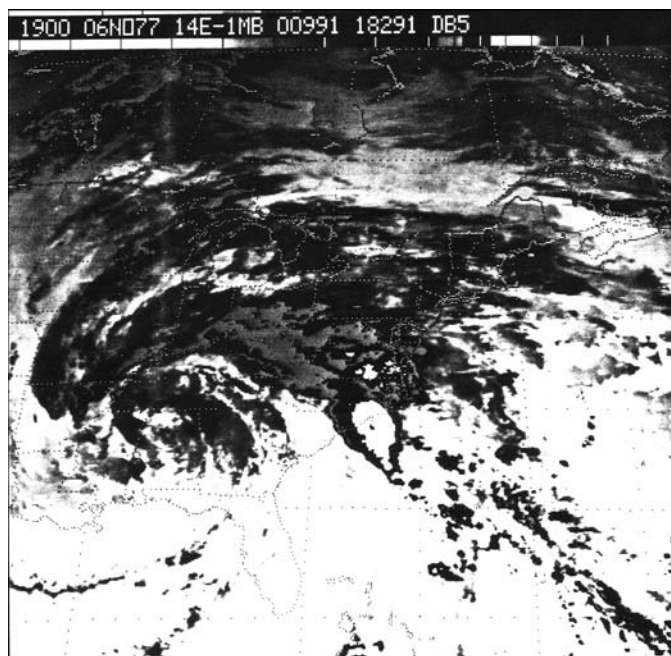
Figure 9-7. Frederick, fully developed hurricane in the eastern Gulf of Mexico at 2018, September 12, 1979 (courtesy NOAA).

of colder cloud top temperatures. Convective clouds can build to higher altitudes as the equator is approached and the temperature of these cloud tops can be colder. Examination of atlases and cross-section analysis of upper air temperatures and the position of the tropopause show the increase of the average height of the tropopause from 8 km in the polar regions to 16 km in the equatorial regions. This indicates the equatorward change potential of cloud vertical development. In general, cloud top development is impeded by the relatively warmer stratosphere, though some individual storms may be able to penetrate or rupture the tropopause boundary for a short time (Crutcher (1967a, 1969b) and Crutcher, Jenne, van Loon, and Taljaard (1971)). Thus, moisture may be injected into the stratosphere. The use of enhanced photographs for manual and visual work and the use of internal computer output for use with rainfall prediction algorithms are used by the NOAA Services (Scofield and Oliver (1977), Woodley (op. cit.), and Woodley and Sax (1976)). Figure 9-8(a)–(f) illustrates both the unenhanced and enhanced photos of a storm situation off the southeastern part of the United States November 6–7, 1977: (a) 1901 Z (unenhanced), and sequence of enhanced photos as (b) 1900 Z, (c) 0330 Z, (d) 0430 Z, (e) 0730 Z, and (f) 0830 Z. The thunderstorm cloud turrets are seen as bumps or indicated by their shadows. (Note, the scale used for the unenhanced photo is different than for the enhanced photos. The development and movement of the storm system to the northeast may be deduced from the sequential position and the changing of the enhanced temperature categories in the central cloud masses. There is dissipation in the mass near the North Carolina coast and development and then dissipation in the mass east of Florida during the afternoon and night. The techniques of reading such photographs are given by Scofield and Oliver (op. cit.). In the photographs above and following, dotted lines indicate coastal or state boundaries.

Figure 9-9 shows the cloud systems over the eastern United States at 2231, June 27, 1978. Lines of cumulus with blowing cirrus tops are clearly visible in the southwest portion of the photographs. The time 2231 Z is near sunset in this area. The eastward projected shadows of the cloud and cloud turrets are easily seen and can be used to compute the heights of the clouds and turrets. Off the southeast coast, southeast of Cape Hatteras, the strong development of cumulus towers (with their shadows) on the lower shield can be seen. But what is important in this photograph is the area of northern Ohio with its strongly developed cumulonimbus clouds and the very strongly developed cloud mass covering the major portion of the state of Pennsylvania. Again, the cumulus towers are quite evident as they push upwards through the entire cloud mass.



(a)



(b)

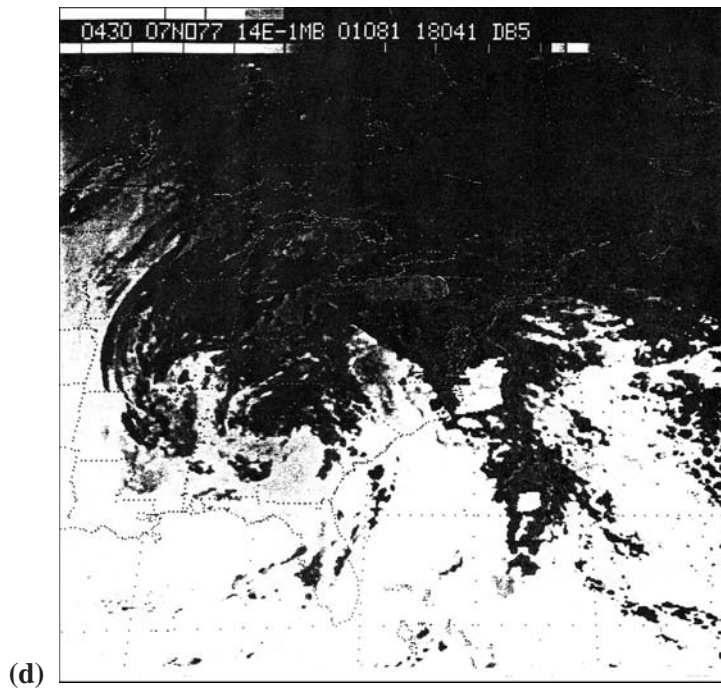
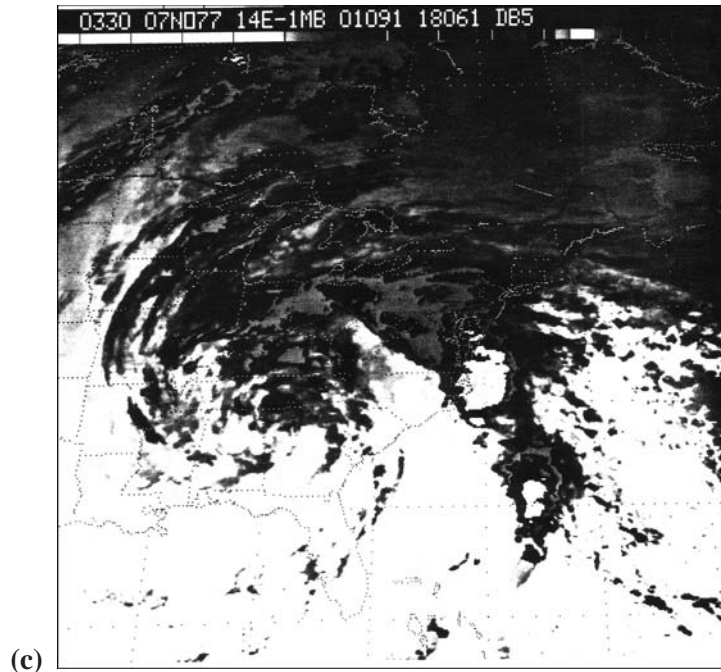


Figure 9-8. Satellite cloud observation of storm over the southeastern United States, November 6–7, 1977: (a) unenhanced photo at 1901 Z and enhanced photos at (b) 1900 Z, (c) 0330 Z, (d) 0430 Z, (e) 0730 Z, and (f) 0830 Z (courtesy of NOAA).

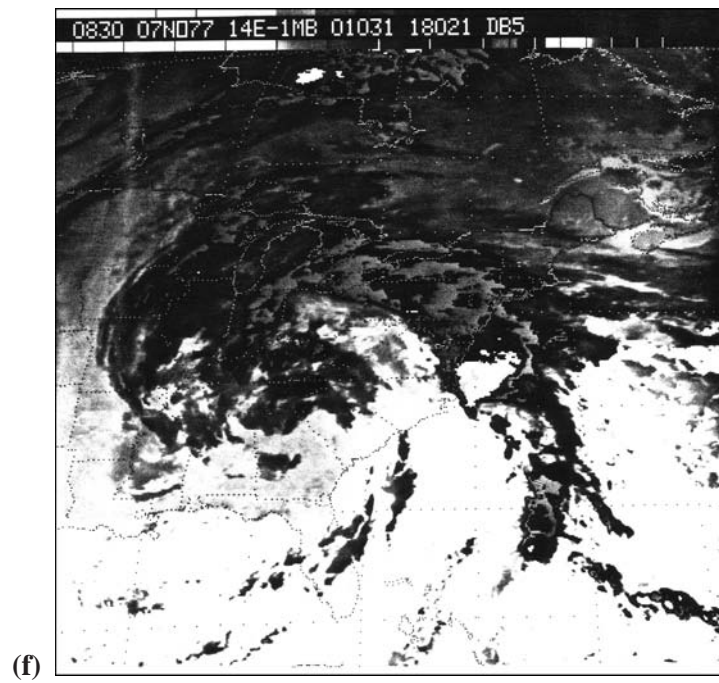
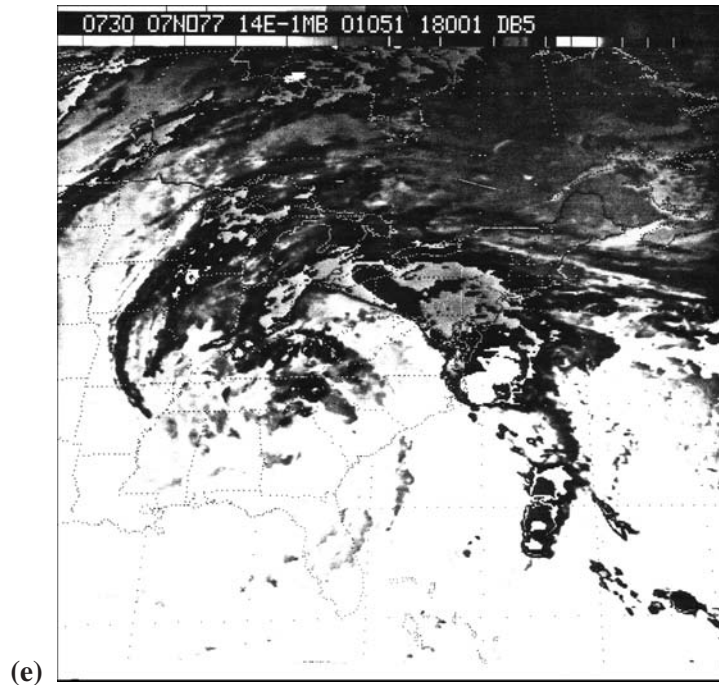


Figure 9-8. Satellite cloud observation of storm over the southeastern United States, November 6–7, 1977: (a) unenhanced photo at 1901 Z and enhanced photos at (b) 1900 Z, (c) 0330 Z, (d) 0430 Z, (e) 0730 Z, and (f) 0830 Z (courtesy of NOAA).



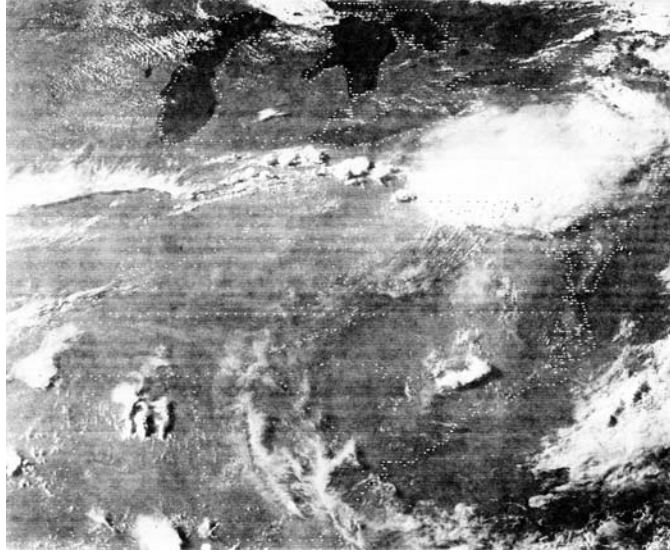


Figure 9-9. Satellite cloud photographs over the eastern United States, June 27, 1978. State borders are indicated for orientation. Note cumulonimbus clouds (courtesy of NOAA).

In the Pennsylvania, northern West Virginia, and Virginia areas in figure 9-9, the cumulonimbus clouds are located on the contiguous state borders. An examination of the records indicates streams running over the banks from the 7.5-cm rains that fell over the border areas but mainly in West Virginia.

The above situation is similar to the July 20, 1977, situation which produced devastating floods in the Johnstown, PA, area. Maddox, Chappell, and Hoxit (1979) describe the synoptic and mesoscale aspects of flash flood events.

Most National Weather Services provide cloud photographs and descriptions to enable their observers to record and code the types of clouds. Scorer (1972) provides a beautifully illustrated cloud atlas in color. Additionally, a bibliography is available in the atlas for those who have a need to or simply want to read further on this interesting and important climate element.

Hasler, Negri, and Piper (1986) and, respectively, Hasler and Morris (1986) describe (1) an interactive system to analyze and display integrated remotely sensed meteorological data sets and (2) hurricane structure and wind fields from stereoscopic and infrared satellite observations and radar data. Figure 9-10 shows two views of Hurricane Allen on August 8, 1980. The latitudinal and longitudinal grid field overlays the hurricane on September 10, 1980. The lower dark crosses indicate the shadow of the overlying grid. Figure 9-11 is a photo of Hurricane Diana on September 11, 1984. This same picture appears on the cover of the July 1985 issue of the *Bulletin of the American Meteorological Society* with the accompanying article by Hasler, Pierce, Morris, and Dodge (1985).

Figure 9-12 is an enhanced photo, similar to those described above, of Hurricane Elena on September 1, 1985, at 1300 Z, from the NOAA-8 visible and 11 micron IR images. The hurricane's position with respect to the southeastern United States is shown. Also overlying the states' outlines and the hurricane are the crosses which represent the intersection of the latitudes and longitudes. Again the underlying dark crosses are the shadows of the crosses projected onto the hurricane. The figures shown above and previously surely indicate to the reader the exciting progress made in climatology (meteorology) in the detection, observation, recording, and study of one of the more important visible features of the atmospheric distribution system for moisture. These further illustrate the computer potential to apply guides to the ordinary output.

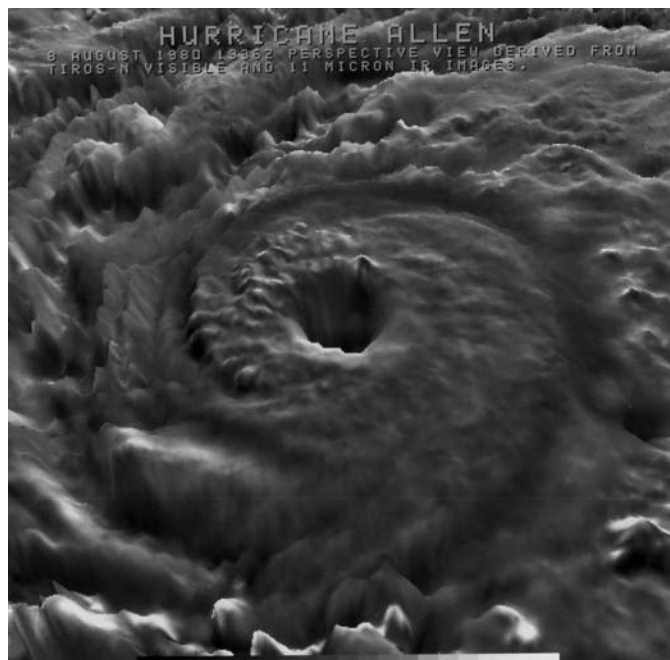


Figure 9-10. Views of Hurricane Allen, August 8, 1980, at 1336 Z. Perspective view derived from TIROS-N visible and 11 micron IR images. Latitude-longitude crosses are locators (courtesy of Hasler-Pierce, NASA Goddard Space Flight Center (GSFC)).



Figure 9-11. Hurricane Diana perspective view derived from TIROS-N visible and 11 micron IR data, September 11, 1984, at 2000 Z (with permission, American Meteorological Society (1985), courtesy of Hasler-Pierce, GSFC).

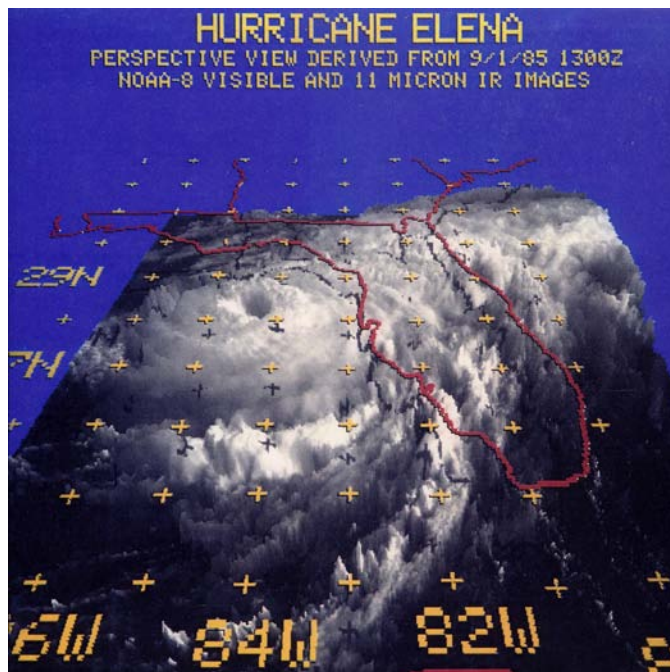


Figure 9-12. Hurricane Elena perspective view derived from September 1, 1985, at 1300, NOAA-8 visible and 11 micron IR images. Superposed crosses are latitude-longitude locations (courtesy of Hasler-Pierce, GSFC).

## 9.5 Summaries

The following are a few more reference summaries:

- (1) Mean Monthly Cloudiness in Percentage of Sky Cover based on conventional data (Landsberg (1945)).
- (2) Global Cloud Cover for Seasons based on satellite data (Clapp (1964)).
- (3) Northern Hemisphere Monthly Cloud Cover based on all available data (USAF-ETAC (1967))
- (4) Analysis of Mean Cloud Amounts for all Landmarks, Winter and Summer Seasons based on satellite data (Barnes (1967)).
- (5) Average Monthly Cloud Cover for the Global Tropics based on satellite data (Sadler (1966)).
- (6) Mean Cloudiness and Gradient-Level Wind Charts over the Tropics, Technical Report No. 215, Volumes I and II, Parts A and B by Gary D. Atkinson and James C. Sadler, Vol. I, pp. 1–22, Vol. II, Charts 1–48, published by the Air Weather Service (MAC), United States Air Force, 1970.
- (7) Comparative Climatic Data for the United States; Cloudiness, mean number of days, clear, partly cloudy, and cloudy through 1978, NOAA, Environmental Data and Information Service, National Climatic Center, Asheville, NC, pp. 47–53.

In any study, there are basic considerations. Global characteristics offer a base. Reference may be made to Haurwitz and Austin (1944), *Climates of the Earth* (after Koeppen); Trewartha (1943), *An Introduction of Weather and Climate*, and Blumenstock and Thornthwaite (1941), *Distribution of the Principal Climates of the Earth*. The above provide some fundamental background information for the serious reader. There are others, prior and post, but these are a start.

For individual stations, the following are available:

- (1) “Mean Sky Cover, Sunrise to Sunset, Monthly and Annual, for the United States,” based on conventional data (United States Weather Bureau, Office of Climatology (1961)).
- (2) The Annual and Diurnal Variations of Cloud Amounts and Cloud Types of Six Arizona Cities,” based on conventional data (Sellers (1958)).
- (3) Mean Cloud Cover Over the USSR based on conventional data (Elliott (1960)).
- (4) “Uniform Summary of Surface Weather Observations” for selected stations, National Weather Records Center.
- (5) Global Cloud Climatologies: A Historical Review by Hughes (1984) is an excellent survey. This contains useful comparative tables and charts.
- (6) London (1957) provides a widely used cloud climatology based on McDonald’s (1938) Atlas of Climatic Charts of the Oceans. Though restricted to the ocean areas, it represents a summary of all ship observational and island and coastal data from about 1850 to 1934. Under the guidance of McDonald

and Leslie Smith, first Director of the present U.S. National Climatic Data Center (NCDC) the U.S. Navy initiated in 1951 an update of all marine data summaries and charts including those involving cloud distributions. But even yet, the first is still a basic reference. The series of the U.S. Navy's Marine Climatic Atlases provide both frequency distributions and isopleth presentations. The first update series 1955 to 1965 were again updated beginning in 1970 but neither the Arctic nor the Antarctic regions are covered. The Morskoi Atlas (1952) of the USSR provides chart information similar to the McDonald atlas for those who cannot obtain a copy of the latter.

### 9.5.1 Computer Simulation

Computer simulation serves all disciplines. With respect to climatology, and specifically with respect to cloud cover, Sherr, Glaser, Barnes, and Willard (1968) provide an example of computer simulation. Based on a cloud cover frequency distribution cover, they derive 29 regions of more or less homogeneous cloud cover characteristics. For each of the regions, they provide five cloud groups, including one for clear and one for overcast, for eight times of the day and for each month of the year. Cloud types and numbers of layers are given. They provide appendices to their study which describe the punched card decks and the magnetic tapes which contain the processing and simulation algorithms as well as the cloud cover data by time periods which range from 3 hr to seasonal and annual increments. The first deck contains 29 maps, regions, and boundaries. The second deck contains the 12 mo of cloud statistics for each of the 29 regions.

An experienced observer knows how difficult it is to observe, assess, and record the observations of seas, wave heights, and frequencies from an unstable platform such as a ship or a boat. The experienced observer also knows some of the difficulties involved in the observing and reporting of cloud cover. The ground-based observer has a limited field of view of the Earth's surface with a radius ranging from about 10 km to a maximum of 50 km, depending on ambient visibility, height above the ground, and obstructions to vision.

Fair weather cumulus with flat bases and vertical sides progressively tend to obscure the observer's line of vision with distance from the observation point. The clouds which tend to have a fixed base above the terrain, due to the Earth's curvature, appear to coalesce into a solid wall of cloud. The observer tends to overestimate the amount of cloud cover of these and other clouds, particularly those with vertical development. Appleman (1962), Lund et al. (1960, 1965, and 1980), McCabe (1965), and Watson (1965) are some of those who have studied and reported on the degree of overestimation. Though the experienced observer knows of these problems and may attempt to lower the expected overestimate, the reported coverage generally still remains too high.

On the other hand, the viewing of cloud cover from an Earth-oriented satellite sensing system or from aircraft platforms also has its own difficulties. Early satellite sensors were deficient in their capability to detect fair weather cumulus as well as high, thin cirrus. Though some of the problems have been partially resolved, the extent of cloud cover is underestimated. The comparison of ground- and space-based observations tend to provide frequency distributions which are dissimilar, so much so that most statistical tests reject or will reject the null hypothesis that they come from the same distribution, even when it is known that they are for the same time and point. From an engineering point of view, in the practical every day application of data as observed and recorded, adjustments are always made. These adjustments are consciously or unconsciously made. Regression techniques may in a sense automatically affect these adjustments. On the other hand, the adjustments may be arbitrarily made by the engineer or user where experience and application provide a base for an intuitive adjustment. An inherent difference in the viewing systems is the fact that parallax effect is affected by viewpoints 180 degrees different; i.e., the sensing cone at the ground-based point opens upward while it opens downward from a space-based point. In the case of astronauts, the visual cone to a surface target changes rapidly from the time the ground-based point is seen and the vehicle passes overhead and beyond. The same may be true for the automatic sensing units which utilize scanning techniques. The result is a time-compressed version of the changing impressions. It will be interesting to see the

results of comparison from reports made by ground- and space-based observers for the same time and point but such observations are yet to be obtained in any quantity. Sherr et al. (1968) discuss these difficulties in more detail.

There are also difficulties encountered in assessment of cloud coverage from both visual and infrared photographs and in attempts to use radar or radiometer data which might be obtained from aircraft. For the moment, the actual cloud cover over a ground-based point presumably is somewhere between the respective overestimates and underestimates of ground-based observers and space-based sensing systems. Sherr et al. (1968) do provide one set of data where ground-based estimates exceed space-based sensing (at Kyushu, Japan). Until more research is done, reasons for this should not be given, except in a speculative sense. That is not done here.

Hahn, Warren, London, et al. (1982) present information on cloud types observed simultaneously over (a) the ocean and (b) the land. Whether comparable studies can be made for other periods is unknown as the cloud observing procedures change. Assumptions must be made in view of the present observing procedures for reporting cloud layers. Such research is not easy!

### 9.5.2 Distributions and Models

Cloud frequency distributions assume several forms. In a converse sense, it may be said that there are several statistical distributions that adequately describe cloud frequency distributions. One of these is the Beta distribution—a general distribution of which there are several subfamilies. Pearson (1898, 1934) describes this distribution and Brooks and Carruthers (1953) describe some empirical distributions as well as some applications. Falls (1973) and Essenwanger (1976) also apply the Beta distribution to cloud amount distributions.

Sherr et al. (op. cit.) provide many examples of the cloud distributions for various climatic regions. They point out the following conditions which are, in a sense, bounding conditions: (1) Over a point, there is only the dichotomous situation of cloud or no-cloud; i.e., overcast or clear, and (2) over larger areas, there is departure from this dichotomy. There seems to be an average 40 percent cover over the entire Earth. This appears to be relatively constant over the time for which there exists an adequate number of recorded observations. Speculatively, slight variations from this 40 percent may be a time of wetness or dryness over the entire Earth.

As areas increase in size from a point, the distributions pass from a two-spike distribution at clear and overcast shading through “J,” reverse “J,” and U-shaped to more normal-shaped distributions; i.e., bell-shaped at rates which depend upon the prevalence of large-scale cloud systems and longer time periods. In the temperate zones in which large cloud systems are the rule, U- or J-shaped distributions are found at the 50-km-scale size of the ground observers view. Though previously it was stated that over a point, cloudiness could be either overcast or nonexistent, there is small chance that a clear sky will exist as a distribution over time for an area of 600-km radius. Thus, it is seen that cloud distributions, among other things, are a function of the area under consideration whether the observations are ground based or space based.

Figure 9-13 (fig. 5-1 from Sherr et al. (1968)) illustrates cloud cover distributions for six stations which appear to show the same general characteristics. Clearly, the summer characteristics follow no nice, easily described model though the early morning distributions form the well recognized U-distributions, while the late afternoon distribution shows a partial modification from the U- to the J-distribution. The regional characteristics are represented by Belleville, IL; Minot, ND; J.F. Kennedy Airport, NY; Bangor, MA; Brandon, England; and Furth, Germany.

J-shaped distributions are exemplified by data from Adak, Alaska; Stanley, Falkland Island; Campbell Island, New Zealand; and Laurie Island, South Orkney Islands. Figure 9-14 (fig. 5-3 from Sherr et al. (1968)) shows the early morning and noon observations for summer and winter for the above locations. The J-shape is only

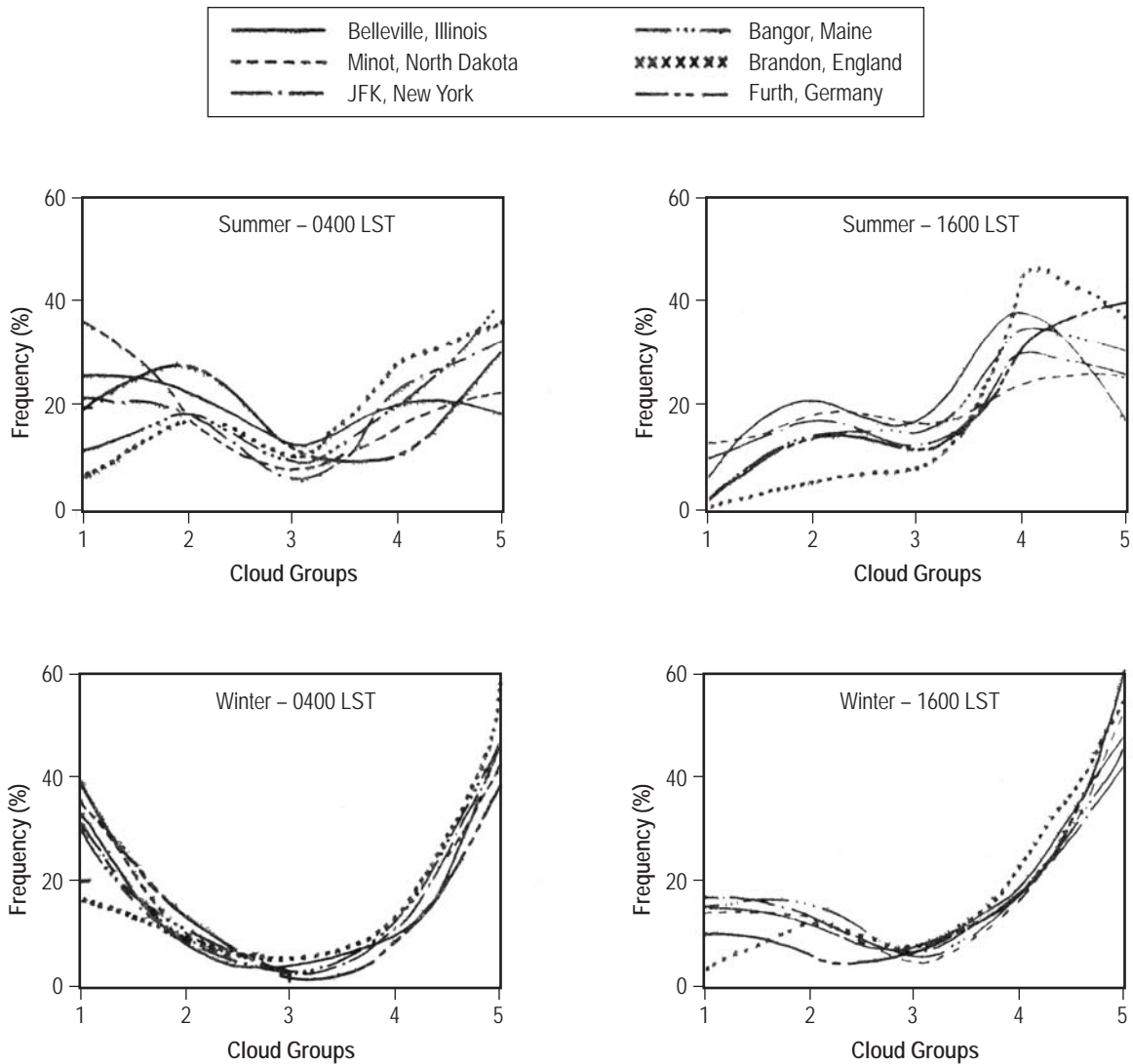


Figure 9-13. Cloud cover distribution curves for six stations—region 11—representing selected regional homogeneous characteristics (courtesy of Sherr et al. (1968)).

one part of the U-shape where clear skies are clearly eliminated. These are essentially maritime stations located in cold Arctic and Antarctic boundary regions.

Reverse J-shaped distributions show the other side of the U-distribution for desert or arid regions as represented by Dhahran, Saudi Arabia; Yuma, AZ; and Alice Springs, Australia. Figure 9-15 (fig. 5-2 from Sherr et al. (1968)) shows the early morning and late afternoon, summer and winter distribution for the above three locations.

Sherr et al. (1968) provide cloud comparison distributions for the above three groups from satellite observations. From the distributions of actual cloudiness, data reduced to digital form, conditional and unconditional, distributions may be developed. In addition, relationships, both on a time and area (space) basis, have been developed and are presented. Studies of the above type are forward steps in attempts to determine and to understand cloud distributions. From this understanding will flow information that will enable us to better guide our destinies.

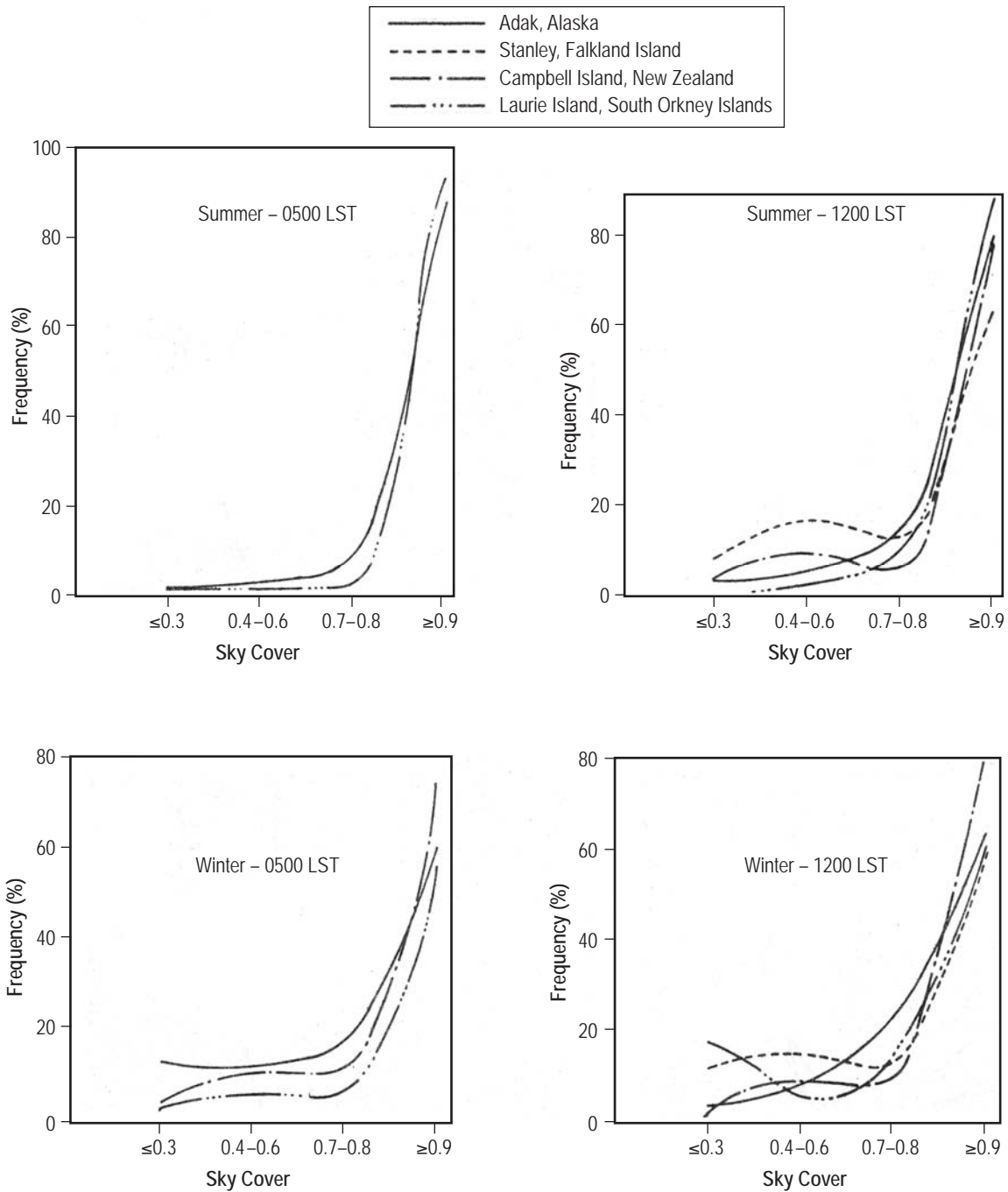


Figure 9-14. Cloud cover distribution curves for four stations—regions 14 and 23—representing J-shaped distributions (courtesy of Sherr et al. (1968)).

There is still another aspect to this situation, which has been briefly mentioned previously. Attempts have been made and will continue to be made to interpret satellite cloud observations in terms of land-based observations. This is an attempt to keep one's footing on known knowledge territory and to tentatively explore other information sources. This is the bridging procedure. One possible outcome of the use of new techniques is an entirely new observational atmospheric structural entity. For example, Winston, Gruber, Gray, et al. (1979), the U.S. Department of Commerce (1979) have published in two volumes the Earth-Atmosphere Radiation Budget Analyses derived from NOAA



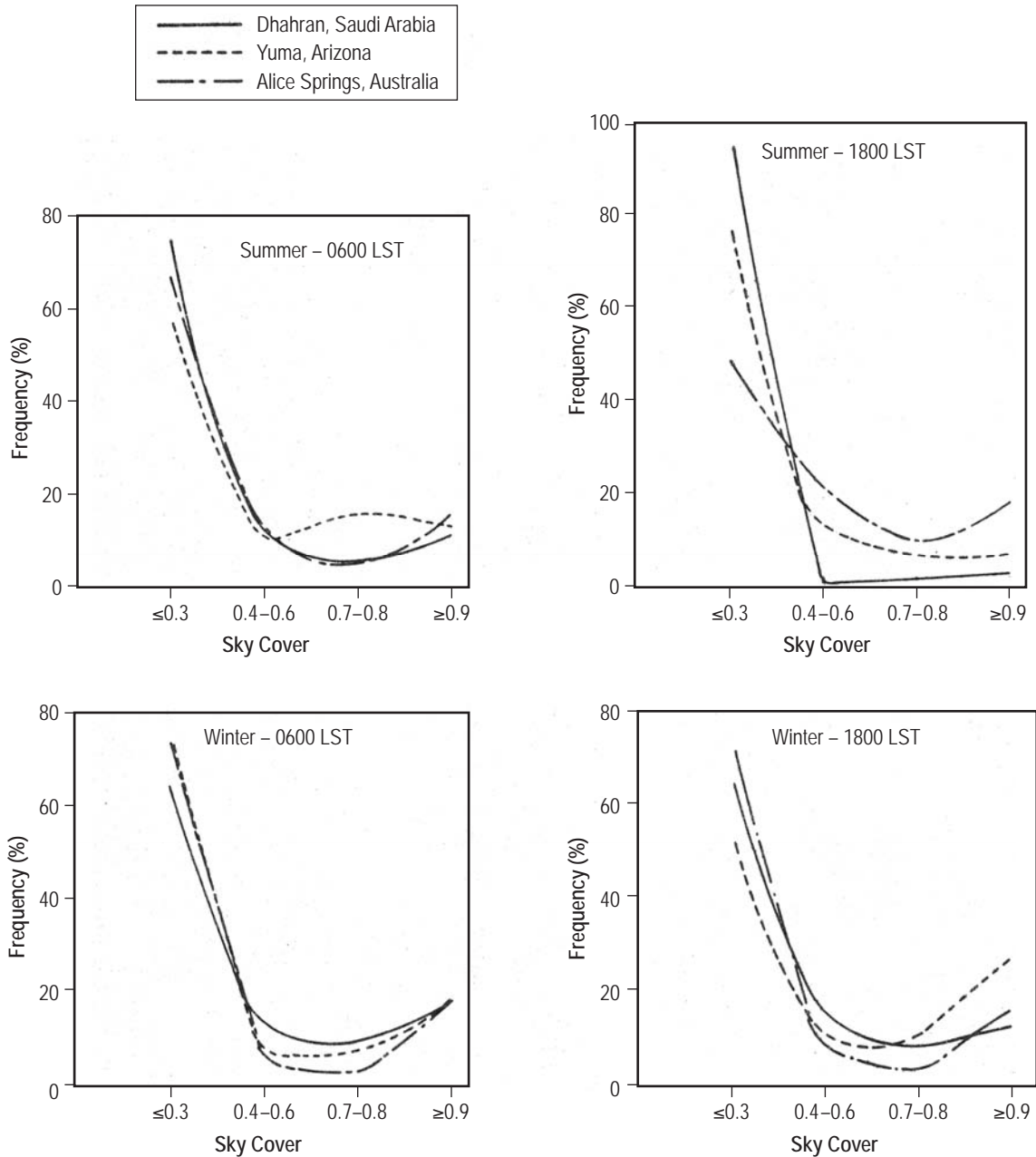


Figure 9-15. Cloud cover distribution curves for three stations—region 1—representing reverse J-shaped distributions (courtesy of Sherr et al. (1968)).

satellite data, June 1974 to February 1978. They present monthly seasonal and annual averages. The quantities displayed are albedo, absorbed solar radiation, outgoing longwave radiation, and net radiation. These two volumes form essentially a new type of atlas which will contribute much to our understanding of the Earth's climate. These will be followed in time with similar information over longer periods of time. Presumably, these will also include some measures of variability when the period of record becomes long enough to provide some precision in the estimates of the statistical parameters.

Following the work of Sherr et al. (1968), the treatment of cloudiness has been increased and the models have been increased in numbers to accommodate four-dimensional models of pressure, temperature, water vapor, and density. In addition, wind information has been added. Reference may be made to Barnes and Chang (1968), Brown (1970), Greaves, Spiegler, and Willard (1971), Spiegler and Greaves (1971), Fowler et al. (1974), Chang and Willard (1972), Spiegler and Fowler (1972), and Fowler, Lisa, and Tung (1975). Thus, in essence, there are seven variates with estimates of their means and variances. These are three models: (1) For clouds, (2) for pressures, temperatures, water vapor, and density, and (3) zonal ( $u$ ) and meridional ( $v$ ) components. In general, there are 3,490 grid points from the surface to 26 km in 2-km intervals with additional wind information at intermediate 1-km intervals. In addition, from the Greenwich meridian westward through 160° E. longitude, information is available from 26 to 52 km at 2-km intervals. These three models are associated with sets of computer programs to simulate meteorological conditions in time and space; i.e., for any point above the Earth's surface to 52-km altitude, with the exception noted above, for any time of the year with expected time changes in the variates.

As examples, figure 9-16(a) and (b) (figs. 3-9a and 3-10a of Fowler et al. (1975)) show Northern Hemisphere stratospheric temperature profiles against height at a station 20° N.–70° W. for January and July, respectively, from 26 to 52 km. Figure 9-17(a) and (b) show similar formation at a mid-latitude station, 40° N.–75° W. Figures 9-18(a) and (b) and 9-19(a) and (b) (figs. 3-11b, 3-11a, 3-12a, and 3-12b of Fowler et al. (1975)) show stratospheric west-east, zonal ( $u$ ) component profiles with one standard deviation band for the same Northern Hemisphere southern and mid-latitude locations. There is a dominance of stratospheric easterly winds (from the east) at two locations. Only in January at mid-latitude stations are the winds generally from the west  $\approx 90$  percent of the time. Only above 40 km are the stratospheric meridional winds predominantly from the south. Below 40 km to 24 km the mean meridional wind is near zero with standard deviation averaging  $\approx 5 \text{ m s}^{-1}$ . Figure 9-20 illustrates this last case.

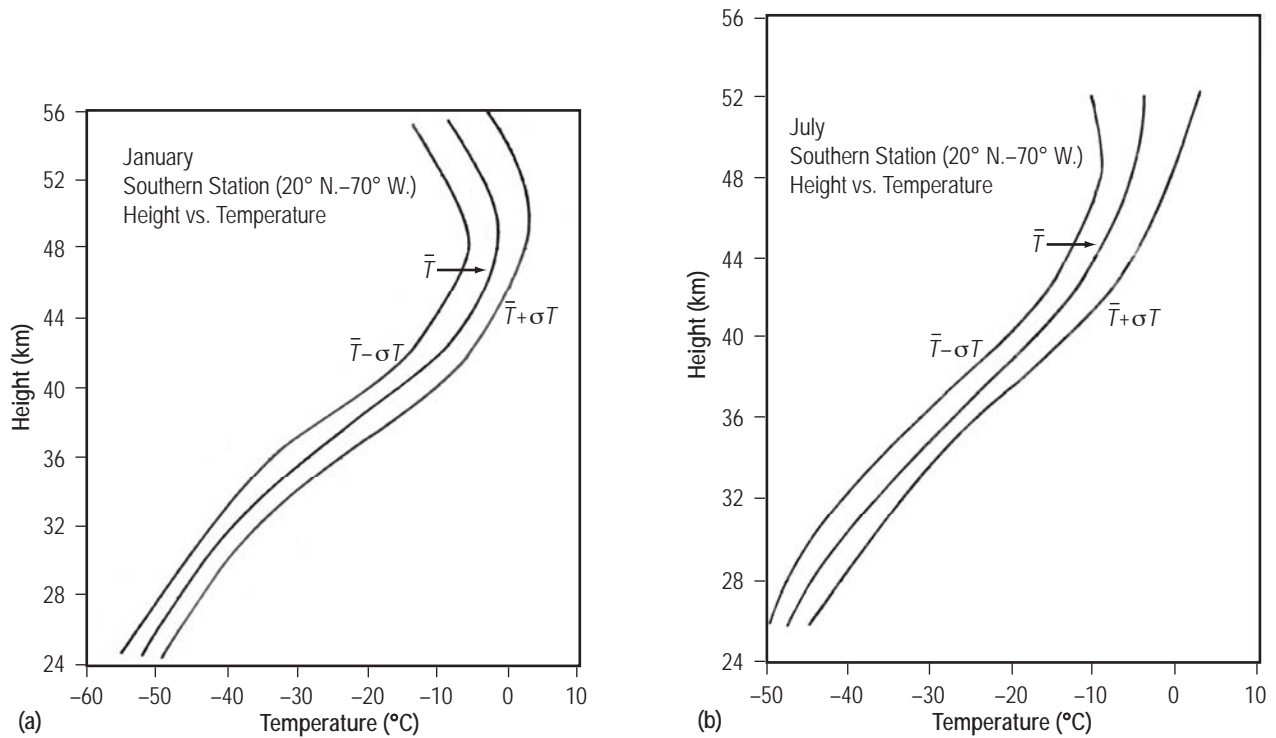


Figure 9-16. Southern station stratospheric temperature profiles, 24–56 km for (a) January and (b) July (after Fowler et al. (1975)).

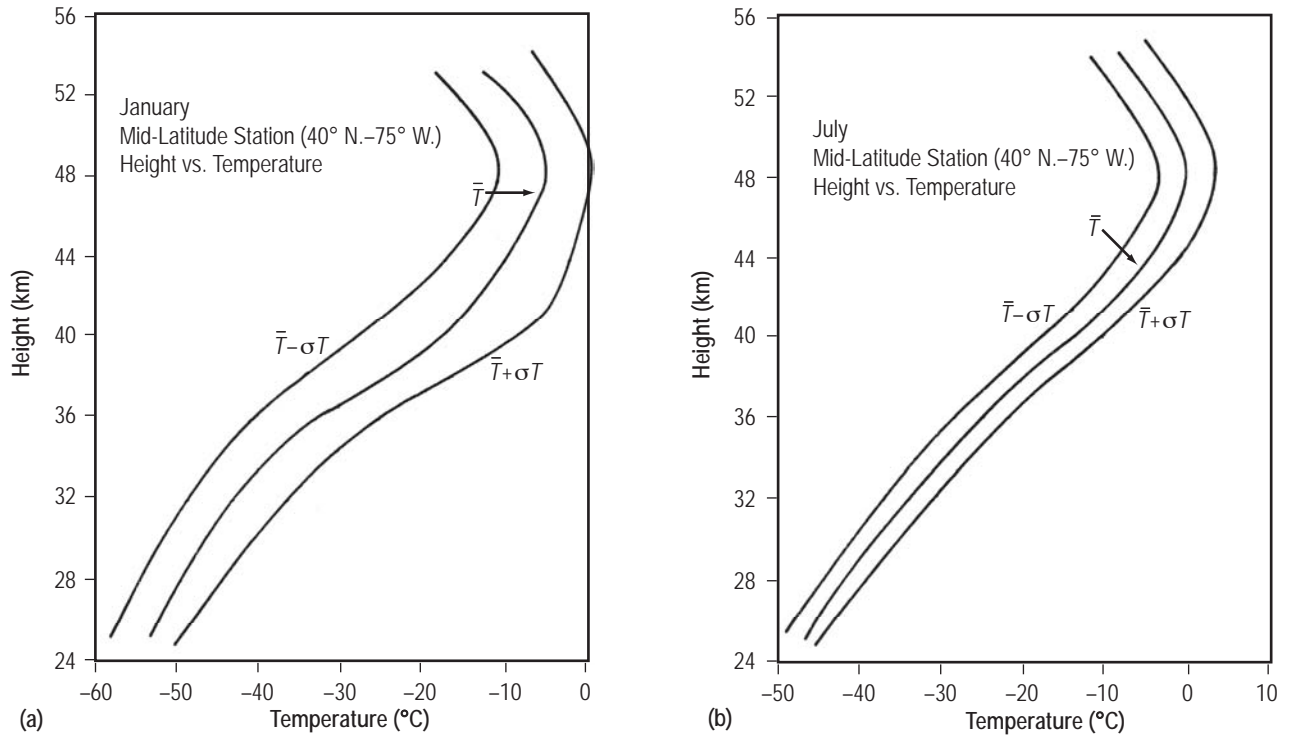


Figure 9-17. Mid-latitude station stratospheric temperature profiles, 24–56 km, for (a) January and (b) July (after Fowler et al. (1975)).

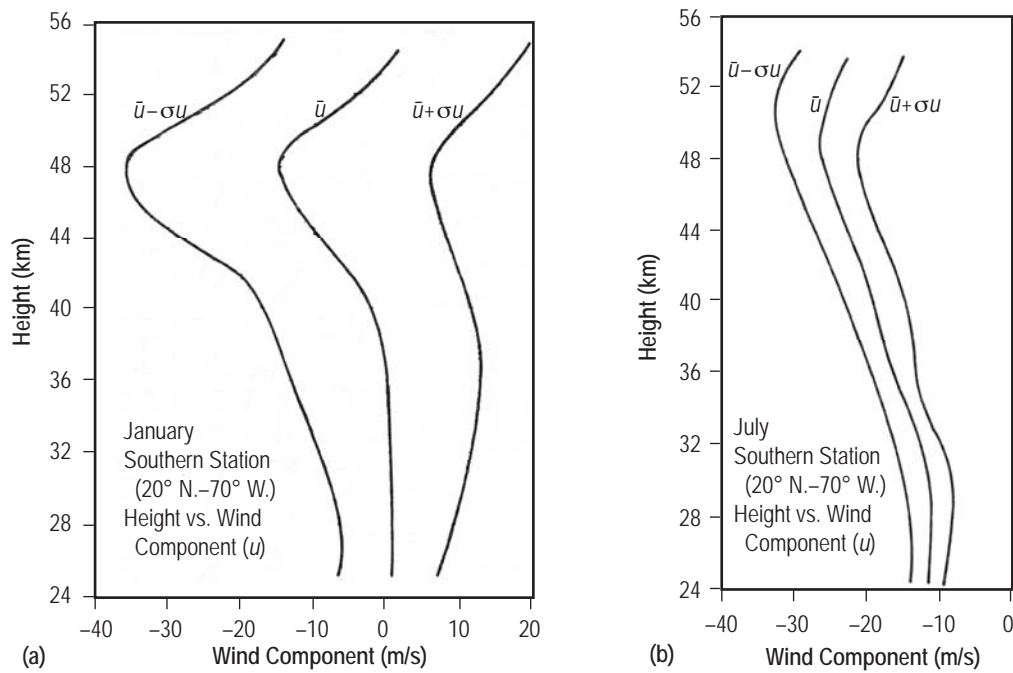


Figure 9-18. Southern station stratospheric zonal winds profiles, 24–56 km, for (a) January and (b) July (after Fowler et al. (1975)).

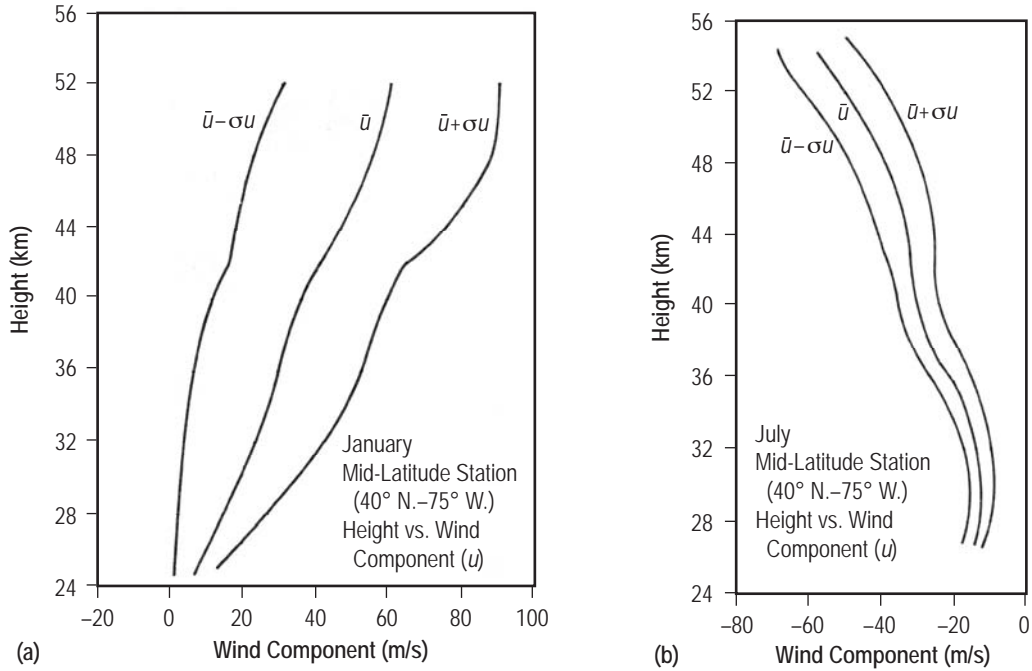


Figure 9-19. Mid-latitude station stratospheric zonal winds profiles, 24–56 km, for (a) January and (b) July (after Fowler et al. (1975)).

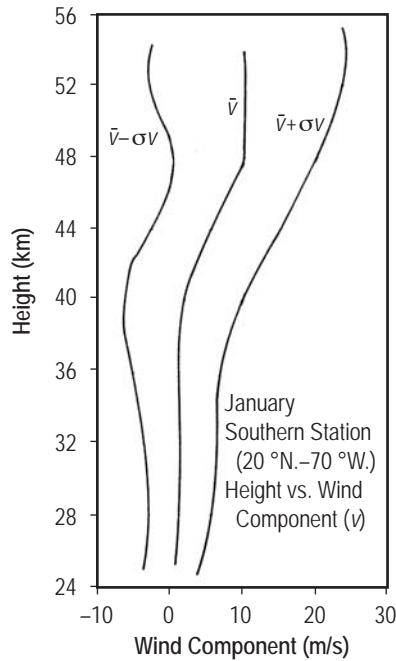


Figure 9-20. January southern station meridional wind stratospheric profiles, 24–56 km (after Fowler et al. (1975)).

The work by Fowler et al. (1975) covers three broad areas designed to improve the existing models:

- (1) The relationship between satellite and surface observed cloud cover using LANDSAT 1 photographs which included cloud shadow effects.
- (2) The extension of the four-dimensional model from an altitude of 25 to 52 km. Point means and variances at 2-km intervals for the elements of pressure, temperature, density, and the  $u$  and  $v$  components of the wind are provided.
- (3) In addition to the original four-dimensional model, the mean and variances of the  $u$  and  $v$  components are added at 1-km intervals from the surface to 25 km.

Their conclusions are as follows: LANDSAT observed cloud cover and observations made from the ground agree well for the one-half degree field of view in the central 60 percent of the distribution. Below 20 percent and above 80 percent cloud coverage, the LANDSAT, respectively, overestimates and underestimates.

In general, cloud shadows add  $\approx 5$  percent to the total coverage estimated from LANDSAT photographs. Below elevation angles of  $30^\circ$  and for cloud coverage between 20 and 50 percent, more than 5 percent is contributed by cloud shadow:

- (1) In the stratosphere, over the limited region from Greenwich Meridian west to  $160^\circ$  E. and from the equator to the North Pole,  $5^\circ \times 5^\circ$  gridpoint values are available as a first cut at a representation of means and variances of pressure, density, temperature, and winds, between 26- and 52-km altitude.
- (2) In the four-dimensional global model of means and variances of pressure, temperature, and density and wind components at 2-km intervals to 52 km, the means and variances at intermediate 1-km intervals have been merged in the layer from the surface to 26 km.

As usual in any research to attain a goal, it is realized along the way that the goal will be reached in its entirety or that only certain phases will be reached. In addition, ideas for improvement of the models are made and entirely new concepts are suggested for consideration. The above developmental work is no different. Here are some of the suggestions made by Fowler et al. (1975) to increase the viability, credibility, and utility of the present NASA configurations of the cloud and the four-dimensional models:

- (1) Continue the comparison of photographs of LANDSAT 1 and LANDSAT 2 to derive better quantitative relationships between Sun angles, cloud cover, cloud height, and cloud shadows, particularly for elevation angles  $< 30^\circ$ .
- (2) Obtain and analyze additional level data of the stratosphere to derive more detailed information on the height dependence of stratospheric profiles.
- (3) Derive grid values of means at variances of pressure, temperatures, density, and winds for the eastern half of the Northern Hemisphere, the Tropical equatorial regions, and the Southern Hemisphere.
- (4) Modify the four-dimensional simulation programs as necessary to curve fit the newly derived parameters at all levels and to provide interpolation to any latitude, longitude, height, and for any season or other selected period of time.

It is realized that the discussion of the four-dimensional model may seem out of place in this section. It is discussed because its development so closely parallels in line the cloud model development and the information is closely related insofar as time periods are concerned. Perhaps later research will tend to consider the interlevel, intralevel, and the interelement relationships. Some of the relationships are available in very limited form. Fowler et al. (1975) further indicate that though they suggest additional data and replacement of certain approximations with measured values, there is little question as to the reliability of the present mode.



## 10. DROUGHT AND EVAPORATION

### 10.1 Drought

Drought exists as an integral part of climate. There is no clearcut demarcation among drought and other features in the day-to-day continuum of weather. In the continuum, the summation of the variable situations, the anomalies, the result is a balance or an imbalance. The imbalance may favor the abundance of moisture or the deficit of moisture. The balance is the portion to which all things adjust to and develop within. The imbalances create stresses against which the ordinary cannot quickly respond.

The geographic configuration of the lands and oceans, the atmospheric circulation patterns and their attendant evaporation, and condensation patterns set the stage.

Arid regions develop. Rain forests develop. Life, existence, agriculture, forestry, and many other features develop within the framework of a "status quo." Vegetation and life are of distinct form and content from the arid regions to other status quo regions.

The anomalies of the weather have been with the Earth in all its existence. The characteristics of the weather have certainly changed, and with these, the patterns and anomalies of climate have emerged. Abundances of precipitation have varied along with the deficits. If it does not rain, drought develops.

Droughts, the deficits, probably never can be defined explicitly. Their effects are quite variable. For example, one cereal grain needs a timing and amount of moisture different from that required by another grain. Before recorded history, forms of drought existed, and certainly in the recorded stories, droughts have been a feature to note. The definition is difficult to formulate. One does try. One tries to develop a guide to defend against the stresses of the anomalies of too much and too little salient features of the hydrologic cycle.

Changnon (1987) describes a running course in the hydrologic cycle from precipitation through runoff; soil moisture, including infiltration; stream flow; and ground water. Evaporation and discharge to the sea must enter this picture also.

The events cited in the above paragraph proceed in the order indicated. In such, a lag is developed in some ways similar to the lag of subsoil temperatures.

McNab, Karl, and Lins (1988) provide an interesting summary-type paper, "The role of climate in the generation of drought." Here is a statement of their summary.

"Precipitation anomalies are a naturally recurring feature of the global climate. These anomalies act on the various components of the hydrologic cycle to produce drought. Climatologies of precipitation, temperature, and moisture provide an indication of the frequency and intensity of precipitation, the correlation of temperature and precipitation, and the atmospheric drying that occur during droughts."

"Climatologies of atmospheric circulation patterns illustrate that drought is associated with persistent or persistently recurring circulations that produce little or no rain; drought does not occur as a result of discernably unique daily circulation patterns. Monthly average circulation patterns indicate the importance of subsidence, dry air advection, and the absence of destabilizing temperature gradients during drought periods. These factors, however,

only provide descriptions of the atmosphere during periods of drought. They do not answer the underlying question: Why do these drought related circulations arise and why do they persist for months and sometimes years?"

"The search for causes of atmospheric drought signals goes far beyond the immediate area affected by drought, because of the global (or at least hemispheric) nature of circulations that produce sustained periods of below normal precipitation. Many current investigations are focused on atmospheric boundary conditions such as SST and soil moisture. Nonlinear processes within the climate system as well as external solar-lunar variations are being investigated as basic causes of drought."

Certainly, the sources of all precipitation, the evaporative processes on land and the oceans themselves, are the prime source. As an aside, evaporative processes on land, particularly during the passage of small storm systems, produce recurrent precipitation. To this extent there will be an overestimate of precipitation available as runoff and infiltration to ground water and as potential return to the sea.

The entire picture of the precipitation/nonprecipitation situation is basically dependent upon the evaporative processes, initially those of the oceans. Radiation, temperature, and winds are effective agents. Thus, marine data and information are quite helpful.

McDonald (1938) provides an excellent base for marine climatology. Jacobs (1942, 1951) was, it is believed, the first attempt to estimate the evaporative processes associated with the oceans on a global scale. Air-sea temperatures are useful in this. The U.S. Navy Marine Climatic Atlas series of the 1950s, the revisions in the 1960s, and the updating in the 1970s continuing McDonald's (1938) publication do provide some data that can be used in the assessment of the evaporative quantities. Of course, the estimation of an item from the means of the individual elements of a process is not necessarily the same as the mean of the process itself. It is sometimes the only measure of the element possible or available. The inclusion of air-sea water temperature differences, the winds, temperatures, and pressures are included as elements of the U.S. Navy Marine Climatic Atlases. Derived elements, such as evaporative processes, were not within the purview of the program.

Drought areas in the sense of precipitation dearth exists over oceans as well as the continents and polar regions. Deficit areas in minerals and food production chains in the seas may be as extensive as those of moisture in the atmosphere. These are allied quite closely with the dynamics in both the hydrosphere and the atmosphere.

Gibbs (1987), for Australia, as large in land area as the United States, describes a drought watch system and includes a drought review of Australia. Rosenberg (1978) edits an AAAS symposium series 15 on North American droughts. The WMO (1986) provides a report on drought and countries affected by drought during 1974–1985. Among many situations, the droughts on the Sahel have received much attention; see Nicholson (1985) on African rainfall applications. See also Todorov (1986) and Quinlan (1986). Even recent articles portray the quandary of researchers in definitions and identification of events. See Druyan (1989) and Agnew (1989), respectively, on Sub-Saharan Drought and Sahel drought: meteorological or agricultural. Namias (1972) and Cayan (1986a) add to the extensive literature, including their own, in their papers on large-scale and long-term fluctuations of atmospheric and oceanic variables. Even the name of the Nobel Symposium 20 where Namias (1972) delivered his paper is indicative of the ever-changing aspects of the Earth. The title was "The Changing Chemistry of the Oceans." Cayan's (1986b) presentation does not indicate a warming of the regions during the period from about 1950 to 1980. This is in contrast to literature statements which appear from time to time.

Cayan (1986b) shows the area average sea surface temperatures (SST) ( $^{\circ}\text{C}$ ) from about 1950 to 1980, a period of about 30 years (fig. 10-1), (a) the North Pacific and (b) North Atlantic. Cayan applies a 12-mo running mean filter to smooth the high-frequency variability. The area extends from  $20^{\circ}$  N. to  $60^{\circ}$  N. latitude. Figure 10-2 (from Cayan and Namias, personal communication) provides a second presentation 1947 through 1990.



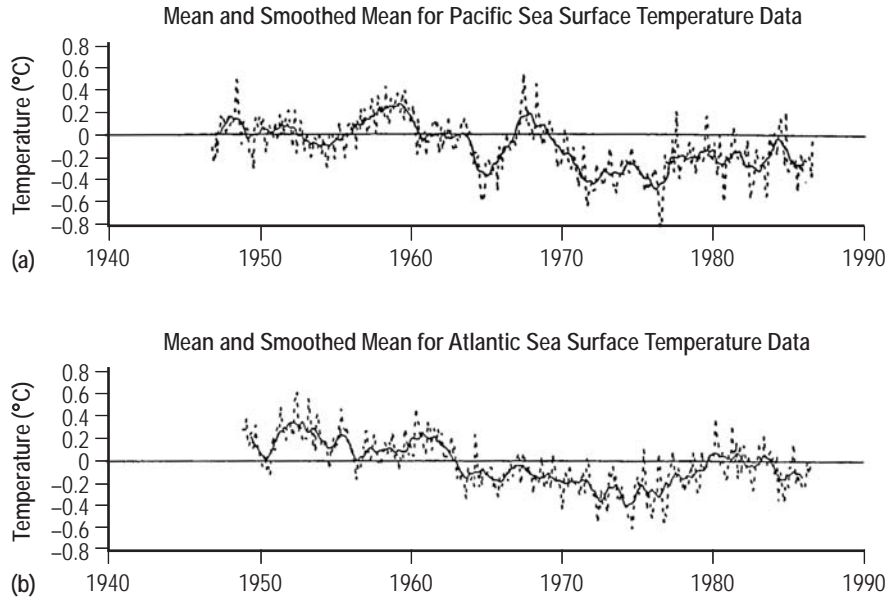


Figure 10-1. Mean and smoothed mean sea surface average temperatures for (a) the North Pacific and (b) the North Atlantic for 20° N. to 60° N., 1950–1980 (after Cayan (1986b)).

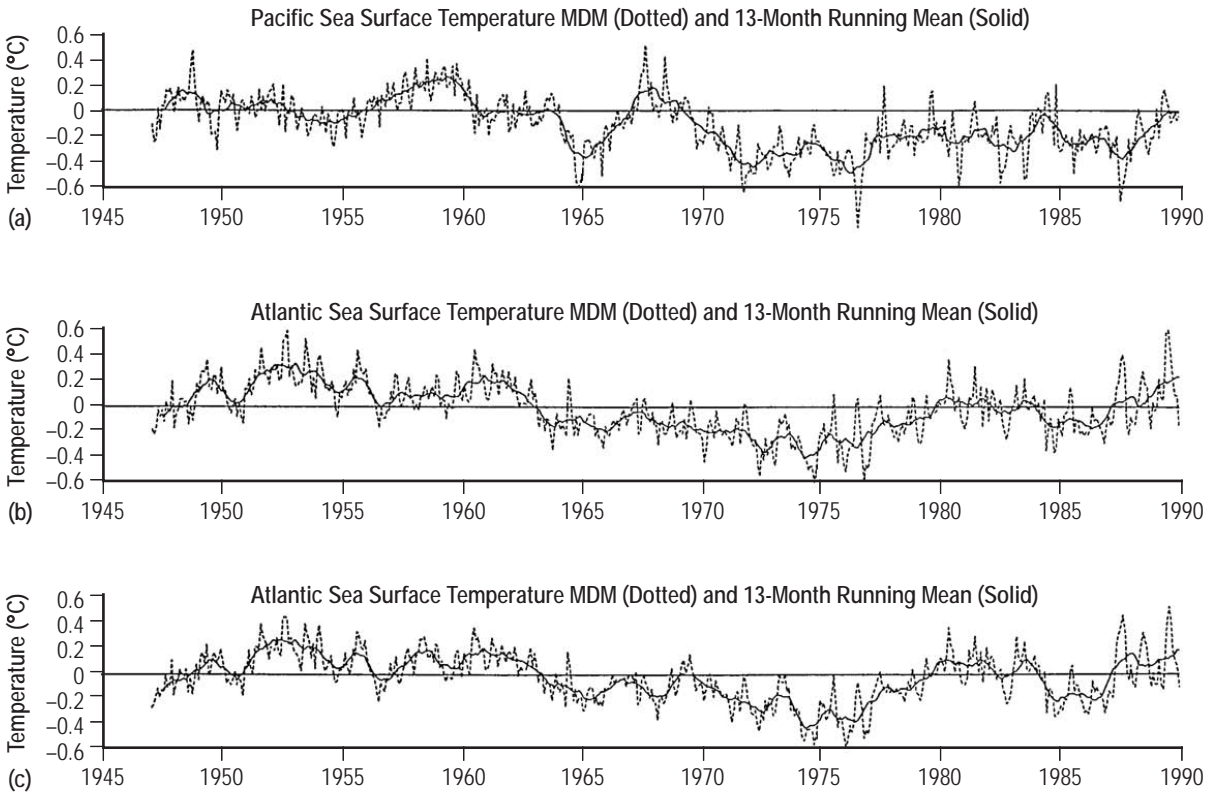


Figure 10-2. Sea surface temperatures for (a) the North Pacific and (b) the North Atlantic, both for 20° N. to 60° N., and (c) the North Atlantic for 5° N. to 60° N., 1947–1990 (courtesy of Cayan and Namias, personal communication (1991)).

The mean deviations from the mean (MDM) are based on the mean for the period 1947–1974 but the data presentation extends to 1990. Parts (a) and (b) present the North Pacific and the North Atlantic for the region, 20° to 60° N. latitude. Part (c) presents information for the North Atlantic for the same period but the region covered for the marine temperatures extends from 5° to 60° N. latitude. The dotted line shows the data while the solid line shows the application of a 13-mo running mean centered on the year of the series. The data and deviations are in Celsius. These data do not imply a warming over the entire period, though a warming effect may be inferred for the last few years.

Climate can be changed by increased forestation or by the destruction of forests. First, the localized climates change. If the forestation or forest destruction increase to cover regions, then the regional climates change and the global climates adjust. The loss of forests leads to loss of soils by aeolian and hydrologic process with subsequent transport over land or in river discharges into the seas. Climates and man are strongly interactive.

## 10.2 Palmer Drought Index

The drought problem is indeed complex. This complexity is induced by the many diverse activities needing definitions peculiar to each activity. One definition cannot serve well for everyone, but a multitude of attempts are made. One such attempt is that described by Palmer (1965). Because no other index, as yet, has supplanted this index, it is often referred to as the Palmer Index. Though it is not a panacea for the problem and is under review and scrutiny all the time, it remains a useful index. Modifications are continually being made by users to fit their individual needs. But perhaps this is why it remains such a useful, though possibly imperfect, index. For these reasons, the index is discussed in some detail and figures are shown to extend the discussion.

Palmer (1965), after almost two decades of work and research, developed an index of drought. This is a definition of meteorological or climatological drought. The foreword of that paper, written by H.E. Landsberg, is pertinent and is quoted here.

“Drought has been cited as a scourge of mankind since biblical times. It still is a major menace to world food supplies. Insect plagues, with which it ranks as a crop threat, can be fought by modern means. Drought remains an unconquered ill.”

“Meteorological science has not yet come to grips with drought. It has not even described the phenomenon adequately. This is certainly the first step toward understanding. And then a long road remains ahead toward prediction and, perhaps, limited control. This paper is an important step toward these goals. It presents a numerical approach to the problem and thus permits an objective evaluation of the climatological events.”

“Although often so classified, drought is not just an agricultural problem. It affects the city dweller, whose water may be rationed, and the industrial consumers of water as well. In fact, water is one of the most vital natural resources. Its lack, regionally or temporally, has the most profound effect on economy. In a country as large as the United States, drought is likely to affect only a part of its territory at any one time. However, no section is entirely spared of droughts and occasionally substantial areas are affected. By severity and duration these events can be calamitous not only locally but for the whole economic structure. Hence knowledge of the probability of their occurrence and their course is an essential element for planning. The thorny problem of a rational land utilization is closely tied in with these considerations.”

“The pioneering work of the late C.W. Thornthwaite on potential evapotranspiration has underlain all modern attempts to assess the water balance. As in his work, the aim of the effort reported on in this paper remains primarily on the climatological aspects. The new method presented here is directed at a quantitative assessment of periods of prolonged meteorological anomalies. We hope it is a step forward and that it can be followed by similar analyses on a broader geographical basis.”

Since the publication of Palmer (1965), drought in various regions of the world has received much more world attention. Examples are the droughts of the Sahel and Ethiopia of which much has been written. The droughts associated with anomalies such as El Niño receive attention and study.

Palmer (1965), in the abstract, states, “Drought can be considered as a strictly meteorological phenomenon. It can be evaluated as a meteorological anomaly characterized by a prolonged and abnormal moisture deficiency. Not only does this approach avoid many of the conflicting biological factors and arbitrary definitions, it enables one to derive a climatic analysis system in which drought severity is dependent upon the duration and magnitude of the abnormal moisture deficiency. Within reasonable limits, time and space comparisons of drought severity are possible. The objective of this paper is to develop a general methodology for evaluating the meteorological anomaly in terms of an index which permits time and space comparisons of drought severity.

The underlying concept of the paper is that the amount of precipitation required for the near normal operation of the established economy of an area during some stated period is dependent on the average climate of the area and on the prevailing meteorological conditions both during and preceding the month or period in question.

A method for computing this required precipitation is demonstrated. The difference between the actual precipitation and the computed precipitation represents a fairly direct measure of the moisture aspect of the weather from normal. When these departures are properly weighted, the resulting index numbers appear to be of reasonably comparable local significance both in space and time. The procedure is tractable for machine data processing by weekly or monthly periods for either points or areas. When this type of climatic analysis has been carried out for a large number of contiguous areas, not only will one obtain drought severity expectancy figures but also other useful items as well. For instance, the analysis will provide wet period expectancies, maps useful in land use capabilities, and material of interest in water resources planning. In addition, some of the derived parameters will very likely prove to be useful in crop yield investigations.”

Palmer (1965) discusses the technique’s use in his model and their limitations. His equations are

$$L_s = S_s^1 \text{ or } (PE - P) , \tag{10.1}$$

whichever is smaller

$$L_n = (PE - P - L_s) S_u^1 / AWC, L_u \leq S_u^1 , \tag{10.2}$$

where

$L_s$  = moisture loss from the surface layer

$S_s^1$  = available moisture stored in surface layer at the start of the month

$PE$  = potential evapotranspiration for the month

$P$  = precipitation for the month

$L_u$  = loss from underlying levels

$S_u^1$  = available moisture stored in underlying levels at the start of the month

$AWC$  = combined available capacity at both levels.

The assumption is made that when field capacity is reached, runoff may occur. Palmer (1965) notes Kohler's (1957) suggestions that this assumption is not always met. There is the problem of the storage during winter times when the ground remains frozen.

Palmer (op. cit.) provides extensive further discussions on the above functional relationship. The Palmer Index is maintained in the computer complexes available to the U.S. National Weather Service (NWS), the U.S. Department of Agriculture, the U.S. National Climatic Data Center (NCDC), and at the other government agencies and in the universities. This index is kept up to date on a weekly basis and is publicized through appropriate channels. Many activities maintain their own specialized variations of the computer program(s) to provide their own version of the index.

To show, in part, the effective output of the Palmer Index programs, figures 10-3(a) and (b) and 10-4, respectively, show drought severity for June 1934, June 1956, and through the week of July 23, 1988. Figure 10-4 shows the immediate effects of rain in the southwestern and central United States after a drought had developed. By this time much of the corn crops had been damaged severely, though the soybean crops were getting rain just when it was needed. The extensive lack of precipitation over the entire Mississippi Basin had reduced the flow of water in the Mississippi River to the lowest point in years. Barge traffic had come to almost a complete halt but was beginning to move by August 1, 1988. Statistics such as these are published by a joint activity of the U.S. NWS and the U.S. Department of Agriculture.

The source of figures 10-3(a) and (b) is NCDC, Historical Climatology series 3-11: Atlas of Monthly Palmer Drought Severity Index (1931–1983) for the contiguous United States. The source of figure 10-5 is the Climatic Analysis Center, NEWS, and NOAA. The series of charts from which this is taken is the Weekly Weather and Crop Bulletin. Myriads of facts or relationships may be given or deduced. One of these is that for the months of July for the years 1934, 1936, 1954, and through July of 1988 (in percent), the total area covered by severe or extreme drought was 61, 44, 45, and 43 percent, respectively.

The Palmer Index is used as a tool by Kunkel and Angel (1989). They provide another perspective on the 1988 midwestern drought in the United States. They indicate that this drought was historic in the fact that it was the worst since the 1930–1940 period. This drought began with the severe dryness of the spring month of May.

Figure 10-5(a) shows the time series of the Palmer Index for the period 1900–1987. To produce this chart, the individual indices for climatic divisions, weighted by the respective division areas, were summed for the entire contiguous area of the United States. This presents only an index in itself of the drought effect on the entire U.S. contiguous area. Whether this is a best representation or not depends upon the perspective which the reader uses. Figure 10-5(b) shows a similar run for the precipitation for the United States.

### 10.3 Other Analyses

Drought is so important from the viewpoint of its potential widespread devastation that steps to provide some lead time guidance is also sought. Extreme drought is associated on a global scale on the low-frequency or long-wave dynamics in the atmosphere and the hydrosphere. Among the many reports on long-term climate data features, Walker (1914) discusses correlations of seasonal weather in the correlations of time and space among the global climate elements. Berlage (1956) studies the phenomenon of the biennial pulse in the southern oscillation through he was not the first to do so or to sense that there was one. Figure 7.2.1.2 from Landsberg, Mitchell, and Crutcher (1959) shows the existence of some power (variance or entropy) in the power spectrum analysis of temperature data from 1870 to 1956 at Woodstock, MD. This was a climatic benchmark station. The power associated

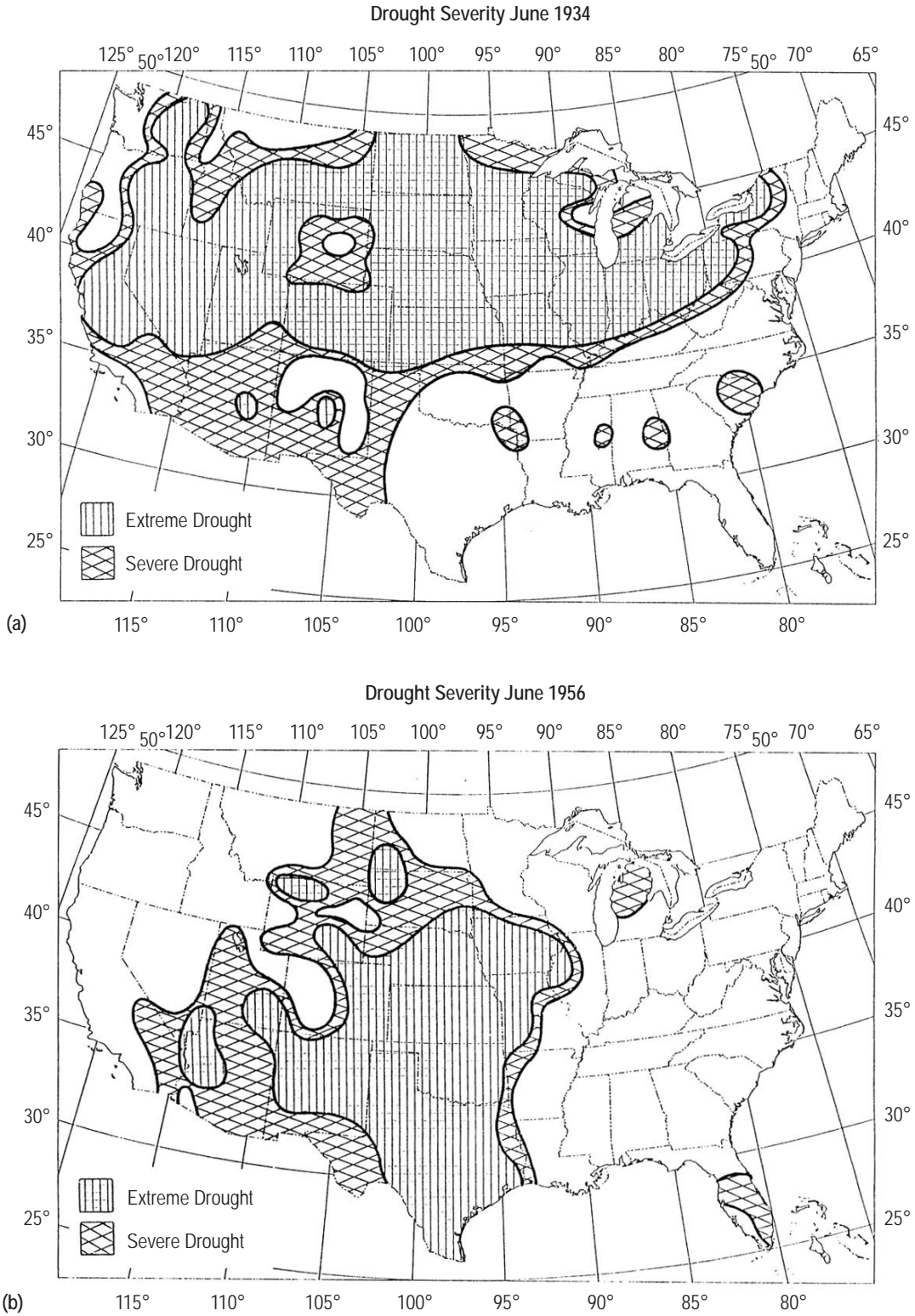


Figure 10-3. Drought severity for (a) June 1934 and (b) June 1956, USA, using Palmer Drought Index analyses (courtesy of NCDC).

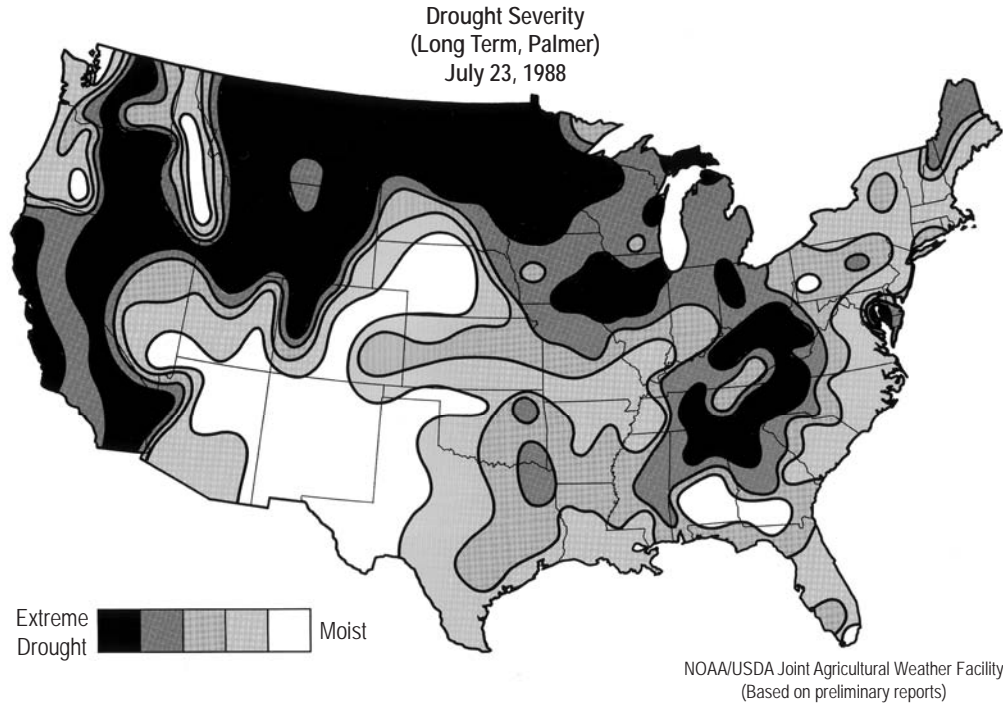


Figure 10-4. Drought severity through week of July 23, 1988, using Palmer Drought Index analyses (courtesy of NOAA, Climatic Analysis Center, NEWS).

with the  $\approx 2$ -yr period is small, yet significant. The periods range from about 1.8 to 2.7 yr. The quasi-biennial oscillation (QBO), previously discussed in section 7 and illustrated in figure 7-7, has the same tendency to be spread over essentially the same periods. Without question, there are longer and shorter periods involved in the neighborhood of 2 yr but these are few. Landsberg, Mitchell, Crutcher, and Quinlan (1963) survey the literature and research on the “biennial pulse.” The Blackman-Tukey (1958) technique was used in which harmonic analysis is applied to autocorrelation functions. See also Panofsky and Brier (1968).

Undoubtedly, allied in some respects to this QBO of the tropical stratosphere and the biennial pulse of the surface climate data are the phenomena of El Niño and the “southern oscillation” utilizing the acronym of ENSO. The features of El Niño are the destructive characteristics to the status quo. The anticyclonic circulations of the oceans are disrupted, the easterly trade winds at the equator weaken, become null, and are replaced by westerly winds. The usual equatorward motion of the atmosphere on the eastern peripheries of the high-pressure areas, the changing of the directions into the easterly trades, and the subsequent shears tend to move to top surface waters away from the coasts. Subsequent upwelling of the nutrient-rich bottom waters provides the base of a long series in the food chain. The subsidence of the atmosphere creates the arid conditions conducive to the great deserts described in an earlier section. The switch in circulation patterns recurrently reverses the equatorial easterly flow with its resultant cooler upwelling waters with equatorial westerly flow with warming surface waters. Most noticeable, south of the equator, this warming feature occurs near the beginning of the Christmas season. For this reason, the appearance of the warm, westerly winds and water currents of this phenomenon was given the name of El Niño for the “Christ Child” (Son). This warm, onshore water effectively caps the supply of nutrient waters and at the same time the warmer, moister air moves overland. The food supply chain of the oceans are disrupted on the equatorial eastern portions of the oceans near the coast, and inland, to and against the Andes, excessive

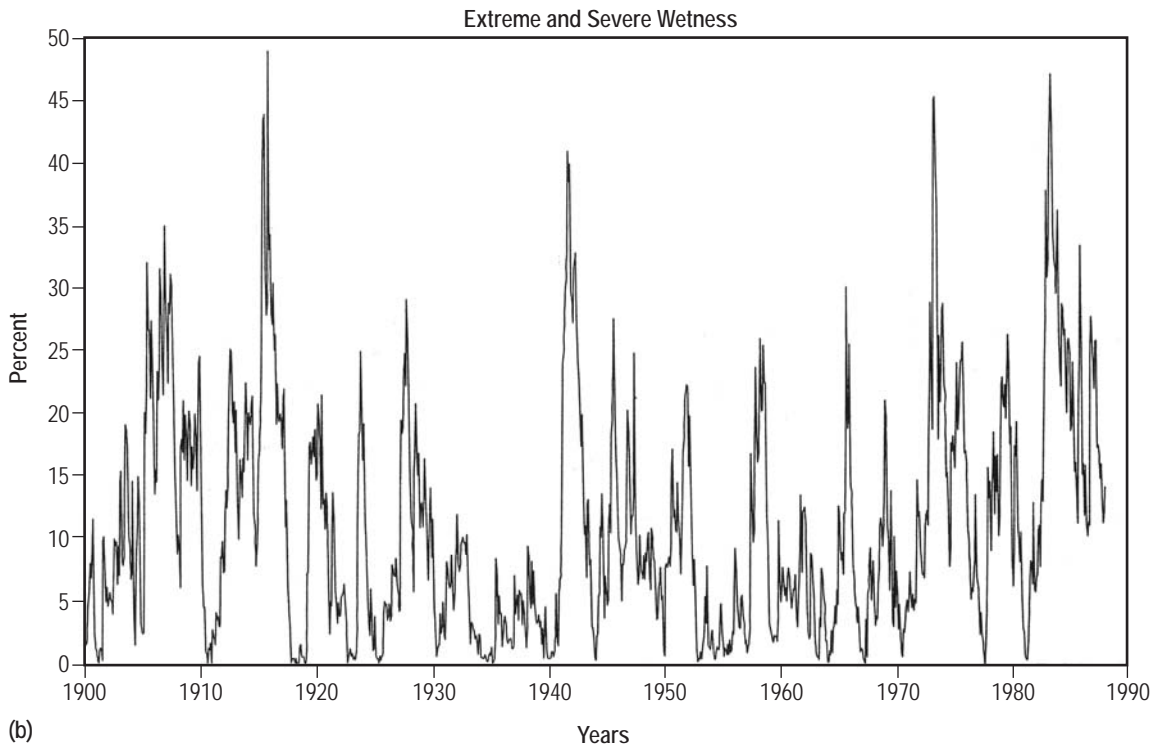
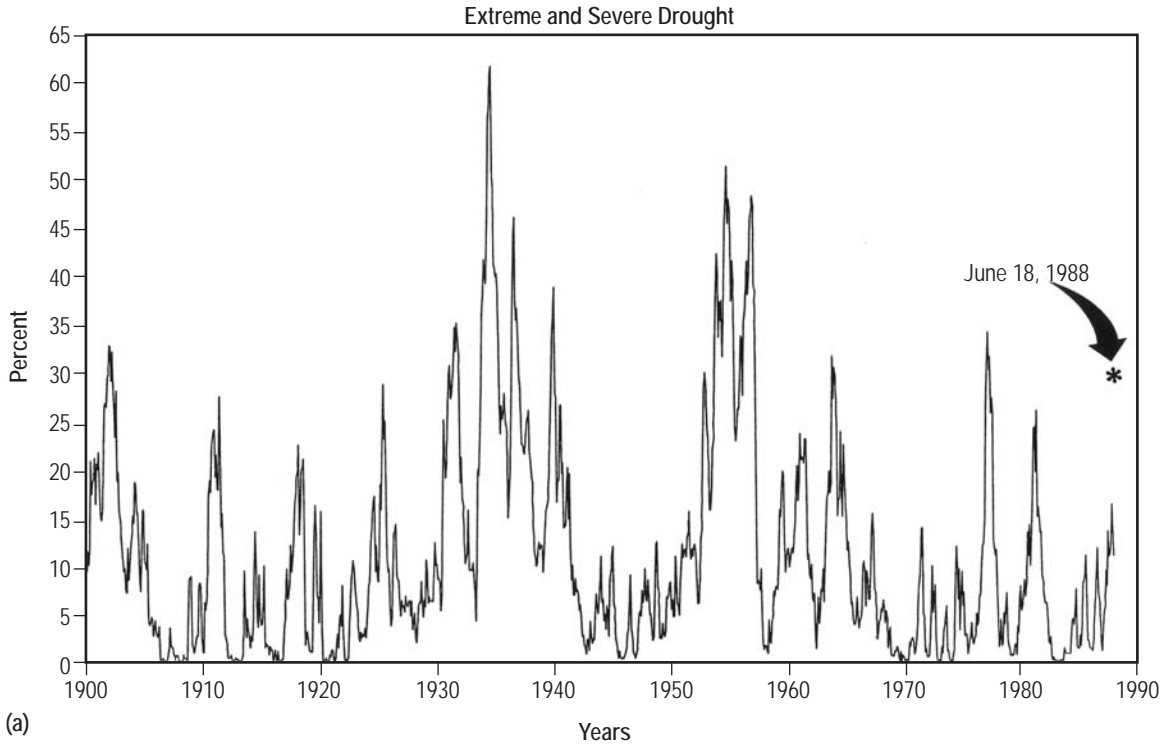


Figure 10-5. Percent area of the contiguous United States having (a) extreme and severe drought and (b) extreme and severe wetness, 1900–1987. The asterisk in (a) denotes the percent area affected as of June 18, 1988 (courtesy NCDC).

rainfalls create floods and destruction in the usually arid regions. If the conditions exist over several years, almost complete disruption and destruction occur. In the latter case, the effects spread far beyond the equator. Recovery is slow. The establishment of the normal easterly tradewind flow has been termed “La Niña” for “The Daughter.” (See Kerr (1988) for attribution.) The disruptions mentioned above also will be associated with altered monsoon seasons of Africa and southern Asia and India. Return to normal will be attended by a slow return of the monsoon weather patterns.

The lack of adequate measurement of the climatic elements on a global extent—both atmospheric and hydrospheric—has prevented and still slows adequate research in the equatorial regions where the effects are noticed strongly. The extreme drought periods are speculatively connected with the ENSO, but considerable research into global dynamics is required.

Many potential ENSO models are under study to determine the best guidance at the present time. Barnett et al. (1988) review three models that, in their opinion, successfully predicted the ENSO of 1986–1987 at lead times of 3 to 9 mo. The apparent key to the technique is the recognition of the particular low frequency-long wave systems that do strengthen and weaken the ENSO. Whether there are other models that do equally well is not known. Also, it is not known how these models performed with respect to the 1988 drought situation in the United States. In any event, a lead of 9 mo will allow some effective planning for all global activities. But, again, the continuum of space and time observational network effectively must be improved and expanded. This includes continental, marine observations which provide ground truth for satellite observations and provide the basic input to the models. These data will better depict the elements of climate.

Folklore often provides a starting point for research and an improved understanding in any activity or discipline. Folklore is based on the vagaries of human experience and an inability to condense or coalesce these into precise and exact statements. Until such condensation can be effected, the historian, folklorist, or the tribal storyteller, is the connective link to the past and to the future. Until adequate language—spoken, written, and understood—forms are developed, the connective links are weak indeed and often dissipate. Until then there will be the believers, the skeptics, and the unbelievers. The livelihoods and the activities of people and the associated and interactive stresses with weather and climate produce folklore. Thus, as one example, in the central and high plains of the United States of North America there are existent stories of precipitation and drought happenings near a people’s generation life and the association of these with the phases of the moon and the position and configuration of the crescent moon. It is realized that changing lifestyles may affect the impressions of a generation; i.e., the age of marriage and childbearing changes inevitably affect the time meaning of the word generation. It is also realized that some regional weather and concepts will change over time but that there is a persistence in the folklore. Thus, what may have seemed to be true a few generations back may not seem to be true in the present.

As indicated in much earlier sections, in order to convince, more than adequate mathematical tools easily and properly manipulated and understood by more than a person need to be developed. Through the past half century, this problem, related to the precipitation and drought of the central and high plains of the United States of North America, and of other regions of the globe, has been under slow, persistent assault. Mathematical tools have been improved and have been augmented. The familiar statistical tools of regression, correlation, lag correlation, harmonic, and other orthogonal polynomial treatments have not presented any essentially clearcut and acceptable results.

Presumably last is the feature of some semblance of quality control and assessments. There has not been and there is no consistent dedication to the production of essentially “clean” data for “climatological benchmark” stations. This was discussed previously in section 2. Adding to this is the incomplete understanding by the researchers of the proper treatment of data and the reverberations in the data sets created by the improper observing, recording, and servicing of data collectives.



Fifty years ago the technique of spectrum analysis was added to those mentioned a paragraph or two above and available for the extraction of information from time series ensembles. See Rice (1944), Tukey (1949), Hamming and Tukey (prior to 1958—unpublished), and Blackman and Tukey (1958). Since then, many papers in many disciplines have been produced. Additionally, the techniques of Blackman and Tukey (op. cit.) have been modified into the maximum entropy spectrum analysis technique. See Landsberg, Mitchell, and Crutcher (1959). Marple (1987) discusses this technique as do many others. Some investigators prefer the Blackman-Tukey procedure while others prefer the maximum entropy procedure. See also the discussions of Macdonald (1989) who prefers the periodogram type of analysis, which predates the development of spectrum analysis. In either case, database imperfections and improperly applied techniques sometimes can lead to the invective aphorism “GIGO” (garbage in-garbage out).

The following comments are included, not to denigrate any of the techniques but to indicate some, just some, of the difficulties or pitfalls facing an earnest and dedicated investigator. In any set of data there usually is a missing or incorrect datum, an occasional datum, more than an occasional datum, breaks in the record, short and/or long shifts in the record induced by sensor change locations or environment, replacement of sensors with new sensors whose range of capabilities are different or unknown, etc. For example, the use of mean data, median data, data selected at random from the data set itself, or from a similar theoretical distribution may present problems in inference.

In any data set, the beginning of the record and the ending of the record form discontinuous jumps from nothing to similar jumps to nothing. Breaks in any record form such discontinuities. The Gibbs phenomenon quite familiar to those working in electrical or electronic subdisciplines is induced by such discontinuities. There are various techniques used to attenuate these effects so that they do not overwhelm the time series work results. The investigator often selects one—one hopes after serious consideration of the problems involved. Some of these are the gaussian, the binomial which is quite flexible and adaptable, trigonometric (sine, cosine, tangential, etc.), gamma, or any other that might be developed by the investigator.

In some data sets, the unwary investigator may replace missing data singly or in groups (intervals) with constant values or with some functional values which induce spurious cycles. The replacement of a missing data interval often is made with constant values such as the mean, the median of the entire available set, or for measures of data containing the interval. The longer the intervals with replacement data of a constant, the more the frequencies of the analysis will be shifted to lower frequencies. There is another problem, usually not discussed except in texts such as that of Conrad and Pollack (1950). That problem is the uneven lengths of the months in days. For example, February has 28 (29), others have 30, and some have 31. Storms do not automatically end at midnight (or some other set hour) of the month’s last day. The data sometimes are severely truncated for each individual month, inducing the “Gibbs” effect into any time series analysis of data.

In the terms of color pasteling (Tukey (op. cit.)), reddening or a pink effect is induced. The shorter the intervals and an increase in the number of these short intervals, say 1 datum or 2 data each, blueing occurs to be confounded with the “Nyquist” frequencies.

Another problem is the tendency of many investigators to overstate the number of degrees of freedom and/or to extend inferences beyond the capabilities of the technique. Due to the apparent nonstationarity of the data information, significant or nonsignificant frequency groups in the spectrum may tend to travel or to increase or decrease their amplitudes including the phase changes. The use of designed filters can only be applied to that frequency region of the design. Interpretation will be involved for these frequencies outside the range in the seriously modified outer regions where spurious induced wave groups appear.

Transformations of data may or may not present problems. Therefore, the investigator must determine whether transformations enhance the research. Such transformations may involve the prewhitening of the data such as extraction of the annual march, the extraction of a trend, or the extraction of a pastelling function. All these tend to leave only the higher frequencies to be studied alone. Each of these may create some inferential problems.

In the sense that both temperature and precipitation, as well as other elements, are involved in the effects of drouth, and in the sense of the short-term QBO, figure 7-8 is first referenced. This was previously used in Section 7, Winds, in conjunction with the presentation of the tropical stratosphere QBO effect in winds. Figure 7-8 is the spectrum for temperature at Woodstock, MD (Landsberg, Mitchell, and Crutcher (1959)). For precipitation at Woodstock, MD, figure 5, p. 292 (Landsberg, Mitchell, and Crutcher, op. cit.) did have several spectral spikes near 3 and 8 mo and near 2.5, 4 to 5, and 16 yr. Though these were individually statistically significant, they were damped in the smoothed spectrum and were judged to be not significant. The annual march had been extracted from these precipitation data as well as the temperature data.

Mitchell, Stockton, and Meko (1979) present a study using Drought Analysis Indices (DAI) deduced from tree ring analyses of the far western mountainous regions of the USNA. These range from Canada to Mexico and from the west coast of the USNA to the plains states. These are proxy data. Tree rings are influenced by several climate variates. There is no spectrum analysis technique as yet of which the writer is aware that has been applied to multivariate ensembles beyond two variates. In the last, there are the two variate spectra, the cross spectrum and the quadrative spectrum analysis. Thus, researchers generally are restricted, in this sense, to using spectrum analysis for one variate where the variate is derived as a function of several other variates whose individual distribution densities may or may not be known. Mitchell, Stockton, and Meko (op. cit.) examine the DAI proxy data with reference to the Palmer Drought Indices (PDI) previously discussed. The series dates back to 1600 A.D. and reflects a statistically significant, well-defined, 22-yr drought rhythm which operates parallel to the Hale sunspot magnetic activity of 22 yr. They use the “pastelling” feature introduced by Tukey and others and deduce that the best null hypothesis base is “pink” and neither “red” nor “white” in the sense of “noise color.”

Mitchell, Stockton, and Meko (op. cit.) present an interesting harmonic dial analysis based on two designed filters. For one of their series where the Palmer Drought Severity Index was  $<1$  and a magnitude of 2.87, the phases are  $360^\circ$  from the minimum of one cycle to the minimum of the following cycle. This then implies that drouths reach a maximum in the far western USNA 2 to 3 yr after the Hale sunspot minima. Given the data and computing the vector variances and covariances, drought strike probabilities could be computed as are hurricane strike probabilities. This requires the integration under the bivariate surface. See Groenewoud, Hoaglin, Vitalis, and Crutcher (1967) and Crutcher, Quinlan, and Hoxit (1971). Drought strike probabilities would be in terms of intensity, timing, and phase. The distribution of vectors, phase, and magnitudes appear to be bivariate normal with a mean phase of  $29^\circ$ .

As mentioned before, one of the items of folklore involves the Moon, its phases, and its declination. That the Moon is involved simply reflects the fact that it and the Sun are the most visible and easily observed elements of the solar system from Earth’s vantage point. This was the best unscientific tool that people in early times could develop. The lunar orbital plane is inclined at an angle of about  $5^\circ 9'$  to the plane of the ecliptic which is the orbital plane of the Earth about the Sun. This angle does vary several seconds. As the Moon moves upwards through the ecliptic (a node) to its highest point above the ecliptic, thence downward through the ecliptic plane (a node) downward to its lowest point and back to the nodal crossing once again of the ecliptic plane by the Moon, a time interval of  $\approx 18.613$  yr has ensued. This is the nutation period. It is equivalent to the forcing function involved in Newton’s discussions. See Mitton (1977), Moore and Hunt (1983), and Currie (1988). This nutation period of 18.613 yr has received some attention over the years. Stockton, Mitchell, and Meko (1983, 1986) reassess their work of 1979 and add information from the Plains States to about  $85^\circ$  W. longitude. They report a better definition of the spectra with the delineation of the 18.6- and the 22-yr rhythms. The QBO is noted in their figures. They include comments on

the analysis of a short record of tree rings from Morocco. These seem to bear out their previous conclusions. Their inferences seem to be that the 22-yr (solar) period is fixed fairly well but that the 18.6 (lunar) period does change phase.

Currie (1989) provides comments on “power spectra and coherence of drought in the interior plains” by I.O. Oladipo (1987). In this paper, Currie (op. cit.) discusses some of the data treatment applications by Oladipo (op. cit.) which he considers to be mistreatments. Where Oladipo (op. cit.) concludes that there is no signal, Currie (op. cit.), using the maximum entropy power spectrum analysis as described by Marple (1987), perceives signals at the periods of 10 to 11 yr and near 19 yr in 64 records from three states—Arkansas, Illinois, and Iowa. Respectively, the periods shown are  $(10.8 \pm 0.05, 10.9 \pm 0.04, 10.7 \pm 0.05, \text{ranges } 10.3, 10.5, 10.2 \text{ to } 11.3, 11.3, 11.2)$  and  $(18.5 \pm 1.4, 19.2 \pm 1, 18.9 \pm 1.4, \text{ranges } 17.1, 18.2, 17.5 \text{ to } 19.9, 20.2, 20.3)$ . The first Currie (op. cit.) calls the solar cycle term and the second the luni-solar cycle term. He uses actual precipitation values and not transformed values. See figure 10-6 adapted from Currie (1988, 1989) and Currie and O’Brien (1990) showing the power spectra described above. The data are prepared by the NCDC, Asheville, NC (Karl (1988), Karl and Williams (1987), and Karl and Williams (1987)). The properly adjusted values are used.

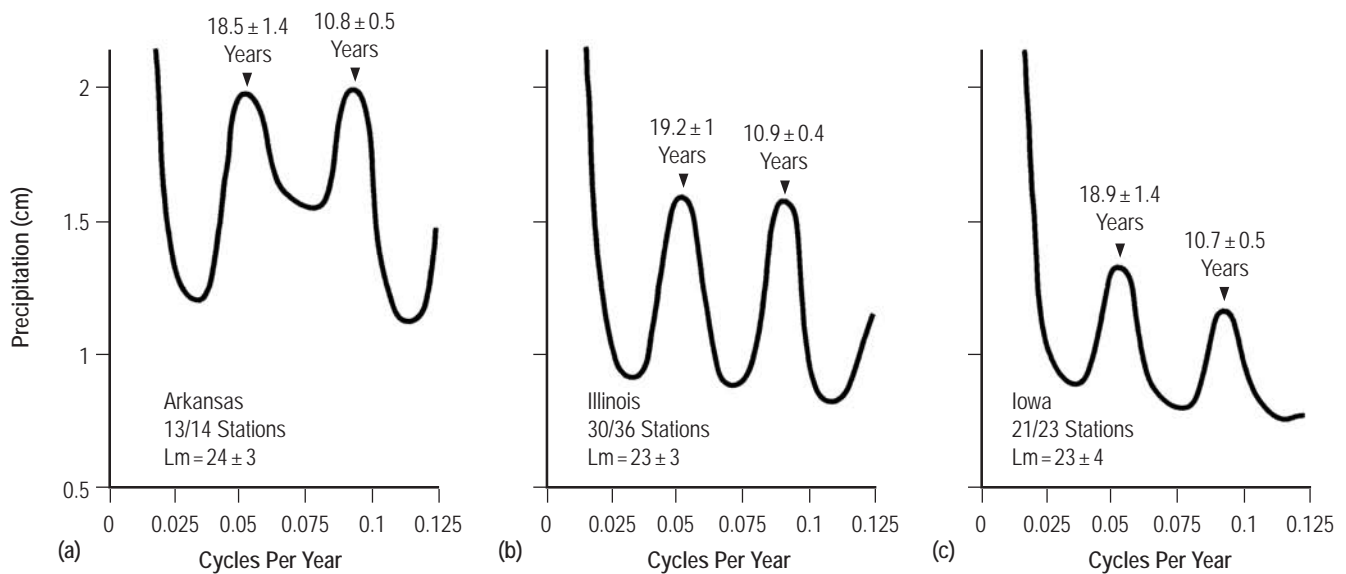


Figure 10-6. Spectrum analyses of precipitation for (a) Arkansas, (b) Illinois, and (c) Iowa (furnished by NCDC; adapted from Currie (1989)).

To deduce some of the reasons for the variability in the solar energy and sunspot cycling activity, Morth and Schlamminger (1979) consider the changes in orbital angular momenta of planets due to their gravitational perturbations. They indicate that the orbital motions of the four giant gas planets—Jupiter, Saturn, Uranus, and Neptune—hold 98 percent of the solar system’s angular momentum. By considering the paired satellite effects and the interaction between the pairs, they indicate 10-, 11-, and 90-yr periods. Thus, in sunspot data, as studied by Morth and Schlamminger (op. cit.), the usually reported 10–11 yr cycle is supported. Whether the same effect is exerted directly on the Earth’s atmosphere and weather by these planetary effects, whether the sunspot activity is actually controlled by the same effects, or whether the planetary effects and the solar sunspot activity reflections of a solar response both affect the Earth’s climate is a matter for serious consideration. At least the solar flare and solar sunspot appear to be likely candidates for consideration as basic climate elements, just as much as those usually considered. As to the 90-yr periods deduced, there have been comments on periods 50 to 90 yr. However, it is difficult to assess

the precision with which such comments can be made due to the relatively short periods of record which restrict the number of degrees of freedom. These various estimates may be the result of different applications of the spectrum analysis techniques, the quality of the data, the regions of the world where the data are procured, etc.

MacDonald (1989) states that “Much of the geophysics involves analysis of time series and much of the data derive from non-linear processes.” He reviews data analysis procedures. He prefers periodogram analysis and provides application examples from orbital mechanics, the sunspot record, and CO<sub>2</sub> variations in an ice core. MacDonald (op. cit.) provides the requisite mathematics and statistics. He prefers the periodogram analysis over spectrum analysis due to the alleged inability of present spectrum analysis techniques to handle nonlinear processes adequately. The dominant term in the Earth’s obliquity as determined by MacDonald (op. cit.) is a period of 41,000 yr. For the sunspot study, he deduces year periods of 9.97, 10.64, 11.04, 11.92, and 98.33 yr with respective variance contributions to the nearest percent of 14, 7, 29, 6, and 11, a summation of 67 percent. The significant periods near 19 and 22 yr discussed previously are not supported by this particular analysis. However, the periods near 9–12 yr are supported. Please note the period near 90–100 yr, which in this analysis, contributes about 11 percent of the variance. Presumably, considerable more work needs to be done to elicit with greater assurance interpretable signals from sunspot information.

There is information in present examination of the waxing and waning of the rhythms. For example, in the case of the stratospheric QBO, the fluctuation was especially strong in the decade of 1955–1965. In the surface data, the effect is not always pronounced as in the above discussion of the Woodstock, MD, USNA data. MacLennan and Lanzerotti (1979) note that while some wave groups are evident in the data at some locations in the eastern USNA, these may not be evident at all stations. Additionally, they noted different contributions to the relative variance, and therefore to the total variance for different data time intervals. They indicate, for example, that a strong QBO in temperature was noted in the 20-yr period 1871–1891 at Baltimore, MD, and Philadelphia, PA, and a weaker fluctuation at New Haven, CT. They noted no enhancement in the data for England in using the Manley temperature series; for central England they did find broad enhancements of power for the 11-yr period in the U.S. data but less enhancement in the central England data. Mason (1976) had reported also the QBO in the England data. An inference from their study is that noted variations such as the QBO, the 11-yr variation, and others may be at times unnoted; their term is “washed out.” This implies that such wave groups develop, rise into statistical significance insofar as the rules seem to require, and then fade away. The action may seem to be that of a “wave train” on the ocean surface. Yet, there may be another artifice effect. An inferential point is made here. Perhaps the QBO is more strongly noted near the region of development. Examination of world records might determine the region of long-term or strongest input, if any. However, this implies the development and maintenance of a world base of good climatological, oceanographical, and other geophysical benchmark stations or areas. The extent of the noted rhythm is a function of the length of record examined. In a short record, the rhythm may be quite obvious as it contributes a large portion of the variability (variance), while against the backdrop of a much longer period, its relative variance becomes small. It becomes imperative then that analyses must be updated. In the experience of this writer, an analysis may be fruitful with a 50-percent increase in record length, will be fruitful in a doubling of the record, and will be very rewarding with a tripling of the record. With all of this, the investigator would be helped if a full number of wavelengths for the rhythm under study are used. Fractional numbers, such as 20.3 wavelengths, allow the development of the “Nyquist” frequencies. This will not mitigate the “Nyquist” frequency effects of other wave trains but it will serve to damp the main ones in the interest region.

The above discussions may seem to be lengthy. The main thrust is to emphasize the point that, as investigative techniques become better and more precise, the effect of “bad” data increases. The investigator needs to become a researcher, more careful, more precise, and better at managing databases.

Among the many problems intertwined in such studies are those induced by the measurement modes and techniques for the various climate elements, including those climate elements, the atmospheric constituency. Much

research and reporting needs to be done in this field. Another important feature of these studies is the defining of the study subject. Just what is drought? What is climatological (meteorological), agricultural—or any other activity drought insofar as rain or lack of rain? In the major portions of work, the studies are made of precipitation amounts and power spectrum analysis is a study of the variation or variability. Presumably, the peaking of rainfall (precipitation) near the 10-, 11-, 19-, or 22-yr periods implies a corresponding peaking period of low or no precipitation (drought). This is an inverse problem.

#### 10.4 Evaporation

The primary sources for water on the continents are the oceans. These water surfaces constitute about three-fourths of the global surface. Fundamentally, for human activities it is important to gauge this transformation from the liquid to the vapor state and the vapor transport. Such measurement is not easy. Inferences based on research constitute most of our estimates. As indicated previously, Jacobs (1942, 1943, 1949, 1950, and 1951) presents inferential work on a global scale. This important contribution is acknowledged. Jacobs (1951) presents charts and tables showing the following:

- The annual values of the rate of sensible heat exchange between ocean and atmosphere,  $Qh$ , over the North Atlantic and North Pacific Oceans.
- Losses, through evaporation from the ocean.
- Losses, through convection from the ocean.
- Losses, total, from the ocean.
- Gains, through sensible heat and latent heat conversion.
- Surplus of energy available in latent energy form.

Flohn (1969) treats the phenomenon of evaporation. He discusses the important work of Thornthwaite (1948) on evaporation and evapotranspiration as well as presenting well these subjects. As these discussions are in volume 2 of the *World Survey of Climatology*, no further discussion is made here except to draw the reader's attention to Farnsworth, Thompson, and Peck (1982). They provide 26 pages of text with enclosed foldout charts. This is the "Evaporation Atlas for the Contiguous 48 United States."

Precipitation and drought is perhaps as complex a process as any other in climatology. The evaporation process is a filtering (fractionation) mechanism that is pressure, temperature, and isotope dependent. In part, this is discussed in the subsections on the hydrosphere and water. Ordinary water ( $^1\text{H}_2^16\text{O}_1$ ) has less mass than ( $^3\text{H}_2^{20}\text{O}_1$ ). As a consequence, it will evaporate more easily. By the same forces, the latter will tend to precipitate more quickly.

Plants and animals will tend to absorb the less massive molecules.  $^1\text{H}_1^2\text{H}_1^16\text{O}_1$  is lighter than  $^2\text{H}_2^16\text{O}_1$  and will evaporate more easily. All the isotopic molecules will differ in physical characteristics. Plant and animal utilization will depend on the isotopic concentrations. Animal materials, plant materials, and the deposition of water as water, snow, or ice reflect their isotopic assimilation. These provide the tools of chronology so important in the study of past climates.



## 11. ATMOSPHERIC COMPOSITION

### 11.1 Chemical (Physical) Elements

#### 11.1.1 Atomic Weights

Table A-11-1 provides atomic weights (in atomic weight units (AWU)) to four significant figures. The letter A in any figure or table number indicates that these will be found in the appendix. Greenwood and Peiser (1988) prepared this table on behalf of the Committee on Teaching of Chemistry of the International Union of Pure and Applied Chemistry (IUPAC) in consultation with the IUPAC Commission on Atomic Weights and Isotopic Abundance. Most chemists prefer the term “atomic weight.” Since 1961, the internationally accepted values have been scaled to the carbon isotope  $^{12}\text{C}$ , carbon 12, taken exactly. Note that carbon (C), the average of all the carbons, itself is 12.01 while oxygen (O) scales to 16.00. This table is reproduced with permission.

These tabulated atomic weights apply to chemical elements in their natural terrestrial isotopic composition. For example, the first three isotopes of hydrogen are  $^1\text{H}$ ,  $^2\text{H}$ , and  $^3\text{H}$  or (H, D, and T), or hydrogen, deuterium, and tritium, respectively. The very short lifespan of tritium, now usually but not totally synthesized by man, leaves only the other two to make up the natural state. The very small amount of deuterium, D or ( $^2\text{H}$ ), compared to H, or ( $^1\text{H}$ ), leaves the atomic weight of the abundance of the natural state as 1.0080 rather than just the abundance of the first isotope,  $^1\text{H}$ , 1.007825. Atomic weights are reviewed and modified every 2 yr. Tabular data of table A-11-1 are not expected to change very much. The given uncertainties establish a range through which the changes may occur. Where a leading superscript occurs with a chemical element symbol, the atomic weight shown is for that isotope alone and not the mixture of isotopes.

This same table (or earlier tables) appears in many chemistry textbooks and references. Each new textbook usually shows the latest approved table. An example of these is Chang (1986). Table A-11-1 so provides the reader with a ready reference to atomic make-up of the major elemental gases of the atmosphere and also to minor and trace elemental gases. Readers also will be better able to assess molecular weights of the gaseous compounds, including those usually not considered by the climatologist. Atmospheric chemistry becomes more important to the climate (meteorological) disciplines with the development of or the discovery of environmental problems. For atmospheric chemistry the reader may refer to Wayne (1985, 1990) and Warneck (1988).

#### 11.1.2 Electronic Configurations

The paragraphs in section 11.1.1 are concerned with the nuclei of the physical-chemical elements. With increasing atomic weights, the mass of the electrons relatively contribute less and less to the weights. But these electrons are extremely important in other aspects.

Electronic configurations are the fields where chemistry is involved. Electrons occupy or fill certain orbitals around an atomic nucleus. Today, many elementary and advanced texts discuss orbitals and orbital theory (Chang (1986)). An orbital may be considered as the probability function ( $\psi^2$ ) that defines the distribution of electronic density in space around the atomic nucleus.

This statement derives from the work of Erwin Schrodinger (1926). The uncertainty principle of Heisenberg (1930) additionally comes into play here. These are also discussed elsewhere. An analogy, even though it is

imperfect—is the attempt to state the location of a three-dimensional vector in a three-dimensional normal random distribution. The probability in the three-dimensional normal random distribution is essentially zero. Therefore, regions are sought where the probability is larger. Of course, it can be stated that an electron, if it is present, is located somewhere within the total space of orbitals. This is similar to the information theory with limits of zero and one.

An atomic orbital has a characteristic energy and a characteristic electronic density distribution. There are three subshells—s, p, and d—with, respectively, 1, 3, and 5 orbitals. In addition, there are three more atomic orbitals, namely f, g, and h, which are not of immediate interest here. Three quantum numbers determine the distribution of electrons. The first three numbers are the principal, the angular momentum, and the magnetic quantum numbers. A fourth quantum describing the behavior of a specific electron—the spin quantum number—completes the description of electrons in atoms.

The principal quantum number is ( $n$ ). It can have integral values of 1, 2, 3, ... It determines the orbital energy. It relates the average distance of the electron from the nucleus but never a distance at any particular moment. The angular momentum quantum number,  $l$ , tells us the shape of the orbital. The magnetic quantum number,  $M_l$ , describes the orbital orientation in a magnetic field. Its range is 0, 1, 2,  $n-1$ . In a magnetic field the electron spin quantum number,  $m_s$ , considers the assumption that electrons act like tiny magnets under the further assumption of the electron spin number of  $1/2$  or  $-1/2$ . These refer to two spinning motions of the electron.

### 11.1.3 Spectral Energy

A person might infer from the foregoing discussions that absorption or emission of electromagnetic energy by an atom or a molecule occurs in only sharp Dirac delta spikes or lines. This is not necessarily true. Atoms or molecules are, to some extent, influenced by their states and by their neighborhoods. An atom is affected by (1) nuclear and electronic spins, and (2) transitions of electrons from one level to another. A molecule is affected, of course, by the atoms of its configuration and also by (1) bonds between the atoms in a molecule and vibrations between and/or among its atoms, (2) rotations of the molecules themselves, (3) translation of the molecules from one place to another (collisions have this affect here also), and (4) flexing or bending of the molecule.

Each of the above has its own energy levels, and its own Hamiltonian and wave functions. These may be summed for a total. Goody and Yung (1989, p. 73) define the quantum-mechanical Hamiltonian operator,  $H$ . To obtain this, one replaces the variables in the usual energy system expressions by operators. The system is the nuclei and the electrons of a molecule.

All of the above involve energy quanta in different portions of the electromagnetic spectrum. Transitions of the above are involved in the ultraviolet, the visible, and the near infrared spectrum from  $10^5$ – $10^4$   $\text{cm}^{-1}$ . Bending energies are involved in this same region. Vibrational bands occur in the near to the far infrared, from  $10^4$ – $10^2$   $\text{cm}^{-1}$ . The rotational bands occur from the far infrared to the microwave region,  $1$ – $10$   $\text{cm}^{-1}$ . Nuclear spin energies are small and occur in the far infrared. The electronic levels (shells or orbitals) are usually separated from their immediate members by only a few electronvolts. These are equivalent to the energies of a few  $\times 10^4$   $\text{cm}^{-1}$ . See Goody and Yung (1989), Moore and Hunt (1983), Chang (1986), Goody and Yung (1989), and Wayne (1988) discuss some or all of the above features. These serve as the basis for this discussion. It is evident that there are several stages or conditions in the energy configurations in an atom or molecule. In a simple case, the spins of the nucleus and an electron are opposite. Absorption of energy (from the far infrared) may induce the electron to change its spin to the same as that of the nucleus. From this higher (excess) energy state, the electron tends to change its spin with emission of energy. The absorption of appropriate photons will induce electronic transitions within the atom(s). Within the ensembles, small and large, of molecules, energy absorption in the infrared may induce changes in vibration between and among molecules, in the far infrared in molecular rotation, and longer wavelength in translational



velocities. Translational velocities is the movement of an atom or molecule from one point to another. If a molecule is moving against the stream of electromagnetic energy, the energy absorbed will come from a higher number. If the motion is with or faster than the stream, the fitting quantum will be found in the lower wave number. The converse exists also. (These “doppler” effects, coupled with collision intensities and with more collisions in translations with the vibrations and rotations, tend to broaden the range of absorption and emission around the main spectral range.) The absorption (emission) bend noted will appear to have wings. Depth (height) will be directly dependent upon the available energy as well as the number of responsive molecules. This effect often is called pressure broadening. Where the translations (velocities) of the molecules are not being further affected, their distributions may be expected to be Maxwellian. This is expected to occur also if emissions balance the absorptions. Where there is an excess of either, the distribution of the total (and the mean) may be expected to be displaced. A noncentral  $X^2$  distribution may describe the situation. This displacement then will be a measure of the warming or the cooling of the ensemble, large or small.

In normal conditions, in solid or liquid form, reactivities are those of ground state (or thermal energy) conditions; i.e., the orbitals are in their lowest energy configurations. With an increase of available photonic energy, electrons are raised to higher energy (orbital) levels. This occurs best when the molecules are in gaseous form as in the upper atmosphere under the onslaught of solar radiation. Though the elements have not changed, their increasing energy forms allows them to participate in reactions which generally would not occur in ground state conditions. Wayne (1989) indicates there is an energy excess. In the ensuing reactions, there is an emission of energy as the new molecules are formed. Such molecules are not often formed in the realm of thermal energies of the ground state structures. The reactions are exothermic. The excess energy is radiated or is redistributed in the bonding, rotation, spin, flexing, and translation of the molecules; i.e., the thermal activities of the molecule. Thus, the incoming absorbed high-energy ultraviolet is degraded into heat and warming of the environs.

Under controlled conditions, laser and/or maser excitation can be used to provide the energies to accelerate chemical processes in manufacturing. In addition to such acceleration of possible reactions, previously improbable reactions can be induced.

The main thrust of this information is that known chemical processes in the upper air are accelerated and that new processes are created; i.e., new processes with respect to those with which the climatologist may be familiar.

The ground state configurations of atoms or molecules are of minimum energy. Ordinarily, these are considered in most chemical reactions and in identification of chemical elements. Though modifications may be attained through thermal means, photochemistry modification—always important—becomes more important. Here, each change in the electronic ensemble of an atom or molecule provides a new atom or molecule with different reactivity or change. One of the results may be ionization.

Photochemistry impacts the atmosphere in its entirety. Light, implying the entire electromagnetic spectrum, is the agent. Visible light; i.e., light that permits human vision, extends from about 400–420 to 750–770 nm. Some humans have vision slightly below and/or above these approximate bounds. Also, there are those individuals who cannot detect portions of this band. Humans, animals, insects, and plants do have sensory organs for other portions of the electromagnetic spectrum. Inanimate material, as indicated above, responds to one or more parts of this spectrum. Figure 11-1 indicates some of the relationships among wavelength, frequency, radiation type, and energy. See tables A-4-1 through A-4-3. Figure 11-1 combines and modifies representations in Chang (1986), Wayne (1988), and others. The internal relationship amongst these is the relationship

$$E = hv \quad , \quad (11.1)$$

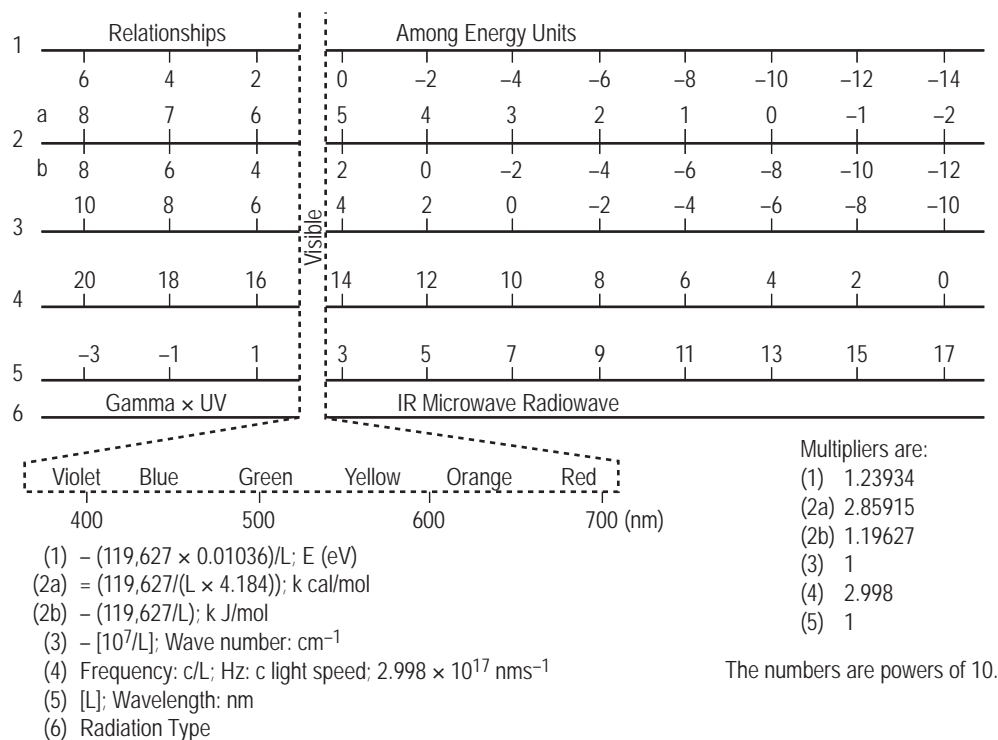


Figure 11-1. Relationships among wavelength, frequency radiation type, and energy (modified from Chang (1986) and Wayne (1988)).

where  $E$  is the energy,  $h$  is the Planck constant, and  $\nu$  is the frequency. Planck's reasoning was that radiation possessed particulate properties and the particles, photons of radiation of specific frequency,  $\nu$ , had with them a fixed energy, momentum, and angular momentum. The magnitude of a photon is the unit ( $h\nu$ ).

An electromagnetic field is composed of photons also called light quanta (Grotthus and Draper, cited by Wayne (1988)). Workers, early in the 19th century, knew that a molecule would undergo a photochemical change by absorption of light of a specific frequency band. An atom (molecule) will respond only to a specific frequency band or to specific bands. Bands may be narrowed or broadened under collision, increasing or decreasing pressure, or doppler effects. It is not necessary that the frequencies be near to each other. Each atom (molecule) acts as a filter, responding to and absorbing the quanta associated with a particular frequency. Each atom (or the atoms of a molecule) has (have) a ground state that has a base of minimum energy configuration. Minimum excitement of an atom is to supply a quantum of energy sufficient to move an electron from one state to the next higher level or orbital. Maximum excitation occurs when appropriate quanta to the same atom are sufficient to move all electrons to the highest levels (orbitals) and beyond the influence of the nucleus. Each quantum absorbed provides the atom (molecule) with an energy surplus to create an energy-rich condition (Wayne (1988)).

In equation (11.1),  $E=h\nu$  implies a linear relation between packets of energy (quanta) and the frequency ( $\nu$ ). Higher frequencies involve greater energies. There is an inverse (nonlinear) relationship with wavelength ( $\lambda$ ). This is discussed also in section 4.

Each  $\text{J mol}^{-1}$  may be converted to  $\text{cal mol}^{-1}$ , eV (electron volts) and  $\text{cm}^{-1}$ . Multiply, respectively, by  $2.390 \times 10^{-1}$ ,  $1.036 \times 10^{-5}$ , and  $8.359 \times 10^{-2}$  (Condon (1958b), Wayne (1988), and Chantry (1984)). Source values differ slightly. Energy of the light quanta vary with the frequency as noted in equation (11.1). A quantum associated

with high frequency (high wave number) will contain more energy than a quantum associated with a low frequency (low wave number). Energy levels of the atoms and molecules vary. The amount of energy required to boost an electron from ground state to the first level (orbital) is not the same as that required to boost it to the next higher level. With small wave number (long wave length), the energy available may be insufficient to boost an electron into the very high orbitals. There may not be enough energy to permit the molecule to dissociate. The effect of sufficient available energy to responsive atoms as discussed elsewhere is (1) to supply energy to excite the atom through all levels (orbitals) including ionization; (2) to provide further energy to increase the vibration, the rotation, or translation of the molecules; and (3) to provide sufficient energy to dissociate the atoms in a molecule.

Energy to dissociate a bond of a molecule will be found in a quantum existing at a specified frequency or higher. Therefore, most bond energy equations essentially provide the frequency (or wavelength) band or continuum at which a specific amount of thermal or photoelectric energy becomes available. As indicated previously, absorption of a quantum of energy greater than the amount required for dissociation provides a source of energy for the dissociation with the remainder being distributed throughout the molecule, producing increased vibration, rotation (spin), translation, and flexing, as well as perhaps additional electron excitation.

The excitation energy is

$$E = N h \nu = N h c \lambda^{-1} \quad , \quad (11.2)$$

where  $N$  is the Avagadro number and  $c$  is the light speed. These provide the molar energy of the photons or light quanta. The following statement provides a numerical form in terms of the wavelength:

$$E = (119.627 \lambda^{-1}) \text{kJmol}^{-1} \quad , \quad (11.3)$$

where  $\lambda$  is in nm (Wayne (1988) and Condon (1958)).

The above discussion indicates that packets of energy, different for different frequencies, may be absorbed by an atom, resulting in the upgrade of an electron to a higher orbital. Such packets of energy, photons (light quanta) may also be absorbed and increase the vibrational, rotational, and translational states without a change in orbit. The more complex the molecule, the more this can happen.

In a sense, the absorption of an energy packet provides a new atom. Potentially, it has a new or different chemical reactivity. As Wayne (1988) indicates, photochemical studies may not have much in common with the thermal reactions of the parent, ground states species. Without question, the consideration of absorption and emission of photons tremendously expands the potential chemical states and reactions; e.g., as Wayne (1988) portrays, potential results involving the absorption act and the fate of the electronically excited species. Although the energies absorbed can later be emitted back along the same schematic pathway to the environment, whatever it might be, this is not necessarily what happens. The potential for energy absorption is particularly great in the upper reaches of the atmosphere. Here, the entire set of energies available from solar radiation may be tapped by atoms, molecules, or variants of these. Once energy has been absorbed by a molecule, such as AB, there may be (1) ionization ( $AB^+ + e$ ), dissociation ( $A+B$ ), direct reaction with a third atom or molecule, E, to obtain ABE,  $AE+B$ , or charge transfers forming radicals  $\bullet AB^+ + \bullet E^-$  or  $\bullet AB^- + \bullet E^+$ , isomerization AB to BA, intermolecular energy transfer with CD ( $AB + :CD$ ), intermolecular energy transfer, a radiationless transition  $AB^+$ , luminescence  $AB + h$ , or interaction with a third body M with physical quenching. Wayne (1988) uses  $NO_2^*$  dissociating with  $NO + (\bullet O \bullet)$  and the reaction  $O_2^* + O_3$  going to  $2O_2 + (\bullet O \bullet)$ , where the asterisk signifies an excited molecule. Figure 11-2 (after Wayne (1985, 1988)) illustrates the above described distribution and redistribution of absorbed energy. That distribution may take any of any one or more channels indicated.

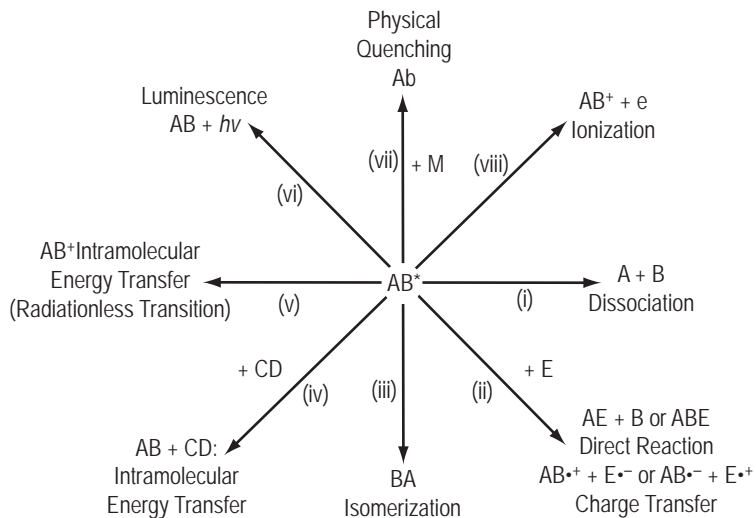


Figure 11-2. Absorption, distribution, and redistribution of energy (with permission, Clarendon Press, courtesy of Wayne (1985, 1988)).

As there are many molecular species and there are many orbitals for each atom and molecule, the potential for reactions is great in this potpourri or mélange of active and reactive participants. Once a gas molecule enters this maelstrom of energies for the quanta to which it is responsive, it will encounter, absorb, and emit specific quanta from and to the entire range presented. The region of the atmosphere where most of the electronic configurations change is known as the ionosphere. However, the foregoing discussion reveals that these changes occur throughout the atmosphere. In fact, ion formation may be one of the least important with the formation activity and reactivities (demise) of the radicals. Other applicable references are Chapman (1951), Phister et al. (1960), Dutsch (1969), and Coulson (1975).

## 11.2 Atmospheric Constituents

### 11.2.1 Comments

Interaction among the interacting structures of Earth, the Moon, and the Sun system drives Earth's climate. In part, the atmospheric constituents, including the radiatively active trace gases, are intimately involved. The primary radiant source is the Sun.

The word element encompasses two meanings in this publication: (1) Climate element, such as precipitation, temperature, sunshine, etc., and (2) the atomic or molecular makeup of the universe, including that of the Earth. Here, meaning of climate element involves both (1) and (2).

In the introduction, some disparaging remarks were made about one's abilities to view and understand much more than one climate element (variate) at a time. This inability is no less evident than in the extrication of information from the "potpourri" of the atmospheric gases (major, minor, trace, and synthetic). There, all sorts of chemical interactions and reactions among these gases, and the photochemical associations with incoming solar radiant energy, produce a mélange of new chemical compounds, including positive, neutral, and negative ions or free-radical forms. In order to isolate and perhaps better understand, for the moment, the situation with respect to each gas, these are presented separately. The reader will note seemingly unnecessary repetitions; i.e., some equations for the reactions of one gas are repeated in other equations, for the same gases may be involved.

As one surveys the literature and the tabular presentations of the latest research results, the number of gases being treated increases rapidly. This simply reflects the *mélange* effect. To adequately begin to understand the import, it will be necessary to develop some clustering or grouping concepts beyond those now being presented. Rationales and techniques exist. Considerable research and work remain. If one attempts to track reactions, physical and chemical buffering will develop and decay as the interactions continue, leading to some sense of frustration in trying to depict the everchanging structures.

Gases of the atmosphere and other constituents may be classified broadly into five categories:

- (1) Major gases
- (2) Minor gases
- (3) Trace gases
- (4) Synthetic gases
- (5) Solids, aerosols, or particulates.

There may be disagreement with these arbitrary categories because of different interpretations of the meanings and their variability. Development of ultrasensitive detection and measurement techniques have revealed previously undetected and therefore unmeasured constituents. Even today, it is suspected that there are complexes in such tiny amounts that routine detectors prove to be inadequate. See Hopke (1988). In environmental work, there are many instances where, though it is known or suspected that certain gases exist, these are below detectable limits and are so reported. Where only one element is considered, estimates of occurrence in the region below the instrumented detection capability may be made by any number of arbitrary algorithms. Where two or more elements are considered, arbitrary assignment of occurrences in the appropriate dimensional space is complicated indeed. Additionally, though some emission and absorption spectra have been detected in stellar radiation and absorption in intergalactic and interplanetary space, all of these may have not been identified yet in the terrestrial continuum. The converse is also true.

Thermodynamic considerations imply that pressure and energy exert major control of any element or combination of elements. The state may be solid, liquid, or gaseous. These may be in radical, ionic, atomic (molecular), or other form. At a certain combination of pressure and temperature (energy), the three molecular states (solid, liquid, and gas) may coexist at the so-called equilibrium triple point. Likewise, under certain conditions, two of the states may exist at a separation boundary: solid-liquid, solid-gas, or liquid-gas. Along the solid-gas equilibrium line, sublimation and the reverse process, condensation may occur. That is, the solid may pass into the gas form, or the gas form may pass into the solid form, without going through the liquid phase. Some frost occurs in this manner. For some elements, there is one point—the critical point—where the liquid and gaseous states become indistinguishable. Any increase of temperature or of pressure, or of both, results in no change. The transition boundary simply disappears.

Molecular sizes, masses, and electronic configurations do have their effects on the state existence. Among the many texts which discuss these, reference may be made to Sanderson (1960).

### **11.2.2 Origin of the Chemical Elements**

An abbreviated discussion of the origin of the universe is given here. Through the ages, origin models have been proposed. Many have already been discarded. Development and demise of models are the products of increasing knowledge. Each one requires an act of faith for consideration and acceptance.

Only one model is mentioned here, though there are other extant models. In this model, the presumption is made that a kernel of pure energy began essentially an instantaneous transformation from energy to matter.

Within the first minuscule time element, transition proceeded to the formation of the many subatomic particles, to vast clouds of hydrogen, some helium, and perhaps some lithium. The transition is presumed to not be smooth and remains nonsmooth today. We see this nonsmoothness in the dynamics associated with the formation and demise of constellations, galaxies, and stars.

All known chemical elements in their many different forms are strewn throughout the known universe and in an isolated local sense, the Earth. The atoms may be in ground state or excited conditions. Chemically, each is different. As noted previously, hydrogen itself is composed of subatomic forms such as the proton, electron, etc. Here, the basic units of the building of the elements were and are vast clouds of hydrogen. The greater the amount of hydrogen available, the more rapid the development and demise of the stellar forms. Those most rapid in their development undergo greater implosion and explosion or rebounding shock waves. It is in these, in a sense, catastrophic features, that the major portion of the elements beyond iron are synthesized or created. Stars of lesser fuel resources may never pass beyond the synthesis of iron, for iron is an energy sink. Our star, the Sun, is a medium star and is not expected to reach the iron stage. Though all elements can be synthesized in the young hydrogen star, the amounts are relatively minuscule.

Most stars today may be considered to be second or more likely later generation stars. That is, they are coalescing points for clouds of nuclear debris created in the catastrophic events of prior stellar explosions and in the interaction of shock waves from several long-gone stars (interstellar shocks) (Duley and Williams (1984)). Thus, a second-generation star will have, to some extent, all created elements embedded in the primary cloud of hydrogen. Thus, the entire solar system is expected to contain residue of many prior stellar explosions and to accrete residue of those and that of future stellar explosions.

It is to be expected as time goes on and techniques and instrumentation are improved that more and more elements will be detected and identified in interplanetary and interstellar space as well as in and on the stars, planets, and moons. The point is made, that in the winnowing processes existent in the galaxies, the star systems and the planetary systems with their quite variable ranges of physical properties of temperature, pressure, gravitation, and radiation, homogeneous clusters will tend to form within these heterogeneous systems. Thus, in a sense, individualities will be developed. For example, Earth is different from Mercury in many ways and similar in other ways.

For a view on the development of interstellar chemistry, see Duley and Williams (1984). They present tables of many of the chemical and physical reactions in interstellar radiation fields. Zeilik (1982) indicates that the search for interstellar gases and their structural pieces started in earnest in the 1960s. The first molecule to be identified was ( $\bullet$ OH). Zeilik lists 60 molecules, inorganic but mostly organic, which had been identified presumably by 1980. Identification of more molecules and of dust debris will continue. See also Wayne (1985, 1988) for discussions of planetary atmospheres.

### 11.2.3 Gases

**11.2.3.1 General Discussion.** Subtly, the meaning of the word “greenhouse” has changed. Now, the enclosure may be any unit, a building, an ocean, an atmosphere, a planet, a solar system, a galactic system, and even the universe. Respectively, the enclosing medium may be a quasi-crystalline compound such as glass, a layer of gas, the atmosphere, planetary space, interplanetary space, and intra- and inter-galactic space of the edges of the universe. The writer must define and the reader must understand the greenhouse to which reference is being made.

Within the confines of the Earth system a gas may be expected to serve just as the glass in an ordinary greenhouse. The concept here is that the gas is collected into one layer composed of nothing but the gas. Under a stipulated temperature and pressure configuration, the depth or thickness of the layer may be measured. A measure is the meter-atmosphere or any derivation thereof, such as the atm-cm (Lapedes (1978)). The layer of gas,

whether confined in a thin, isolated layer or mixed throughout a deep, diffused layer, serves the same purpose and acts in the same fashion as the glass of the ordinary greenhouse. In the first, it is unconfined; in the second, there is confinement. Just as the characteristics of glass changes with its composition, so does the characteristics of Earth's atmosphere. For example, pure silicon dioxide or quartz glass is transparent to ultraviolet. Admixture of lead or other adulterants change the transmittance, absorption, and emission characteristics. So too changed are the characteristics of the Earth's atmospheric responses to changes in its constituency. Similarly, the Earth's oceans' characteristics change. The changing of the atmospheric constituency is the prime reason for the inclusion of this extended subsection and other subsections on trace gases in section 11. These changes are important in the pollution and greenhouse aspects.

Abetti (1957) indicates that helium was discovered on the Sun at the 1868 eclipse and that it was not discovered on Earth until Ramsey isolated it from gases extracted from the mineral cleavite. Helium has no known triple point and requires temperatures far beyond atmospheric temperatures to absorb and emit energy. Other examples are the chlorofluoromethanes (CFMs) which exist in the Earth's atmosphere from known synthesis and introduction by man. Natural processes produce one of the simpler methanes, methyl chloride ( $\text{CH}_3\text{Cl}$ ) (Cowan et al. (1973), Watson et al. (1980), and Warneck (1988)). See Warneck (1988) for a detailed discussion. Whether all of these existed in the atmosphere naturally is not known. Therefore, for the moment, these are classified as synthetic gases in the foregoing classification.

Ramanathan, Cicerone, Singh, and Kiehl (1985) report on potential climatic effects of the radiatively active trace gases that have been detected in the atmosphere. These and the many other studies emphasize the importance of these gases as climatic elements in themselves. Thus, the measures of climate, climatic effects, and past, present, and future climates are expanded beyond the temperature, pressure, moisture, and radiation generally considered as climate elements. Ramanathan et al. (op. cit.) report on more than 30 trace gases and indicate that the effects are equivalent to those of carbon dioxide. The UN World Meteorological Organization (WMO) (1982) summarizes the issues as of 1982 and provides a listing of many studies that have been made on the subject of the trace gases.

Boatman et al. (1988) report on the beginning of climatology of trace gases in the atmosphere (1987). McPeters (1988) develops a climatology of only one gas, nitric oxide, in the upper stratosphere, mesosphere, and thermosphere. The period was 1979 through 1986. Eisele (1988) reports on ion chemistry, the natural and anthropogenic negative ions in the troposphere. That many of these trace gases are sensitive to each other and to time of day is evidenced by many researchers who, wherever possible, maintain their observations over the 24-hr period.

Krysell and Wallace (1988) report that the CFMs—dichlorodifluoromethane ( $\text{CCl}_2\text{F}_2$ ) and trichlorofluoromethane ( $\text{CCl}_3\text{F}$ ), methyl chloroform ( $\text{CH}_3\text{CCl}_3$ ), and carbon tetrachloride ( $\text{CCl}_4$ )—now have been measured in the Arctic Ocean deep waters. They further stipulate that oceanic and atmospheric inventories of these compounds result from known anthropogenic (man-made) releases. These make good transient tracers of oceanic circulation for these are essentially nonreactive under these conditions. This may not be necessarily true and probably is not true in the stratosphere and upper atmosphere. There, pressure is low and energetic ultraviolet radiation can weaken the bonding. This would allow halogens to escape and interact with the energetic, reactive, unstable ozone molecules. Jeffers and Wolfe (1989) and a response by Wallace and Krysell (1989) discuss the hydrolysis of carbon tetrachloride ( $\text{CCl}_4$ ) under varied temperature and pH. They further indicate that methyl chloroform ( $\text{CH}_3\text{CCl}_3$ ) would be lost over 40 yr and would not serve as a long-term tracer as would carbon tetrachloride ( $\text{CCl}_4$ ). As usual, the plea is made for more research. The halogenated alkanes will be discussed later in a separate section.

The following tabular presentations of gases are based on the research and surveys of others. Haurwitz (1941) attributes a portion of his table on the main constituent gases of the atmosphere to Paneth (1937) and presents an abbreviated form. Tables A-11-2 through A-11-7 contain this abbreviated form and other gases with additional information on melting and boiling points where available at standard atmospheric pressure from Sanderson (1960),

Huheey (1978), and U.S. Department of Defense (DoD), AFCRL (1985). Many texts and references provide some, if not all, of the same information. Attribution is also made to Guggenheim (1950), Glueckauf (1951), Zemansky (1951), U.S. DoD AFCRL (1960), Chang (1986), Weast (1988), and Warneck (1988).

This section deals with the atmospheric gases which are probably most familiar and some which are not so familiar. This does not belittle the importance of some of the other gases or some of the other elements or their compounds. There are important particulate materials in the atmosphere, on land, and in the oceans. Small enough to remain in suspension in the air, these particulate materials may be purged from the air by coalescence processes or precipitation scavenging. Saharan dust has often been carried over northern Europe and over the Central American regions. In fact, many of the suspensoid particles act as coalescing points for water vapor and other absorbing gases. Some of these are simple grains of quartz (silicon dioxide) or granitic material. Others are molecular aggregates of chemical combinations of various gases. Others are crystals of various salts raised in dust from desiccated regions. Still others are the molecular aggregates of various gases and their reactions, such as photolytic reactions, with their environment. Such gases are produced in automobile use of petroleum fuel. Peroxyacetyl nitrate, so noticeable as a participant in the smog phenomena and an eye irritant, is one of these. See Stephens et al. (1956), Stephens et al. (1961), and Leighton (1961). Ozone ( $O_3$ ) is a byproduct of these reactions.

Yet, others may be ejected in droplets from the oceans resulting from wind and wave action. These ionic forms upon evaporation may be changed to crystals or hydrated crystals and lifted by mechanical and convective action. In either form, these may serve as landing (adsorbing) platforms for water vapor molecules and other gases. Water droplets and crystals (ice) serve as landing and chemical reaction platforms for atmospheric gases, including water vapor. When grown to sufficient size and weight, the atmosphere may be unable to support them and physical deposition occurs. Collision with shrubbery, trees, and the hills and mountains permits some deposition.

Tabular data are arranged as follows:

Table A-11-2: Main constituent gases of the atmosphere

Table A-11-3: Minor and some trace gases of the atmosphere

Table A-11-4: Additional trace gases of the atmosphere

Table A-11-5: Synthetic gases

Table A-11-6: Aerosols, including particulates, SMIC (1971), AFCRL (1985, p. 18–19)

Table A-11-7: Some comparative weights, melting points (m.p.), and boiling points (b.p.) of some chemical compounds, some of which are constituents of the atmosphere.

It may be noted in table A-11-7 that with increasing weight (or increasing carbon atoms) of the alkanes (methane, ethane, etc.), the boiling points (b.p.) increase. The melting points of the even-numbered alkanes are higher than the next higher odd numbered homologues. Though the alkanes are chains, they are not linear chains; i.e., the chains are zig-zag chains. The melting and boiling points for the methyl ( $CH_3$ ) halides increase with increasing weight. The same holds true in both tables A-11-5 and A-11-7 for the carbon tetrahalides, though the boiling points for carbon tetrabromide and carbon tetraiodide are not given (see below). The carbontetrahalides tend to decompose at high temperatures.

It is not likely that methyl iodide, carbon tetrachloride, carbon tetrabromide, and carbon tetraiodide will exist in the atmosphere as gases for a long period of time due to their high melting and boiling points. If these halides were carried aloft as solids or liquids by convection and mechanical action, ultraviolet radiation or near ultraviolet radiation could supply sufficient energy to volatilize the molecules. However, the chances are great that the molecule itself earlier would be decomposed and would no longer be recognizable as a unit. Some of the very reactive halides would be released.



It must be emphasized here that the values given in the foregoing tables may not agree precisely with other sources. The reasons are varied. Most occur because better determinations are always being made. For example, it is not always possible for an investigator to know the 100 percent natural makeup of a molecule. There will be a few values given which do not agree with some other individual sources. Any errors must be attributed to this writer.

An atom or a group of atoms may behave as a unit through a variety of reactions. Each singleton or group of atoms is called a radical. A radical which has unpaired electrons is called a free radical. The cleavage or breakup of the radicals requires energy. Some energy is available from heat and chemical reaction but a great, essentially nonending source is solar radiation. The solar radiation covers a wide range of energies useful in many reactions within the total atmosphere and hydrosphere.

A word about the free-radical symbol used in this paper: A closed circle or dot ( $\bullet$ ) is used to denote an unpaired electron. In this paper, such a dot is placed ahead of the symbol unless space requirements suggest another location such as after or to the side of the symbol. For example, take the chlorine ( $\text{Cl}_2$ ) and oxygen ( $\text{O}_2$ ) molecules which are in themselves radicals. Chlorine has one unpaired electron while oxygen has two unpaired electrons. These molecules—( $\text{Cl}_2$ ) and ( $\text{O}_2$ )—when broken produce ( $\bullet\text{Cl}$ ) and ( $\bullet\text{Cl}$ ) plus ( $\bullet\text{O}\bullet$ ) and ( $\bullet\text{O}\bullet$ ), two free radicals of chlorine and two free radicals of oxygen. In this paper, positiveness (+) and negativeness (−) symbols are generally not used. The total space around a radical is available for placement of a dot or dots. If other symbol placements are used, their position takes precedence over the placement of the free-radical dot ( $\bullet$ ).

Wuebbles et al. (1989) provide a well-balanced treatment of the role of atmospheric chemistry in climate change. This appears in the *Journal of the Air and Waste Management Association* (JAPCA), formerly the *Journal of the Atmospheric Pollution Control Association*. As was mentioned in the introduction to this publication, it seems necessary to treat climate in a many dimensional context, not in the linear sense and one element at a time. The Wuebbles et al. (op. cit.) paper discusses the many reactions among gases of the atmosphere. The sources and sinks of some of the gases are indicated. Their discussions center around several major topics, namely chemical interactions involving hydroxyl radical ( $\bullet\text{OH}$ ) and ozone in the troposphere and ozone and water vapor in the stratosphere. Hydroxyl radical ( $\bullet\text{OH}$ ) also is produced in the upper reaches of the atmosphere by photolytic action on water. The radical form may be written with prior or post dots such as  $\bullet\text{H}$  and  $\bullet\text{OH}$ . Ozone ( $\text{O}_3$ ) is created there also from oxygen ( $\text{O}_2$ ). The two molecules almost instantaneously mutually destruct each other. Wuebbles et al. (op. cit.) provides useful, well arranged tabular material augmenting the information in tables A-11-2 through A-11-7. As they indicate, hydroxyl radical ( $\bullet\text{OH}$ ) is the primary tropospheric scavenger (or prey, as the case may be) of carbon monoxide ( $\text{CO}$ ), methane ( $\text{CH}_4$ ), the halocarbons, and the sulfur compounds. They also indicate that to understand and integrate all the interactive effects in detail will require global tropospheric-chemical models not yet available. Such modeling will require a base knowledge of the hydroxyl radical. Such is not yet available, and as far as is known, no such database development has been initiated for this very important interactor.

Rhodes et al. (1980) and Crutcher, Rhodes, Graves, et al. (1986) provide discussion and techniques pertaining to studies of the statistical distributions of simultaneous climatological (meteorological) and chemical data. These are discussed in more detail in a following section. Wuebbles et al. (op. cit.) will enable one to obtain a better understanding of the complexities of the situation. Perhaps the reader will realize the polylemma situation and comprehend better the limitations of explorations on one item at a time. This does not belittle the excellent and detailed research being done in this fashion. Undoubtedly, the researcher hopes that a particular research approach will yield the one and only answer. Thus, though carbon dioxide ( $\text{CO}_2$ ) is one of the main radiative gases of the atmosphere and though an increase of carbon dioxide may increase the temperature of the troposphere, such warming may set in motion other events which tend to nullify, if not negate, the warming effect insofar as the effects on the animate and the inanimate. There is a driving need to know.

**11.2.3.2 Sources and Sinks.** Knowledge of the sources and sinks of the atmospheric gases is a prime requisite to an understanding of climate in other than the usual statistical or descriptive terms. The very dynamics of the system is made more understandable. For example, carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>) are both sinks for carbon (C) and oxygen (O<sub>2</sub>). Atmospheric losses to outerspace represent a sink for all gases. The flow is more rapid for some. Oceanic absorption and/or absorption of carbon dioxide (CO<sub>2</sub>) is a sink. Biosynthesis, using carbon dioxide (CO<sub>2</sub>), nitrogen (N<sub>2</sub>), oxygen (O<sub>2</sub>), and water (H<sub>2</sub>O) in both land and sea plants and animals represents a considerable sink. Lost to space, the gases are unrecoverable. Stored in plant and animal tissue, including the skeletal and exoskeletal features, they are later recoverable. These sinks are future sources. Carbonates formed in chemical synthesis, and not necessarily biosynthesis, form another sink which later may become a source. Changing alkalinity of the oceans or subduction of sea floor carbonates with later exhalation by volcanoes represents a change from sink to source. Another change from sink to source is the burning (oxidation) of plant and animal tissues and of stored hydrocarbons in coal and gas.

**11.2.3.3 Clathrates.** Another sink-source for atmospheric gases is now mentioned. In section 11.7 in the discussion on methane (CH<sub>4</sub>), this sink-source is the gas clathrate hydrates. Appropriate references are provided in that section. All atmospheric gases, and many others, are subject to the encaging (clathrating) of a gas molecule by a water structure. Where this structure is crystalline they are known as gas clathrate hydrate ices. Such encaging is not unique to water. Where the encaging structure is quartz (SiO<sub>2</sub>), the clathrate silicates are known as clathrasils. Clathrasils are not discussed to any extent here. But, it is interesting to note these remarkable features of water and sand. The hydrogen bonding in water in the gas clathrate hydrates seemingly, in general, precludes the encaging of any hydrogen-bonded gas. There is no chemical interaction between the water and the gas. Once encaged, the gas can enter no chemical reaction and therefore remains, by any chemical means, undetectable. The almost totally inert gases such as argon (Ar), krypton (Kr), and xenon (Xe) are the favorite of those who study clathrate structures by physical means. Where the encaging material is carbon, the name clathracarbs seems to follow. Perhaps another, more relevant identification can be synthesized. Again, see section 11.7.

### 11.3 Atmospheric Losses

The makeup of the atmosphere has evolved over a considerable time period and continues to evolve. See Walker (1977), Wayne (1985), and Warneck (1988). Presumably at one time, the amount of oxygen was almost 30 percent, which would be poisonous to some forms of life today. The anaerobic life could presumably adjust to this balance as was probably the case aeons ago and as in the case near the thermal vents in the sea floor. Nitrogen presumably would have been below 70 percent, allowing for some percentage of all the other atmospheric gases. Today, the relative amounts are near 78 and 20 percent for nitrogen and oxygen, respectively. Zeilik (1982) describes another scenario. As cited by Warneck (1988), Jeans (1916) first described the thermal escape of a gaseous constituent from the Earth system on the basis of kinetic theory.

The Maxwellian distribution for the motion of gas molecules assumes that the motion is isotropic; i.e., independent motions in the  $(x,y,z)$  space. The term Rayleighian often is applied to the distribution of the molecular speeds whether on a line  $(x,y, \text{ or } z)$  or a plane  $(x,y), (x,z) \text{ or } (y,z)$  or in the  $(x,y,z)$  space. If these are noncentral and the motions are correlated, the assumption of isotropic motion is not valid. Most texts on thermodynamics or on statistical mechanics show various derivations of the central Maxwellian or Rayleighian distributions. Groenewoud, Hoaglin, and Vitalis (1967) provide tables and Crutcher (1967b) provides application for the central and noncentral bivariate distributions which may be called  $X^2$  distributions in two space; i.e., two degrees of freedom. The noncentral case can occur with addition or extraction of energy.

In the three-space of the atmosphere in the case of the molecules or in the case of dissociated molecules, the ionized atoms, or the free radicals, the average path between collisions is called the mean free path. At the very diffuse or a critical level edge of the exosphere, there exists a region which may be labeled the exobase (Walker

(1977)). Above this base, collisions of molecules are not frequent, while below the base, collisions are more frequent. At this exobase, the molecules still have a Maxwellian distribution of velocities. As Walker (1977) and Jeans (1954) indicate, the exobase location is an arbitrary one. They define the exobase to be the altitude from which a fraction  $1/e$  of molecules traveling straight up with enough energy to escape Earth's gravitational attraction will do so without any further hindering collisions. Warneck (1988) provides an excellent discussion.

Hydrogen, helium, and other gases continue to be exhaled or outgassed by the seemingly solid Earth. Hydrogen perhaps exists in solid, liquid, or gaseous form deep in the Earth's interior. It also becomes available in the dissociation of the water molecule into its hydrogen radical and hydroxyl radical components, ( $\bullet\text{H}$ ) and ( $\bullet\text{OH}$ ), particularly in the upper reaches of the atmosphere. A large source of helium exists in the vast pools of natural gases which lie near the Earth's surface. Radioactive disintegration processes produce helium. Methane comprises the larger part of these pools of natural gases. Known production rate would increase the accumulation of hydrogen and helium relative to the total atmospheric content. However, there is no significant accumulation. One possible answer is the continual loss of the lighter gases which have risen to the exobase and then pass through and above the exobase. The assumption is that the effective Maxwellian distribution of molecular velocities assures that some will escape the pull of Earth's gravity. In these regions, the molecules essentially have ballistic trajectories, many of which return to the exobase, but some do not and are lost, essentially forever, insofar as Earth is concerned. There are four sources for helium, two of which are primordial and radiogenic. In the latter, the fissioning of radioactive material expels alpha particles (radiation), which on gaining electrons, form helium atoms.

Ratios of gases may be used to keep check on the production, accumulation, and abundance of the outgassing materials. These ratios remain relatively constant. For further details, the reader may refer to any number of texts, such as Walker (1977); Wayne (1985), "Chemistry of Atmospheres"; Chamberlain and Hunter (1986), "Theory of Planetary Atmospheres"; Budyko, Ronov, and Yanshin (1987), "History of the Atmosphere"; and Warneck (1988), "Chemistry of the Natural Atmosphere." Through convective mechanical turbulence and diffusion processes, all other gases will reach the exosphere and the exobase. The Maxwellian (Rayleighian) distribution applies to each of these also. But due to their sizes and weights, and therefore densities, these will not be as easily lost by the Earth. This writer assumes but is not certain that the Maxwellian distribution is representative of the velocities of the dissociated molecules at the exobase region.

The *Handbook of Geophysics and the Space Environment*, DoD, DAF, AFGL (1960, 1985) contains good bases for the formulation of an extensive climatology of the atmospheric gases. This continuum contains the atmospheric structure and the distribution and characteristics of the many gases in molecular, atomic, radical, and ionic form which reaches from the surface to the outer atmosphere.

## 11.4 Gas Radiative Characteristics

### 11.4.1 General

Each chemical element has its own radiative characteristics in absorption and emission. If each gas were able to act as a true blackbody, which it does not, it would effectively reradiate energy as received. Monoatomic, diatomic, and triatomic molecules such as O, O<sub>2</sub>, or O<sub>3</sub> and their ionic forms have their own absorption and emission characteristics. Signatures of these are seen in the observed and recorded spectra.

Solar radiation is effectively an output of all the energies given up as the various elemental forms condense; i.e., as electrons cascade downward through discrete energy levels (shells or orbitals) of the atomic structure. Existence of gases between an energy source, such as the Sun or other star, and an observing point, such as the Earth, is implied when those gases absorb energy and deplete the energy such that expected radiation receipt does not occur. Thus, clouds or obstruction region effects occur in any or all regions of the electromagnetic spectrum. The

occurrence of a few void spectral frequencies or wavelengths may lead to identification of intergalactic, interstellar, or interplanetary gases or material, provided that their spectral signatures are known. These absorption spectra (lines) are known as Fraunhofer lines.

### 11.4.2 Absorption Spectra for Selected Gases

The foregoing discussion and general tables provide a reference base. The mixture of gases which constitute the atmosphere is complex. Spectral characteristics help to identify the constituents of the atmosphere. Molecular spectra are more complicated than atomic spectra.

This discussion is essentially general and limited. The following subsection will discuss some, but not all, of the individual gases. The order will follow more or less that presented in the tabular material. As thermal energy is supplied in a beam to an atom and as energy is absorbed by the atom in small packets (quanta), an electron or electrons is (are) elevated from a ground state to a higher energy level (shell or orbital) farther from the nucleus. These jumps may be from any level (orbital) to any higher energy orbital or completely outside the attractive influence of the nucleus. This absorption depletes the energy of the beam in the frequency or wavelength of the spectrum to which the atom or molecule is responsive. This region of depletion in the spectrum will then appear relatively less intense than before or if completely absorbed, will not appear in the beam which has passed through the gas. In a bright, original spectrum of all frequencies (wavelengths), these regions will now be void of such frequencies (wavelengths). These spectral absorption regions will appear as dark lines or will be missing.

Energized or excited atom(s), with no further incoming energy, will tend to revert to the original ground state of nonexcitation. Reversion is accompanied by release of quanta in dropping from the higher energy levels or orbits through all levels, in single level steps or in jumps of several steps at a time. The energy excess which becomes available at each step or jump is emitted as radiation. Each step or jump exhibits its own characteristics. In a relative sense, there will be bright emission lines.

The absorption and emission lines (dark and/or bright), called Fraunhofer lines, help to identify the particular atom. These characteristics have also been discussed in section 4. The series of radiation jumps mentioned were the Brackett, Paschen, Balmer, and Lyman series. Ions and molecules are similarly affected and may be identified by their absorption and emission spectra. However, it is more difficult in the molecular case as more energies are absorbed and emitted via translational, rotational, vibrational, and electronic motion (Liou (1980)). Where the electrons exist in a high, intense excitation state, even to the point of escape, the cessation of input energy may permit the capture of (a) loose electron(s) and a radiative cascade of energy releases in inward steps and jumps that create a wide range of frequencies (or wavelengths) in the emission spectra. For discussions of fluorescence, phosphorescence, and chemiluminescence, see Wayne (1988). The Aurorae Borealis and Australis is one example. So-called neon lights are other examples. Those interested in these features may wish to examine the shells, energy states, or the orbitals through which the electrons pass. Substantive information is available in almost any current chemistry or physics textbook.

In the best of cases, it might be expected that a line spectrum would appear as a Dirac delta spike, the narrowest possible line. However, this purest line is not observed. These lines are broadened, according to Chantry (1984, p. 176), by radiative damping, collisional, and Doppler broadening. Pressure broadening is a part of the second. Chantry (op. cit.) provides over 1,500 references on aspects of long-wave optics. As indicated previously, the atmospheric mixture of gases is complex. From an examination of infrared transmission characteristics, it may be difficult for the beginner and even the experienced worker to identify that portion of the absorption attributable to any one gas or a group of gases. Additionally, it is difficult to assess just how much energy is absorbed or emitted. Thus, from a basic elementary tutorial point of view, it is helpful to examine the characteristics of single gases first. This involves preparation of pure gas samples or so-called synthetic atmospheres. All the gases themselves are not

synthesized but a sample of one and only one gas is prepared. Following this, binary and tertiary mixtures of gases may be prepared and utilized. Howard, Burch, and Williams (1955, 1956) present infrared transmission characteristics of some “synthetic” atmospheres, each atmosphere consisting of one gas only. Figure 11-3 (from Howard (1960)) shows the near infrared absorption spectra of CO, CH<sub>4</sub>, N<sub>2</sub>O, O<sub>3</sub>, CO<sub>2</sub>, HDO, and H<sub>2</sub>O over the range of 1 to 15 (10<sup>3</sup> to 15 × 10<sup>3</sup> nm) or (10<sup>4</sup> to 650 cm<sup>-1</sup>). Additionally, at the bottom of this figure is shown a simulated, typical absorption spectrum for solar radiation through a clear sky. The absorption runs from zero percent at the top of each small subfigure to 100 percent at the bottom. The small figures are arranged so that the reader may either actually or visually combine the absorptions. For example, slightly below 8 μ, about 1,250 cm<sup>-1</sup>, CH<sub>4</sub>, N<sub>2</sub>O, and H<sub>2</sub>O, as well as other gases, to some extent absorb infrared and emit infrared radiation. Emission is omnidirectional. As another example, in order of magnitude of absorption and emission in the range of 4–5 (2,500–2,000 cm<sup>-1</sup>), there are CO<sub>2</sub>, N<sub>2</sub>O, H<sub>2</sub>O, CO, and O<sub>3</sub> species.

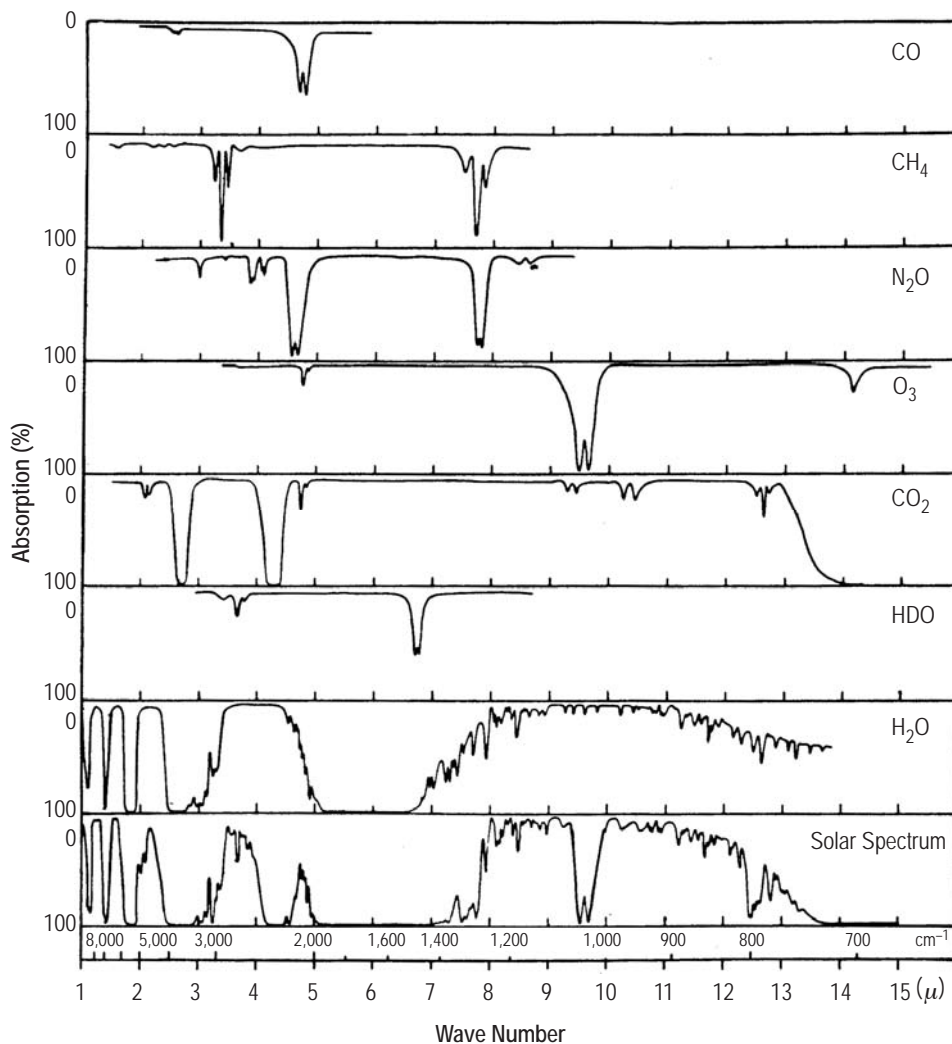


Figure 11-3. Infrared transmission of some “synthetic” atmospheres (with permission, AFCRL (1960), courtesy of Howard (1960)).

The major gases nitrogen ( $N_2$ ) and oxygen ( $O_2$ ) are not treated in detail. These are nonpolar. Except for their bonding energies, in the molecular sense, these are nonresponsive. However, in their excited states and in their dissociated ionic, radical, and electronic configuration forms, they are quite responsive and active.

Here is an important point as shown by Howard, Burch, and Williams (1956) and cited by Goody and Yung (1989). Transmission of energy in the bands, assuming no correlations, is the product of the transmission percentages of the individual gases. The conditions of temperature, pressure, and path length must be the same. The importance is that as a gas is added to a mixture, the combined effect is greater than the simple addition. Thus, with the addition of atoms and molecules with modified electronic structures, the transmission effects are changed.

Following a different approach, Kyle and Goldman (1975) present an interesting aspect of infrared absorption characteristics of the atmosphere. Figure 11-4 (a) and (b) show examples of the results of computing atmospheric transmission characteristics rather than making the observation (Kyle and Goldman (1975)). The technique, based on actual observations and reports of many investigators, does allow future investigators to compute expected transmission features for any particular gas or mixture of gases at altitudes above the surface. The gas relevant characteristics used are those of  $H_2O$ ,  $CO_2$ ,  $O_3$ , and  $N_2O$ ;  $CH_4$  are those of vibration and rotation; and the pure rotational transitions of  $H_2O$  and  $O_3$  as well as those of  $O_2$ . The levels selected for computation were the 4, 14, 30, 40, 45, and 54 km which divide the selected atmosphere into seven homogeneous layers and have effective pressures of 0.29, 1.2, 2.5, 8.3, 36, 106, and 390 mb. Three spectral resolutions used are 0.1, 5, and 20  $cm^{-1}$ . Tables for each of the gases above are provided by Kyle and Goldman (1975), if one wishes to work at one time with only one of the above gases. Figure 11-4(a) and (b), respectively, exemplify the use of most of the gases mentioned above. The resolution is 20  $cm^{-1}$ . The wave numbers are, respectively, 2,500–1,250  $cm^{-1}$  and 1,250–zero  $cm^{-1}$ . These figures are for radiation transmittance from the top of the atmosphere to the specified height levels. Therefore, though the shapes are similar to those in figure 11-3, the ordinate scales are inverse, transmittance versus absorption. Figure 11-3 (Howard (1960)), for absorption covers the wave number range from 1,000 to 750  $cm^{-1}$  (1–15  $\mu$ ). Reference may also be made to Howard, Burch, and Williams (1955) and to Burch, Howard, and Williams (1956). Note the broadening of the line spectrum contributes to the widening of the spectrum with the decrease in altitude above the surface of the Earth. Such broadening is brought about by (1) damping of vibrations, (2) perturbation due to absorbing molecule collisions as well as absorbing and nonabsorbing molecules, and (3) the doppler effect created by the different velocities of atoms and molecules. See Liou (1980) and Chantry (1984). Although outside the scope of this section, the reader is referred to the spectra of night airglow emission discussed by Phister, Keneshea, Oliver, et al. (1960). There, some of the ionic characteristics of radiation absorption and emission may be examined.

There are many other references and texts concerning the all-important phenomenon of solar radiation and the absorption and emission characteristics of the terrestrial (tellurian) atmosphere. Among the many, a few are noted: (1) Berry, Bollay, and Beers (1945); (2) Mitra (1948); (3) Kuiper (ed., 1949); (4) Malone (ed., 1951); (5) U.S. DoD, DAF (1960, 1985); (6) Kruse, McGlaulin, and McQuistan (1962); and (7) Murray and Goldman (eds., 1981). Many of the above have extensive bibliographies. Additionally, a few others are provided in section 4 of this publication. See also McClatchey et al. (1973), Rothman and McClatchey (1976), Rothman (1978, 1981), Rothman et al. (1978, 1981, 1983a, 1983b), and USAF, AFGL-TR-88-0177 (1988). The reader may purchase electronic computer magnetic tapes which contain information that can be used to produce combined spectra. These tapes were and are produced under the auspices of the U.S. DoD, USAF (1975 to present); they are available at cost from the National Climatic Data Center in Asheville, NC.

### 11.4.3 Bonding Energies

In the development of molecular configurations, some of the atoms or groups of atoms are more closely bonded or less closely bonded than others. For example, the carbon molecule,  $C_2$ , can be triply bonded. These bonds can be broken, dissolved, or cleared by the supply of and the absorption of a certain quanta of energy. That is,

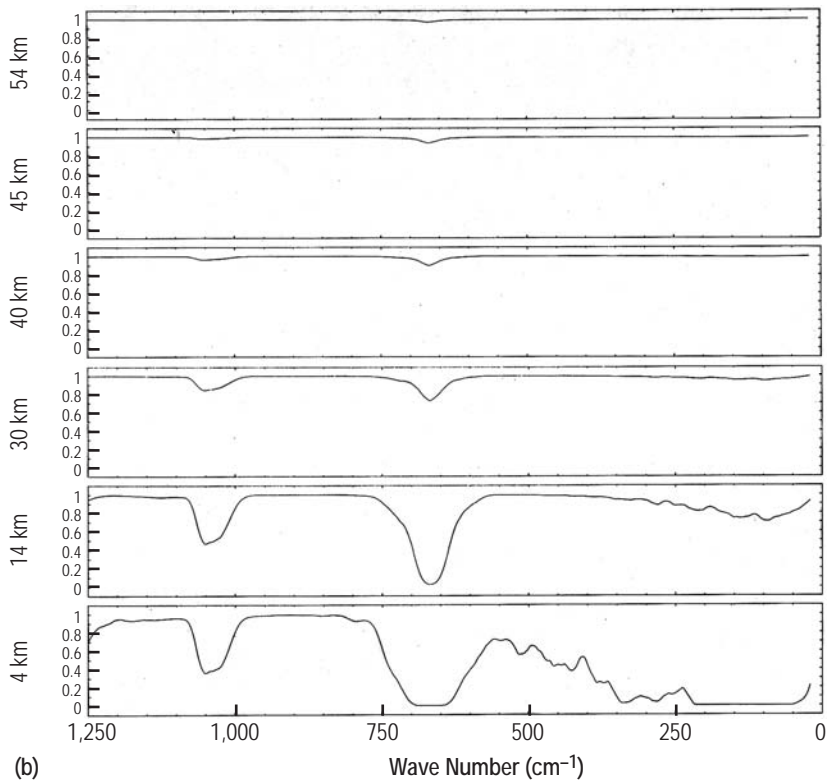
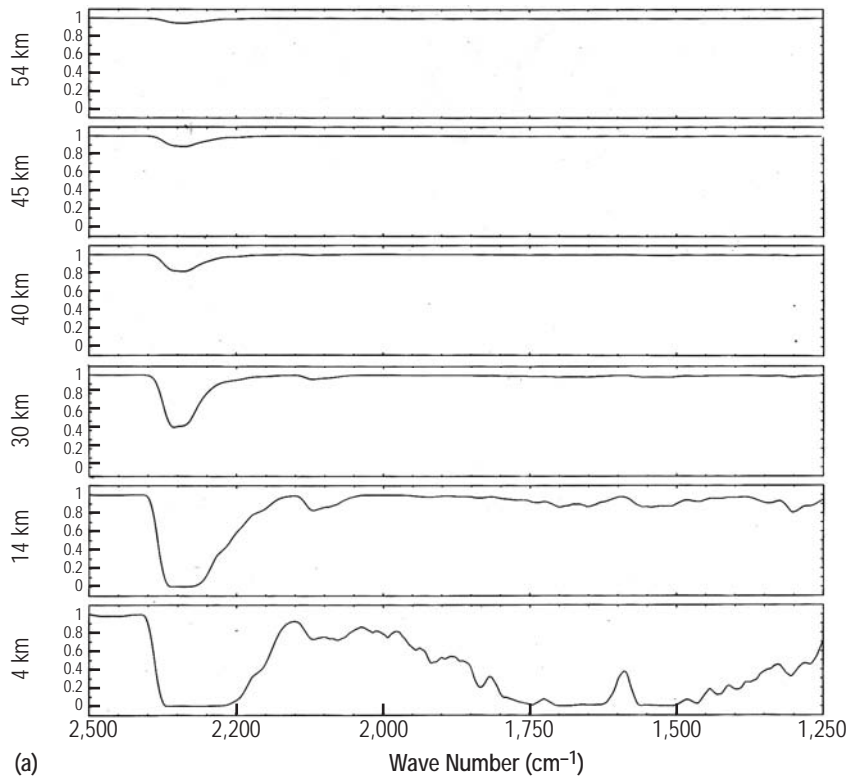


Figure 11-4. Example of computing atmospheric transmission characteristics rather than making the observation, from wave number (a) 2,500 to 1,250 ( $\text{cm}^{-1}$ ) and (b) 1,250 to zero ( $\text{cm}^{-1}$ ) (after Kyle and Goldman (1975)).

the carbon molecule can be dissociated if the precise amount of energy can be supplied in quanta. As indicated previously, the molecules must be responsive. If not responsive, the molecule simply remains unaffected even though energy is available. To break the triple bonds of carbon  $C_2$  ( $C \equiv C$ ),  $812 \text{ kJ mol}^{-1}$  of  $C_2$  gas are necessary. The quanta available are in the electromagnetic spectrum at  $\approx 147 \text{ nm}$  wavelength,  $6.80 \times 10^4 \text{ cm}^{-1}$  wave number, or about  $2 \times 10^{15} \text{ Hz}$ . Such a packet of energy is only available in the ultraviolet region or x-ray regions and below in wavelength shorter or higher in wave number or Hz.

Tables A-4-1 through A-4-3 and other tables in appendix A show relationships among some energy units. Figure 11-1 also shows some of these same relationships among energy units. The units are electron volts (eV),  $\text{kcal mol}^{-1}$ ,  $\text{kJ mol}^{-1}$ , wave number ( $\text{cm}^{-1}$ ), frequency (Hz), wavelength (nm), and types of radiation. The vertical strip, representing the human visual region of the electromagnetic spectrum, is expanded to indicate the color wavelengths ranging from about  $400 \text{ nm}$  ( $0.4 \mu$ ) to about  $770 \text{ nm}$  ( $0.77 \mu$ ). The lower left-hand portion of the figure represents the six items mentioned above. The numbers, in powers of ten, are to be used with the appropriate multiplier for each item. For example, for item 5, wavelength, at  $1 \times 10^7 \text{ nm}$ , the multiplier is 1. The wavelength is then  $10^7 \text{ nm}$ . Interpolation in any logarithmic or exponential field is difficult so some care is necessary. Here, as elsewhere, the wavelength of  $1 \times 10^7 \text{ nm}$  is associated with  $1.23934 \times 10^{-4} \text{ eV}$ ;  $2.85915 \times 10^3 \text{ kcal mol}^{-1}$ ;  $1.19627 \text{ kJ mol}^{-1}$ ;  $1 \text{ cm}^{-1}$ ; and  $2.998 \times 10^{10} \text{ Hz}$ . Likewise,  $2.998 \text{ Hz}$  associates with a wavelength of  $10^{17} \text{ nm}$  and a wavenumber of  $10^{-10} \text{ cm}^{-1}$ .

Table A-11-12 provides the bonding (disbonding) energies for several atmospheric gases. See Kerr and Trotman-Dickenson (1981) and Weast (1988) and other editions for information on bonding energies for other gases. For a more detailed and comprehensive treatment on bonding, see Murell, Kettle, and Tedder (1985). A molecule can have several bonds. Those under consideration are indicated. In the case of nitrogen, a triple bond is indicated, while for oxygen, a double bond is implied. The dissociation of these bonds requires a certain amount of energy—thermal or photoelectric. If such bonds are reestablished, an equivalent amount of energy is released. In addition, the wavelengths (in nm) of the minimum disbonding energies are indicated where such energies become available. Excess energies are available in shorter wavelengths. Excess energies absorbed will be redistributed in the molecular complex.

The cleavage of bonds depends upon the type and location of the bonds and upon ambient conditions. The very generous mixture of gases—major through trace—provides a situation where it is difficult to decide just where to start to assess the structure and activities of the atmosphere. Here, we start with incoming solar radiation to provide the energies and with the three gases—nitrogen ( $N_2$ ), oxygen ( $O_2$ ), and argon (Ar). The first two are nonpolar while the third is a singlet. These, in themselves, are not too reactive. For this reason, ozone ( $O_3$ ) and water ( $H_2O$ ) are invoked here though each earns a separate subsection.

Each of the above molecules must be photolyzed and allowed to react to provide information later. Subsections are, therefore, numbered and identified briefly as nitrogen ( $N_2$ ) (11.5), oxygen ( $O_2$ ) (11.6), argon (Ar) (11.7), methane ( $CH_4$ ) (11.8), carbon dioxide ( $CO_2$ ) (11.9), ozone ( $O_3$ ) (11.10), chlorine ( $Cl_2$ ) (11.11), water ( $H_2O$ ) (11.12), halocarbons (HCFs and CFCs) (11.13), radon (Rn) (11.14), and aerosols (11.15). Methane reflects the hydrocarbons, carbon dioxide encompasses carbon monoxide (CO), and water includes hydrogen and hydroxyl groups. The halocarbons could be called carbons or methanes (alkanes). As indicated previously, absorption of the appropriate photoelectric energies will excite or ionize the atoms or molecules or may cleave the molecules with a distribution of excess energies if any. Minimum ionization energies are generally greater than the dissociation (cleavage) energies. Wayne (1985, 1988) provides a table containing ionization potentials for a series of atmospheric species. The values are given in electrovolts, their equivalents in  $\text{kJ mol}^{-1}$ , and their equivalent wavelengths. (See also Weast (1988)). Wayne (1985, 1988) also provides an excellent discussion of the increased reactivities of excited atoms and the development of exothermic tendencies in subsequent reactions. In following discussions, an asterisk superscript

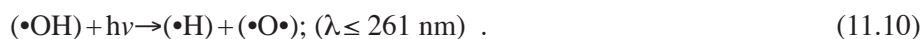
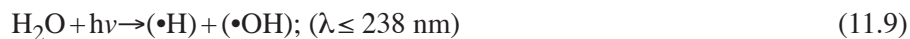


will denote an excited atom. The extent of excitation is not shown. Stages of excitation are generally shown by alluding to the shell structure changes. Only one has been used here and that is the excited oxygen atom ('O).

Now let us examine a few of the reactions within the nitrogen-hydrogen-oxygen community. Atoms are used to form the molecules but here the molecules are used as a source of atoms. The photolytic disbonding of the oxygen and ozone molecules are one example. The well-known Chapman model for ozone formation is used (Chapman (1930)). Also see Wayne (1985, 1988).



The invocation of a third body, M, is made to resolve the dissipation of energy from excited atoms so that they can form bonds. Such energies must be removed or forming molecules will fly apart before they form a bond that holds. Because nitrogen (N<sub>2</sub>) and oxygen (O<sub>2</sub>) form almost 99 percent of the atmosphere, the probability is high that most third-body molecules involved will be nitrogen or oxygen molecules. However, this cannot be certain for there are other atoms and molecules present. However, the third body must be available and present before the forming complex shakes apart. It removes the excess energy in collision with the joining atoms. In the equations above, lone oxygen atoms and ozone triplets, O<sub>3</sub>, are formed and canceled. Not as much energy is required to disrupt the ozone molecule as the oxygen molecule, so the longer wavelengths (lower frequencies) of the ultraviolet make their play. Water (H<sub>2</sub>O) may be decomposed as in



Discussion of these same equations will be made in sections on oxygen and water.

Table A-11-13 presents some atmospheric gas absorbers and emitters with the corresponding spectral regions (Smith (1985)). These are the trace gases with the exception of oxygen (O<sub>2</sub>). Presentation order is that of subsequent subsections of section 11.

See figure 11-1 to change GHz to wavelength in nm or use the following formula:

$$\text{Wavelength } (\lambda) \text{ nm} = c/\text{Hz} \quad (11.11)$$

where *c*, the speed of light in nms<sup>-1</sup>, is 2.998 × 10<sup>17</sup>. The absorption and emissivity of these gases are the basis of many remote sensing techniques, especially those which use Earth satellites. Please note that while the halocarbons are yet small in amount in the atmosphere, their proportional amounts are increasing due to man's activities.

Note also these responses in the regions of the infrared and microwave regions. The use of the trace gas responses to interrogation by satellite or remote sensing is another facet of the trace gas importance in climate research.

## 11.5 Nitrogen

Nitrogen ( $N_2$ ) as a gas constitutes roughly about three-quarters of the Earth's present atmosphere whether consideration is volumetric or mass. A few of its chemical and physical characteristics are given in table A-11-2. Due to its preponderance in the atmosphere, it acts as a buffer to many chemical reactions but is also involved in reactions of its own. It may be used to exclude oxygen and thereby act as a preservative. However, there are several hydrides and oxides which, if too abundant, become a problem in environmental situations to plant and animal life. Some of these are NO (nitrogen oxide),  $N_2O$  (nitrous oxide),  $NO_2$  (nitrogen dioxide),  $NO_3$  (nitrate),  $NH_2$  (nitrogen dihydride),  $NH_3$  (ammonia), and  $HNO_3$  (nitric acid), which can be classed as trace gases. The general formula for the oxide is  $N_yO_x$ , where  $y, x$  ranges upward from 1 to 5. At this point, it is essential to remark that with these or other chemical combinations, there are some that do not or cannot exist.

An electronically-excited  $N_2$  molecule will react with an oxygen molecule ( $O_2$ ) to form ( $\bullet N_2O$ ) and a free atom ( $\bullet O\bullet$ ) (Wayne (1985)). In this compound ( $\bullet N_2O$ ) (nitrous oxide), see figure 11-3, some absorption is indicated from 2 to 9  $\mu$  ( $5,000$  to  $1,100\text{ cm}^{-1}$ ) with strong absorption near 4.75 and 7.75  $\mu$  ( $2,100$  and  $1,250\text{ cm}^{-1}$ ). Figure 11-5, derived from figure 11-3, visually places the ( $\bullet N_2O$ ) absorption curve close to the simulated atmospheric absorption curve. This permits easier comparison. As  $CH_4$  (methane) absorbs and radiates near 7.75  $\mu$  ( $1,250\text{ cm}^{-1}$ ), the characteristics bolster those of ( $\bullet N_2O$ ). Of course, atomic and ionic forms of nitrogen have their individual absorption and radiation characteristics. These are mentioned here but are not discussed in detail. At an altitude of around 100 km, both nitrogen and oxygen are affected by ultraviolet radiation. Each molecule may be broken (dissociated) into atomic form. Later, precipitating energetic electrons to either or both of these two provide the visual and magnetic phenomena of the polar lights, the aurorae. The infrared radiation absorption and emission of the nitrogen is relatively small. Nitrogen, the molecule with triple bonds, is essentially nonpolar. Its main energy absorption in the ultraviolet or higher wave number regions tends to increase the atomic vibration until the bonds are weakened and broken. It is similar to oxygen in this respect. The reader is referred to U.S. DoD, AFCRL (1960, 1985), Chantry (1984), and Warneck (1988). The last two references discuss nitrogen and its compounds at some length. Included are discussions of the latitudinal and diurnal variability. These provide reference spectra of many of the compounds. The production and dissociation of ozone is also discussed. Rhodes et al. (1980), in examples of clustering of eight variates, shows the relatively well-known general inverse relationship of the nitrogen oxides and ozone; i.e., when one is high, the other is low. One removes the other. With absorption of radiation, ozone is changed to an ( $O_2$ ) and ( $\bullet O\bullet$ ); the ( $\bullet O\bullet$ ) coalesces with the oxide of nitrogen.

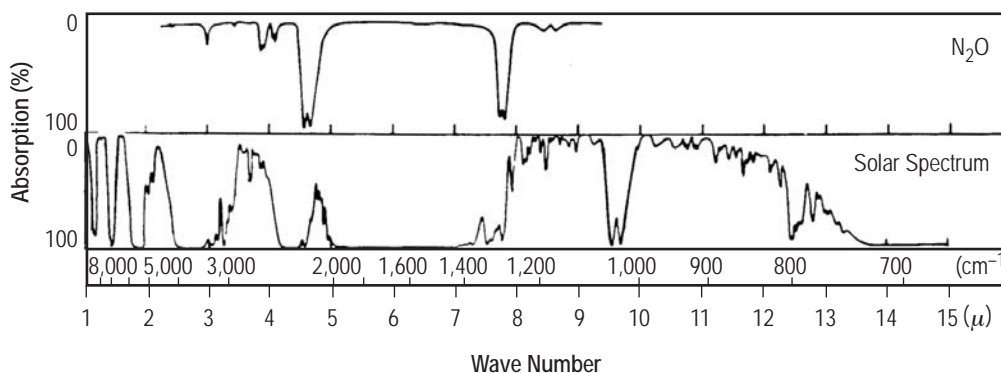


Figure 11-5. A modification of figure 11-3. The upper portion is the nitrous oxide ( $N_2O$ ) infrared absorption spectra. The lower portion is the simulated atmospheric solar absorption spectra. The range is from 1 to 15  $\mu$  (courtesy of Howard (1960)).

The term “free radical” refers to any atom or group of atoms such as a molecule that has one or more unpaired electrons. This term or its shortened form “radical” is occasionally used elsewhere in this publication. It is applicable to any element. Although a “free radical” has no positive or negative charge, it is highly reactive because of its unpaired electron(s). Ions do have positive and negative charges and are known as “cations” and “anions.” The free radicals may initiate reactions which in turn release other “free radicals,” not necessarily the same. These repetitive steps may continue until the free radicals are destroyed or trapped. The number of steps which occur before no free radical is produced is known as the “chain length.” This chain length varies with the type of free radical and the reacting counterpart. In the free-radical chlorination of a hydrocarbon, such as methane, the chain length may be  $\approx 10,000$  (Fessenden and Fessenden (1986)).

It is iterated here that the modifications of the electronic configurations of the nitrogen atoms (molecules) as well as for oxygen atoms (molecules) occurs as described previously. Also, the many avenues of action remain open just as for the general molecule (AB) used as a previous example. Khalil and Rasmussen (1988) discuss the trends and global mass balance of this active gas, nitrous oxide ( $N_2O$ ), over the past 3,000 yr. This becomes particularly important in the dissolution of ozone. Nitrous oxide occurs naturally in the atmosphere but its amount is being increased by man’s activities. Based on data cited by Hileman (1989), the rising trend of nitrous oxide levels during the period 1977–1986 over the Northern Hemisphere ranges from about 300 to about 306 ppbv.

Equations (11.12) through (11.15) (courtesy of Wayne (1990)) pictures the steps in which nitrogen oxides are involved in the oxidation of methane. Here again, the use of molecules of the gases of the atmosphere is involved many times without prior discussion. Such discussion will follow. There are, of course, other pathways by which methane may be oxidized. The schematic here with ( $\bullet NO$ ) and ( $\bullet NO_2$ ) is cyclic in the regeneration of the hydroxyl group ( $\bullet OH$ ) which is needed to initiate the oxidation here. The source of the hydroxyl group may vary but here it is regenerated.

There are many potential reactions open for ( $\bullet NO_2$ ). Nitrate radicals can form as in



where this reaction is a sink for ozone ( $O_3$ ). The ( $\bullet NO_3$ ) radical may be photolyzed as follows:



or it may in a three-body collision with ( $\bullet NO_2$ ) form  $N_2O_5$  as



The second of the above reactions may be classed as a multireaction while the third is a sink for the NO. Because it is available for immediate photolytic dissolution, it may be better described as a holding cycle, though it constitutes only  $\approx 5$  percent of the  $NO_x$  (Wayne (1985)). But it does represent a later source ( $\bullet NO_2$ ) and ( $\bullet NO_3$ ), the first being a destructive agent for ozone as shown in reaction equation (11.12). Also as Wayne (op. cit.) notes, other holding cycles become important particularly for nitric acid formation:



The formation of the nitric acid reservoir as above holds about one-half of the stratospheric  $NO_x$ . See Hanson and Mauersberger (1988a,b). Their studies are directly related to the chemical reactions involved in the chlorine destruction of ozone in the Antarctic and Arctic polar regions in conjunction with ices of the chemical reservoirs associated with the extremely low temperatures of the polar stratospheres.

## 11.6 Oxygen

Oxygen ( $O_2$ ) is the second major gas contribution to the mass and volume of the Earth's atmosphere. It is absolutely essential to all life as it is known. In its atomic form ( $\bullet O \bullet$ ), particularly in its radical form, it is highly reactive; i.e., it is extremely corrosive or destructive. With nitrogen, it forms compounds  $N_x O_y$  where  $x$  and  $y$  may take on any value up to 5. Several of the oxides were mentioned in the foregoing section but  $N_2 O_5$  (nitrogen pentoxide) is mentioned here. These oxides are all trace gases but, because of their activities, are important in the atmosphere. In excess, the oxides are involved in many pollution problems, such as those of sulfur (S) associated with water and scavenged by precipitation. Warneck (1988) has an interesting discussion on the budget and cycles of oxygen (p. 615) and indicates that there is much uncertainty in the budget. According to Warneck (op. cit.), the major reservoirs of oxygen are the sulfates in sea water and in evaporites and  $Fe_2 O_3$  in sedimentary rocks. Of the total oxygen available on Earth, in the seas, and the atmosphere, only  $\approx 4$  percent (one 25th) is in the atmosphere; as such, it constitutes about one-fifth of the atmosphere. As Warneck further indicates, the oxygen and the ozone are the principal absorbers of radiation in the ultraviolet region. He presents the oxygen absorption as a function of the wavelength. The prominent features as he shows are the Schumann continuum (115–175 nm), the Schumann-Runge band (175–208 nm), and the Herzberg continuum (208–235 nm).

The oxide of oxygen,  $O_3$ , or ozone, is a trace gas but its importance is such that it is given a special section (sec. 11.6) for discussion. Harries (1977) provides a stratospheric emission spectrum from on board a Comet aircraft at an altitude of 12 km. Included are spectral peaks of  $O_2$ ,  $O_3$ , and  $H_2 O$ . Weak spectral peaks for oxygen are noted at about wave number 12, 14, 23.5, and  $25.5 \text{ cm}^{-1}$ .

Oxygen ( $O_2$ ) is a very stable gas within the atmosphere. Machta and Hughes (1970) state, "All reliable oxygen data since 1910 fall in the range of 20.945–20.952 percent by volume." The instrumental accuracy (bias) was  $\pm 0.006$  percent. This stability and its responsiveness to radiation allows it to be used with satellite probes to sound the structure of the atmosphere (Christy (1990)).

As indicated previously, the nonpolar molecule of oxygen, as in nitrogen ( $N_2$ ) is relatively inactive. Photolytic or other reactions will decompose the oxygen ( $O_2$ ) molecule into its very active oxygen ( $\bullet O \bullet$ ) atoms. These may be excited or ionized. Along with the very active components of the decomposition of water ( $H_2 O$ ) into the hydrogen ( $\bullet H$ ), hydrogen ( $H_2$ ), hydroxyl ( $\bullet OH$ ), and oxygen ( $\bullet O \bullet$ ) parts, an even higher potential for reactivity is introduced.

Already indicated is the general formula  $N_y O_x$  for the nitrogen oxides. Also, there is the general formula for the hydrogen oxides ( $H_y O_x$ ). Because of their activities, these assume great importance in atmospheric processes. These are discussed in section 11.12.

## 11.7 Argon

The noble gases were previously thought to be nonreactive; however, a few compounds involving the noble gases have been synthesized, with the exception of helium.

Argon is one of the six known, previously called, "Noble" gases. These, along with their approximate atomic masses, are to the nearest unit mass: (1) Helium (He, 4); (2) Neon (Ne, 20); (3) Argon (Ar, 40); (4) Krypton (Kr, 84); (5) Xenon (Xe, 131); and (6) Radon (Rn, 222). In the chemical Periodic Table, this group is the 8A series. Helium (He), argon (Ar), and radon (Rn) are products of radioactive decay of the uranium (U, 238) and the thorium (232) series. Radon (Rn) remains radioactive with a half-life of  $\approx 3.82$  days. There is continued resupply of helium (He) lost from the gravitational field and the radon (Rn) and other radioactive decay. Helium (He), due to its atomic mass of 4, can escape and presumably does escape the Earth's gravitational field. Argon exceeds the average molecular weight of the atmosphere, about 28.5, by  $\approx 40$  percent.

Argon (Ar, 36-40), including isotopes, does not escape easily from the Earth's gravitational field. Argon (Ar) continues to increase though very slowly. At the present time, Argon (Ar) constitutes almost 1 percent of the Earth's atmosphere; generally, this is quoted near 95 percent. Haurwitz (1941) citing Paneth (1939) provides values of 0.93 and 1.28 for the percent by volume and mass, respectively, in the atmosphere. Glueckauf (1951) citing Moissan indicates the relative worldwide constancy of  $\approx 0.9343$  percent of the atmosphere with a standard deviation of 0.0006. Warneck (1988) provides a mixing ratio,  $\approx 9,340$  ppmv, essentially the same as shown by Gotz (1951).

Essentially nonreactive, Argon (Ar) aids in electric incandescent and fluorescent light bulbs and tubes, manufacture and use in smelting processes to prevent oxidation processes, and in any other process where it hinders contamination. Ionization of argon (Ar) by alpha, beta, and gamma-ray production and its chemical nonreactivity allows it to be used in detectors and counters of radioactive disintegrations. Argon (Ar), as well as other lone or combined gases, plays an important role in laser (Light Amplification by Stimulated Emission of Radiation) techniques and use. See Herbert (1980), Huheey (1978), Chang (1986), Warneck (1988), and Wayne (1988).

### 11.8 Methane (an Alkane Hydrocarbon)

Methane ( $\text{CH}_4$ ), the fully reduced form of carbon (C) is important to mankind for at least three reasons:

(1) Methane ( $\text{CH}_4$ ), in an ever-increasing demanding world, is a fuel, raw material, and energy source.

(2) Methane ( $\text{CH}_4$ ) is a physically, chemically, and radiatively responsive constituent of the atmosphere. Carbon dioxide ( $\text{CO}_2$ ) and water ( $\text{H}_2\text{O}$ ) are the ultimate gas products of its oxidation. All three absorb and emit radiation in a large part of the infrared electromagnetic spectrum.

(3) Methane ( $\text{CH}_4$ ) is available as a major constituent of natural gas from underground sources which include gas fields, permafrost, and/or petroleum sources, from coal fields (mines), from anaerobic gas formation; from thermo and calagenic gas formation; and from synthetic production.

As a fuel and energy source, methane ( $\text{CH}_4$ ), on burning, provides heat and subsequently work. It serves as a raw material for many industrial processes including the development of other fuels. It is a clean-burning gas with primary products of carbon dioxide ( $\text{CO}_2$ ) and water ( $\text{H}_2\text{O}$ ). However, if atmospheric air is used as the oxygen source, and there is insufficient oxygen for complete combustion, carbon monoxide (CO) is formed as are the other oxides of nitrogen. Lethal quality develops when oxygen is excluded and these gases become suffocants. Methane ( $\text{CH}_4$ ) is explosive in confined spaces with oxygen. Uncontrolled, it is dangerous to life and property. The lethal quality of carbon monoxide (CO) for man and most animals is well known. It binds to hemoglobin, thus blocking the uptake and transport of oxygen by blood circulation. Also, the oxides of nitrogen ( $\text{N}_y\text{O}_x$ ) are participants in atmospheric chemical reactions and, in general, are considered pollutants. Due to their small amounts in the atmosphere, each is categorized as a trace gas, though its radiative absorption and emission characteristics affect the thermal balance of the atmosphere. These are important. The byproducts of methane's ( $\text{CH}_4$ ) combustion processes carbon monoxide (CO), carbon dioxide ( $\text{CO}_2$ ), water ( $\text{H}_2\text{O}$ ), and the oxides of nitrogen ( $\text{N}_y\text{O}_x$ ) spread the radiative absorption and emission over the infrared spectrum, thereby augmenting methane's effects.

Water photolyzed or otherwise broken into the hydrogen and hydroxyl forms furnishes the ubiquitous and very reactive hydroxyl ion which also initiates destruction of the  $\text{CH}_4$  (methane) molecule. The ubiquitous hydroxyl ion ( $\bullet\text{OH}$ ) derives from many chemical interactions. (Quite ubiquitous it is; i.e., it is found nearly everywhere. Yet it is so reactive that it is solitary only for short intervals of time.) It reacts with methane ( $\text{CH}_4$ ), oxidizing methane which creates water ( $\text{H}_2\text{O}$ ) and a methyl ion ( $\bullet\text{CH}_3$ ) which is also very reactive. This process is a source of water in the lower stratosphere. Jones et al. (1986) estimates that this is a contribution in excess of 6 ppm. Later, photolysis in the upper stratosphere again photolyzes the water molecules providing hydrogen ( $\bullet\text{H}$ ) and hydroxyl ions ( $\bullet\text{OH}$ ). See also section 11.12 for further discussion on water and the hydroxyl and hydrogen groups.

The U.S. Bureau of Mines, Department of Energy, Morgantown, WV, maintains a distribution center for information on petroleum minerals and gases, all participants in energy sources. One of its publications, an extensive bibliography, will lead the interested researcher to other equally extensive bibliographies and to other pertinent papers. It is the use or venting of natural gas and the use of fossil fuels for energy which provide one of the steps in potential changes in the Earth's climate. Just what the subsequent steps will be in the very co-reactive climate system is not known. There are proponents for dissimilar scenarios.

Figure 11-3 from Howard (1960) shows at the bottom a simulated atmospheric infrared absorption spectrum of solar radiation. For comparison, laboratory absorption spectra of a few individual selected gases are shown. The two major gases— $N_2$  and  $O_2$ —are nonpolar and absorb only small amounts of energy. Only one oxide of nitrogen spectrum, that of  $N_2O$ , is shown.

Figure 11-6, a modification of figure 11-3 for easier comparison, shows only the simulated atmospheric solar and the methane ( $CH_4$ ) infrared absorption spectra. Table 11-1 shows some of the physical properties of methane ( $CH_4$ ). In addition, some physical characteristics of methane's constituent atoms or molecules, carbon and hydrogen, are provided. Reference will be made to the table later.

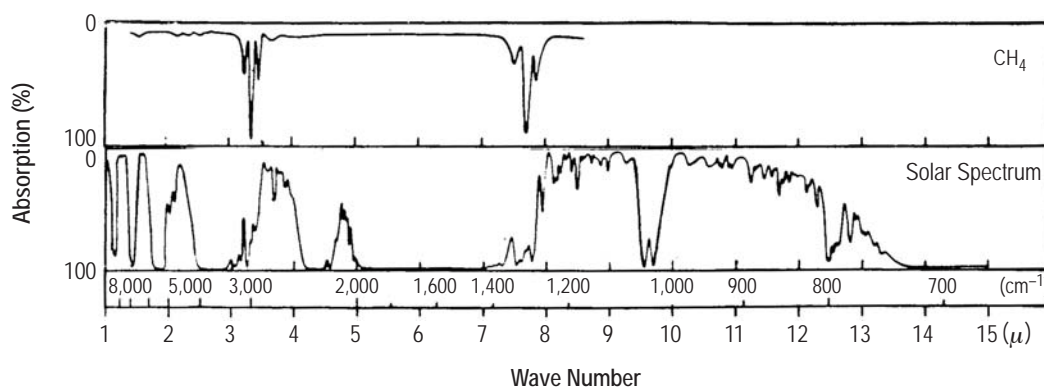


Figure 11-6. A modification of figure 11-3. The upper portion is the methane ( $CH_4$ ) infrared absorption spectra. The lower portion is the simulated atmospheric solar absorption spectra. The range is from 1 to 15  $\mu$  (courtesy of Howard (1960)).

Duley and Williams (1984) (p. 111) provide a scenario for the formation (syntheses) of methane ( $CH_4$ ) within interplanetary, interstellar, and intergalactic regions. Presumably, such syntheses occur within the systems themselves. Once formed, it has its own unique characteristics. Methane ( $CH_4$ ) radiation absorption in the far ultraviolet and in the range of 105 to 150 nm ( $9.5$  to  $6.6 \times 10^4$   $cm^{-1}$ ) results in its dissociation into molecular forms ( $\bullet CH_2 + H_2$  (Wayne (1988)) or ( $\bullet CH_3 + \bullet H$ ), ( $\bullet CH_2 + H_2$ ), and ( $\bullet CH + (H_2) + \bullet H$ ) (Duley and Williams (op. cit.)) who attributes this to Okabe (1978). As the latter indicate, this could result from the sublimation of solid methane from dust grains which may serve passively;  $C_{60}$ , a buckminsterfullerene, will be discussed later. Further speculation is that these dust grains may be  $C_{60}$  molecules. Warneck (1988) and Wayne (1988) also discuss these same reactions. Wayne (op. cit.) indicates that photoionization occurs at wavelengths  $<96.7$  nm. Duley and Williams (op. cit.) also provide an approximation to the measured radiation flux in interstellar transparent regions. The point here is that the photodissociation (photolysis) of the simple molecules of methane ( $CH_4$ ) and other atmospheric gases provides myriads of progeny which then are free and available to participate in the formation of various substances and compounds. As association-dissociation continues, the overall radiation absorption and emission characteristics change. These along with chemical reduction and oxidation (redux) processes induce a continued

Table 11-1. Methane (CH<sub>4</sub>) physical properties.

Element (atom or molecule)	Hydrogen (H <sub>2</sub> )	Carbon (C)	Methane (CH <sub>4</sub> )
Weight (atomic or molecular)	2.016*	12.01 <sup>†</sup>	16.042
Density at 0 °C	0.0899*	—	0.7168*
Melting point (°C)	-259.14*. <sup>†</sup>	>3550 <sup>†</sup>	-184.0* -182.48 <sup>†</sup>
Boiling point (°C)	-252.8*. <sup>†</sup>	4827 <sup>†</sup>	-161.5*. <sup>†</sup>
Critical density (g.cm <sup>-3</sup> )	0.0310*		0.162*
Critical temperature (°C)	-239.9*. <sup>**</sup>		-82.5* -83.0 <sup>**</sup> -82.1 <sup>†</sup>
Critical pressure	12.8 <sup>†</sup>		45.8 atm (bar)*. <sup>**,†</sup>
Triple point (°C)	-259.39 <sup>†</sup>		45.6 <sup>**</sup>
Percent contribution to the atmosphere:			
1. By volume	50 × 10 <sup>-6</sup> *		1.4 × 10 <sup>-4</sup> *
2. By weight	3.48 × 10 <sup>-6</sup> *		7.75 × 10 <sup>-5</sup> *
Reduced thickness (atm-cm, NTP)	39.9768 × 10 <sup>-2</sup> *		1.11935*

\*AFCRL (1985), \*\*Chang (1986), <sup>†</sup>Weast (1988), <sup>‡</sup>Greenwood and Peiser (1988).

Note: This isotope <sup>12</sup>C atomic mass is defined as 12 exactly. The value of 12.01 given in the table is the average of the contributions of all carbon isotopes presently measured for the Earth.

change of atmospheric physical, including radiative, properties, and chemical states. Each atmospheric gas becomes important from consideration of its active and passive states, as well as its buffering and catalytic potentials.

The following more extensive discussion for methane (CH<sub>4</sub>) is not intended to depreciate the importance (influence) of the other gases already discussed and those to be discussed. The extended discussion, including the subsection on clathrates, eliminates the need to discuss all gases in such detail. All gases serve as sources and sinks of energy as long as these absorb and/or emit energy. Warneck (1988) gives a 13-step description for the thermal oxidation of methane (CH<sub>4</sub>) to the intermediate products and to the end products of carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O). Table 11-2, taken from Warneck (1988) with permission, illustrates the reactive mechanism. Free radicals may be intermediate products but these are so reactive that they exist as such for only a very short time. In addition, other free radicals from photodissociation processes may accelerate or disrupt this oxidation process. For example, a hydroxyl group (•OH) may initiate the process.

Please note that cycling is not unusual in chemical reactions. However, in trace gases, these cycling processes are very important. In each trace gas discussion, cycling will be a feature. Note here that the hydroxyl radical (•OH) recycles; i.e., it is used and later produced to be used again.

### 11.8.1 Methane Sources

The sources of methane (CH<sub>4</sub>) on Earth are:

- Presolar and solar: Syntheses in large stellar processes.
- Thermogenesis: Decomposition and thermal transformation of plant and animal (organic) material at depths by heat and pressure.

Table 11-2. Reaction mechanism for the thermal oxidation of methane (adapted from Warneck (1988)).

(a)	$\text{CH}_4 + \text{O}_2 \rightarrow (\cdot\text{HO}_2) + (\cdot\text{CH}_3)$	Initiation step
(b)	$(\cdot\text{CH}_3) + \text{O}_2 \rightarrow \text{CH}_2\text{O} + (\cdot\text{OH})$	
(c)	$(\cdot\text{OH}) + \text{CH}_4 \rightarrow \text{H}_2\text{O} + (\cdot\text{CH}_3)$	First chain
(d)	$(\cdot\text{OH}) + \text{CH}_2\text{O} \rightarrow \text{H}_2\text{O} + (\cdot\text{CHO})$	
(e)	$(\cdot\text{CHO}) + \text{O}_2 \rightarrow (\cdot\text{HO}_2) + \text{CO}$	Second chain
(f)	$(\cdot\text{HO}_2) + \text{CH}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + (\cdot\text{CHO})$	
(g)	$\text{H}_2\text{O}_2 + \text{M} \rightarrow (\cdot 2\text{OH}) + \text{M}$	Chain branching
(h)	$(\cdot\text{OH}) + \text{CO} \rightarrow \text{CO}_2 + (\cdot\text{H})$	
(i)	$(\cdot\text{H}) + \text{O}_2 + \text{M} \rightarrow (\cdot\text{HO}_2) + \text{M}$	Third chain
(j)	$(\cdot\text{HO}_2) + \text{CO} \rightarrow \text{CO}_2 + (\cdot\text{OH})$	
(k)	$(\cdot\text{OH}) + (\cdot\text{HO}_2) \rightarrow \text{H}_2\text{O} + \text{O}_2$	
(l)	$(\cdot\text{HO}_2) + (\cdot\text{HO}_2) \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	Chain termination
(m)	Loss of $(\cdot\text{HO}_2)$ and $\text{H}_2\text{O}_2$ at the walls of the vessel	

Note: M indicates physical or chemical constituent which acts mainly as an energy transfer agent. This is also known as the third body in a three-body collision. It is involved in no other way.

- Biogenesis: Decomposition of plant and animal (organic) material by living organisms.
- Syntheses: Syntheses by man.

**11.8.1.1 Presolar and Solar.** There are several views on the development of the solar system. See Goldsmith and Owen (1980) who discusses two of them. One is based on Laplace's model which implies that the planets and moons coalesced from essentially homogeneous debris containing all stellar-produced material. The second model discussed seems to imply a source of homogeneous clusters or regions of materials different from one cluster to another.

Our Sun is a small to medium star which has not yet passed through the carbon (C) burning phases. Others may class it as a more than medium star. It is still in the initial hydrogen burning phase and is not expected to continue beyond the carbon burnout phase. Though carbon (C) and intermediate nuclei can be formed in the hydrogen to helium burning phase, the amounts can only be minuscule relatively. Thus, although carbon forms in the Sun itself, the primary source of carbon in the solar system and in interstellar space is believed to be the debris of presolar stellar implosion-explosion processes where the burning phases have passed beyond that of carbon. Thus, many stars including our Sun can be considered, from one point of view, forming out of debris prior stellar explosions, to be second, third, or later generation stars.

Methane ( $\text{CH}_4$ ), being one of the simpler molecules, built from hydrogen ( $\cdot\text{H}$ ) and carbon (C), initially has a greater chance of being present than other gases such as nitrogen ( $\text{N}_2$ ) and oxygen ( $\text{O}_2$ ), as in general, these are formed later in stellar development. Methane ( $\text{CH}_4$ ) is not unique, just as many other gases are not unique in being present in the solar system, in interplanetary, interstellar, and galactic space. See Duley and Williams (1984, p. 111) for a model for the generation (synthesis) of methane ( $\text{CH}_4$ ) in interstellar space. See also Kuiper (1949), Mitton (1978), Henbest (1979), Goldsmith and Owen (1980), Menzel (1970), Moore and Hunt (1983), and Lunine and Stevenson (1985). Tsurutani (1989) describes the odyssey of the spacecraft Voyagers 1 and 2, 1977–1989. In particular, the trip of Voyager 2 and the identification of methane ( $\text{CH}_4$ ) and other gases are noted for the two giant gas planets, Uranus and Neptune. The colors noted are greenish-blue due to the absorption of the red and the reflection of the blue-green by methane ( $\text{CH}_4$ ). However, it should be noted that methane ( $\text{CH}_4$ ), by itself, on Earth cannot be seen,



smelled, or tasted by man. It is hoped that the continuing trip of Voyager 2 will provide some information about the planet Pluto as well as information on the heliopause, that region which forms the boundary between the solar system and intergalactic space. Methane ( $\text{CH}_4$ ), if present on Pluto, would be difficult to detect due to the expected temperatures below the melting point of methane ( $\text{CH}_4$ ). See table 11-1. The melting and boiling points of methane ( $\text{CH}_4$ ), respectively, are approximately  $-182.5\text{ }^\circ\text{C}$  (90.7 K) and  $-161.5\text{ }^\circ\text{C}$  (111.7 K). The computed equilibrium temperature of Pluto is estimated to be  $-210\text{ }^\circ\text{C}$  (63 K) (Menzel (1959)). The calculated temperature, attributed to Cruikshank and Silvggio (1980) by Hartmann (1983), is approximately  $-230\text{ }^\circ\text{C}$  (37 K). The inference is made that at these temperatures, most of the gases, with the exception of hydrogen and helium, would be deposited as frost. Except where tied to or being an integral part of the planet cores (shells), the solid portions in the planet, the hydrogen and helium would have been lost in space. The estimated mean atmospheric temperatures of the gas giants Saturn, Uranus, and Neptune are approximately 88, 59, and 48 K with daytime ranges of 120–160, 50–110, and 50–110 K. These imply the existence of solid, liquid, and gaseous methane ( $\text{CH}_4$ ). The surface temperature regimes of the inner four terrestrial planets—Mercury, Venus, Earth, and Mars—is enough to keep most of the lighter compounds in vapor form, yet subject to photolysis and loss to space. One can only conjecture as to whether methane ( $\text{CH}_4$ ) was ever allowed to remain physically in the plastic core solidification of the inner planets. If so, and if it still remains, it is below the detection level of the available instrumentation and techniques. Only continued space exploration with remote sensing techniques may be able to give acceptable answers if methane continues to be outgassed.

The above discussion leads to the following scenario which is speculative on the author's part:

(1) It has been implied that methane ( $\text{CH}_4$ ), being one of the simpler molecular configurations, will be produced and essentially distributed throughout space, or at least the galaxy of which the Sun is a star and the solar system is a part.

(2) Presumably it will have been or will be proportionally present in galaxies and planetary systems.

(3) It is conjectured that outgassing material from planets will be forced by stellar (solar) winds towards the edges of the planetary system.

(4) The cooler temperatures towards the edges will permit the gases to approach liquefaction and solidification stages. The fact is that the inner terrestrial planets (excluding Earth) seem to have little or no atmospheric methane, while from Mars outward, the relative amounts of methane ( $\text{CH}_4$ ) seem to increase. In a sense, the gas methane ( $\text{CH}_4$ ) is boiled away from the inner planets, forced (blown) outward, and condensed onto or coalesced with the giant gas planets, Jupiter, Saturn, Uranus, and Neptune. The slow swing of the gas giants around the Sun and the continued flow of methane outward allows the giant gas planets to sweep the outer regions and collect the methane ( $\text{CH}_4$ ) or its ions. The above scenario would apply to all gases but with less effect as the increasing molecular weights lessen outgassing and transport. The configuration and motions of the great gas planets assures a good cleanup; they make good sinks.

Lunine (1989) discusses the origin and evolution of the outer solar system atmospheres. As noted above, these present atmospheres are distinctly different from those of the inner planets, Earth included. Lunine (op. cit.) reviews the current understanding of the evolution of the giant gas planets' atmospheres on the basis of key molecular species. Infall of icy and rocky planetesimals accompanies the assumed model formation of the giant gas planets. Many believe that this infall continues. As Lunine (op. cit.) indicates, this would explain the enrichment of the atmospheres with methane and deuterated species. Of course, the atmospheric materials of all the solar system planets have been undergoing evolution prior to and during the solar system's existence of about 4.5 or 4.6 billion years. These have been subjected to the transforming and winnowing (fractionating) processes which involve the wide range of energy and material in the solar and galactic systems.

### 11.8.1.2 Thermogenesis.

Methane (CH<sub>4</sub>) thermogenesis involves the following two aspects:

(1) The physical and chemical synthesis of methane (CH<sub>4</sub>) is based on availability of carbon (C) and hydrogen (H). MacDonald (1983) discusses the abiogenetic potential for methane in the Earth's interior. Duley and Williams (1984, p. 111) provide an interstellar model given the energy of the ultraviolet and carbon (C) and hydrogen (•H) nuclei.

(2) The temperature and pressure treatment of once living plant and animal debris in an anaerobic environment which limits oxidation. Continued deposition of layers of silt over the debris provide the necessary mechanism to increase both temperature and pressure. Thus, in coal, petroleum, or gas regions, methane may be synthesized naturally. Due to the varying types and amounts of debris material and to the varying temperature and pressure treatments, various amounts of methane (CH<sub>4</sub>) will be produced. Some natural gas sources contain 40 percent methane while others contain 90 percent. Hammerschmidt (1934) shows more than 80 percent of natural gas in the Texas-Oklahoma region to be methane (CH<sub>4</sub>). Katz (1945) shows a range of 55 to 93 percent. Thermogenesis may precede, be contemporary with, or follow biogenesis.

**11.8.1.3 Biogenesis.** Warneck (1988) discusses the bacterial (microbial) methane (CH<sub>4</sub>) production from once living material. In general, the environments are anaerobic; i.e., without oxygen. Such environments are found in the gut of living organisms such as herbivores, carnivores, and omnivores (including man), termites and other insects, and in soils such as paddy (rice) soils, marshes and in lake, sea, and ocean bottoms. Garbage, especially in landfills, offers suitable anaerobic environments with a good food (energy) supply for the anaerobic bacteria. See Kaplan (1974) for natural gases in marine sediments. See Hodgson (1978) with respect to the search for natural gas. This search is unending.

Increasing populations require more food (energy). Increased crop production will provide the requisite energy. Though carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O) will be used in the crop production, carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O), and methane (CH<sub>4</sub>) from the anaerobic environments will be released to the atmosphere.

In marshes, the gas byproducts of the anaerobic bacterial use of once living matter effervesced or "bubbled." These gases long were known and still known as "marsh" gas(es). In mines, methane was and is known as "fire-damp." In order to compare the tendencies of gases to rise, some of the relative molecular weights of gases follow: (1) hydrogen (H<sub>2</sub>), (2) helium (He), (3) methane (CH<sub>4</sub>), (4) water (H<sub>2</sub>O), (5) nitrogen (N<sub>2</sub>), (6) carbon monoxide (CO), (7) ethane (C<sub>2</sub>H<sub>6</sub>), (8) oxygen (O<sub>2</sub>), (9) argon (Ar), (10) carbon dioxide (CO<sub>2</sub>), and (11) propane (C<sub>3</sub>H<sub>8</sub>). Respectively to no decimals are: (1) 2, (2) 4, (3) 16, (4) 18, (5) 28, (6) 28, (7) 30, (8) 32, (9) 40, (10) 44, and (11) 44. See table A-11-1 for atomic weights. In an atmosphere with no convection or mixing, the gases will separate into layers. With convection, diffusion, and mixing, as in the Earth's atmosphere, the gases will be essentially fairly well mixed. It is expected that the lighter gases will tend to rise the fastest, will tend to be photolyzed, and/or lost to space. Note that methane is comparatively light.

**11.8.1.4 Syntheses.** As indicated previously, methane (CH<sub>4</sub>) may be synthesized by natural processes. Witness to this is the detected and identified existence in most of the solar system. That man can mimic a few of these syntheses processes is known.

Conant ((1933), p. 45) describes a process wherein carbon monoxide (CO) in an atmosphere of hydrogen (H<sub>2</sub>), under elevated temperature and pressure and in a more enriched supply of hydrogen (H<sub>2</sub>) in the presence of a nickel (Ni) catalyst, methane (CH<sub>4</sub>) and water (H<sub>2</sub>O) are produced. In the Lurgi process, where the source of carbon (C) is a bed of burning coal, under pressure, and with steam, the carbon monoxide necessary above is produced. See Fessenden and Fessenden (1986, p. 108). Conant (op. cit.) also describes the production of methane (CH<sub>4</sub>) from aluminum carbide (Al<sub>4</sub>C<sub>3</sub>) and water (H<sub>2</sub>O). The byproduct is aluminum hydroxide Al(OH)<sub>4</sub>. In all three of the

above processes, methane (CH<sub>4</sub>), the simplest of the alkane hydrocarbons, is produced. The Lurgi process is used to produce commercial quantities, albeit it may be an economically expensive process. If iron (Fe) is used as a catalyst in the above Lurgi process, the Fischer-Tropsch process (Fessenden and Fessenden (op. cit.)) is induced, in which methane, other alkanes, and other hydrocarbons are produced. Where only a subscripted carbon (C<sub>x</sub>) is indicated in the literature, the “x” denotes the number of types of hydrocarbons produced. For example, C<sub>1</sub> indicates that only one hydrocarbon is produced in the synthesis. A C<sub>4</sub> indicates that four hydrocarbons are produced, say methane, ethane, propane, and butane.

The Lurgi or the Fischer-Tropsch, in some cases, may be the only source of energy in the gas or liquid form. Coal is used. In other cases, the processes are alternatives where gases and liquids are otherwise available. Economic considerations determine whether coal will be exploited extensively. At the present time, in an economic sense, a price of oil 30 1990 U.S. dollars a barrel probably would make profitable commercial production of methane (CH<sub>4</sub>). A relative rise in petroleum prices and improvement of the production processes, including the elimination of environmental pollutants, will accelerate the use of Fischer-Tropsch processes. Haggin (1990) discusses the steady progress in the Fischer-Tropsch technology; a conceptual scheme illustrates F-T synthesis and power generation. Cost-competitive production is expected by the late 1990s.

As an aside, most research and production do not consider the unused byproducts which can only add to the disposal problems, and the addition of gases to the atmosphere and the oceans. All these affect climate in one way or another.

The general alkane formula is C<sub>n</sub>H<sub>2(n+1)</sub>, where *n* is 1 or more. The second alkane is ethane (C<sub>2</sub>H<sub>6</sub>). Where *n* is two or more and the constant 1 is changed to 0, the alkenes are produced, C<sub>n</sub>H<sub>2n</sub>. An example is ethylene (C<sub>2</sub>H<sub>4</sub>). Where *n* is 2 or more and the constant is changed to -1, the general formula for alkynes is C<sub>n</sub>H<sub>n</sub>. C<sub>2</sub>H<sub>2</sub> is an example. Respectively, single, double, and triple carbon bonds, respectively, occur in the alkanes, alkenes, and the alkynes. See Chang (1986). Of the first ten alkanes, under normal temperature and pressure, the first four, methane through butane, will be gases while the last six, pentane through decane, will be liquids. See Chang (op. cit.) and tables A-11-2 and A-11-7 for some comparative boiling point (b.p.) temperatures.

## 11.8.2 Isotopes

### 11.8.2.1 Isotopes.

$$n_t = n_o e^{-kt} \quad , \quad (11.16)$$

where *n<sub>o</sub>* is the number of <sup>14</sup><sub>6</sub>C nuclei present at *t<sub>0</sub>*, time zero, while *n<sub>t</sub>* is the number of <sup>14</sup><sub>6</sub>C nuclei present *t*, somewhat later (Getman and Daniels (1931)). The radioactivity constant is *k* using any one radioactive mass, say <sup>14</sup><sub>6</sub>C. By measuring the rate of decay, the number of electrons emitted at two different times the decay constant for <sup>14</sup><sub>6</sub>C can be determined. For <sup>14</sup><sub>6</sub>C, *k* = 1.21 × 10<sup>-4</sup> y<sup>-1</sup> (Chang (1986)). An easy ratio to use is one-half; i.e., the time when one-half of the original number of <sup>14</sup><sub>6</sub>C nuclei remain—the others have reverted to <sup>14</sup><sub>7</sub>N nuclei. Then,

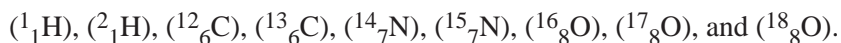
$$t_{0.5} = 0.693k^{-1} \quad , \quad (11.17)$$

where *t<sub>0.5</sub>* is the half life in years if the constant *k* has that dimensional unit. For <sup>14</sup><sub>6</sub>C, this half-life is 5,730 yr.

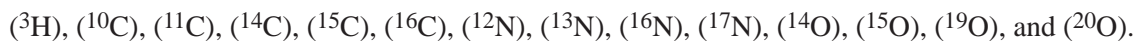
The number of isotopes of known hydrogen (H), carbon (C), nitrogen (N), and oxygen (O) are, respectively, 3, 7, 6, 7 (Weast (1980)). These are:

(<sup>1</sup><sub>1</sub>H) through (<sup>3</sup><sub>1</sub>H), (<sup>10</sup><sub>6</sub>C) through (<sup>16</sup><sub>6</sub>C), (<sup>12</sup><sub>7</sub>N) through (<sup>17</sup><sub>7</sub>N), and (<sup>14</sup><sub>8</sub>O) through (<sup>20</sup><sub>8</sub>O).

Respectively, there are 2, 2, 2, and 3 stable isotopes:



The subscript notation for the atomic numbers, except for the uranium series, will not be used further. The unstable (radioactive nuclei) are:



If the half-life and the decay constant are known for any radioactive element (mass), Libby (1955) suggests that the length of time that the radioactive substance has been decaying without replenishment can be estimated (Chang (1986)). The equation for this is

$$t = \frac{2.303}{K} \log \frac{\text{fresh supply decay rate}}{\text{old supply decay rate}} \quad (11.18)$$

The half-lives of the above unstable nuclei, with two exceptions— $(^3\text{H})$  and  $(^{14}\text{C})$ —range from a few milliseconds to slightly more than 20 yr. The half-life of  $(^3\text{H})$  is  $\approx 12.26$  yr (Weast (1980)) while that of  $(^{14}\text{C})$  is  $\approx 5,730$  yr (Chang (1986) and Stuiver (1986)). Tritium ( $(^3\text{H})$ ) and  $(^{14}\text{C})$  in the short and medium range terms then may serve as tracers in weather and climate. The assurance that the samples have not been replenished with radioactive isotopes is difficult. Only very short periods for tritium ( $(^3\text{H})$ ) are best while the  $(^{14}\text{C})$  periods range best from 1,000 to 50,000 yr or about 10 half-lives for  $(^{14}\text{C})$ , when about one-thousandth of the original mass remains. For the first, bottom waters of the seas and oceans are sources clear of  $(^{14}\text{C})$ , while for the second, fossil fuels.

Tree-ring (dendrochronology), varve,  $^{18}\text{O}$ , coral, and ice field analyses are beset with difficulties. Varves are the periodic (annual) depositions of sediment. Yet these offer good hope that the difficulties may be resolved, and dependable tree-ring analyses may be determined. So the snow (ice) cores of the permanent snow regions/the Arctic, Antarctic, and those of high-altitude mountain peaks in their worldwide distribution, and coral developments of the oceans past and present will be investigated more and more. These do provide some bases to examine the effects of manmade excursions in the atomic (nuclear) bomb use, testing and nuclear power incidents. Schwert and Ashworth (1990) report on another of the many techniques to check and cross-check on the glacial and interglacial effects on the world's plants and animals, flora and fauna, through the techniques of radiocarbon dating. In this case, it is the fossils of insects which form the material of the dating. According to Schwert and Ashworth (op. cit.) the concept was pioneered in the late 1950s by G. Russel Coope of England's University of Birmingham.

To present another phase of the perspective of ages, in the long term, the decay of the uranium series provides a tool to estimate rock ages of the Earth. The oldest rocks found on Earth carry an age of about 4.5–4.6 billion years (Chang (1986)). The estimated age of the galaxy within which the Earth formed and is embedded, is roughly 12–15 billion years, while that of the universe in which this galaxy is embedded is roughly 20 billion years.

Previously, the implication was made that the solar system, including the Earth, is star-dust derived. Thus, all things, animate and inanimate, on Earth contain or may have contained all elements including their isotopes. As in the above-mentioned carbon-14 and U isotopic ratio dating techniques, the dating potential exists to use various combinations from the mélange of isotopes. But with this vast potential there exists also the enormous difficulties involved to produce viable and precise dating techniques. For example, there are 13 thorium isotopes and 16 uranium isotopes listed in Weast et al. (1980)). Uranium decays to thorium as follows: In one line of degradation, uranium-238 ( $^{238}_{92}\text{U}$ ) emits alpha radiation and decays to thorium-234 ( $^{234}_{92}\text{Th}$ ). Upon emitting beta radiation, this decays to proactinium-234 ( $^{234}_{91}\text{Pa}$ ), which with subsequent beta radiation, decays to Uranium-234 ( $^{234}_{92}\text{U}$ ). This

form of uranium, then, upon emission of alpha radiation, decays to thorium-230 ( $^{230}_{90}\text{Th}$ ). The respective half-lives of these stages are (1)  $4.51 \times 10^9$  years, (2) 24.1 days, (3) 6.7 hours, (4)  $2.47 \times 10^5$  years, and (5)  $8 \times 10^4$  years (Weast (op. cit.) and Chang (1986)).

Extensive research in this field continues. Bard, Hamelin, Fairbanks, and Zindler (1990) announced the refinement of the uranium-thorium (U-Th) ratio techniques to provide better accuracy in dating techniques. Their suggestion is that this technique application may be used to help calibrate all the other techniques' results. However, they conclude that for the moment, good precision is obtained for the past 10,000 yr. Their inferences are that the  $^{14}_6\text{C}$  dates at about 10,000 yr should be actually about 11,500 yr, very roughly an 11-percent error. There is an increasing divergence of estimates with increasing time before the present (b.p.). This divergence is apparently created by the Earth's changing magnetic field which affects the production of  $^{14}_6\text{C}$  by the incoming energetic nuclei of the cosmic rays. Presumably,  $^{14}_6\text{C}$  dates should be moved backward in time. There exists, therefore, in the various disciplines, material and techniques to cross-correlate the results of the various dating techniques. Some of these techniques involve dendrochronology (tree ring), varves,  $^{18}\text{O}$ ,  $^{14}\text{C}$ , and coral developments of oceans, past and present. By so doing, the climatologist will obtain information on a better database. This will allow the climatologist to better assess past climates, the present climate, and the status of future climate.

It is not known whether the following point is discussed in prior literature. Timing has been possible in the past century. That is a short span in the lifetime of the uranium series. Timing of short-lived species indicates a first-order process. Thus occurs the thought that perhaps the decay process is more than a first-order process. If so, then the speculative ages of the Earth, the solar system, the galaxy, and other galaxies ought to be modified when that larger order process may be identified.

**11.8.2.2 Isotopic Ratios.** Consideration of relative amounts (percentages) and percentage ratios of atoms permits the development of a consistent perspective. That perspective is that the atomic percentages of the more stable atoms is a most probable state and that the percentages of the unstable atoms are small indeed. However, just as trace gases are important in climatology and the understanding of climate processes, so, too, are their trace atoms, the radioactive atoms. Thus, though this section concerns methane ( $\text{CH}_4$ ), which involves only the carbon (C) and hydrogen atoms (H), comparative data are shown below for two other atoms—nitrogen (N) and oxygen (O). Nitrogen ( $^{14}\text{N}$ ) is the basic source for  $^{14}\text{C}$  and some of the oxides of nitrogen. Discussions of methane are extensive as it is the first of the trace gases to be discussed. Additionally, the discussions are applicable to the others. No depreciation of the effects of the others is intended when the same items, such as clathrates, are not discussed in such detail. The reader should make this transference. The oxides of carbon will be discussed in more detail in section 11.9, carbon dioxide ( $\text{CO}_2$ ). Included are relative percentages and some ratios (Weast (1980), Chang (1986), and Stuiver (1986)). These do not include all isotopes. Here, only ( $^3\text{H}$ ), ( $^{16}\text{N}$ ), and ( $^{14}\text{C}$ ) are unstable.

#### 11.8.2.4.1 Percentages:

( $^1\text{H}$ ), 99.985; ( $^{12}\text{C}$ ), (98.89); ( $^{14}\text{N}$ ), (99.63); ( $^{16}\text{O}$ ), 99.759;  
( $^2\text{H}$ ), 0.015; ( $^{13}\text{C}$ ), (1.11); ( $^{15}\text{N}$ ), (0.37); ( $^{17}\text{O}$ ), 0.037;  
( $^3\text{H}$ ), — —; ( $^{14}\text{C}$ ), ( $10^{-12}$ ); ( $^{16}\text{N}$ ), (— —); ( $^{18}\text{O}$ ), 0.204.

#### 11.8.2.4.2 Ratios:

( $^{14}\text{C}/^{13}\text{C}$ ), ( $9 \times 10^{-9}$ ); ( $^{17}\text{O}/^{18}\text{O}$ ), 0.181; ( $^{14}\text{C}/^{12}\text{C}$ ), ( $1 \times 10^{-12}$ ); ( $^{18}\text{O}/^{16}\text{O}$ ), 0.205;  
( $^{13}\text{C}/^{12}\text{C}$ ), ( $1.12 \times 10^{-12}$ ); ( $^{17}\text{O}/^{16}\text{O}$ ), 0.038.

Again, it must be noted here that the amounts of radioactive nuclei are small and must be considered to be within their rounding error calculations of the totals for the stable nuclei.

The information above utilizing only the nuclei of hydrogen (H), carbon (C), nitrogen (N), and oxygen (O) reveals that the number of configurations of potential molecules is great. For example, considering three isotopes of hydrogen and five isotopes of carbon, there are at least 255 separate potential methane (CH<sub>4</sub>) molecules, each different from the others in their isotopic makeup. The most probable natural configuration for methane, of course, is (<sup>12</sup>C<sup>1</sup>H<sub>4</sub>), which would occur more than 98 percent of the time. Also, because of the half-lives of <sup>14</sup>C and <sup>3</sup>H, and the other radioactive carbons, methane configurations involving these should not be found in coal, petroleum, or natural gas, which are underground and not accessible to contamination by newly formed <sup>14</sup>C. There is usually a caveat involved with any statement. The caveat here requires that these not be near any nitrogen or neutron sources for the production of <sup>14</sup>C. Uranium or thorium contamination of coal beds or oil pools would present problems. Yet, if uranium and thorium are present and confound the <sup>14</sup>C procedures, these in themselves offer dating potential.

Recently formed <sup>14</sup>C will be found in methane derived from biogenesis. This, along with <sup>3</sup>H provides good estimates of time in recent formation of plants and their debris. Those may be in sediments, in the gases of decomposition or combustion, or in water.

Stuiver (1986) discusses many of the problems associated with the application of the <sup>14</sup>C and the isotope ratio techniques. Tree ring chronologies are discussed and references are provided to many research works such as Stuiver and Polach (1981), Stuiver and Quay (1980), Ferguson and Graybill (1983), Long (1982), and Freyer (1986).

Both <sup>14</sup>C created in the outer atmospheric regions and the radioactive hydrogen and oxygen isotopes will form radioactive compounds such as methane (CH<sub>4</sub>), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O), hydrogen (H), ozone (O<sub>3</sub>), and oxygen (O<sub>2</sub>). Living matter uptake of these is, among other things, temperature dependent. In examination of once-living material, therefore, these do offer guides to former climate temperatures. Assimilation of these would appear to be physically (mass and temperature) dependent as they are not different chemically. Thus, evaporative processes and living organisms discriminate among the various isotopic complexes. For example, fish die in heavy water. There is an indicated decrease in the <sup>13</sup>C/<sup>12</sup>C and <sup>14</sup>C/<sup>12</sup>C ratios from 1,750 to 1,980. This decrease may be associated with both the burning of fossil fuels which presumably contain no <sup>14</sup>C and to deforestation and agricultural tilling practices (Stuiver (1980)).

Where dendrochronology information diminishes with increasing past time, these isotopic ratios in varves provide an extension of climate records into the past. These proxy data provide a reading medium for the records of past climatology. However, as with all such type of records, it may be difficult to extract information about one particular physical or chemical attribute during the time in which the varve, or other proxy feature, was being formed. For example, in response to surface methodology, there are various physical-chemical combinations which will produce a stipulated product. Therefore, the record may have been produced in one of several avenues. Care must be exercised.

### 11.8.3 Atmospheric Methane

**11.8.3.1 Atmospheric Methane (CH<sub>4</sub>) Sources and Sinks.** The foregoing sections show that methane (CH<sub>4</sub>) may be considered to be spread throughout the planetary system as well as the galaxy, if not the universe. In the case of Earth, methane exists in Earth's crust, oceans, and atmosphere. The mantle also is considered to be a source of methane as well as many other gases. As a gas, it can escape the confines of the crust, into the oceans, into the atmosphere, and into interplanetary space. It may not make it that far due to interaction with other atmospheric constituents or be photolyzed (dissociated) so that it is no longer methane. The lifetime (not half-life) of atmospheric methane (CH<sub>4</sub>) seems to be around 10 yr (Goldsmith and Owen (1980)). It is the sink reaction with the very reactive hydroxyl (•OH) ion that exerts great control on the tropospheric lifetime of methane (CH<sub>4</sub>). Water (H<sub>2</sub>O), as pointed out previously, is one product of this oxidation. This is a water source for the stratosphere. The amount

in the atmosphere has been increasing slowly but the rate of increase has been increasing also. Natural outgassing, petroleum and gas well flaring, the incomplete burning of natural gas during production to diminish the methane ( $\text{CH}_4$ ) hazards of suffocation and dangerous explosions, and outgassing from coal are other sources. Sources also are the incomplete combustion processes of man's industries and losses in transportation and transmission.

**11.8.3.2 Identification—Sources and Statistics.** Glueckauf (1951) and Warneck (1988) indicate that Migeotte (1948) identified methane ( $\text{CH}_4$ ) as a constituent of the atmosphere by its spectroscopic signature. As mentioned previously, it had been known as “marsh” gas. It had been used as a fuel for many years. Glueckauf (op. cit.) indicates that Prof. F.W. Libby analyzed atmospheric methane ( $\text{CH}_4$ ) and concluded that the  $^{14}\text{C}$  content coincides with its biological production. These carbon isotopic ratios and signatures are also used to deduce methane ( $\text{CH}_4$ ) sources by Cicerone and Oremland (1988), Lowe et al. (1988), and Wahlen et al. (1989). Anaerobic sources are discussed by Cicerone and Oremland (1988). Crutzen and Andreae (1990) discuss the effects of biomass burning on atmospheric chemistry and biogeochemical cycles. They estimate the biomass burning methane ( $\text{CH}_4$ ) atmospheric input to range from 11 to 53  $\text{Tgy}^{-1}$ . A teragram is  $10^{12}\text{g}$ . See table A-2-1. Methane ( $\text{CH}_4$ ) derived from coal, petroleum, and natural gases generally contains no radioactive carbon (C) or hydrogen (H) due to their half-lives. Both have long since decayed almost completely. According to Glueckauf (op. cit.), Prof. Libby suggests an annual biological production of more than  $10^7$  tons. The determination of the amount of methane still needs to be better determined. Glueckauf (1951), Moore and Hunt (1983), and U.S. DoD, AFCRL (1985) provide in percent by volume, respective estimates of 1.2, 1.5, and  $1.4 \times 10^{-6}$ . Methane ( $\text{CH}_4$ ) is essentially a clean-burning gas; it is the simplest alkane. As such, it is in demand for energy production. The general formula for the alkanes is ( $\text{C}_n\text{H}_{2(n+1)}$ ). It absorbs and emits radiation in several portions of the electromagnetic spectrum including the far ultraviolet and the infrared. Though it is only a trace gas, it becomes important in the diminution of infrared radiation loss from the Earth. See again figures 11-3 and 11-6 for the comparison of the absorption spectrum of methane ( $\text{CH}_4$ ) with a few other single gases and the simulated atmospheric absorption spectrum of solar radiation.

In addition to the biological production of methane ( $\text{CH}_4$ ), there is the increasing use of natural and synthetic gases in industry, commerce, transportation, and dwellings. Natural gas from below the Earth's surface contains mostly methane ( $\text{CH}_4$ ), some ethane ( $\text{C}_2\text{H}_6$ ), very small amounts of other alkanes ( $\text{C}_n\text{H}_{2(n+1)}$ ), along with scant amounts of nitrogen, carbon dioxide, hydrogen, hydrogen sulfide, and helium. As shown previously, the decay of  $^{14}\text{C}$  is to  $^{14}\text{N}$  and the change of  $^{14}\text{N}$  to  $^{14}\text{C}$  includes the formation of hydrogen. Unless there is a neutron source, say decay of the uranium or thorium series,  $^{14}\text{C}$  will disappear. In the case of methane,  $^{14}\text{CH}_4$  becomes  $^{14}\text{NH}_4^+$ , presumably in charged form, the ammonium ion. The amount is small indeed as is the amount of  $^{14}\text{C}$ .

In the thermal oxidation of methane, several intermediate products may be created (table 11-2 previously shown) (Warneck (1988; table 2-1, p. 49)). These are methyl groups, formaldehyde, and the oxides of hydrogen ( $\text{H}_x\text{O}_y$ ), the hydrides of carbon, and carbon. The primary oxides of hydrogen important in the study of the atmosphere are ( $\bullet\text{OH}$ ),  $\text{H}_2\text{O}$ , ( $\bullet\text{HO}_2$ ), and  $\text{H}_2\text{O}_2$ . In figures 11-3 and 11-6, note that, in the infrared, methane ( $\text{CH}_4$ ) absorption and emission spectra bracket the stronger oxide absorption, carbon dioxide ( $\text{CO}_2$ ). Photolysis, in the upper air, and chemical reactions, in the troposphere, may produce the hydroxyl radical ( $\bullet\text{OH}$ ). This ( $\bullet\text{OH}$ ) then can enter the oxidation process of methane ( $\text{CH}_4$ ) and accelerate the thermal oxidation process. See step 3 in table 11-2.

The oxide of hydrogen (in vapor form), water ( $\text{H}_2\text{O}$ ), has a larger number of frequencies (wave numbers or wavelengths) in which it is a good receptor and radiator. Another point made is that oxidation of methane in the stratosphere also produces, as end products, both carbon dioxide and water. Then in the upper stratosphere, radiation disrupts the water molecule into hydrogen radical and hydroxyl radical. See table A-11-4 for the energy necessary to do this and also to cleave the methane molecule. In the latter, about  $410 \text{ kJ mol}^{-1}$  are required to remove each hydrogen. There is some ultraviolet which reaches the Earth's surfaces. If absorbed by a water ( $\text{H}_2\text{O}$ ) molecule, the hydrogen ( $\bullet\text{H}$ ) and the hydroxyl ( $\bullet\text{OH}$ ) radicals will be produced. The hydroxyl radical, ( $\bullet\text{OH}$ ), is one of the more reactive gases and is involved in many rapid chemical reactions. In the atmosphere, the hydroxyl radical ( $\bullet\text{OH}$ ) is

active in the decomposition of methane to ( $\bullet\text{CH}_3$ ), another active radical before final oxidation. Khalil and Rasmussen (1983) discuss the sources, sinks, and seasonal cycles of atmospheric methane. As methane can react with and deactivate chlorine, it can act as a buffer in the catalytic reactions of chlorine and ozone interactions as well as stopping the immediate destruction of an ozone molecule. In fact, a mixture of methane and chlorine can explode.

No attempt is made in any preceding section, this section, or the following sections or subsections to merge estimates of data. Estimates are presented above and sources are provided. This realm of merging statistics (e.g., means, variances, and proportions including the pooling of estimates) is meta-analysis. (Even if the researcher knows the intent and the goals of the research, that these are the same in the several different data sets and that the interactive aspects within the sets and between the sets are the same, the effect known and discussed as “Simpson’s paradox” may create problems. See Hedges and Olkin (1985), Paik (1985), Bailar and Mosteller (1986), Tan (1986), Wainer (1986), Schwandt and Halpern (1988), Hunter and Schmidt (1989), and Iyengar (1991). This paradox appears when two or more data sets, which individually apparently show the same features, are combined, yet the total effect may be reversed. The words “Simpson’s paradox” alludes to another, different situation as discussed by Goody and Yung (1989) with respect to atmospheric radiation.

However, though the use of meta-analysis is expanding into and over many disciplines, the reader should be aware of the views of the proponents and the opponents. Mann (1990) reviews some works and mentions a study (an overview) of more than 750 cloud seeding experiments. This study presumably is that of Todd and Howell (1985, 1987). The subject is an evaluation of weather modification. It is referenced here, rather than in section 8, Precipitation. The conclusion is that under the rules established for cloud seeding experiments and the study, there is a positive response somewhat stronger in summer than in winter. For further details and some of the problems, please see references.

Steele et al. (1987) report on the global distribution of methane in the troposphere. The study provides 2 yr of data (1983–1985). Steele et al. (op. cit.) citing Ramanathan et al. (1985) indicates that methane is one of the most important radiatively active trace gases with a significant potential to contribute to climatic change within the next century. They report on the 2 yr of data gathered at 23 globally distributed sites in the NOAA/GMCC cooperative flask sampling network. For the above reasons, as is done here, consider the chemical compound methane to be an important climatic element. As with all data-gathering efforts, including those dealing with methane ( $\text{CH}_4$ ), good, reliable benchmark stations (locations) need to be established and maintained. Databases derived from these must be established, maintained, and serviced. Funds must be made available. Instrumental documentation and observational procedures should be included in these databases.

Figure 11-7 from Khalil and Rasmussen (1990) shows the global methane increase in the atmosphere from mid-1980 to mid-1988. This is slightly more detailed than in the presentation by Blake and Rowland (1989). The mean appears to be  $\approx 1,600$  ppbv with some trend slowing in the last years to a top value of 1,680 ppbv.

Figure 11-8, adapted from Boden, Kanciruk, and Farrell (1990) shows the estimated methane content derived from ice cores and present-day measurements including those shown in figure 11-7. The user should not be misled by the logarithmic scale used here and for carbon dioxide in the next section, section 11.9. The reader easily can see the rise in atmospheric methane from the beginning of this record 160,000 yr before the present, the fall, and then again the slow rise at 10,000 yr and then the faster rise beginning 1,000 yr ago. These data are derived from ice cores and the NOAA/CMDL flask sampling network. The methane measured in the ice cores was trapped in the air bubbles. Also indicated was the existence of methane ice, the clathrate hydrate.

*Trends* (Boden, Kanciruk, and Farrell (1990)) includes the contributions of many researchers. All data presented in *Trends* are available in digitized form from CDIAC at Oak Ridge at the address provided at the end of section 11.9, Carbon Dioxide ( $\text{CO}_2$ ).



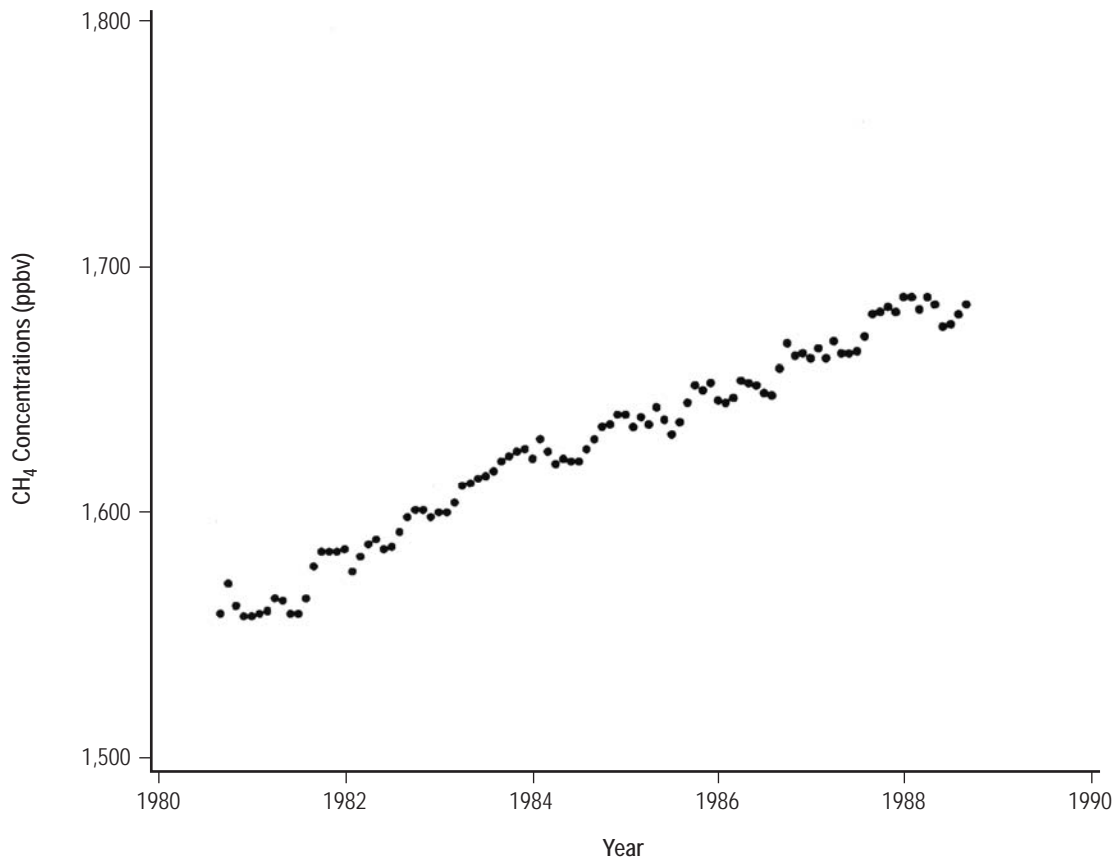


Figure 11-7. Global methane increase in the atmosphere from mid-1980 to mid-1988 (ppbv) (courtesy of Khalil and Rasmussen (1990)).

Figure 11-9 shows the same global distribution, seasonality, and trend of methane (CH<sub>4</sub>) plus three more years of data from the GMMC network through the courtesy of L.P. Steele (Fung et al. (1991)). A modification to the isometric axes would make the viewing easier. The arrow indicates the equatorial position. They show a distinct annual variation as well as rise in amounts during the period. For those who are interested in methane modeling on the global scale, the information provided by Steele et al. (op. cit.) will provide useful constraints on local, regional, and global scales.

Good (1985) presents a vertical distribution of methane (CH<sub>4</sub>) derived from various research reports. Distribution curves for equatorial regions, 25–35°, 40–60°, and greater than 60° latitude are presented. In the mid-latitude, in the troposphere, the amounts shown are steady, but above 10 km, there is a steady decrease. In the equatorial and polar regions, there is a steady decline through the vertical. The inference is that convection and turbulence are effective in the troposphere such that there is quick transport upwards. Good (op. cit.) also presents vertical distribution curves for ethane, propane, and acetylene (C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>2</sub>H<sub>2</sub>).

Warneck (1988) discusses the methane budget. Warneck (op. cit.) provides the contribution of a number of authors to the study of the average methane tropospheric mixing ratio. He shows the ratio of the mixing ratios for comparison of the Northern and Southern Hemispheric mixing ratios. These were reported for the decade of 1973–1983. The average ranged from 1.35 to 1.65 and the Northern/Southern Hemisphere ratios ranged from 1.03 to 1.07.

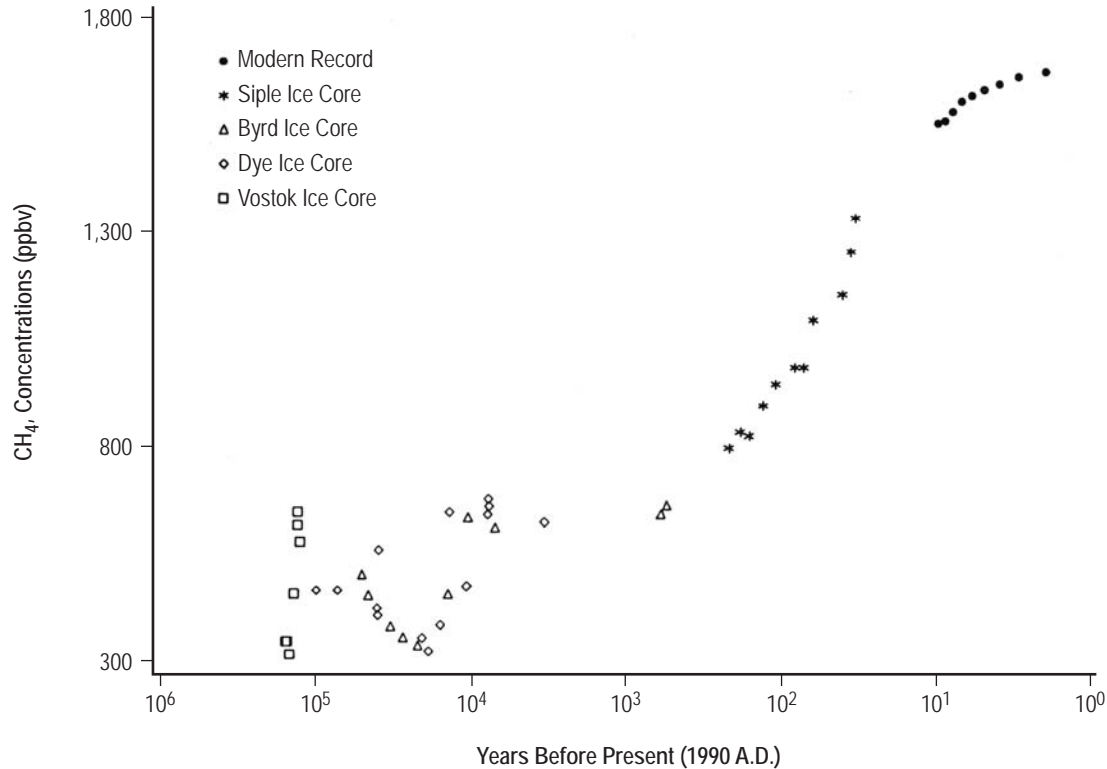


Figure 11-8. Estimated methane amounts derived from ice cores and present-day measurements. Derived from ice cores and the NOAA/CMDL flask sampling network (courtesy of Department of Energy, Oak Ridge National Laboratory, Boden, Kanciruk, and Farrell (1990)).

Monitoring techniques have been improving. The data imply a methane rise of  $\approx 20$  ppbv per year. The reader may refer to Rasmussen and Khalil (1981), Fraser et al. (1981, 1984), and Blake et al. (1982). All references indicate a prior lower level of methane in the atmosphere, being about 0.7 ppmv before 1700 A.D. Since then there has been almost an exponential increase almost to 1.7 ppmv (Warneck (op. cit.)) which is the same indicated by Blake and Rowland (1989). Warneck (1988) presents in his figure 4.3 a rather level amount of methane ( $\text{CH}_4$ ) ratio 0.7 ppmv from about 10,000 yr to 300 yr before the present. Beginning in the late 18th century, a steady increase is noted up to about 1.4 ppmv.

Revelle (1983) indicates that the atmospheric methane concentration is increasing at a rate of 1 to 2 percent per year, or  $\approx 0.07$  GT of methane per year. Rasmussen and Khalil (1981) expect the absolute amount will double in the next 40 to 50 yr to an equivalent of  $\approx 7.2$  GT of carbon. The amount of carbon entrapped in the  $\text{CH}_4$  hydrate form is uncertain, but is believed to be large (Kvenvoldin (1988a)). As more exploration occurs, a better estimate will likely become available. The reader will find the above references and those in their bibliographies good reading. The hydrate storage feature is discussed in more detail later.

Watson (1986) displays a linear increase of methane in the atmosphere from 1977 through 1985 of almost 16 ppbv  $\text{y}^{-1}$ . An annual wave is displayed. The assumption is made that this oscillation is created by biological processes due to the increases in the summer hemisphere temperatures. Also displayed are halocarbon increases through the same period at Ragged Point, Barbados, WI.

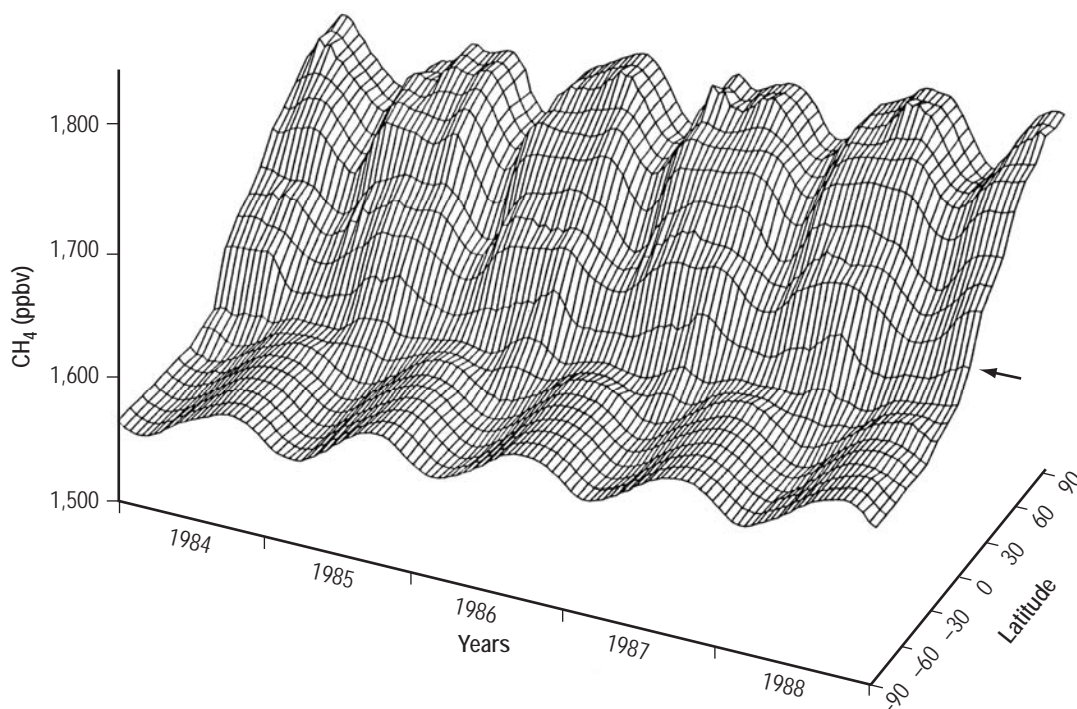


Figure 11-9. Isometric presentation of global latitudinal methane distribution amounts, 1984–1988 (courtesy of NASA, L.P. Steele (Fung et al. (1991))).

Zander et al. (1989) utilize the years of 1951, 1975, and the 4-yr period, 1984–1987, to reevaluate the vertical column abundance of methane ( $\text{CH}_4$ ) above Jungfraujoch Station, Switzerland. Infrared solar spectra are used. The 1984–1987 period permits the identification of a seasonal swing in the halocarbon data as was indicated for Ragged Point, Barbados, WI, above. They indicate a  $\pm 10$ -percent variation around the mean for the annual wave. They indicate a yearly increase of  $(0.7 \pm 0.1)$  percent  $\text{y}^{-1}$  between 1951 and 1986 but, of course, cannot present any long-term variation. They deduce mixing ratios of  $1.28 \pm 0.08$  ppm for 1951 and  $1.64 \pm 0.9$  ppm for 1985–1987. The latter falls in the neighborhood of the data shown in figure 11-9.

Conway and Steele (1989) indicate a 95-percent correlation coefficient ( $r^2$ ) between atmospheric carbon dioxide and methane. This correlation was noticed particularly in the Barrow, Alaska, region but not near the dew-line locations. At Barrow, this seemed to be in the pollutants transported from other regions. Yet another inference might be a greater primary supply of methane, only part of which undergoes oxidation to carbon dioxide. As noted previously, methane's ( $\text{CH}_4$ ) average life span in the atmosphere is  $\approx 10$  yr. Resupply was more than sufficient in the region as indicated by the continued rise in atmospheric methane ( $\text{CH}_4$ ) amounts.

Khalil and Rasmussen (1987) state that their analysis of the record for methane over the past 10,000 yr (from the end of the last ice age) shows that up to 1700 A.D. the methane contribution to the atmosphere remained relatively low and constant at  $\approx 700$  ppbv. Between 1700 and 1900, their charts showing results at different locations, by various authors, indicate a rise in methane cumulation at a rate of  $1.5$  ppbv  $\text{y}^{-1}$ . Between 1900 to 1925, the increase was  $\approx 2.2$  ppbv  $\text{y}^{-1}$ , and between 1927 and 1956, the increase was  $\approx 6.4$  ppbv  $\text{y}^{-1}$ . Between 1962 and 1973, the increase was  $\approx 11$  ppbv  $\text{y}^{-1}$  and during the last decade, the rate has been  $\approx 17$  ppbv  $\text{y}^{-1}$ . Methane in ice cores is the main base for the earlier part of the construct. However, in comparison of figures 11-7 and 11-8, the increase seems to still be  $\approx 15$  ppbv  $\text{y}^{-1}$ .

Chapellaz et al. (1990) report on the study of the deposition of atmospheric methane in ice cores at Vostok, Antarctica. They indicate that atmospheric methane doubled when going from full glacial conditions (350 ppbv) to interglacial periods (650 ppbv). The period covered is  $\approx 160,000$  yr (b.p.). Please note the present approximate 1.72 ppmv (Warnech (op. cit.)) or 4,900 Tg. One Tg is equal to  $10^{12}$ g or 1 million metric tons. They do not indicate whether any part of this was in clathrate storage. See the extensive discussion on clathrates in section 11.8.5. They report that spectrum analysis indicates periodicities close to those of orbital variations. They also suggest that associated warming during deglaciation is 30 percent of that due to carbon dioxide. Already pointed out is that methane can be oxidized to carbon dioxide with a resultant decrease of atmospheric methane and an increase of atmospheric carbon dioxide. They do discuss the potential of methane forcing climate by (1) direct radiative effect, (2) chemical feedback, and (3) climate feedback. See Craig and Chow (1982), Rasmussen and Khalil (1984), Stauffer et al. (1985), Rinsland et al. (1985), and Zander et al. (1989a and 1989b).

#### 11.8.4 Clathrates

Exploration and research point to continued discovery of methane clathrate hydrate fields in permafrost regions and in ocean sediment regions. Oceanic acoustic reflecting phenomena bottom simulating reflectors indicate potential fields of energy in either gas or gas clathrate form. See Dillon et al. (1990). Considerable exploration is underway. Because methane ( $\text{CH}_4$ ) and other allied gases are an energy source and because the release of these gases and their oxidation products, and some of their other compounds such as methylchloride ( $\text{CH}_3\text{Cl}$ ), tend to increase the radiative trace gas potential, it seems desirable to discuss the clathrate phenomenon to some extent. In the past 60 yr, this phenomenon has increased its status as an atmospheric trace gas source.

Ubiquitous water has been discussed extensively in sections 1 and 3. Nine forms of water ice—eight crystalline hexagonal and one cubic (Ic)—were mentioned. In this section, the latter form is a main item. This also plays a part in Earth's climatic scenario. Powell (1948) uses the word "clathrate" with specific reference to this feature. Miller (1973) describes a clathrate. A clathrate hydrate is a cubic crystalline ice-like, open-lattice network of host water structures that serve as guest housing for molecules. Any molecule may participate in a "clathrate" phenomenon. Clathrate, from the Greek and Latin languages, means cage. (Originally it meant a peg, key, or lock.) A similar word, "incarcerate," comes from the Latin language. Cram (1989) as noted by Cole (1989) coins the word carceplex to denote such cages for the delivery of medicines within the body. Others have used the word clathrate. See Pauling (1961) and Miller (1961) with respect to "pro" and "con" anaesthesia. The phenomenon as used today is an action of an ensemble of molecules imprisoning a molecule. Gentler words for the "jail" or "cage" and the "prisoner" are "host" or "housing" and "guest." It seems to be not an "antagonistic" but a "cooperative" action.

As an example, where the host is an ensemble of water ( $\text{H}_2\text{O}$ ) molecules, the words "clathrate hydrate" are used. In the ordinary sense of hydration, water molecules surround molecules or ions in one or more shells. Where gas molecules are enclosed, the words "clathrate gas hydrates" are used. Except where noted otherwise, only the words "clathrate hydrate(s)" will be used, as this discussion pertains to the gases which are a part of the atmosphere, oceans, or solid (plastic) Earth. In some disciplines only the words gas hydrates are used but there is some chance for confusion. Vinogradov and Linnell (1971) discuss the propensity for the formation of layers of hydration shells in water. Recent research by Yang and Castleman (1989) indicate the possibility of clathration in water where a hydroxyl or hydronium ion may be a guest of the clathrate hydrate shell,  $(\text{H}_2\text{O})_{20}$ . See also survey article by Dagani (1991).

As a second example, where the host is a cage or grid ensemble of silicon dioxide ( $\text{SiO}_2$ ) molecules, the word(s) "clathrate silicate" or "clathrasil" are (is) used.

A third example is one which has only been deduced within the last two decades. Here the encaging material is carbon. Quite a few researchers have experimented with cluster beam techniques. See Pitzer and Clementi

(1959), Dietz et al. (1981), Smalley (1990), and Curl and Smalley (1988). The most stable of the cages is the  $C_{60}$ ; i.e., 60 carbon atoms, though many others exist, with carbon atoms always in multiples of 2. Due to the appearance of the cages, idealized, to be like geodesic domes, these are often called fullerenes after the well-known architect Buckminster Fuller. Analogous to the clathrate hydrates and the clathrate silicates mentioned previously, these might be called clathrate carbons or clathracarbs. If the guests are gas molecules, these could be labeled gas clathracarbs or, if the gas argon is the guest, argon clathracarbs. These will be discussed again. Whether these clathracarbs are important in climate is unknown. The existence of these are brought to the reader's attention so that a better understanding of the atmospheric composition may be possible. There are many fast-developing facets to the fullerene science. The housing of guests is only one facet. Schwartz (1991) indicates that  $C_{60}$  will house helium or neon. The clathracarbs are believed to form a part of the interstellar and interplanetary media as well as planetary composition. Work continues on the identification of those participants that provide spectral lines near 200 nm. Webster (1991) indicates that the fullerane,  $C_{60}H_{60}$ , a saturated fullerene hydride, produces nearby spectral lines. Saunders (1991) implies that the hydride  $C_{60}H_{36}$  is a more stable form. Webster (op. cit.) says that this stabler form produces equivalent IR spectral lines to those which, as yet, have not been identified. Please see the discussions by Edelson (1991) and the short summary survey by Baum (1991).

As mentioned above, any atmospheric gas may participate in the clathrating process. See Goldberg (1963) for the possibilities for free radicals and reactive molecules in clathrate cavities. Atmospheric gases participate in the radiation processes. Though the gases nitrogen ( $N_2$ ), oxygen ( $O_2$ ), oxides of nitrogen such as ( $\bullet N_2O$ ) and ( $\bullet NO_2$ ), and argon (Ar) have been discussed previously and are subject to the clathrate process, discussion of the process has been delayed to the present section on methane ( $CH_4$ ). Methane ( $CH_4$ ) and its oxidized products of carbon monoxide (CO) and carbon dioxide ( $CO_2$ ) are often considered first in a discussion of the radiational features commonly referred to as "greenhouse" warming.

As the discussion here is extensive, and is applicable in a general sense to any of the atmospheric gases or mixtures of those gases, reference to such clathrate hydrates in any other subsection will be very brief.

The isolating features of gas clathrate hydrates provide both a sink for atmospheric gases and a storage mechanism for potential later release. Existence of other clathrates such as the "clathrasils" is acknowledged. Though these may be important in Earth's climate, only the hydrate form where water forms the cages will be of immediate interest.

The word sink is a relative term. Here it designates the phenomenon of something being removed from active participation in any process. The period of removal is variable. Therefore, for any discussion, the length of the period and the phase ought to be mentioned. In some respects, the sinks are transient. Following this argument, Earth itself is an ensemble of many transient sinks. Light gases, ions, and atoms are continually being lost to galactic space; i.e., galactic space is a sink. These are removed from immediate active participation in Earth processes. Cycling of materials occurs in many instances, such as carbon dioxide as a gas, as in the carbonic ions and in the carbonates. Thus, for example, the methane clathrate hydrate is a sink form which will disintegrate once the physical pressure temperature constraints are exceeded. Both water and methane are freed.

**11.8.4.1 History.** There are several papers which include histories of the discovery and development of the clathrate phenomena and research. Among these are those of Schroeder (1927), Davidson (1973), Miller (1973), Berecz and Balla-Achs (1983), and Sloan (1990).

Sir Humphrey Davy in 1810 is credited with the discovery of a chlorine hydrate by cooling a water solution of chlorine below 9 °C (Miller (1973)). This was corroborated by Faraday in 1823 (Sloan (1990)). Little was done until the last of the 19th century. Miller (1973) and Sloan (1990) as well as others reference the work of Villard and DeForcrand. For example, Villard (1894) and DeForcrand (1902) studied several hydrates among which were those

of methane ( $\text{CH}_4$ ), carbon dioxide ( $\text{CO}_2$ ), and propane ( $\text{C}_3\text{H}_8$ ). These molecules and others are of increasing interest today due to their radiational characteristics in the gaseous form. The field laid dormant until the 1920s and 1930s when the clathrates became and still remain a problem in energy fields in transmission of natural gases and petroleum. See Hammerschmidt (1934), Deaton and Frost (1937, 1939, 1948), Miller (1973), Makogon (1965, 1974, 1988), and Sloan (1990). Curl and Smalley (1988) report on their work on a hosting by carbon of the gas argon (Ar). See also Curl and Smalley (1991) for an up-to-date discussion of the buckminsterfullerenes, -fulleranes, and -fullerides. That the clathrate phenomenon extends throughout the solar system and is a feature of climates is discussed by Curl and Smalley (op. cit.), Miller (1973), and Lunine and Stevenson (1985). Lunine and Stevenson (1985) suggest the formation and accretion of the gas clathrate hydrates and silicates.

There may be some interest in a more personal introduction. See Sawyer (1967) concerning a general chemistry experiment on clathrates. See also Brown (1962) for a more general treatment. The words are "inclusion compounds" which treat other types of inclusion in addition to the cage structures.

**11.8.4.2 Chemical Problems.** One of the bigger problems involved in the study of clathrates is that once a gas molecule is caged, it is removed from active chemical participation. It can enter no chemical reaction and therefore cannot be tested chemically. It is hidden and is inactive in its chemical responses. Only if the hydrogen bonding of the water cages is broken; i.e., dissociation occurs in the imprisoning material, then and only then can appropriate chemical responses for identification of the freed gas(es) be obtained. Where, in any chemical formulae, there are whole numbers of participating atoms deducible, the formulae are called stoichiometric. An example is common table salt, sodium chloride ( $\text{NaCl}$ ). Another example is water ( $\text{H}_2\text{O}$ ). Where whole numbers of participating atoms are not deducible with respect to one of the other participating atoms, the formulae are known as nonstoichiometric. An example is methane clathrate hydrate,  $\text{CH}_4 \cdot 5.75 (\text{H}_2\text{O})$ . Such is generally the case with clathrate hydrates but a troublesome feature is that the numbers deduced may not be consistent, for not all cages may have an occupant. This certainly leads to confusion, which will be alluded to later.

**11.8.4.3 Physical Considerations—General.** Physical means, such as irradiation with x rays and now nuclear magnetic resonance techniques and dielectric absorption techniques, can elicit responses from the caged material. Thus, the caged material(s) may be identified. The number of identified clathrates increases. Between 1973 and 1978, 26 new clathrates were identified (Davidson and Ripmeester (1978)), which also will be alluded to later. By 1987, as indicated by Ripmeester et al. (1987), over 120 clathrates had been identified. Von Stackelberg and Muller (1951, 1954) report on the work of their group (1948–1954) in the deduction of the crystalline structures of clathrates by means of x-ray diffraction. These are structures I and II. Pauling and Marsh (1952) made the first determination of a structure I hydrate. Claussen (1951c) guessed at the structure II hydrate by modeling which was verified by Stackelberg and Muller (1951, 1954) and Miller (1973). Jeffrey (1984) proposes a number of other structures while Ripmeester, Tse, Ratcliffe, and Powell (1987) propose a new structure which they call Structure H, a hexagonal type structure. They mention the fact that large hydrocarbon molecules may be encapsulated by this crystalline form of water.

Figure 11-10 exemplifies a Structure I hydrate ensemble (Pauling (1961)) which is reproduced with permission. As Miller (1973) indicates, this is a 12-cubic-unit cell which contains 46 water molecules and 8 cages of two types. The vertices represent the oxygen atoms of the water molecules while the hydrogen atoms involved in the hydrogen bonding process lie along the lines that connect the vertices. Structure II has a 17 Å cubic unit cell which has 136 water molecules with 8 large cages and 16 small cages.

Sloan (1990), among others, discusses the polyhedra now generally associated with the clathrate hydrates. Sloan (1990) is the best book known to the author at the present time on the subject of the gas clathrate hydrates. The hydrogen bonding is important. Sloan (op. cit.) assembles considerable information on water structures.

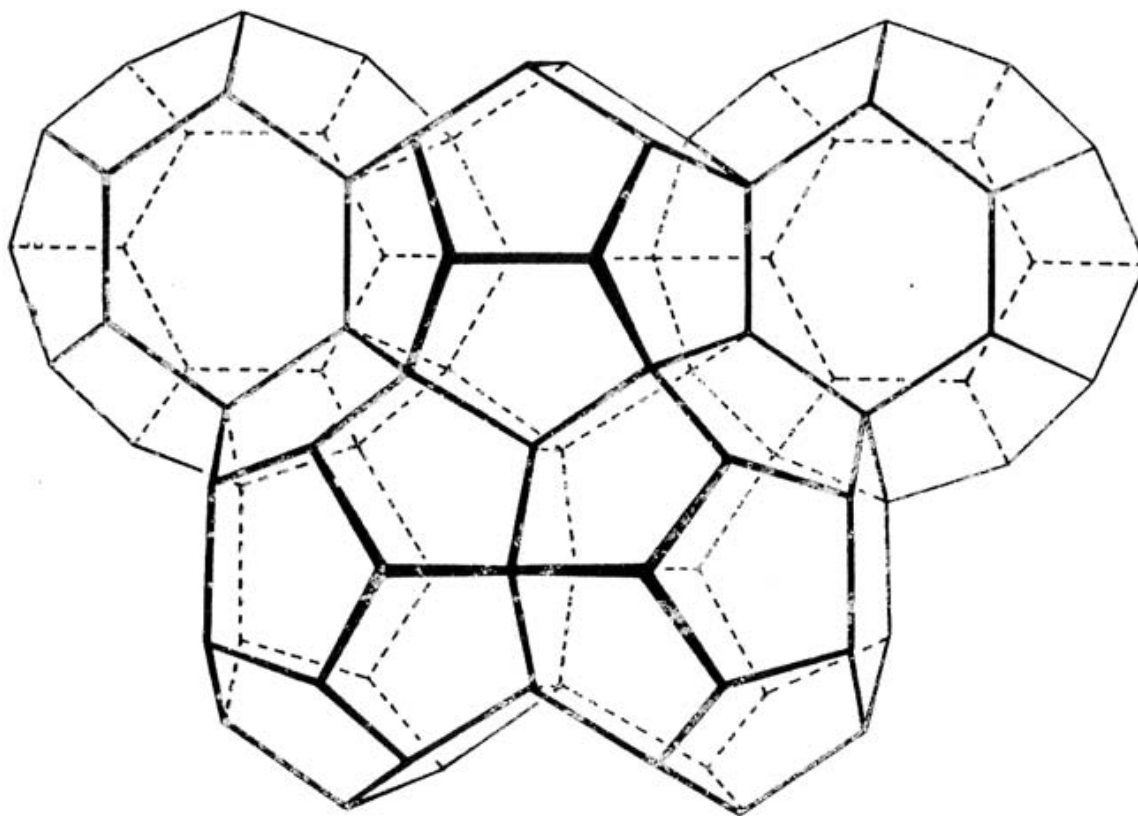


Figure 11-10. Structure I ensemble for a clathrate hydrate. The 12-A hydrate crystals. One dodecahedron is shown in the side center. Around it are the tetrakaidecahedra which provide room for somewhat larger molecules than fit in the dodecahedra. There are six tetrakaidecahedra and two dodecahedra per unit cube (with permission, AAAS, *Science*, courtesy of L. Pauling (1961)).

He references many works including those of Jeffrey and McMullan (1967), Jeffrey (1984), and Davidson and Ripmeester (1984). The general cage nomenclature form suggested by Jeffrey (1984) is  $(n_i m_i)$ . For the  $i$ th type,  $n_i$  is the number of edges while  $m_i$  is the number of faces. The 12-, 14-, and 16-hedra cavities are then described by  $5^{12}$ ,  $5^{12}6^2$ , and  $5^46^4$ . The dodecahedron,  $5^{12}$ , has 12 pentagonal faces. The tetrakaidecahedron,  $5^{12}6^2$ , has 12 pentagonal faces and 2 hexagonal faces. The hexakaidecahedron then has 12 pentagonal faces and 4 hexagonal faces. In each case the superscript additions indicate the number of faces, respectively, 12, 14, and 16. In addition, there are larger polyhedral cages.

Hydrate cavities (fully closed, without guests, empty cages) are not stable in pure water (Jeffrey (1984)). A gas molecule in a cavity, closed or not, stabilizes the cavity. Stabilized enclosed cavities; i.e., closed cubicles each with a single gas molecule resident, help to stabilize nearby cavities or cubicles. If the majority of cavities enclose gas molecules, one only to a cavity, the entire structure is stabilized. Thus, in a methane clathrate hydrate, 1 m<sup>3</sup> of such an ice structure may have all cubicles filled or only two-thirds of the cavities filled. When the cubic meter of methane clathrate hydrate (ice) decomposes at normal temperature and pressure, various estimates are that 120 to 180 m<sup>3</sup> of gas are released. Kvenvolden and McMenamin (1980) indicate 160–164 m<sup>3</sup>. The number of cubicles filled is variable, depending on the pressure-temperature configurations at formation time and the formation rate. Therefore, the ratio of number of gas molecules released to the number of water molecules is variable. Different investigators attempting to formulate relationships determine different and inconsistent formulae. The formulae

may differ for different gases. For methane and other atmospheric gases, the best ratio seems to be  $\text{CH}_4 \cdot 5.75$  ( $\text{H}_2\text{O}$ ) or  $8\text{CH}_4 \cdot 46 \text{H}_2\text{O}$ . These formulae are nonstoichiometric; i.e., a whole number of host water molecules is not associated with one guest gas molecule. Another variation enters into the picture when the cubicles are  $5^{12}$ ,  $5^{12}6^2$ , or  $5^{12}6^4$ . Though only one gas molecule is associated with one cubicle, the number of water molecules vary, respectively, as 20, 24, and 28. The volumes also are different. In the usual form of hexagonal ice (Ih) the typical distance between the oxygen nuclei is 0.276 nm (Sloan (1990)). The covalent bonded protons (hydrogen nuclei are  $\approx 0.1$  nm from an oxygen nucleus while hydrogen bond distance to another oxygen nucleus is  $\approx 0.176$  nm. Sloan (1990) following Durrant and Durrant (1962) shows the ice forming as a “puckered” hexagonal ring structure. The external and internal diameters of these hexamers (hexagons) are about 0.552 and 0.422 nm. Presumably, in a symmetric lattice of such ice, molecules  $< 0.422$  nm in diameter could pass easily through the ensemble. This feature will be discussed again at the end of this subsection on clathrates. Sloan (1990) further indicates that the cavities  $5^{12}6^4$  and  $5^{12}6^2$  have the capacity, respectively, to contain molecules as large as 0.66 and 0.60 nm. There seems to be a relationship between the cavity (house) sizes and the gas molecule (guest) sizes which helps to determine those cubic structures which best serve. A ratio near 1 or more of cavity to molecule size indicates difficult fitting which may include cavity distortion. A ratio of 0.7 indicates difficulty in the guest stabilizing the potential host cavity. Much lower than this, no stabilization occurs. Thus hydrogen, helium, and neon form no known clathrate hydrates. It would seem that in the  $5^{12}$  structures where total impermeability is not attained because there are no face-to-face orientations, these three gases may perfuse through the structure or even through the cavities stabilized by nearby stable cavities. However, with other gases available as helping gases, such as propane, hydrogen sulphide, carbon dioxide, etc., impermeable mixes (layers) may and probably will develop.

Sloan (1990) provides tables and figures for the comparison of diameter ratios of cavities to molecules and of cavities, guest molecules, and potential cavity configurations. Where Sloan (1990) indicates (figure 2-8, p. 49) that no clathrate hydrates exist, Ripmeester et al. (1987), not then available to Sloan, indicate the determination of those which accommodate molecules of diameter greater than about 0.75 nm. They propose a new structure “H” for clathrates in addition to the many potential forms suggested by Jeffrey (1984). The likely cavities for the supporting (helping cavities with helping gases) cavities are a  $5^{12}$ , a  $4^35^66^3$ , and the main host is the a  $5^{12}6^8$  cubicle. NMR techniques are used to deduce the structure, and to identify the guests (Ripmeester et al. (1987)).

Bulky molecules, such as methylcyclohexane, may be encapsulated in the above ensembles where the helping gases are xenon (Xe) and hydrogen sulfide ( $\text{H}_2\text{S}$ ) at about atmospheric pressure and 0 °C (273 K) (Ripmeester (op. cit.)). If methane itself is used as a helping gas, then such clathrate hydrate formation can be induced if the pressure is increased to  $\approx 20$  atm. The helping gases usually occupy the smaller cavities. In the larger cavities, the occupying molecule is free to rotate about a long axis.

Nitrogen ( $\text{N}_2$ ), oxygen ( $\text{O}_2$ ), argon (Ar), methane ( $\text{CH}_4$ ), carbon dioxide ( $\text{CO}_2$ ), and other atmospheric gases may participate as guests, one to a cubicle in structure I (Miller (1973)). Molecules of larger dimension, such as those of propane, will be guests of structure II ensembles, although smaller molecules may also be guests, but again only one to a cage. In the case of the carbon cage,  $\text{C}_{60}$ , for argon,  $\text{Ar} \cdot \text{C}_{60}$ , the structure appears like a volley ball. The intermediate dot in the case of clathrates implies that the  $\text{C}_{60}$  cage structure encloses an argon molecule. In these cases, the dot does not indicate a radical nor a multiplication. The  $\text{C}_{60}$  molecule mentioned previously has recently (1990) received much attention and will be further discussed.

It should be noted here that clathrates may be transported along with their gas cargos. The Canadian National Research Council groups have been in the forefront of investigations of the clathrate phenomena. Reference may be made to Davidson (1971, 1973, 1981), Davidson et al. (1977, 1978, 1981, 1984, 1986, 1987a,b), Ripmeester et al. (1977, 1981, 1987, 1988), Tse (1987, 1980), and Tse et al. (1982, 1983a,b, 1984, 1986, 1987a,b,c). For other references, see Sloan (1990).



11.8.4.3.1 Formation. Clathrate structure formation seems to be an amicable affair within the pressure and temperature constraints. Both the host(s) and guest(s) must be present and both seem to be involved in the process. As previously discussed, there are eight known forms of the ordinary hexagonal forms of water ice. The clathrate host water structure is a cubic, not a hexagonal, structure, except for structure H. In the embedding process of the gas molecule, its size, configuration, and its rotational and vibrational characteristics apparently help in the determination of the space-shape required for free movement as the pentagonal and hexagonal platelets are formed, erected, and joined. Sometimes, apparently, during the structure development of near neighboring cubicles, a cubicle may be closed and empty before a “guest” is involved. As indicated previously, this leads to problems in determining the nonstoichiometric formula. Where there are cubicles with no guests, the counts will not be a maximum. The number of empty cubicles depend on conditions during clathrate formation. Too many empty cubicles and the structures disintegrate. Of course, plenty of water must be available.

Here, it should be mentioned, as noted in several references above, that a mixture of guest gases may make the hydrate formation easier (under not as strict constraints). This seems to be the case where mixtures of large molecules and small molecules are used, such as propane and methane. For example, in a mixture of methane and water where methane tends to build or affect the smaller cubicles, the addition of propane enables the building of small cubicles which in turn help to support the larger cubicle structures. The methane occupies the smaller cubicles, one molecule to a cavity.

In analogy, if one has ever watched a bird build a nest, the bird, after placing a feather, twig, or piece of twine, will sit in the forming nest, move up and down, and turn around and around in forming a circular and evenly smoothed bed. In the case of clathrate hydrates, the interior free space of the cubicles will form roughly in spheroidal shapes. The spherical cavities will be formed for those molecules whose vibrational, rotational, or spin characteristics will allow the guest molecule to move freely. Ellipsoidal shapes will serve those that have short and long axes, allowing spin, rotation, and vibration about the longer axis but no spin around one or both about a shorter axis. The form swept out will be football or discus shaped. However, the face plates will generally be pentagons or hexagons. The outside surfaces will not be smooth. Over time, the varied cubicle sizes are assumed to reach an average shape and size.

**11.8.4.4 Pressure-Temperature Constraints.** Some clathrates are formed under normal pressure, temperature, or pressure-temperature regimes just as the first known clathrate chlorine hydrate was developed in 1810 by Sir Humphrey Davy. On the other hand, some clathrate hydrates exist under wide-ranging conditions. Also, as noted above, some mixed hydrates have formation and dissociation points outside the constraints for any one of the participating gases when that gas is used alone. See also Barrer and Stuart (1957). These will be discussed in more detail in the next subsection.

**11.8.4.5 Methane Ice.** Natural gas may be outgassed or obtained from sediment. Water, methane, or any other gas may form a gas hydrate or clathrate hydrate, which means that the methane is enclosed in a solid water cage. Under specific pressure and low temperature conditions, this gas hydrate exists in cubic forms, not hexagonal. See Davidson et al. (1986). Generally, hexagonal ice melts at 0 °C and 1 bar of pressure (atm). Clathrate hydrates may form and decompose in a range of temperatures including temperatures above 0 °C. Just as with hexagonal ice, there are several forms for the clathrate hydrates. Several clathrate structures are assumed. Such pressure and temperature conditions are met in sediments of the oceans and in permafrost (4 °C) near areas of the polar regions. As methane gas forms and/or rises through sediments with the right temperature and pressure conditions, methane caging occurs, only if sufficient water and methane are present. A methane clathrate ice is permeable by itself. Particularly, if larger molecules, such as propane, are available as helping gases, a methane-propane clathrate ice mixture may become impermeable. This solid clathrate hydrate forms and may act as a barrier to gases still rising from below. See Kobayashi and Katz (1949) for a discussion of methane hydrates at high pressures. See Marshall

and Kobayashi (1964) and also Baker (1974) for experiments on hydrocarbon gas clathrates in unconsolidated sand. There is some indication that when there is a great amount of water in the sediment, but no great quantities of methane, small, isolated layers of clathrate ice may form and many small patches and clathrate crystals may form and cement (stiffen) the sediment layers. Cores have been obtained where the sediment appears to be studded with small crystals. See also Evrenos et al. (1971) on impermeation of porous media.

Figure 11-11 shows the burning of methane ice. The methane is being released as the water crystal structure disintegrates in the open air at normal pressure. This photograph is used with the permission of the Morgantown, West Virginia, U.S.A., Energy Tech Center of the U.S. Department of Energy. This same photograph serves as a frontispiece to Sloan (1990), which he describes as a burning snowball. From personal experience in the gas fields



Figure 11-11. Methane ice burning (courtesy of the Morgantown, WV, USA, Energy Tech Center of the U.S. Department of Energy (1990)).

of Oklahoma choked pipelines, removal of the ice and purging of the lines provided clumps of such methane ice (or snow balls) which burned very well. See also Hammerschmidt's description of the problems. Today, there are several ways to prevent this formation; one is to dry the gas before it is pumped.

Carson and Katz (1942), Katz (1945), Unruh and Katz (1949), Robinson and Hutton (1967), Makogan et al. (1972), Davidson and Ripmeester (1978), Kvenvolden and McMenamin (1980), Khalil and Rasmussen (1983), MacDonald (1983, 1988), Revelle (1983), Lachenbruch and Marshall (1986), Ratcliffe and Ripmeester (1986), and Collins et al. (1987) consider the gas or clathrate hydrate problem. The process of caging, in the case of methane and water as well as for other gases, seems to be a mutual affair. (The molecular sizes are compatible such that linking of the water molecules into the forming polyhedra entrap the methane molecule, provided such a molecule is there.) The lower value given above simply indicates that all of the cage spaces were not filled by the gas as they became available. Once the cage formed, no gas molecule much larger than any cage face could enter into the cage because of its size. A molecule slightly larger than a polyhedral face can slip through the faces if pressured much like a cotton ball. Getting out is a different matter. The larger number simply indicates that all available spaces were filled as they became available. As indicated previously, the nonstoichiometric formula then may vary from experiment to experiment but is often given near the value  $\text{CH}_4 \cdot 5.75 \text{H}_2\text{O}$ . In attempts to force a stoichiometric structure, earlier versions gave a stoichiometric value of  $\text{CH}_4 \cdot 6 \text{H}_2\text{O}$ . In addition to the pressure-temperature constraints, there must be ample water supplies as well as a corresponding supply of methane or other gas(es). In the ocean sea bottom sediments, and perhaps in the permafrost regions, there may not have been sufficient water or sufficient methane or other alkanes to provide a continuous sheet of the gas clathrate hydrate. But there may have been localized areas where these clathrates could form in the sediment and so stabilize or cement the sediment layer. This sediment layer, cemented, in appearance, and studded with clathrate groups or crystals, would eventually become impervious to gas being generated below, rising from fissures in the crust or from the mantle. Drilling would perhaps not show the clathrates as drilling proceeds through the sediment layer. See Sloan (1990) and Dillon et al. (1990) concerning the acoustic sounding of these buried methane hydrate cemented layers called bottom simulating reflectors.

The nonstoichiometric nature of the gas clathrate hydrate systems has made it difficult to assess the hydration numbers. These may vary, depending on the gases being enclosed and the resultant cages being developed. X-ray diffraction, the recently improved expanded neutron powder diffraction measurements, and dielectric absorption techniques are tools now used and are especially helpful in deducing crystalline structures (Pauling (1961), Davidson (1981), Miller (1985), Ripmeester et al. (1987), and Ripmeester and Ratcliffe (1988)). Miller (1985) presents a concise and revealing discussion of the general clathrate phenomena. Sloan (1990) presents an extensive up-to-date summary and discussion of the clathrate hydrates of natural gases. This is recommended reading for both the novice and the professional in the field of clathrates. Ripmeester (1989, personal communication) provides the following short discussion on the structure and gas content of gas hydrates:

“The relationship between apparent stoichiometry and actual gas content becomes clear with referral to the structure of the clathrate hydrates. For structure I clathrate hydrate, the unit cell (from x-ray diffraction) contains 46 water molecules. Each unit cell contains 6 large cages (14-hedra) and 2 small cages (12-hedra), so that the formula for one unit cell can be written  $6M_1 \cdot 2M_2 \cdot 46 \text{H}_2\text{O}$ .”

“When all cages are full, this leads to the formula  $G \cdot 5 \frac{3}{4} \text{H}_2\text{O}$  ( $G =$  guest molecule). For methane hydrate, essentially all of the  $M_1$  cages and about  $\frac{3}{4}$  of the  $M_2$  cages are filled, leading to a hydration number close to 6. For  $\text{CO}_2$  hydrate, the guest molecule is too large for the small cage, so that only most of the  $M_1$  cages are filled, leading to a hydration number close to  $7 \frac{2}{3}$  ( $\text{CO}_2 \cdot 7 \frac{2}{3} \text{H}_2\text{O}$ ).”

“For structure II, the situation is similar. The unit cell formula is  $8M_1 \cdot 16M_2 \cdot 136 \text{H}_2\text{O}$  if all cages are filled (as for Kr, Ar,  $\text{O}_2$ ,  $\text{N}_2$ ) the formula is  $G \cdot 5 \frac{2}{3} \text{H}_2\text{O}$ .”

“For molecules larger than  $\approx 6$  Å diameter, only the large cages are filled, leading to a formula of  $G \cdot 17$  H<sub>2</sub>O (e.g., for propane hydrate). For gas mixtures containing both large and small molecules (e.g., methane and propane), the situation is more complex, with propane present only in large cages and methane distributed over both sites, but primarily in the small cages. There is no experimental evidence of multiple occupancy of any of the hydrate cages.”

The hydrogen bonds are relatively weak but are quite sufficient to strongly structure the water cages. If the pressure is decreased or the temperature increased, or both, these bonds may dissociate, the cages collapse, and thereby release the methane. Those who drill through the permafrost must use special techniques to keep clathrates—the gas hydrates—in the permafrost from dissociating. Without such precautions, this gas released, superpressures and oil well blowouts occur. This is dangerous to men, equipment, and especially to the permafrost. The same dangers exist in the ocean, where the sediments themselves form layers impervious to rising gas(es). In addition, with appropriate pressure and temperature conditions, clathrate hydrate layers impervious to passage of gas(es) may form. Ocean platforms used for oil drilling purposes must expect problems if drilling through suspected clathrate ices. However, acoustic and seismic sounding may show the base of potential clathrate layers (Kvenvolden (1988a)). Not much more is known. Sloan (1990) discusses these problems and describes the techniques involved to minimize drilling, transportation, or transmission problems.

Large stores of methane and presumably other gases were encaged long ago (and are still being encaged) molecule by molecule. The total is not known but it could be extremely large (Kvenvolden (1988b)). Kvenvolden estimates about  $10^4$  Gt (10 Tt) of carbon. This amount is greater than the other known sources of carbon fuel. The deeper layers, impervious to the passage of gases of all types, further trap gas being exhaled from bottom sediments and perhaps the sea beneath or from still deeper Earth. Most authors consider two problems occasioned by release of methane from bottom structures and dissociating gas hydrates; both release methane to the atmosphere. The end result may be an atmospheric warming through trapping of infrared radiation, which on emission, causes warming of permafrost and further clathrate dissociation. A reinforcing cycling action occurs. Another problem may occur and that is the collapse of water ice cages with subsequent subsidence. Close to coastlines, this could result in flooding and further permafrost degradation. This, of course, could release more of the old stores of methane into the atmosphere. But in all of this, one must consider the long, long time necessary for the heat transfer; presumably this may be centuries away.

Kvenvolden and McMenamin (1980) include schematic diagrams of the permafrost and the methane gas hydrate stability region. Figure 11-12, adapted from their work, illustrates the possible depth of occurrence. The thermal gradient in permafrost is assumed to be  $0.018$  °C m<sup>-1</sup>. The methane clathrate hydrate region is shown between the gradient line and the curve. The depths of the hydrate stability zone extend from about 200 to 1,150 m with corresponding temperatures ranging from about  $-10$  to  $14$  °C. Below  $0$  °C, ice exists, and above  $0$  °C, water exists. The thermal gradient in the nonfrozen sediments is  $\approx 0.027$  °C m<sup>-1</sup>. Sodium chloride and other salts are excluded from the clathrate region. As with any such clathrate formation by hosts and guests, there exists those critical points and planes which separate the phases. In the case of methane clathrate, there are the phases, water, methane, hydrate, the water methane, the ice-water, the ice-methane, and the ice-water-methane-hydrate mixtures. The existence of other guest gases complicates the situation.

At this point, a digression is made. In section 11.8.2.1 the existence of methane (CH<sub>4</sub>) in interstellar and interplanetary space was discussed. Also, the now known existence of methane (CH<sub>4</sub>) on Earth and on the giant gas planets was discussed. The thermal and pressure conditions are quite different on Earth compared with those of the gas planets, Jupiter, Saturn, Uranus, and Neptune. Miller (1985) hypothesizes the existence of clathrate hydrates as major features of the outer gas planet structures. Lunine and Stevenson (1985) discuss the thermodynamics of clathrate hydrate at low and high pressures with application to the outer solar system. Figure 11-13 is adapted from

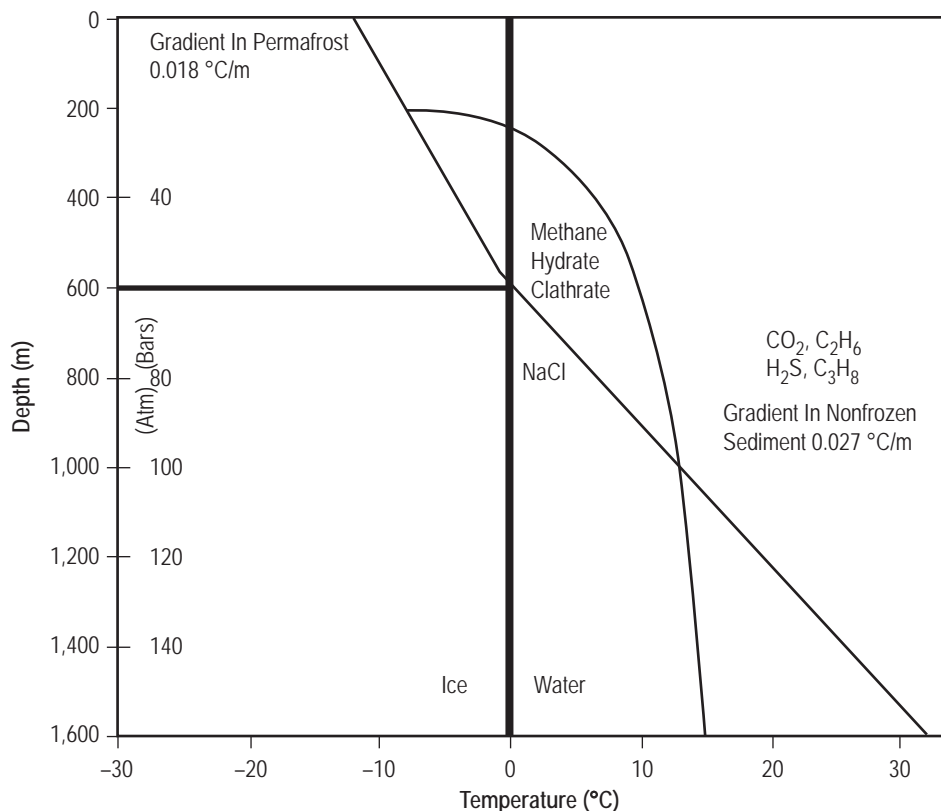


Figure 11-12. Schematic diagram of the permafrost and methane hydrate stability region (courtesy of Kvenvolden and McMenamin (1980)).

their figure 2, p. 497. It is similar to and supplements that of Kvenvolden and McMenamin (op. cit.) but is modified and rotated for easier comparison with figure 11-12. The small, central outline square represents the part covered in figure 11-12.

In figure 11-13, the envelope lines enclose the region in which the clathrate, thermodynamically, is preferred relative to water ice or liquid plus the co-existing components. The X represents methane in this case, but the figure can be interpreted roughly for other gases. The dashed line represents the water ice-liquid phase boundary. Superimposed are the dotted lines representing the vapor-liquid phase boundary, A, and the liquid-solid phase boundary values of the pure component X. This figure indicates that the methane clathrate can exist at low pressures if the temperatures are sufficiently low. Lunine and Stevenson (op. cit.), also in tabular material, provide for the following selected gases—the temperature (K) associated with the dissociation pressures (bars): (1) CH<sub>4</sub>, 180, 0.419; (2) CO<sub>2</sub>, 200, 0.366; (3) H<sub>2</sub>S, 273, 0.968; (4) C<sub>2</sub>H<sub>4</sub>, 180, 0.03; and (5) SO<sub>2</sub>, 271, 0.290. These combinations do occur in the Earth and its atmosphere. Davidson (1981) in his table 1 gives the structure, hydration number, and dissociation pressure (atm) of methane (CH<sub>4</sub>); I, 5.9, 26 °C. Any or all of these gases may be sequestered at the same time as methane; however, the water cages would be more complicated. As to the sequestering of ozone, as far as the author knows, no work has been done, but Lunine (1989) (personal communication) indicates that the dissociation pressures should be lower than O<sub>2</sub> but higher than CO<sub>2</sub>. Ripmeester (1990) (personal communication) indicates that if it exists, it will have a hydration number between 6 and 7 with structure I. If it exists, such a sequestering represents a potential ozone sink.

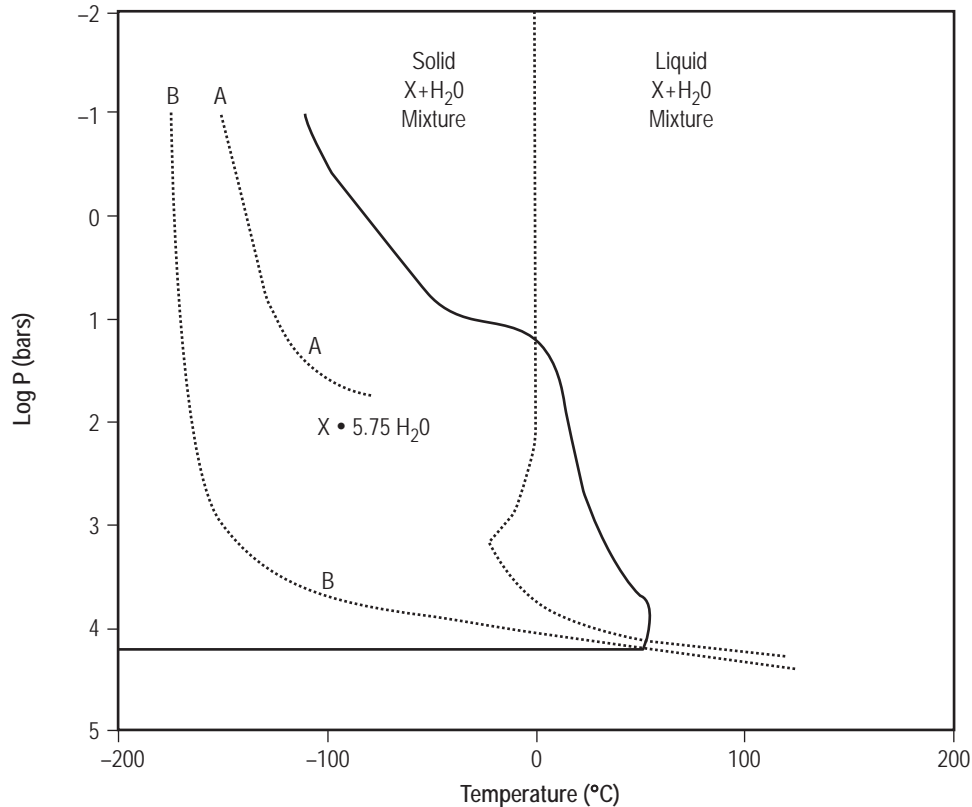


Figure 11-13. Pressure temperature constraints for clathrate hydrates (X is any gas) with general application including solar interplanetary and planets. Central square-modification after Kvenvolden and McMenamin (1980). See figure 11-12 (adapted with permission, Lunine and Stevenson (1985) and Kvenvolden and McMenamin (1980)).

**11.8.4.6 Further Comments on Hosting.** Geometric as well as orbital and thermodynamic considerations play a part in this scenario. Lunine and Stevenson (1985) extend a statistical mechanical model of clathrate formation originally developed by van der Waals and Platteeuw (1959) to predict the formation conditions and composition of clathrate hydrate under a wide range of situations. Particular interest lies in the solar system.

In previous subsections, the assumption has been made that only one occupant or guest per cavity is to be considered. As mentioned by many authors, such lone occupancy is noted. Further, both Sloan (1990) and Ripmeester (personal communication) indicate that no experimental evidence is available to show anything more than single occupancy.

Suggestions or ideas that double or multiple occupancy may be possible are presented by van der Waals and Platteeuw (1959). Lunine and Stevenson (1985) explore these ideas and provide geometric and theoretical work. One example noted is the suggested double occupancy of a cavity by methane ( $\text{CH}_4$ ) and hydrogen ( $\text{H}_2$ ). Thus, a wide field of research is open to investigation. But as this section on clathrate hydrates indicated and the difficulties associated with such studies imply, the research will be most difficult.

The subject is important from the viewpoint of the sequestering and release of atmospheric gases during changing climate regimes.

**11.8.4.7 Clathrate Summary.** For those interested in the subject of physicochemical storage of gases, reference may be made to texts on inclusion compounds, intercalation structures, nonstoichiometric compounds, and clathrates, including clathrate hydrates, clathrate silicates, and clathrate carbons. Encaging of gases and chemical compounds is an intriguing and important subject. To the climatologist, this is so because it represents potentially important sources and sinks for atmospheric gases. According to Miller (1985) and Shoji and Langway (1983), clathrated air is found in polar ice fields (cores); i.e., atmospheric air is encaged by water cavities. It is not a new feature but seldom receives much attention in undergraduate studies in physics, chemistry, and much less so in geology and climatology. The encaged species undergo no chemical reactions. Their presence or nonpresence cannot be ascertained by chemical techniques. Only physical techniques, primarily those of radiative techniques, can be used successfully. The cages also may be described as tubes, sandwiches, dimples, etc. See Brown (1962), Hagan (1962, 1963), Mandelcorn (1964), Whittington, Stanley, and Jacobsen (1982), and Atwood, Davies, and MacNicol (1984). The papers by Brown (op. cit.) and Whittington, Stanley, and Jacobsen discuss other modes of isolation in addition to the cages discussed here. Once encaged, under suitable conditions the sequestered materials may be transported. Here, for methane and other atmospheric gases, the preferred encaging polyhedra seem to be the 12-, 14-, and 16-sided faces, formed of pentagons and hexagons. If all of the polyhedra are of the same form, complete packing of all space is not necessarily possible. Mixtures of polyhedra allow for complete packing and, in the case of methane clathrates, the potential formation of impervious layers and/or masses. Figure 11-10 (courtesy of S. Miller) from Lunine and Stevenson (1985) and from Pauling (1961), with permission from Pauling, is one illustration of one proposed polyhedral form for methane clathrate hydrate. Vinogradov and Linnell (1971), Jeffrey (1984), and Brown (1962), among others, present similar representations. See also Collins et al. (1987) on other clathrate hydrates of  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ ,  $\text{PH}_3$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_3\text{H}_6$ . These are often found mixed with methane ( $\text{CH}_4$ ). As mentioned previously, it is chemically impossible to determine the nature of the “guest” or “prisoner” molecules enclosed within the structure of “host” or “jailer” molecules. Until the “guests” are released at the disintegration of the “host” structural framework, the “guests” cannot be identified chemically. The pressures at the temperatures where the host structures break down are dissociation pressures. However, with infrared techniques (Davidson (1981)) x-ray and neutron diffraction techniques and the development of NMR techniques, both the identity of the “guests” and the physical structure of the “hosts” can be determined by physical (not chemical) means. See also Ratcliffe and Ripmeester (1986),  $^1\text{H}$  and  $^{13}\text{C}$  NMR studies on clathrate hydrates, and Ripmeester et al. (1987).

The main point now is that clathrating is not restricted to methane and the host cages are not necessarily water. Argon (Ar), one of the “noble” or relatively inert gases, often has been used as the “guest” to a large number of different “hosts.” One of the latest is reported by Curl and Smalley (1988) where the “host” lattice cage is the carbon-sixty,  $\text{C}_{60}$ . Speculatively, Smalley (1988) suggests that this clathrate exists in interstellar space as well as in and on Earth. This basis is ascribed to known spectral bands which may be associated with Argon encaged by the carbon. Where the cage has not formed and locked and the partial caging continues, spiraling forms of “soot” in burning processes is noted. (See also recent survey articles by Baum (1990, 1991)). Usable amounts of these clathracarbs are being produced such as  $\text{C}_{48}$ ,  $\text{C}_{60}$ , and  $\text{C}_{72}$ ; the larger proportion goes to  $\text{C}_{60}$ . Many other gases may be caged, such as  $\text{N}_2$ ,  $\text{O}_2$ , Kr, and CO. See Davidson et al. (1987a) on a clathrate hydrate of carbon monoxide (CO). That paper includes a discussion as to how the material was determined to be CO encaged by water.

Guyer and Koshland (1990) discuss the buckminsterfullerene  $\text{C}_{60}$  in their article on Diamond: Glittering prize for materials science. The  $\text{C}_{60}$  molecule has the shape of a volleyball or a soccer ball, and because Buckminster Fuller did much work with polygons in building construction, the fullerenes are often called buckyballs. The fullerenes have an even number of carbons such as  $\text{C}_{50}$ ,  $\text{C}_{60}$ ,  $\text{C}_{70}$ , etc.;  $\text{C}_{60}$  seems to have the most stable configuration. Progress in laboratory techniques permit production in grams per day. There is some speculation that these, if care is not used, may constitute a respiratory health hazard. Because they are also so stable (chemically unreactive), they may be very abundant in the universe. They can only be detected by physical probing with selective electromagnetic radiation.

Gibbons (1990), writing in *Science: Astro-1: From the jaws of defeat*, and reflecting statements of the mission scientists, provides the speculation that the researchers may be able to determine whether the primordial dust that condensed still exists and is detectable. These scientists apparently have strong evidence to show that the dust is carbon. Presumably this would be graphite, C<sub>60</sub> or another buckminsterfullerene or buckminsterfullerane.

Davidson (1981) in his table I gives the structure, hydration number, and dissociation pressures (atm) at 0 °C of several gases, among which is methane: (1) N<sub>2</sub>, II, 5.8, 150; (2) CH<sub>4</sub>, I, 5.9, 26; (3) H<sub>2</sub>S, I, 6.1, 0.95; (4) CO<sub>2</sub>, I, 7, 12.4; (5) C<sub>2</sub>H<sub>6</sub>, I, 8.2, 5.2; (6) C<sub>3</sub>H<sub>8</sub>, II, 17, 1.73; and (7) I-C<sub>4</sub>H<sub>10</sub>, II, 17, 1.12. This information is included so that the reader will not infer that all clathrates have a hydration number of 5.75.

Ripmeester et al. (op. cit.) propose a new structure II in addition to the clathrate hydrate structures I and II. Structure I is associated with the 14-hedra while structure II is associated with the 16-hedra. See Davidson (op. cit.) for illustrations. There are also other numbered structures. Basic structures are suggested by Brown (1962) and Jeffrey (1969, 1972, 1984). It is noted that where there is a mixture of gases, which may include methane, the cages may be larger for the larger molecules (such as for argon), smaller for the smaller molecules, and larger and not necessarily symmetrical for large and small molecules encaged in the same cavity. Ripmeester et al. (1987) indicate that over 120 guest species of the hydrate hosts have been identified. They also discuss briefly the clathrasils where the hosts are cages composed of silicon dioxide (SiO<sub>2</sub>). Ripmeester (1990), personal communication, indicates that, as yet, there is no indication that more than one guest can occupy a cubicle.

The study of the climates of all planets is done to be able to better deduce the past, present, and future climate(s) of the Earth. For those who are interested in the climates of the outer planets where the temperatures and pressures equal or far exceed those of Earth, the serious study of clathrate features is encouraged. Lunine and Stevenson (1985) discuss the thermodynamics of clathrate hydrate at low and high pressures with application to the outer solar system. The modeling by Lunine and Stevenson (op. cit.) clearly indicates the potential for clathrate formation in Earth's atmosphere. Whether such actually happens is not known; as for the moment, there are no known and available applicable observational techniques. The situation remains highly speculative.

In view of the recent exposure of some of the features of the outer planets by the remarkable journey of the satellite explorer, Voyager 2, new advances will be made in understanding. As Berry (1989a,b) indicates, Neptune's cloud decks are of methane and the atmosphere is methane-hydrogen rich. Speculatively, explainability of some of the noted surface features of the outer planets may be in terms of gas clathrate hydrates, clathrasils, or other encaging compounds. But of more immediate importance to man are those Earth clathrates which undergo association and dissociation as features of long-term climate.

Considerable discussion has been made in this section about methane clathrates because this phenomenon may help to fill in some features of the global climate. MacDonald (1990) treats this subject in some detail. An estimate of about 1,000 Gt of carbon by MacDonald (1990) is compared to about 10,000 Gt of carbon (Kvenvolden (1988b)). The methane clathrates constraints of pressure and temperature have been presented. In the scenarios of the glaciation and interglacial features, under the glaciating regions, clathrate sequestering of methane may be initiated and accelerated. The time period is long—hundreds to thousands of years. At the same time, the evaporation and removal of water from the oceans and its transport to the glaciation regions lowers the sea level. The changing temperature and the pressure regimes of the oceanic regions of sequestered methane releases the stored methane. The releasing time is shorter than the sequestering time. With reversal of the climate effects of the two regions, permafrost regions have their turn in methane release while the ocean regions again initiate their sequestering actions. MacDonald (1990) provides estimates of 10,000 and 60,000 yr, respectively, for the formation (stabilization) and the degradation (destabilization) of the gas clathrates to great depths. Undoubtedly, some destabilization (release) of methane from the clathrate form goes with any surface warming as the temperature wave progresses downward.



### 11.8.5 Methane Interactions

The formation of methane and its oxidation have been briefly discussed. The formula for methane, CH<sub>4</sub>, serves as a base for further discussion. However, what is given here is also applicable to many of the other alkanes, the alkenes, and the alkyls. The molecule can be ionized; it can be decomposed and the parts radicalized, making them very reactive. The hydrogens may be replaced one by one by any one of the halogens or by methyl groups or by other atoms or complex groups.

Table A-11-8, bond energies, allows some assessment of the relative stabilities of compounds and to predict the run of chemical reactions (Fessenden and Fessenden (1986) and Chang (1986)). For example, in the chlorination of methane (or methylation of chlorine), the cleavage of the Cl-Cl bond requires 243 kJ mol<sup>-1</sup> of energy. This amount of energy can be supplied by the heat of chemical reactions or that available in quanta at wavelengths (wave numbers) of ≈492 nm (7.03 × 10<sup>4</sup> cm<sup>-1</sup>). This energy is available in the visible spectrum near the ultraviolet, which ranges from about 400 to 700 nm. The breaking of the hydrogen bond from the methyl group occurs with the absorption of 435 kJ mol<sup>-1</sup> of energy near the wavelength (wave number) of 265 nm (3.64 × 10<sup>4</sup> cm<sup>-1</sup>) which lies within the ultraviolet. These cleavages produce the radicals of methyl, chlorine, and hydrogen. A subsequent reaction produces methyl chloride (CH<sub>3</sub>Cl) and hydrogen chloride (HCl). To disrupt the methyl chloride and the hydrogen chloride bonds requires, respectively, 350 and 430 k J mol<sup>-1</sup>. Comparing the sums of the two groupings, (243+435=678) and (350+430=780) kJ mol<sup>-1</sup>, the second is larger than the first; i.e., it takes more energy to disrupt the resultant bonds than the bonds of the initial methane and chlorine. The difference, ≈102 kJ mol<sup>-1</sup> (almost 24.5 k cal mol<sup>-1</sup>) implies that the formation of methyl chloride and hydrogen chloride releases 102 kJ mol<sup>-1</sup>. The reaction is exothermic. That is, it is almost an automatic process once initiated and there are no buffers or other intervening reacting gases, ions, or radicals. In similar fashion, other gas bond cleavages and combinations can be examined. The above reaction can be written as



and



where bond energies\* equal ΔH<sup>o\*\*</sup> (kJ mol<sup>-1</sup>).

The dots before the groups imply that these are radicals with unpaired electrons left after the destruction of the previous bonds. These and all other radicals may be characterized “in electronic computer game nomenclature” as atmospheric “Pac Men.” Nowhere is this most evident than in the chain reactions of chlorine involved in the destruction or consumption of ozone. The energies with the negative sign are energies emitted; these are exothermic reactions.

The above reaction also implies that this will naturally occur in the atmosphere and hydrosphere. The latter includes the lakes, rivers, ponds, and marshes of the world where bacterial action produces methane among many other products. The chlorine in the air and water also occur naturally, often being available in the venting volcanoes below and above ocean surfaces. Thus, methyl chloride is another trace gas involved in the absorption of energy

and the reradiation of energy. Such energies absorbed in the infrared result in the increase of the rotational, vibrational, and other aspects dealing with molecular configurations. Emission of energy simply permits the molecules to become relatively quiescent, but the surroundings will be warmed.

The halide reactions become less exothermic with increasing atomic weights; i.e., in the order of fluorine, chlorine, bromine, and iodine. In fact, the methane-iodine reaction after bond disruption is slightly endothermic. On the other hand, the fluorine reaction is much more exothermic, so much so that it is a dangerous reaction, as is the chlorine reaction, if partially confined. Coupled with the explosive nature of methane, the procedure is still more dangerous in confined spaces. Thus, it is not likely that the iodide reactions would provide methyl iodide as a serious contender in the atmospheric greenhouse phenomenon.

Again, this discussion on bond dissolution and subsequent reactions does not imply that the electromagnetic solar energy output is the sole bond-breaking option.

Also, it is emphasized that table A-11-12 could be extended. This is left to the reader who may refer to Weast (1988), Huheey (1978), Chang (1986), Fessenden and Fessenden (1986), and others. A separate section is reserved for a bit of discussion of the halocarbons and the problems associated with them.

### 11.8.6 Importance to Climate

Mitchell (1989) presents a figure which is quite informative. The atmospheric warming curves attributed to polyatomic carbon dioxide and methane show a decrease in the trend of warming with an increase of the two gases in the atmosphere. For a methane increase of 4.5 ppmv, a relative heating of  $2.75 \text{ Wm}^{-2}$  will be noted. For a carbon dioxide increase of 250 to 500 ppm, a relative heating of  $325 \text{ Wm}^{-2}$  will be attained. The heating rate on one ppmv basis will be for methane and carbon dioxide, respectively,  $0.61$  and  $0.013 \text{ Wm}^{-1}$ ; the ratio is almost 50. It appears that methane on a molecule-for-molecule basis is 50 times more effective as a warming agent than carbon dioxide. Thus, as methane is apparently increasing at an actual rate of 1.6 ppmv per decade while carbon dioxide is increasing at 1.42 ppmv per decade, the ratio of 50 to 1 for the effectiveness of methane to carbon dioxide remains. For more, see the discussion in section 11.9 on carbon dioxide.

Methane ( $\text{CH}_4$ ) (Goody and Yung (1989)) absorbs and emits radiation near the following wave numbers or wavelengths—1,303, 1,311, 1,534, 3,010, and 3,019  $\text{cm}^{-1}$  with overtones and combinations at 2,612, 2,822, 2,830, 3,062, 4,223, 4,340, and 4,540. As Mitchell (1989) and Dillon et al. (1990) indicate, neither carbon dioxide ( $\text{CO}_2$ ) nor water vapor ( $\text{H}_2\text{O}$ ) absorb or emit radiation in the region from  $8 \mu$  to about  $12 \mu$ , approximately  $1,200$  to  $800 \text{ cm}^{-1}$ . See also figure 11-3 adapted from Howard (1960). Note that 1,303 and  $1,311 \text{ cm}^{-1}$  is just beyond the  $1,200 \text{ cm}^{-1}$ . Broadening of the methane ( $\text{CH}_4$ ) absorption band at  $1,303 \text{ cm}^{-1}$  due to increased methane amounts, warming, and collision may induce the wings of the band to spread and overlap slightly, from below  $1,200 \text{ cm}^{-1}$  to wavelengths slightly longer than  $8 \mu$ . Thus, methane ( $\text{CH}_4$ ) would close slightly the window open for radiation as far as carbon dioxide ( $\text{CO}_2$ ) and water vapor ( $\text{H}_2\text{O}$ ). More partial closing of this window will be indicated in the section on ozone ( $\text{O}_3$ ) and the halocarbons.

The energy involved in the absorption or emission by a molecule is the energy of the one associated photon at a specific wavelength or wave number. If wavelengths in nm or wave numbers  $\text{cm}^{-1}$  are used, the respective equation is as follows (Wayne (1988)):

$$E = \frac{119,627}{\lambda} \text{ kJ mol}^{-1} \quad (11.23)$$

or

$$E = 119,627\tilde{\nu} \times 10^{-7} \text{ kJ mol}^{-1} , \quad (11.24)$$

where  $\lambda$  is the wavelength and  $\tilde{\nu}$  is the wave number. A doubling of the wave number (or halving of the wavelength) will double the associated energy. Methane has two fundamental bands—overtone and combination. Two fundamental bands are selected at 1,302.77 and 3,018.92  $\text{cm}^{-1}$  (Goody and Yung (1989) p. 211). The associated energies are 15.5846 and 36.1149  $\text{kJ mol}^{-1}$ .

Please note that fundamental methane ( $\text{CH}_4$ ) bands operate to partially close some windows not closed to both absorption and emission by water ( $\text{H}_2\text{O}$ ) and carbon dioxide ( $\text{CO}_2$ ). In addition, please note that both methane ( $\text{CH}_4$ ) and nitrous oxide ( $\text{N}_2\text{O}$ ) operate in the same band region of 7.7  $\mu$ . These two fairly well blanket this band.

## 11.9 Carbon Dioxide

Minor and trace gases are minor and trace only in their amounts relative to the major gas amounts. Some of the minor and trace gases are effective as dampers and controls of the Earth's climate because they can act as buffers, sources, and sinks to other gases; as such, their influence is extensive. Their interactions, both physically and chemically, spread these control features. These gases, as well as the major gases nitrogen ( $\text{N}_2$ ) and oxygen ( $\text{O}_2$ ), may be considered elements of climate. These are so considered here. The present extensive research by persons and organizations in so many different disciplines attest to the importance accorded to these gases. All these gases are participants in the energy and food chains (the basic support of all life). These gases are important radiatively, physically, chemically, and in the biochemical sense.

Carbon dioxide is used by both plants and animals as structural and food building material and in life process regulation. It is released in both plant and animal respiration—on land and in the oceans—in the degradation of plant and animal material, by burning of fossil fuels, and by geologic processes within the lithosphere and the mantle. It is absorbed and released by the hydrosphere. The rates of absorption and release are functions of temperature, pressure, and ionic mixtures. Its capability as a climate control or modifier rests in its capacity to absorb, retain, and reradiate energy, particularly in the long-wave or low-frequency region. This modifies the sensible temperature regime of the Earth and its atmosphere, as well as the lithosphere and hydrosphere. Water precipitated as liquid or solid scavenges carbon dioxide ( $\text{CO}_2$ ) from the atmosphere. The mixture becomes a change agent for some rocks, soil, and the skeletal remains of land and sea animals.

From and Keeling (1986) reassess late 19th century measurements of atmospheric carbon dioxide concentrations. The original data were published between 1880 and 1950. According to From and Keeling (op. cit.), a British engineer, C.S. Callendar, interpreted these data, and these and other data permitted From and Keeling (op. cit.) to deduce that the mean annual concentration of atmospheric carbon dioxide was near 290–292 ppm in the period 1880–1905.

According to a report by the U.S. National Research Council, National Academy of Sciences (1979), the carbon dioxide ( $\text{CO}_2$ ) in the atmosphere had risen from  $\approx 314$  ppm in 1958 to 334 ppm in 1979, an increase of 6.4 percent. As with other so-called “greenhouse gases,” this increase of carbon dioxide ( $\text{CO}_2$ ) in the atmosphere, which results in part from the increased use of fossil fuels, is a matter of concern to many people. The ability of carbon dioxide ( $\text{CO}_2$ ) to absorb and reradiate thermal energy is expected to change the thermal structures of the atmosphere and the thermal and acidic properties of the hydrosphere. In the same U.S. National Research Council, National Academy of Sciences report (op. cit.), it is stated that if the use of fossil fuels continues to grow at the rate of (a) 4 percent, (b) 2 percent, or (c) zero percent per year, doubling of the carbon dioxide ( $\text{CO}_2$ ) in the atmosphere will occur, respectively in (a) 50, (b) 70, and (c) 150 yr. The increased absorption, translocation, and reradiation of energy are expected to make some changes in climate. Models generally are linear and do not consider chemical and physical buffering of other constituents of the Earth's spheres except in proxy or surrogate form. A good

prior comparative database is not available. Another good reference is Williams (1978). More about this gas and its potential effects will be discussed later.

Table A-11-1 includes atomic weights for carbon (C) and oxygen (O) which compose the bonded elements of carbon dioxide (CO<sub>2</sub>). Table A-11-2 gives some physical characteristics for the atmospheric gases including (1) melting point (m.p.), (2) boiling point (b.p.), and the (3) critical temperatures (°C), (4) pressure (atm), and (5) densities.

Carbon dioxide (CO<sub>2</sub>), as an atmospheric minor or trace gas, contributes a known increasing amount to the atmosphere. Known recent bounds are ≈292 ppm on the low side and 355 ppmv on the high side. Lesser and greater contributions have occurred and will continue to occur. Glueckauf (1951), citing Callendar (1940), indicates a relatively stable 292 ppm carbon dioxide (CO<sub>2</sub>) content from about 1,865 to 1,895. After 1,895, he indicates a steady rise to 1,935 to about 318 ppm with extrapolated values of near 330 ppm by 1950. Figure 11-14 and table 11-3 of monthly values are graciously provided by Keeling (1990) through the Carbon Dioxide Information Center (CDIC) of the Oak Ridge Laboratories of the U.S. Department of Energy. Figure 11-14 is based on measurements made at the Mauna Loa Observatory in the Hawaiian Islands up to 1988. The 330 ppmv extrapolated by Callendar for 1950 was not reached at the Mauna Loa Observatory until about 1975. However, the steadily increasing slope of the data presentation has helped to create real concern in the people of the world. There is ample reason to investigate, study, and report on this phenomenon. There will be a tendency to extrapolate these rates exponentially rather than linearly. Such extrapolations may be misleading. See also Beardsmore and Pearman (1987) and Conway et al. (1988). This same figure and tabular data are shown by Boden, Kanciruk, and Farrell (1990). The units are ppmv<sup>-1</sup>. Addition of data since 1988, Boden et al. (1994) and others imply a slowing of the carbon dioxide rise. The annual averages are the averages of the monthly means. The values are rounded to the nearest tenth.

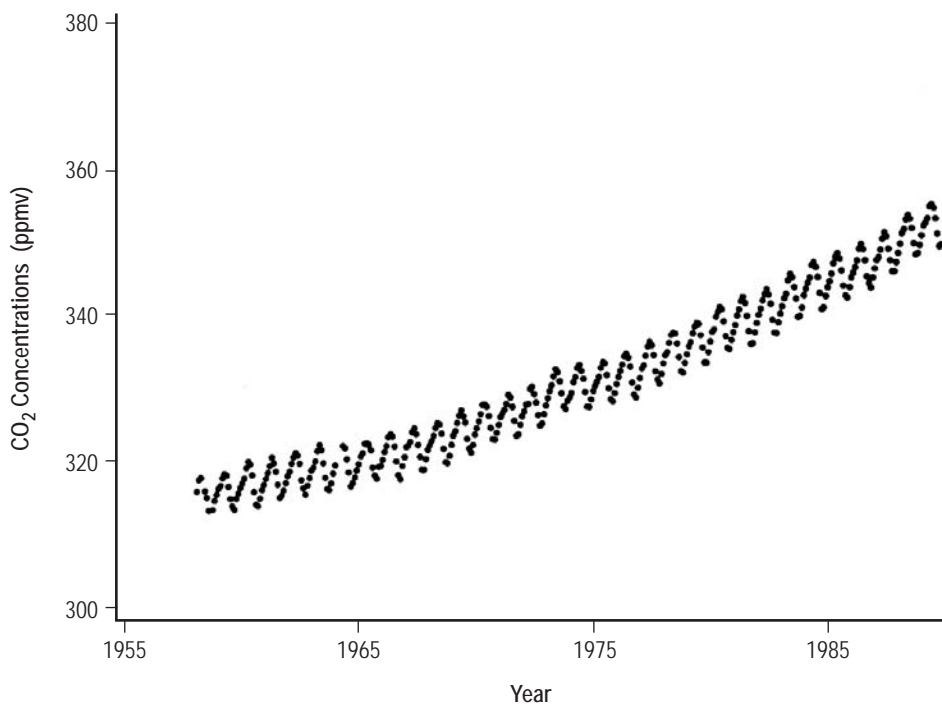


Figure 11-14. Carbon dioxide (CO<sub>2</sub>) monthly concentration values (ppmv) at Mauna Loa Observatory, 1958–1990, showing the seasonal oscillation and the increasing trend (courtesy of C.D. Keeling (1990) for preliminary data and the CDIC, ORNL).

Table 11-3. Atmospheric concentrations of carbon dioxide\* (CO<sub>2</sub>) at Mauna Loa, Hawaii, 1958–1989 (with permission of U.S. Department of Energy, Oak Ridge National Laboratories, courtesy of C.D. Keeling (1990) and Boden, Kanciruk, and Farrell (1990)).

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Ann
1958			316.0	317.6	317.8		316.1	315.2	313.4	313.5		314.8	
1959	315.6	316.4	316.8	317.8	318.4	318.2	316.7	315.0	314.0	313.6	315.0	315.8	316.1
1960	316.5	317.1	317.8	319.2	320.1	319.7	318.3	316.0	314.2	314.1	315.1	316.2	317.0
1961	317.9	317.8	318.5	319.5	320.6	319.9	318.7	317.0	315.2	315.5	316.2	317.2	317.7
1962	318.1	318.7	319.8	320.7	321.3	320.9	319.8	317.6	316.5	315.6	316.9	317.9	318.6
1963	318.8	319.3	320.1	321.5	322.4	321.6	319.9	317.9	316.4	316.2	317.1	318.5	319.1
1964	319.6				322.2	321.9	320.4	318.6	316.7	317.2	317.9	318.9	
1965	319.7	320.8	321.2	322.5	322.6	322.4	321.6	319.2	318.2	317.8	319.4	319.5	320.4
1966	320.4	321.4	322.2	323.5	323.8	323.5	322.2	320.1	318.3	317.7	319.6	320.7	321.1
1967	322.1	322.2	322.8	324.1	324.6	323.8	322.3	320.7	319.0	319.0	320.4	321.7	322.0
1968	322.3	322.9	323.6	324.7	325.3	325.2	323.9	321.8	320.0	319.9	320.9	322.4	322.8
1969	323.6	324.2	325.3	326.3	327.0	326.2	325.4	323.2	321.9	321.3	322.3	323.7	324.2
1970	324.6	325.6	326.6	327.8	327.8	327.5	326.3	324.7	323.1	323.1	324.0	325.1	325.5
1971	326.1	326.6	327.2	327.9	329.2	328.8	327.5	325.7	323.6	323.8	325.1	326.3	326.5
1972	326.9	327.8	328.0	329.9	330.3	329.2	328.1	326.4	325.9	325.3	326.6	327.7	327.6
1973	328.7	329.7	330.5	331.7	332.7	332.2	331.0	329.4	327.6	327.3	328.3	328.8	329.8
1974	329.4	330.9	331.6	332.9	333.3	332.4	331.4	329.6	327.6	327.6	328.6	329.7	330.4
1975	330.5	331.1	331.6	332.9	333.6	333.5	331.9	330.1	328.6	328.3	329.4	330.6	331.0
1976	331.6	332.5	333.4	334.5	334.8	334.3	333.0	330.9	329.2	328.8	330.2	331.5	332.1
1977	332.8	333.2	334.5	335.8	336.5	336.0	334.7	332.4	331.3	330.7	332.1	333.5	333.6
1978	334.7	335.1	336.3	337.4	337.7	337.6	336.2	334.4	332.4	332.2	333.6	334.8	335.2
1979	335.9	336.4	337.6	338.5	339.1	338.9	337.4	335.7	333.6	333.7	335.1	336.5	336.5
1980	337.8	338.2	339.9	340.6	341.2	340.9	339.3	337.3	335.7	335.5	336.7	337.8	338.4
1981	338.8	340.1	340.9	342.0	342.7	341.8	340.0	337.9	336.2	336.3	337.8	339.1	339.5
1982	340.2	341.1	342.2	343.0	343.6	342.9	341.7	339.5	337.8	337.7	339.1	340.4	340.8
1983	341.3	342.5	343.1	344.9	345.8	345.3	344.0	342.4	339.9	340.0	341.2	342.9	342.8
1984	343.7	344.6	345.3	347.0	347.4	346.7	345.4	343.2	341.0	341.2	342.8	344.0	344.3
1985	344.8	345.8	347.2	348.1	348.7	347.9	346.3	344.2	342.9	342.6	344.0	345.3	345.7
1986	346.0	346.7	347.6	349.2	349.9	349.2	347.7	345.5	344.5	343.9	345.3	346.6	346.9
1987	347.7	348.1	349.1	350.6	351.5	351.0	349.2	347.7	346.2	346.2	347.4	348.7	348.6
1988	349.9	351.2	351.9	353.2	353.9	353.3	352.1	350.0	348.5	348.7	349.8	351.1	351.2
1989	352.5	352.8	353.4	355.1	355.4	354.9	353.4	351.3	349.6	349.9			

\*Atmospheric CO<sub>2</sub> in parts per million by volume (ppmv). Annual averages based on monthly means. All numbers have been rounded to the nearest tenth. Addition of data since 1988, Boden et al. (1994) and others imply a slowing of the carbon dioxide rise.

Figure 11-15, from Boden, Kanciruk, and Farrell (1990), provides a glimpse of the probable course of atmospheric carbon dioxide (CO<sub>2</sub>) over the past 160,000 years. This figure is based on the derivation from the Vostok and Siple station ice cores and the information presented in figure 11-14. See Barnola et al. (1983), Barnola et al. (1987), Delmas et al. (1980), Lorius et al. (1985), Neftel et al. (1982), Neftel et al. (1985), Raynaud and Barnola (1985), and Schwander and Stauffer (1984). Reference may be made to the numerical data associated with the ice core depths (Boden, Kanciruk, and Farrell (1990)). Please note in figure 11-15 the low values (≈200 ppmv) at about 160,000 years, the relatively high values (≈300 ppmv) at 150,000 years, the low value at ≈90,000 years BP, then the rapid rise to 240 ppmv, the plateau region, and the rapid rise beginning ≈300 years ago. Visually, do not be misled

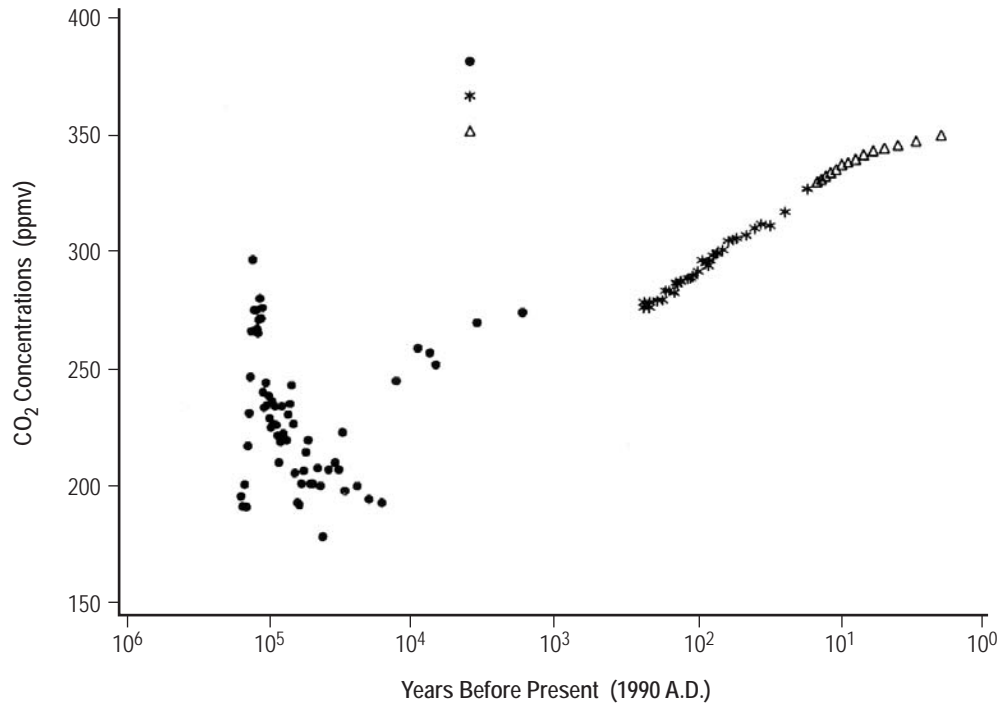


Figure 11-15. Annual atmospheric carbon dioxide ( $\text{CO}_2$ ) concentrations (ppmv) during the past 160,000 years (derived from the Vostok and Siple ice cores and Keeling's Mauna Loa record) (courtesy of DOE, ORNL, CDIC, Boden, Kanciruk, and Farrell (1990)).

by the logarithmic time scale. Comparison with figure 11-8 for methane ( $\text{CH}_4$ ) for the same time period shows similar features. These appear to be equivalent except for scaling. This is not surprising due to the slow oxidation of methane ( $\text{CH}_4$ ) to carbon dioxide ( $\text{CO}_2$ ).

Various investigators have attributed the increasing amount of atmospheric carbon dioxide to power production using carbon-based fuels and the atmospheric oxygen. The close parallel of the rise in both fossil fuel consumption and carbon dioxide concentration implies the anthropogenic (man's) influence; but this is not explicit.

Clearly evident in figure 11-14 is the seasonal fluctuation of the measured  $\text{CO}_2$  at Mauna Loa. This seasonal feature is characteristic at other locations but is reversed in the Southern Hemisphere. The amplitude is greater in the Northern Hemisphere. This implies a tropospheric mixing time of about a year. The inference may be made that vegetative use of carbon dioxide during the growing season participates in the annual oscillation. Examination of the seasonal fluctuations as the polar regions are approached shows considerable damping. This simply reflects the lessened activity of the biosphere, particularly the vegetative activity.

Figure 11-3, as previously indicated, provides the comparative radiation absorption characteristics of selected atmospheric gases. Reference may be made also to Yao (1981), who provides a combined transmission depiction (after Gates (1965)) of the  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{O}_3$  gas mixtures. Figure 11-3 is a replicate of the synthetic atmosphere absorption presentation of figure 16-10 (Howard (1960)). To facilitate comparison, figure 11-16 shows only the simulated atmospheric solar absorption and the carbon dioxide and monoxide absorption curves; these are extracted from figure 11-13. With absorption, there is no transmission. Strong absorption by  $\text{CO}_2$  of infrared radiation is noted at about  $2.8 \mu$ ,  $4.2 \mu$ , and from about  $12.7$  to  $16 \mu$  with weak absorption at  $2$ ,  $4.7$ ,  $9.2$ ,  $10.2$  and  $12.6 \mu$ . Corresponding wave frequencies are  $3,571$ ,  $2,380$ ,  $787$ , and  $625 \text{ cm}^{-1}$ . Carbon dioxide absorbs over a very

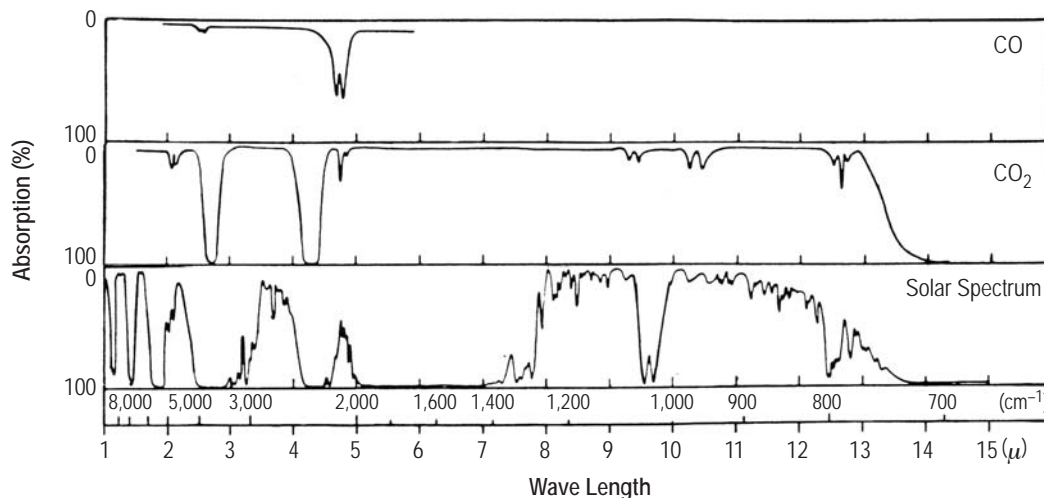


Figure 11-16. Carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>) infrared absorption curves shown with the simulated solar radiation spectrum from 1 to 15 μ (courtesy of Howard (1960)).

wide infrared wavelength or wave number range. The combined absorption effect of the synthetic atmospheres is extensive. With carbon dioxide as a good absorber and reradiator, increasing amounts of the gas can only lead to a warming of the atmosphere if no subsidiary or ancillary cooling scenarios develop. This feature has long been recognized. The “greenhouse” effect is potential.

### 11.9.1 Sources and Sinks

Presolar sources for carbon monoxide (CO) and carbon dioxide are acknowledged as for methane. These gases, along with other gases, such as water (H<sub>2</sub>O), are exhaled (degassed) continually from the Earth’s interior from and through the mantle and through the crust. Additionally, plant life uses, processes, and stores carbon dioxide (CO<sub>2</sub>) in tissues. These, on death, form a source for regeneration. Carbon dioxide (CO<sub>2</sub>) is a part of the gas mixture extracted from coal and petroleum fields. It is stored in sea water as a gas in a loosely hydrated form known sometimes as “carbonic acid” and as a part of carbonate compounds found in sea beds and fossils. Sea water’s ability to hold or not hold CO<sub>2</sub> is strongly temperature and alkalinity dependent. Thus, sea water acts as a buffer, absorbing, transporting, and releasing carbon dioxide (CO<sub>2</sub>) dependent upon temperature, alkalinity, wind, and pressure considerations. In addition, the encaging of gases, including carbon dioxide (CO<sub>2</sub>), as the so-called gas hydrates or clathrates, does store some amounts of carbon dioxide (CO<sub>2</sub>) within the water cages. See the extensive discussion on clathrates in the preceding subsection on methane. Clathrate hydrates are sinks for they sequester the carbon dioxide or other gases. Clathracarbs may serve a similar function but, for the moment, this is highly speculative. These gases then cannot enter into any chemical reaction. See Unruh and Katz (1949), Takenouchi and Kennedy (1965), Davidson (1981), Bell (1982), Ratcliffe and Ripmeester (1986), and Conway and Steele (1989)). Progress in research techniques now indicates that the hydration number is near 7, having changed from 5.75 (Takenouchi and Kennedy (1965)), to 6 (Davidson (1981)), to 7 (Ripmeester (1989), Personal Communication). This variation in any new and uncertain phenomena is to be expected.

Under the tremendous pressures in the ocean floors and in the permafrost, mixed gas clathrates may form an impervious layer. Beneath such an impervious layer, gases could accumulate. When the clathrate hydrate hydrogen bonds dissociate, the gases may rapidly escape to the surface. This phenomenon was discussed more extensively in section 11.8 on methane.

Carbon dioxide (CO<sub>2</sub>), so necessary to food production, is stored in storage units such as sugars, starches, etc., and in plant and animal tissues including the skeletal forms. These are sinks for CO<sub>2</sub> on both land and sea. With a relative molecular weight greater than that of the atmosphere, CO<sub>2</sub> tends to stay low and not escape so readily through the top of the atmosphere as do hydrogen and helium. However, diffusion and turbulence will carry carbon dioxide (CO<sub>2</sub>) upwards into the stratosphere.

Massive burning in forests, on prairies, and on or within the Earth's hydrocarbon (oil and gas) fields yields immediate and perhaps more than massive injection of trace gases, carbon dioxide (CO<sub>2</sub>) being one of these. Crutzen and Andreae (1990) discuss one feature of today's ecological world and that is the burning of the tropical rain forests. They estimate that in permanent deforestation and burning, 200–700 Tgy<sup>-1</sup> of carbon (C) and 2–7 Tgy<sup>-1</sup> of nitrogen (N) are released each year. They also estimate that 1,600–4,100 Tgy<sup>-1</sup> of carbon dioxide (CO<sub>2</sub>) are introduced into the atmosphere. They further indicate that all of this introduction is equivalent to that of the industrial world production. Eventually, with the tropical forests disappearing, this injection will cease. The load of these then should not be the increase noted over the last few centuries. The increased amount will influence on a first order the sensible energy of the atmosphere. But the potential second-order reaction leads to many scenarios. Some will oppose others insofar as the restricted scenarios permit. Simply stated, the main job of the climatologists in all disciplines will be to monitor, record, study, report, and perhaps to make venture forecasts of climate and climate change. But first of all, as pointed out previously, it is necessary to define climate and to determine its variability. Until that is done, untenable forecasts will continue to be issued.

The oxidation of methane (CH<sub>4</sub>) is also a source of carbon dioxide (CO<sub>2</sub>) in the atmosphere, particularly in the stratosphere. The burning (oxidation) of methane (CH<sub>4</sub>) results in three products—carbon dioxide, water, and available energy heat. There are several intermediate products. The following equation (Conant (1933) and Warneck (1988)) shows this:



Through the years, there have been many studies of various phases of thermal methane (CH<sub>4</sub>) oxidation. Warneck (1988) brings them together in his table 2-1, p. 49: it was reproduced with permission as table 11-2. As Warneck indicates, the first reaction is slow in the thermal regime but may be hastened in part by photodissociation processes.

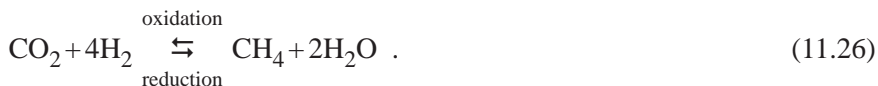
For the formation of a methyl free radical (•CH<sub>3</sub>), photons at ≈275 nm (≈435 k Jmol<sup>-1</sup>) will split a hydrogen (•H) from the methane (CH<sub>4</sub>) molecule. The methyl radical (•CH<sub>3</sub>) is then available for step (b). (See table A-11-8.) Thus, the intermediate photochemical and thermal reaction may speed the process. Note the production of the radicals •CH<sub>3</sub>, •CHO, •OH, and •HO<sub>2</sub> which are always extremely reactive. They have unpaired electrons and will actively engage a suitable partner for a stable configuration. Another feature of this table is the grouping of the chain reactions and branching, producing carbon dioxide (CO<sub>2</sub>) at the end of the third chain. The fourth chain terminates the process with the loss of the two molecules •HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>. However, an oxygen (O<sub>2</sub>) remains to interact with methane (CH<sub>4</sub>). As noted in each chain by Warneck (op. cit.), a reacting molecule is destroyed and regenerated. It is also important to emphasize that the (•OH) radicals of (b), (g), and (j) are so active that that particular formed radical may not be available for a step (c), (h), or (k) due to encountering another molecule or radical before these encounter a CH<sub>4</sub> or CO.

Refer to Levy (1971), who proposes that the oxylys and formaldehyde concentrations will remove the monoxide CO to such an extent that the half-life is ≈0.2 yr, ≈2 mo. Traub et al. (1990) discuss stratospheric hydroperoxy measurements.

Given CO<sub>2</sub>, H<sub>2</sub>O, and energy, carbonic acid or oxygen production result. Photosynthesis also provides a pathway. Also note the difference between the atmospheres of Earth and Venus.



As Warneck (1988) indicates, Miller and Urey (1959) suggest the following reaction for the formation of methane from carbon dioxide and water and an energy supply where the hydrogen comes from the dissociation of water:



The above reaction requires supplies of hydrogen and water. Miller and Urey (1959) indicate that with temperatures above 300 K, the production of carbon dioxide and hydrogen would be favored, while at cooler temperatures, the formation of methane and water would be favored. To break the first carbon-oxygen (C=O) double bond requires  $\approx 536 \text{ k Jmol}^{-1}$ . (See table A-11-8.) To break the remaining carbon monoxide (C≡O) triple bond requires  $1,072 \text{ k Jmol}^{-1}$ . Energies to do this are available in the electromagnetic spectrum, well into the ultraviolet region, at wave lengths of 110 nm or less. (See figure 11-1.) Whether consideration of CO is a viable and important option in today's atmosphere needs to be studied as to the concomitant availability of the hydrogen, water, and methane, carbon dioxide, radiation, and temperatures. Whether viable and operating in Earth's atmosphere, these processes may not be important in the total radiative sense. Both gases are radiatively active and, acting in concert, cover more of the infrared spectrum. If one could be totally converted to the other, say all methane is converted to carbon dioxide, the methane windows would be opened. But the carbon dioxide absorption and radiation would be improved. It seems apparent from the above discussion that the use of fossil fuels can result in an increase in the blanket effect of the radiatively active trace gases. But as indicated previously, this is only one step in a complicated complex scenario of Earth's climate.

Raw sink materials may be utilized to produce carbon dioxide which is then injected into the atmosphere by burning coal, petroleum, natural gas, and wood or plant fiber, by dissolution of carbonates, by volcanic exhalations, by changing oceanic alkalinities, and dissociation of the carbon dioxide clathrate hydrates. The dissociation pressure for carbon dioxide at 0 °C is 12.5 atm as compared with 26 atm for methane (Miller (1973)). See also Kvenvolden and McMenamin (1980) and Lunine and Stevenson (1985) for the pressure-temperature phase diagrams for atmospheric gas clathrates shown in section 11.8 on methane. Mixtures of gases will associate and/or dissociate the clathrate ice structures at higher temperatures than can a pure gas. This seems to be better realized if there are large and small molecules leading to structure II crystalline ensembles. Storage times are generally long and storage is slow in itself. Thus, perturbations in the amount of CO<sub>2</sub> in the atmosphere may be created whenever a storage source is exploited or depleted.

Carbonates carried to great depths in the Earth by subduction will be processed chemically and the carbon dioxide exhaled from the Earth. This is an ongoing process. Volcanoes form good exhalation vents.

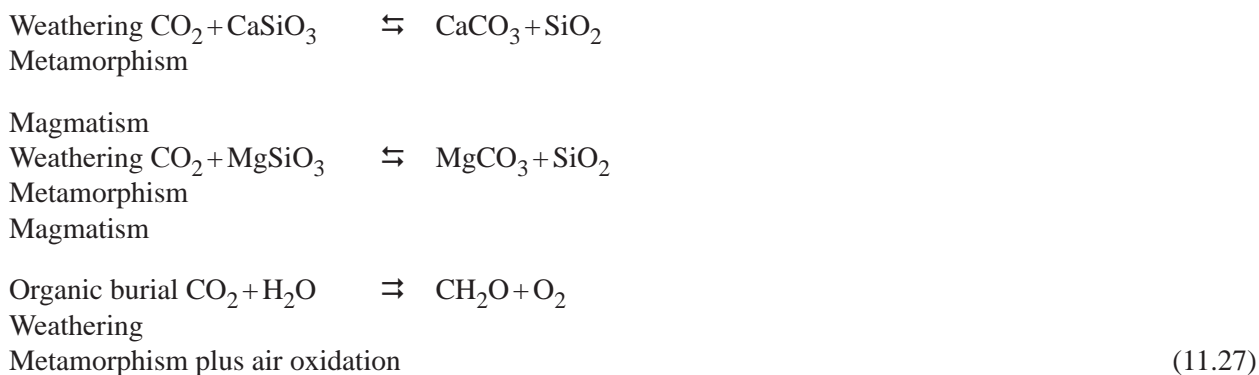
**11.9.1.1 Earth-Venus Comparisons.** Here again, it might be important to mention to the reader the difference between the Venusian (Venus) and the Tellurian (Earth) atmospheres with respect to carbon dioxide. Apparently, there is little or no water or plant life on Venus. Plant, insect, and animal life on Earth sequester (in the process of living) carbon dioxide and its atoms in their tissue structures. On death, much of this sequestered material remains sequestered. These are sinks for carbon dioxide. Chemically-forming carbonates, outside of the life processes, also are sinks. Water is a useful agent in all of these processes. Thus, the chemical and life processes on Earth represent an avenue to reduce the carbon dioxide content of its atmosphere and to maintain such a limitation. Consequently, carbon dioxide physically constitutes only a minor or trace effect in Earth's atmosphere. Its radiative absorption and emission properties are another matter. In the case of the Venusian atmosphere, it is a major gas both in its proportional amount (Mitton (1978)) and in its radiative properties.

See the discussion on planetary atmospheres in Wayne (1985), Goody and Yung (1989), Warneck (1988), and others. The higher temperatures of the Venusian atmosphere as compared to the Earth are probably due to its closer proximity to the Sun. Even with considerable water in the atmosphere, the temperatures do not decrease to the condensation temperature for the water vapor; a runaway greenhouse exists.

With little or no life on Venus there is no good mechanism presently known to sequester and remove carbon dioxide from the atmosphere; it accumulates. Fifty years ago estimates of Venusian surface atmospheric pressures were 20 times that of the Earth's; now, the estimates are greater than 90 (almost 100) times that of the Earth's. The depth of the atmosphere is now estimated to be at least 125 km, though the tops of the clouds are estimated to be  $\approx 80$  km. Surface temperatures are estimated to be  $\approx 750$  K. Interplanetary probes furnish the basis for newer estimates. Radar mapping from satellites is now underway, though some mapping has been done from Earth.

**11.9.1.2 Biogeochemical Aspects.** Already discussed are the proxy data associated with analysis of air bubbles trapped in glacier ice. This applies to other gases too. Berner, Oeschger, and Stauffer (1980) discuss the carbon dioxide cycle from the study of ice core data. See also Berner, Lasaga, and Garrela (1983)). Two of these papers propose a model for the development of a reversible silicate to carbonate geochemical cycle. This proposed sequestering and release of carbon dioxide through geochemical processes is discussed by Berner (1990). The time span is the phanerozoic, the time since plant life began on Earth. Here, as in all other aspects of this publication, so-called "proxy data" are, if developed properly, assumed to be good indicators of past climate. Because they are the result of time averaging as well as physical and chemical environmental conditions, they in themselves form a distinct type of record. There remains the caveat that the research performed by any individual or group of individuals must be reliable and dependable. As an example, there is the element of surface air temperature. There may be a person (or persons) who says that a temperature observed and recorded is a pure item. However, there is concern as to whether the temperature was measured in or beneath a shelter, above arid ground, water, or a vegetative cover such as short grass, long grass, in areas representative of the region, in clear sky, partly cloudy, or cloudy conditions, whether one meter, ten meters, or hundreds of meters from a building, where from building to building the radiative characteristics vary. There are other aspects of the problem. The above is not to denigrate the observation and recording of today's temperatures but to emphasize that there are problems with so-called "real" data as there are with "proxy" data. Berner (1990) constructs a new model to calculate the atmospheric level of carbon dioxide over the past half billion years (570 million years). Berner's (1990) model indicates that carbon dioxide levels were high during the mesozoic and early paleozoic and low during the permo-carboniferous.

Berner (1990) provides an aspect of the geo-bio-chemical-physical process as surveyed for the phanerozoic period. This is the interaction of the silicates and carbonates. Three reactions are indicated, the last being the biosphere participation:



As Berner (1990) indicates, the first two reactions are the well-known Urey chemical reactions. The third reaction is that generally considered in photosynthesis and respiration but which refers to their biological equivalents. In Berner's (op. cit.) words, in going from left to right, the reaction refers to net photosynthesis or the difference between global synthesis and respiration as represented by the burial of organic material in sediments. Much work remains to be done for this model. The degassing, or outgassing, of carbon dioxide and the relationships with plant life must be better assessed in reliable quantitative terms.

### 11.9.2 Survey

Literature on carbon dioxide is considerable due to its importance to all life and climate. Stepanova (1953) prepared a set of references of 229 articles and books which appears in the American Meteorological Society publication, *Meteorological Abstracts and Bibliography*. Since that time, carbon dioxide literature and associated bibliographies have expanded. The Carbon Dioxide Information Analysis Center was established at the Oak Ridge National Laboratory in Oak Ridge, TN, by the U.S. Department of Energy. That Center has supported the preparation of a publication index. The title is “An Annotated Inventory of Climatic Indices and Data Sets.” Many individuals from many countries collaborated in the preparation of this inventory. This publication, assembled by Hattemer-Frey, Karl, and Quinlan (1986), contains a number of supporting illustrations and tables and describes 34 prominent climatic indices. It also provides an annotated listing to help meet the information needs of those who are evaluating the effects of increased atmospheric carbon dioxide levels. The broad range of indices, as noted in the introduction to the publications introduction, covers 10 subject areas. (See also the spring 1990 CDIAC communication previously discussed in section 11.8 on methane.)

Trabalka and Reichle (1986) edit 27 contributions from 52 contributors concerning the study of the changing carbon cycle, a global analysis. The first contribution is authored by Gammon, Kohmyr, and Peterson. The article is entitled, “The Global Atmospheric CO<sub>2</sub> Distribution 1968–1983: Interpretation of the Results of the NOAA/GMCC Measurement Program.” Their table 1.1 provides provisional monthly mean carbon dioxide concentrations from continuous measurement at four GMCC/NOAA baseline observatories in Barrow, Mauna Loa, American Samoa, and the South Pole. The Barrow data ranges from a low of ≈334 ppm at the beginning of the period (1973) to ≈346 ppm at the end (1983). The range at the Mauna Loa Observatory varies from ≈333 ppm beginning in May 1974 to ≈345 ppm. The Samoan data range from ≈330 ppm to 343 ppm beginning in 1976. At the South Pole, beginning in 1975, the values range from ≈329 ppm to 342 ppm. These values were selected provisionally for background conditions and are expressed in the WMO X81 mole fraction scale, ppm with respect to dry air. According to the winter 1989 *CDIAC Communications*, the November 1988 measurement at the Mauna Loa Observatory was 349.77 ppmv. All these data represent a consistent rise in carbon dioxide concentration.

One of the CDIAC’s primary objectives is to compile and distribute carbon dioxide-related information. Some materials and services which may be requested are free. At the present time (1990) carbon dioxide information about the carbon cycle, climate, vegetation, resource analysis, and decision making is delivered to 3,900 persons in 149 countries. Those who want to participate can do so through the Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831–6335.

Another aspect of the carbon dioxide problem is given by Sundquist and Broecker (1985), editors of “The Carbon Cycle and Atmospheric CO<sub>2</sub>. Natural Variations Archaen to Present.” The lead article by Revelle is important in that it provides an introduction to the scientific history of carbon dioxide. This book consists of a multidisciplinary treatment, as indeed, almost all collections today are and need to be. A review of the hundreds of articles is far beyond the scope of this section.

The U.S. National Research Council (1983) in the Report of the Carbon Dioxide Assessment Committee also presents an overview in a report on changing climate. Another assessment (1982) is available: the Institute for Energy Analysis (1983) publishes the *Proceedings of the Carbon Dioxide Research Conference*. Clark (1982) edits the Carbon Dioxide Review for the Institute of Energy Analysis. Again, this is a multidisciplinary study dealing with those items that affect climate. The U.S. National Research Council (1984) reports on a workshop on Glaciers, Ice Sheets, and Sea Level Effect of a CO<sub>2</sub>-induced climatic change. MacCracken and Luther (1985) edit a collection of selected contributions concerning detecting the climatic effects of increasing carbon dioxide. Nine papers by 15 scientists are included.

The Oak Ridge National Laboratory published and publishes many reports. Four of these are (1) Olson, Allison, and Collier (1980), V1 and V3; (2) Olson (1980); (3) Watts and Allison (1983); and (4) Chilton, Allison, and Talmage (1981a,c). These reports contain pertinent edited bibliographies on the global and related aspects on carbon dioxide and research. These will be helpful to anyone starting research on this important aspect of climate—carbon dioxide. Quinlan, Karl, and Williams (1987) provide the U.S. Historical Climatology Network Serial Temperature and Precipitation Data. This is in printed form as well as on microfiche. Karl et al. (1990) provide an update. Environment Canada (1979) presented a workshop and published *Proceedings of the Energy/Carbon Dioxide Issues and Impacts*, Environment Canada, pp. 1–64.

Plagues and wars serve to limit human populations. The advent of the Industrial Revolution and the development of remedial cures permit the steady increase in populations of both human and animal. Carbon dioxide will increase but the increase should only balance that used to produce the necessary foods. There is, in a sense, a partial recycling of the carbon dioxide.

The slow climate changes leads to oscillations of total global carbon dioxide amounts. Past records, in the terms of “proxy” data, layers of sediment and of ice, support the idea of these swings. The recent rapid increase of carbon dioxide, as well as some other trace gases, parallels, in a sense, the use of fuels. Estimates of fuel use can be ascertained, in some cases, from those used in industrial development, in transportation, and in creating and modifying environmental conditions suitable for expansion of habitable regions. Therefore, it seems plausible to estimate from use of inventory supplies the amount of carbon dioxide being released to the atmosphere. In terms of small units, the numbers are large so the generally accepted unit, to make the estimates conceptually more understandable or managed, is the gigaton, Gt. This unit is equivalent to 1 billion metric tons,  $10^9$ t. The word gigaton is preferable here as the words billion or trillion may have different interpretations.

Watson et al. (1990) with at least 31 supporting authors for the period 1850 to 1986 indicate the release of  $312 \pm 40$  GtC. Fossil fuel burning releases are  $195 \pm 20$  GtC while land use and deforestation contribute  $117 \pm 35$  GtC. Amounts of carbon monoxide and carbon dioxide produced would be reduced by the multipliers (12/28) and (12/44) to obtain the actual carbon amounts indicated. These simply are the ratios of the atomic masses of carbon (C) to oxygen (O) and to oxygen ( $O_2$ ) as shown in table A-11-1. The above authors provide other estimates. As a survey of the past status and the present status of the atmospheric trace gases, the above referenced work provides relevant material.

One more instance, out of the many existent worldwide, is now given. The U.S. Department of Energy maintains a Carbon Dioxide Information Analysis Center (CDIAC) at the Oak Ridge National Laboratory. This Center is a part of the Environmental Sciences Division of the Oak Ridge National Laboratory and was established in 1982. The CDIAC provides information support to the international, policy, and education communities for evaluation of complex international issues associated with elevated atmospheric carbon dioxide, including potential climate change. CDIAC activities include obtaining and evaluating data, articles, and reports; producing digital numeric data and computer model packages (NDPs and CMPs); distributing carbon dioxide-related reports; and producing the *CDIAC Communications* with worldwide distribution of over 5,500 subscribers in 151 countries. To date, there are 38 NDPs and CMPs available, 11 issues of *CDIAC Communications* have been distributed, and CDIAC has responded to more than 16,000 requests. The above information is written by Bob Cushman in the Spring 1990, *CDIAC Communications*. The mailing address for the program is: Carbon Dioxide Research Program Atmospheric and Climate Research Division, ER-76, U.S. Department of Energy, Washington, DC 20545.

It should be mentioned here that one of the fundamental services of the CDIAC is the provision of fully-documented, machine-readable, carbon dioxide-related data sets and computer models to the international research and policy-making communities. Information can be obtained on 9-track magnetic tape and on 3.5- or 5.25-inch floppy diskette, IBM7 PC format. Presumably, other models will be developed and become available. The Spring

1990 *CDIAC Communications* lists and describes 38 available NDPs and CMPs. With respect to other disciplines, other Centers exist and likely will be developed.

## 11.10 Ozone

Boville in MacDonald (1963) succinctly presents reasons for the importance of ozone. It protects surface life and provides warming of the middle atmosphere, the stratosphere. The latter is a control in the Earth's energy budget.

Ozone, in major part, is formed in the upper reaches of the atmosphere by absorption of solar energy followed by dissociation of diatomic oxygen and recombination of the diatomic and atomic forms in three-body collisions. Ozone serves as a shield from ultraviolet radiation for the Earth's life forms at the bottom of the atmosphere and in the hydrosphere. During the nighttime hours, ozone ordinarily tends to slowly dissociate to the less energetic diatomic form, the oxygen molecule. Ozone slowly descends to greater pressure regions and receives more protection. At 30 to 20 km, its destruction and resupply essentially balance. Here, a security blanket or reservoir becomes established. In particular, dynamic circulation on a seasonal basis carries ozone downward and poleward (Danielson (1985)). On a global basis, the ozone maximum is near 25 km above sea level. With abundant production of ozone but increased dissociation, though a stable security blanket can develop, it is less secure.

Excellent basic references on the upper atmospheric structure and characteristics are those contained in the American Meteorological Society's *Compendium of Meteorology* of 1951. Especially with respect to ozone, the contributions of Angstrom (1951), Cauer (1951), Chapman (1951), Craig (1951), Glueckauf (1951), Gotz (1951), Mitra (1951), and Moller (1951) are important. See also London (1985) for an excellent treatise on ozone. With respect to oxygen and nitrogen, Mitra (1951) provides additional information on spectral regions and reactions.

Within the atmospheric boundary layer, ozone is not believed to be produced directly in significant quantities and is believed to be equivalent to that transported downward from the stratosphere through the troposphere. Under temperature inversions in moist layers, concentrations may occur. Storms do transport ozone to the surface behind cold fronts where mixing and destruction in the boundary layer quickly follows. Chemically, ozone is a highly reactive gas. Some ozone formation is attributed to lightning or electrical discharges. However, the major portion is formed in the chemical reaction processes among various atmospheric pollutants, including automobile exhaust gases and in the oxidation of methane. Resultant chemical and photochemical reactions usually produce smog and the very irritating peroxyacetylnitrate compounds. Ozone is recognized as one of the many components of photochemical smog. Many times, proposed reactions are speculative. Because ozone is so highly reactive, potential destroyers exist in manmade gases such as nitrous oxides, in vegetation, in rubber, etc. Main sources of nitrous oxides are internal combustion in engines, nitrogen fertilizers, and volcanic eruptions. A relatively early international symposium on chemical reactions in the lower and upper atmosphere was arranged by the Stanford Research Institute (1961). Considerable extensive work continues on this chemistry, and it is expected that all governments and organizations have programs and personnel studying, measuring, and reporting on such chemistry. The proceedings of that symposium is a synthesis in three major areas of atmospheric chemistry at that time—ionospheric research, geochemistry of the troposphere and stratosphere, and photochemical reactions and contaminants.

### 11.10.1 Tropopause—The Naming

Kites have been used since the middle of the 18th century to carry meteorological sensing equipment aloft. These were and are restricted to the lower portion of the atmosphere. The highest known ascent for a kite observation is 10 km. These meteorological observations augmented the surface observations. Balloons also were used to carry meteorographs to as high an altitude as possible. Many were lost, but the few instrument packages that were

found added important information. With the advent of aircraft, the aircraft were used to carry meteorographs. Some of these were still operational in the mid-1940s. Today, these may be used in special research.

In the years prior to 1900, many people were involved in the launching of balloons with meteorographs. The French, Germans, and British were deeply involved. Around the turn of the century, Assmann of Germany and Teisserenc de Bort of France and their groups maintained an intense rivalry. Ohring (1964) provides an interesting story on this in his article "A Most Surprising Discovery." Ohring (op. cit.) reviews the entire program leading to the "surprising discovery." The then current theories and philosophy indicated that the temperature of the atmosphere should decrease continuously from the surface upwards except for the shallow surface temperature inversions. Here, a side comment is made. If these flights had been made in the depths of the Antarctic winter, theories would have not been disproved. There is no stratospheric inversion in the Antarctic wintertime. Perhaps a greater upset would have occurred when the summer stratospheric inversion appeared.

As is often the case, the first of the soundings which showed a decrease and isothermal layers were considered to be in error. Convinced after a time and with more than 200 flights for confirmation in 1902, Teisserenc de Bort informed the French Academy of Sciences. One month later, Assmann (1902) made his announcement. But sometimes, in these neck-and-neck type of races, one's announcement takes precedence only because the group being informed has an earlier meeting. Both groups had been working on the same phenomena and it seems reasonable to assume essentially contemporaneous reporting in this case. According to Thiessen (1946), Teisserenc de Bort, before the German Meteorological Society in 1908, suggested the names of the troposphere (the mixing sphere) and stratosphere. The paper apparently never was published. The demarcation between the troposphere and the stratosphere, indicating a slowing of, halt of, or inversion of the temperature lapse rate was eventually named the tropopause.

### 11.10.2 Ozone

Ozone ( $O_3$ ) is the third of the oxygen forms,  $O_1$ ,  $O_2$ , and  $O_3$ , respectively, the oxygen atom, the oxygen molecule, and the ozone molecule, again, respectively, the mono-, di-, and triatomic forms. Unless otherwise specified, these refer to the simplest of the isotopic forms.

Schonbein (1840, 1854), who discovered ozone, had observed that the odors attending lightning discharge, electric sparks, and that accompanying the electrolytic decomposition of water were essentially the same. This test for this sameness was a simple qualitative chemical test, the blueing of a paper impregnated with a potassium iodide starch solution. Schonbein (op. cit.) eventually conjectured that ozone was a constituent of the atmosphere.

Fabry and Buisson (1913), through their spectrographic work, showed that the major part of ozone was located in the stratosphere. As implied by Gotz (1951), Schonbein's difficulties lay in the ozone variability in the surface layers. There, the day-to-day variability in any one month is larger than the annual variation of the monthly means. As the amount of ozone in the surface layers is small, the day-to-day passage or movement of the surface air masses with their turbulent motions would be a variation source. Meetham (1937) indicates that a 0.01 cm increase in the amount of ozone is accompanied by a rise of 3 °C, in the potential temperature at 18 km. A lowering of the tropopause by 1 km results. Haurwitz (1938) discusses these problems and indicates that as a cyclone passes, (1) the total ozone content increases by 0.01 cm, (2) the potential temperature increases by 3 °C, and (3) the tropopause height decreases by 1 km.

Gotz (1951) indicates the amount of ozone at standard temperature and pressure to be small, just a few millimeters (2–5 mm). These amounts are equivalent to 200–500 DU (Dobson unit). Oxygen, the source of this trace gas amount at its main source at the top of the stratosphere, along with the ozone, absorbs extraterrestrial (solar) radiation. Certain wavelengths or regions of wavelengths are more effective than others. (See figures 4-4 and 4-5

and table A-11-8.) The oxygen ( $O_2$ ) dissociates into the atomic form ( $\bullet O_1 \bullet$ ). Resultant combinations of another  $O_2$  and ( $\bullet O_1 \bullet$ ) provides radiation emission in wavelengths below 2,900 Å (290 nm). (See the discussion on the Rydberg series.) Presumably, Hartley (1881) was the first to report this, and Fabry and Buisson (1921) confirmed this feature. These characteristics and the great amount of atmospheric oxygen largely deplete the powerful solar ultraviolet radiation before it penetrates too deeply into the atmosphere. Ozone itself will absorb radiation below 1,150 nm with a resultant rise in temperature and some dissociation. See figures 4-4 and 4-5. See also Mitra (1951)).

As indicated briefly above, Oxygen ( $\bullet O_1 \bullet$ ) is the base building unit of oxygen ( $O_2$ ), the oxygen linear diatomic molecule, and oxygen ( $O_3$ ), the planar triatomic molecule. Energy absorption by oxygen ( $\bullet O_1 \bullet$ ) of the higher energy ultraviolet radiation also may provide an excited atom; i.e., at least one electron is raised to a higher energy level or orbital. Energy absorption by oxygen ( $O_2$ ) results in vibration of the two atoms as well as possible excitation of one or both oxygen atoms ( $\bullet O_1 \bullet$ ). Of course, the absorption bands are not necessarily the same. Energy absorbed by the triatomic planar molecule can be greater than the diatomic form because there are two bonds—one single and one double bond—instead of one bond as in the molecule ( $O_2$ ). There are more ways for energy to be absorbed and assimilated. These have been discussed previously. The spin-rotation features of the molecule also are influenced.

The odd oxygens, ( $\bullet O_1 \bullet$ ) and ( $O_3$ ), are the highly reactive forms. Oxygen ( $O_2$ ) is well mixed through the entire atmosphere below the levels where intense energy absorption keeps all elements in the dissociated ionic state. (That region aptly is called the ionosphere.) Oxygen ( $O_2$ ) has the energy absorption characteristics which leads to the formation of the oxygen ( $O_3$ ) ozone layer. Oxygen ( $\bullet O_1 \bullet$ ), oxygen ( $O_2$ ), and oxygen ( $O_3$ ) absorb maximal energy in several regions of the electromagnetic energy spectrum. However, it is in the overlapping absorption regions but not necessarily the maximal regions that allows the formation and consistent supply of ozone ( $O_3$ ). See Gotz (1951)).

Haurwitz (1938) points out that ozone can absorb energy 10 to 100 times greater than that absorbed by oxygen. Wuebbles et al. (1989) indicate a dual role of ozone in climate. Ozone, once formed, is the major absorber of ultraviolet radiation at wavelengths  $>200$  nm. Although forming a small percentage of the total atmosphere of about zero to  $5 \times 10^{-8}$  percent, and a very thin layer from a standard temperature and pressure concept, it shields the Earth from the intense shortwave solar radiation. The Dobson unit is used to express the amount of ozone present in a column. If the amount of ozone in the column is brought to a pressure of 1 atm, 100 DU would measure 1 mm in thickness. As will be seen later, the normal total column atmospheric ozone averages about 300 DU, or 3 mm in thickness. See glossary in Anthes (1989). Ozone also is an absorber and radiator of energy in the spectral infrared region. It thus can act as a “greenhouse gas.” As Gotz (1951), p. 287, writes: “If a gas, such as ozone at its upper boundary, absorbs mainly in the ultraviolet part of the spectrum but emits accordingly to the laws of temperature radiation, then its temperature must rise to a rather high value before incident and emitted radiation will attain equilibrium.”

A third climate effect may be postulated. Ozone, as a very reactive gas, enters into many chemical interactions in the atmosphere, destroying and being destroyed in the process. Its action may be considered beneficial or harmful, depending on the point of view of the person making the decision. For example, the protective layer of ozone is considered a plus. Its effect on direct contact with life forms extremely is deleterious. The effect on climate then depends on the resultant of all the interactions of the reactive atmospheric constituents.

### 11.10.3 Ozone Sources and Sinks

The primary source of oxygen, ozone ( $O_3$ ), lies in the availability of oxygen ( $O_2$ ) and the energy of the intense extraterrestrial (solar) ultraviolet radiation packets or quanta. Presumably, 90 percent of the ozone lies within the stratosphere.

Figure 11-17 derives from figure 11-3 from Howard and Burch (1960). This compares the ozone (O<sub>3</sub>) infrared absorption of solar radiation with that by the simulated total atmospheric absorption of solar radiation. The latter includes the first. Secondary sources are those chemical reactions in the atmosphere, particularly the troposphere, which produce ozone as a byproduct. Some of these will be briefly mentioned later.

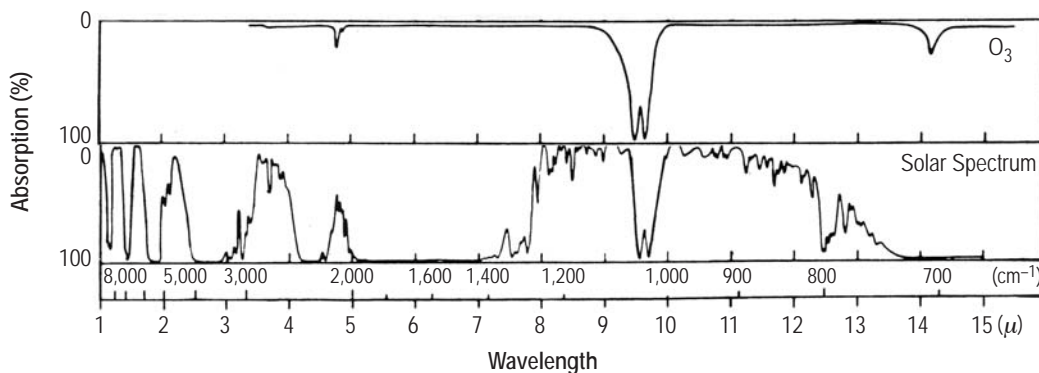
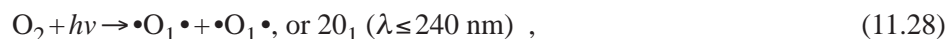
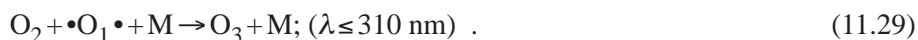


Figure 11-17. Comparison of ozone (O<sub>3</sub>) absorption of infrared solar radiation with the absorption by the atmosphere of the infrared solar radiation (courtesy of Howard (1960)).

Dave and Furukawa (1966) provide tables for scattered radiation in the ozone absorption bands. Photo disassociation of the oxygen (O<sub>2</sub>) molecule and ozone formation are discussed by Wulf (1937), Chapman (1943, 1951), Bamford (1942), Craig (1951), Gotz (1951), Liou (1980), Chantry (1984), Warneck (1988), and Wuebbles (1989). Chapman (1930) formulated the theory of ozone formation. His model was based on the work of Regener (1906) cited by Gotz (1951) and the information concerning the energy absorption in the Schumann-Runge and Herzberg bands. The region of contact between oxygen molecules and the incoming radiation is in the upper and middle portions of stratum in which the stratosphere forms. See Schumacher (1930, 1932), Khrgian (1973), and Khrgian, Kusnetsov, and Kondrat'eva (1967) for extensive survey work. The primary reaction leading to ozone formation is that described by the above authors and others. (Generally, if the lone atom is considered here it may help to visualize the reaction where the "O" is subscripted as (•O<sub>1</sub>•). If no other notation is made, the (•O<sub>1</sub>•) is assumed to also be written as (•O<sub>1</sub>(<sup>3</sup>p)•) which includes the ground state orbital configuration:



where  $h$  is Planck's constant and  $\nu$  is the frequency of radiation. Some authors indicate 255 nm. The  $h\nu$  is a photon or quantum. Ozone then is formed by a three-body collision of an oxygen molecule (O<sub>2</sub>), an oxygen atom (•O<sub>1</sub>•), and a third body, M:



The third body can be any other atom or molecule including oxygen or ozone. Ozone can come to an unstable rest with loss of energy, that energy being transferred to the third body, thereby increasing that body's rebounding momentum. Ozone (O<sub>3</sub>) itself can absorb sufficient energy from suitable infrared radiation to loosen an oxygen atom from the remaining oxygen molecule:





This is not a total sink as it allows for almost immediate recombination. A potential sink also exists in the collision of ozone with an oxygen atom ( $\bullet\text{O}_1\bullet$ ):



Here, the odd oxygens nullify each other. Another reaction may occur as



Again, the third body, M, will have a different momentum or a redistribution of its internal energies after impact and rebound. The above five reactions are known as Chapman (1930) reactions. These are the beginning of the stratosphere formation. See also Wayne (1985) for a description of a Chapman function. The above five reactions take place so closely in time that equilibrium conditions can be shown. See Craig (1951) and Liou (1980).

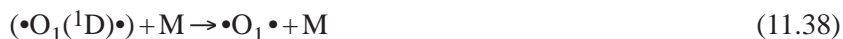
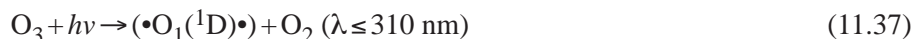
A catalytic reaction is one in which an element or a substance may initiate, participate in, or accelerate a chemical reaction and be eventually recovered intact or essentially unchanged upon completion of the reaction. Bates and Nicolet (1950) suggested that catalytic atmospheric gas reactions were possible. Catalytic ozone destruction reactions occur as another sink:



The “X,” for example, represents an oxide such as nitric oxide ( $\bullet\text{NO}$ ) or hydrogen oxide ( $\bullet\text{OH}$  — the hydroxyl radical), atomic hydrogen ( $\text{H}_1$ ), or chlorine ( $\text{Cl}_1$ ). As Liou (1980) indicates, these reactions produce the net results:



If  $\text{O}_3$  (ozone) itself absorbs in the ultraviolet, then one of the oxygen atoms ( $\bullet\text{O}_1\bullet$ ) may be excited; i.e., an electron or more than one electron may be lifted to a higher energy level or orbital. For one such atom, the following may occur:



Here, the ( $^1\text{D}$ ) indicates a lift to the D orbital configuration from the ( $^3\text{P}$ ) configuration. For example, the reaction in equation (11.28) could have been written as  $\text{O}_2 + h\nu \rightarrow 2(\bullet\text{O}(^3\text{P}))$ . See Wuebbles et al. (1989). The above also illustrates formation of nitric oxide ( $\bullet\text{NO}$ ). Reference is now made to the general equation (11.35) where nitric oxide, NO, is “X.” A cycling sequence may form, such as



This cycle destroys both odd oxygens— $\text{O}_3$  and  $\bullet\text{O}_1$ . Both these odd oxygens are necessary to maintain ozone in the middle atmosphere. The even oxygen,  $2\text{O}_2$ , is the net result as shown by Wuebbles et al. (1989).

As pointed out previously, it is the increase and warming of ozone by radiation absorption that, in part, as the ozone moves into the middle atmosphere, creates the warm inversion stratum called stratosphere. With no ozone production, that stratum warmth decreases and the stratum weakens and disappears as it effectively does in the polar winter, especially the Antarctic.

The above reactions are essentially in the forms suggested in Gotz (1951), Liou (1980), and Wuebbles et al. (1989). As Wuebbles et al. (op. cit.) indicate, based on the work of Molina and Rowland (1974), an especially effective catalytic cycle involves the chlorine atom. The action follows the same schematic as that for nitric oxide. See Wayne (1985) and Whitten and Prasad (1985) for more details on these cycling mechanisms:



Again, the “X” factor is regenerated to enter another cycle destroying both odd oxygens. This chain cycling will continue until the chlorine atom is removed from its action with ozone by reacting with some other atmospheric constituent. The chain lengths may be 100,000 reactions long. Rowland (1991) estimates such for the chain length of ClOx. The hydroxyl radical can undergo the same cycling scheme with ozone:



The last two, ( $\bullet\text{OH}$ ) and ( $\bullet\text{HO}_2$ ), are perhaps more searchers and destroyers than is ozone. Craig (1951) provides considerable material in his chapter on radiative temperature changes. He indicates that warming of the upper part of the ozone layer results from ozone’s absorbing qualities. The bands usually associated with these are: (1) the Hartley bands, 200 to 320 nm; (2) the Huggins bands, 320 to 360 nm; and (3) the Chappuis bands, 480 to 780 nm.

#### 11.10.4 Stratosphere Formation

In the tropics and midlatitudes, solar radiation impinges on the upper air more strongly than in polar latitudes. Essentially, the impingement is directly overhead twice a year at the equator, twice a year at latitudes between the two tropics, and once a year at the Tropics, Capricorn and Cancer. The impingement is inclined the rest of the year.

Prior to the work of Assmann (1902) and Tesserenc de Bort (1902), the assumption was made that the temperature of the atmosphere decreased with height throughout its depth. It was a startling discovery then that this was not accurate, at least at the latitudes where research was being done.

Ozone ( $\text{O}_3$ ), as the triatomic molecule of oxygen, an allotrope of oxygen, is a superoxide. Its molecular weight is 48, as compared to 32 for  $\text{O}_2$  and 16 for  $\bullet\text{O}_1$ . In tables A-11-2 and A-11-3, with the exception of krypton, xenon, and radon, it is the heaviest of the gases shown. It is also one of the more dense, and it tends to settle

downward. Additionally, ozone ( $O_3$ ) is warmed by radiation (as shown in sec. 11.6.2 above), both by the ultraviolet and infrared radiation. Also, as indicated in section 11.9.2, if a body absorbs mainly in the ultraviolet spectral region and emits according to the laws of temperature radiation, then its temperature must rise before equilibrium is attained (Gotz (1951)). Thus, ozone must warm and be warmed. Downwelling ozone molecules are replaced by newly forming ozone molecules in daylight. As ozone settles downward, it becomes less vulnerable to the destroying longer wavelength ultraviolet radiation, though it was created, in part, by shorter wavelength ultraviolet radiation. As ozone settles downward, entering protective higher pressure regions and, escaping the ultraviolet radiation, it begins to encounter infrared radiation of the Earth and of other gases. This also can destroy ozone, as indicated previously, but the process is slow. Eventually, the system reaches an equilibrium where ozone destruction concentration balances downwelling ozone concentrations. Photolytic decomposition of ozone provides two lighter units ( $O_2$  and  $\bullet O_1 \bullet$ ) of which  $\bullet O_1 \bullet$  will tend to upwell by its own buoyancy while  $O_2$  can only move upwards, as before, by slow convection. The entire atmospheric structure will have been warmed to this point or level. Stratospheric ozone will radiate in the infrared in all directions with a net result of warming above as well as the troposphere. The levels where warming stops locates the tropopause. This is the feature described by Assmann (1902) and Tesserenc de Bort (1902).

### 11.10.5 Instrumentation

Dobson (1930), working in meteorology to apply and to augment guidelines initiated by Fabry and Buisson (1913), developed the well known Dobson photospectrometer. Relying on ozone absorption at different radiation wavelengths, approximate heights and thicknesses of ozone layers may be established. The technique is the “umkehr” method. Well-described instrumentation pictures are provided by Gotz (1951). Essentially, this procedure is based on differing absorption and radiation characteristics of ozone at frequencies (wave numbers) which are selectively identified with and responsive to ozone.

The standard instrument in the Global Ozone Observing System is the Dobson photospectrometer (Dobson (1957a,b)). The instrument is a quartz double monochromator which measures the relative intensities of paired wavelengths in the Huggins ozone absorption band (300–350 nm) from which the total ozone in a vertical column of the atmosphere may be deduced.

Lindemann and Dobson (1922) had encountered the warm layer of the stratosphere in their study of the incandescence of incoming meteors and their attempts to determine the altitude of this incandescence. Few of the Dobson photospectrometers remain, but due to resurgence of interest in ozone, those that do remain have been rehabilitated and are maintained by various countries in good condition. The WMO assists in coordinating the programs. These instruments provide the basic ground truth for all total ozone observations. Satellites provide good, continuous coverage of many things, including the all-important ozone. However, sensors on satellites for ozone, as well as other elements, sometimes suffer degradation. There are insufficient satellites to allow cross-satellite calibrations. From a reliability point of view, the use of sensors manufactured by the same process would not necessarily be a solution. Thus, techniques of the Dobson photospectrometer system remain the one good base to calibrate other systems. See Planet, Miller, and Angell (1988) for a discussion of the present system.

Dobson (1957a,b) and Dobson and Normand (1962) provide necessary information for the use and calibration of Dobson photospectrometers; all such spectrophotometers have been numbered. Komhyr et al. (1989) report the results of an International Dobson spectrophotometer and Brewer spectrometer calibrations session in Arosa, Switzerland, in 1986. Fifteen countries with their numbered instruments participated. The reference spectrophotometer was the World Primary Standard spectrophotometer No. 83 of the Dobson Spectrophotometer Central Laboratory in Boulder Observatory. Komhyr, Grass, and Leonard (1988) indicate the ozone measurement precision of instrument No. 83 has been maintained to within an uncertainty of 0.5 percent. Three countries had Brewer

instruments which were compared to the master instrument No. 83. From a quality assurance point of view, these international comparisons should be maintained and calibrated.

**11.10.5.1 Vertical Structure.** The foregoing discussion concerned primarily horizontal structures or layers. Essentially, this amounts to the total ozone amounts as determined by “umkehr” techniques. The radiosonde era begins with the initial work of Moltchanoff (1928). There was increasing development in Europe, particularly during 1937–1938 at several observing stations in the United States. These primarily were observation locations for pressure, temperature, and humidity in the vertical. The radiosonde is attached to and carried aloft by a balloon. With appropriate sensors and a transmitter, it can transmit information to a ground station. From this telemetered information, the vertical distribution of temperature, pressure, and moisture can be determined. Visual or radar theodolite observations of the balloon trajectories permit the determination of wind. Radio theodolite observations can be made day and night and in other conditions where visual methods cannot be used. Sensors were developed and used (and are used) for ozone, for other gases, for turbulence, and for radiation. Also, other sensors have been developed and still others possibly could be developed. The ozonesonde is a balloon-borne instrument used in conjunction with thermodynamic information to determine the vertical structure of ozone concentration of the atmosphere. Rocketsondes also can carry and release ozone-sensing equipment. That equipment is not described here. Angell and Korshover (1978, 1980) are two consistent reporters of temperature, wind, and ozone structures of the atmosphere based on data obtained. Rocketsonde networks were established and continue to operate on an irregular basis, generally on lines from one polar region to the other, along the North American-South American corridor. Further discussion here is limited by time and space. No denigration of the importance of these instrumental techniques is intended in limiting discussion. A Total Ozone Measuring Satellite system now is deployed.

Court (1942) reported on the disappearance of the tropopause at Little America, Antarctica, during the winter. Figure 11-18 presents a temperature-pressure profile read by eye from charts which Court (op. cit.) presented. This is the Little America, Antarctica, mean temperature profile, September 1940, 15 observations. The U.S. Marine Climatic Atlas, Vol. IX (1965) presents mean graphs for all Antarctica stations including Little America. These present essentially the same picture of the polar tropopause waning and waxing. Rubin (1953), Schumacher (1955), and Wexler and Rubin (1956) also discuss features of the disappearance of the Antarctic tropopause during the Antarctic winter. They also provide comparative soundings for seasons in the Antarctic and the Arctic. In January 1963, the Air Force Cambridge Research Laboratories initiated a 1-yr program network of 11 stations in North America to study the vertical ozone distribution (Hering, ed. (1964)). This network covered the North American region from Fairbanks, Alaska, and Thule, Greenland, to Balboa in the Panama Canal zone. The program was extended to cover the International Quiet Sun Years (IQSY) time period 1964–1965.

Hering (ed.), Vol. I (1964), Hering and Borden (eds.), Vol. II, (1964), Hering and Borden (eds.), Vol. III, (1965), Hering and Borden (eds.), Vol. IV, (1967), and Hering and Dutsch (1965) report on the above-referenced project 8631 of the U.S. Air Force Cambridge Research Laboratories to make ozonesonde observations over North America. These reports are an extensive compilation of data in the year 1963 and during the IQSY of 1964 and 1965. Ozone observations were obtained by use of chemiluminescent-type ozonesonde developed by Regener (1960). Regener (1960), Vol. 1, contains both data and ozonograms at 11 stations extending from Fairbanks and Thule, southward to Balboa. A special series of ascents were made at La Paz, Bolivia.

As a part of the IQSY, 1964–1965 program, the U.S. Department of Commerce, ESSA operated or supported operation of nine ozonesonde stations in the Western Hemisphere and in Antarctica (Komhyr and Stickel, Vol. 1 (1967) and Komhyr and Grass, Vol. 2 (1968)). Komhyr and Grass (1968) report on the ozonesonde observational program at 11 stations: (1) Amundsen Scott, Antarctica, (2) Byrd, Antarctica, (3) Canton Island, South Pacific, (4) U.S.N.S. Eltanin, (5) Fairbanks, Alaska, (6) Hallet, Antarctica, (7) Hilo, Hawaii, (8) La Paz, Bolivia,

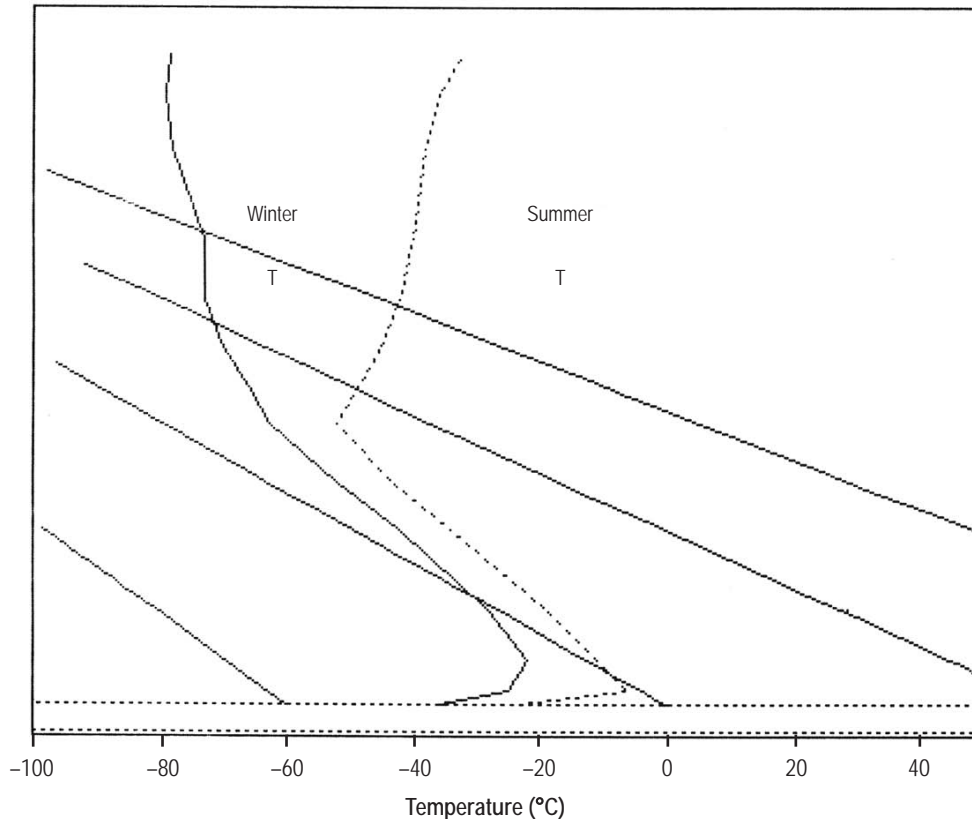


Figure 11-18. Little America, Antarctica, winter and summer temperature (°C)-pressure (mb) profiles. The winter profile is based on 15 observations in September 1940. These are estimated from those presented by Court (1942) (courtesy of American Meteorological Society).

(9) Puerto Montt, Chile, (10) Sterling, Virginia, and (11) Wilkes, Antarctica. The period of observation covers the IQSY (1964–1965). Three different ozonesonde types were used: Regener (1960) chemiluminescent, Brewer-Mast electrochemical, and the then newly developed carbon-iodine instruments (Komhyr (1964)). The authors discuss problems associated with each and the procedures to work with each. The report itself contains the ozonograms. These stations supplemented those of the Air Force Cambridge Research Laboratory (AFCRL) cited above. Western Hemisphere ozonograms have been published in Vol. 1., Supplementary data—coded values of ozone, temperature, and wind—applicable to standard and significant levels for all soundings, including 1962 Antarctica soundings, appear in *Ozone Data for the World*. This was published by the Meteorological Branch, Canadian Department of Transportation in cooperation with the WMO.

According to these publications, computer tabulation sheets for Volumes 1 and 2 are available from the National Weather Records Center, now the National Climatic Data Center, Asheville, NC. This is no longer certain. The World Ozone Data Center address is: World Ozone Data Centre, Atmospheric Environmental Service, 4905 Dufferin Street Downsview, Ontario, Canada M345T4. See Environment Canada, *Ozone Data for the World*, Index No. 22, and Vol. 29, No. 2 as examples. The 1962–1966 ESSA ozone data when combined with data from the AFCRL North American ozonesonde network, 1963–1965, and data from the National Center for Atmospheric Research sounding program at Boulder, Colorado, Dutsch, provide nearly 2,500 direct measurements of the vertical distribution of ozone in the Western Hemisphere and Antarctica (Komhyr and Grass (1968)).

Figure 11-19(a) and (b), taken from Komhyr and Grass (1968) with permission, depict a winter and a summer sounding at Byrd Station, Antarctica, July 7, 1965, and December 22, 1966. These allow the comparison of ozone and temperature vertical profiles. The variates are partial pressure of ozone ( $\mu\text{mb}$ ) and temperature ( $^{\circ}\text{C}$ ) against atmospheric pressure (mb). During the winter season, in this case July 7, 1965, the temperature trace may extend below the chart range. However, the temperature data are easily deduced. Additionally, the total, integrated and residual ozone amounts in Dobson units are (285, 263, 22) and (331, 279, 52). The total amounts are derived from spectrophotometer (“Umkehr”) measurements while the integrated amounts are derived from ozonesonde measurements. The difference between these two is the residual ozone remaining in the atmosphere above the last level of ozonesonde data. The Dobson unit is equal to 1 milli-atm-cm ozone or  $10^{-3}\text{cm}$  ozone at STP. Due to increasing interest in the current Antarctic winter and mid-spring ozone apparent deficits, programs have been started to increase the ozone measurement program along with the measurement of other trace gases. Komhyr, Oltmans, and Grass (1988) describe some results from one of the programs initiated in 1986. The abstract of their paper reprinted with permission follows:

“Vertical-profile ozone distributions and variations, as well as the annual course of total ozone, are described for South Pole, Antarctica, from observations made throughout 1986 with electrochemical concentration cell (ECC) ozonesondes and a Dobson spectrophotometer. Ozone decrease in the stratosphere in September and October months was the highlight of the measurements. From mid-August to October 7, total ozone decreased by about 40%, with the bulk of the decrease occurring between 12 and 21 km. Within this region the maximum rate of ozone decrease, with an exponential decay half-life of 11 days, was observed between September 20 and October 15, when column ozone and ozone volume mixing ratio at  $16 \pm 1$  km decreased by 78% and column ozone between 12 and 21 km decreased by 50%. This time interval was characterized by virtual cessation of ozone flux into the stratosphere above South Pole that might have resulted either from movement of the polar vortex or from ozone advection from lower latitudes. In contrast, ECC ozonesonde data obtained in 1971 show ozone to have arrived at South Pole above 30 mbar in mid-September and above 100 mbar in late September, 6 and 3 weeks, respectively, earlier than it did in 1986. Supporting evidence for a temporal change in the time of ozone transport to Antarctica by atmospheric circulation comes from 1974–1986 surface ozone observations at South Pole, which show a negative surface ozone growth rate during summer months, a positive growth rate during winter months, and an increase in the amplitude of the annual cycle by a factor of 2. A correspondence is shown between El Niño-related highs in sea surface temperature anomalies in the equatorial Pacific Ocean and lows in October–December total ozone averages that were observed at South Pole in the 1960s and 1970s. Such ozone lows occurred during years of increased circumpolar vortex stability, late stratospheric warming, and late ozone arrival in Antarctica. It is suggested that the 1982–1983 El Niño, which was of unprecedented intensity, similarly affected the transport of ozone to Antarctica, thereby contributing to the observed springtime ozone decrease. The transport of air parcels from  $50^{\circ}$  to  $60^{\circ}$  S latitude into the tropopause and low stratosphere region of Antarctica, as suggested by 10-day, isobaric back trajectory analyses, may also contribute to the Antarctica springtime ozone decrease and warrants further investigation.”

Table 11-4 (with permission, Komhyr, Oltmans, and Grass (1988)) provides mean monthly South Pole, Antarctica, total ozone data for 1986 derived from Dobson spectrophotometer observations. Note the low values of October, the spring season.

Komhyr, Grass, and Leonard (1986) discuss the total ozone decrease at the station, South Pole, Antarctica 1964–1985. Also Komhyr et al. (1988) report on Electrochemical Concentration Cell (EEC) ozonesonde observations at the station, South Pole, Antarctica during 1987. They note an early October low of 127 DU compared with the early October 1986 low of 150 DU. They present a figure which shows an ozone decline from near 280 DU in

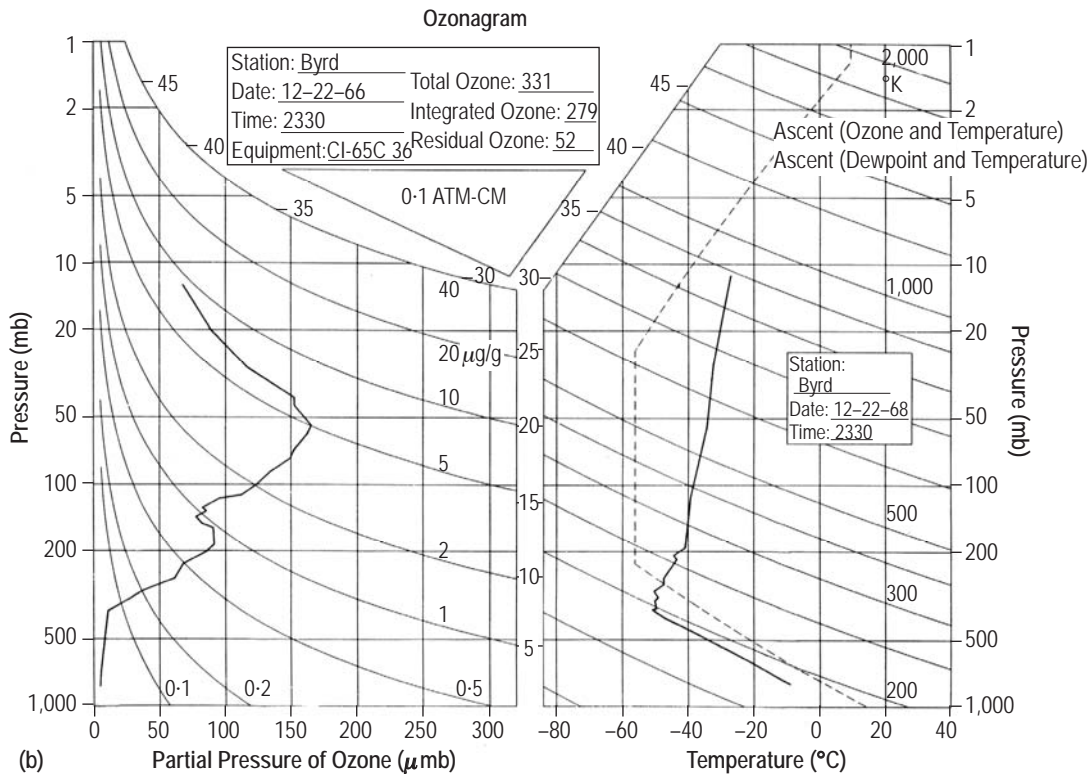
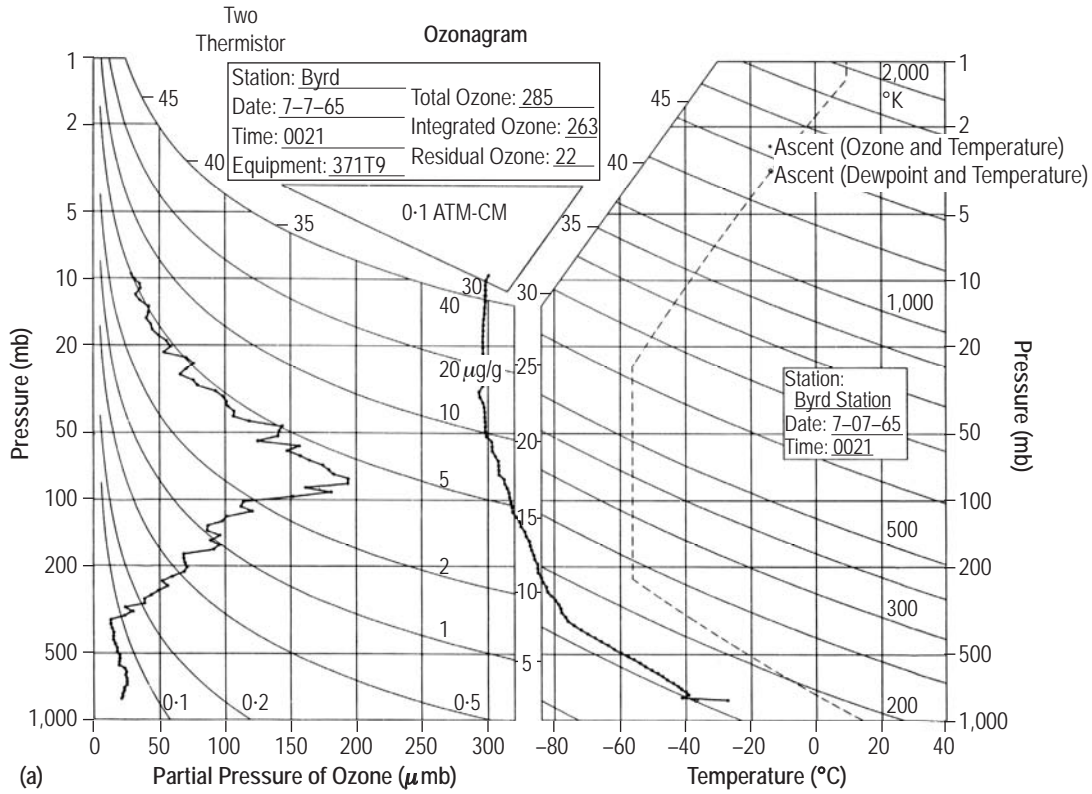


Figure 11-19. Byrd Station, Antarctic, ozonagram temperature ( $^{\circ}\text{C}$ ), ozone partial pressure (nb) versus pressure (mb) for (a) winter, July 7, 1965, and (b) summer, December 22, 1966 (courtesy of ESSA, NOAA, with permission Komhyr and Grass (1968)).

Table 11-4. Mean monthly, South Pole, Antarctica, total ozone data for 1986 derived from Dobson spectrophotometer observations (courtesy of the American Meteorological Society, from Komhyr, Oltmans, and Grass (1988)).

Month	Number of Observations	Total Ozone	
		DU*	s.d., DU*
January	26	280	8
February	23	261	15
March	6	228	8
April	7	221	7
May	8	230	4
June	5	243	4
July	6	240	5
August	3	250	10
September	–	–	–
October**	10	184	6
November	27	313	63
December	28	321	24

\* Dobson unit (DU) is equal to 1 milli-atm-cm ozone; s.d.; standard deviation.

\*\*The ozone value for October represents observations made during the latter half of the month.

1980 to a 1987 low of 127 DU. This decline has been attributed variously to the use of nitrates in agriculture, the halocarbons, and to the severe El Niño episode of the beginning at about the same time. At this time, only the halocarbon influence seems to be important. See the scientific assessment of stratospheric ozone, 1989 report prepared under the auspices of the WMO.

Komhyr, Oltmans, and Grass (1988) also provide ECC ozonesonde data showing development of the ozone hole over the station, South Pole, Antarctica. For example, to help do this, they present examples of the paired sequence of days through the year where earlier soundings in a month may be compared with a later sounding. See figures 11-20 and 11-21 for the summer (Nov. 20 to Dec. 28, 1986) and winter-spring (Aug. 19 to Sept. 15) seasons. See also figure 11-22 from the same paper where six graphs of paired ozone profiles are shown with a base date of August 19, 1986, and then six graphs of paired soundings where the base date is August 17, 1971 (g)–(1). The latter figures present total ozone amounts in DU for comparison. During 1971 the total ozone amounts increased from 197 DU to 215 DU in early October to 342 DU in mid-October (g through l). During the 1986 period, ozone amounts decreased from early August 1986 readings of 263 DU to 247 DU in early September 1986 to 172 DU in mid-October 1986. In general, the profiles indicate a lessening of ozone concentrations with time through the base August 9, 1986, (winter) profile and total ozone amounts appear to be greater in 1986 than in 1971. For the entire period, the authors provide values (260 DU versus 200 DU), a decrease of  $\approx 23$  percent. To further elucidate the expected spring increase of ozone, they examine 10-day isobaric back trajectories at the 300-, 200-, 70-, and 50-mb surfaces. These studies seem to indicate incursions of ozone into the region of minimum ozone. Thus, dynamic as well as static considerations are suggested.

Komhyr et al. (1989a) report on the observational program of 1987. Robinson et al. (1988) describe the long-term air quality monitoring at the South Pole by the NOAA program geophysical monitoring for climatic



change. Their discussion emphasizes GMCC South Pole air chemistry record for carbon dioxide, total ozone, surface ozone, methane, halocarbons, nitrous oxide, and aerosol concentrations.

Robinson et al. (op. cit.) provide the trends in trace gases measured at South Pole, Antarctica, 1977–1987. Here are the trend characteristics as read from their figures 13–16, and given in tabular form in table 11-5.

Methane ( $\text{CH}_4$ ) shows a clearly marked annual wave. Robinson et al. (op. cit.) also show an equally marked annual wave in condensation nuclei: As nuclei have a lower bound of zero, the authors choose to use logarithms of the condensation nuclei amounts as the variate against time. These four gases and ( $\bullet\text{NO}_2$ ) are among many that are involved in the catalytic destruction of ozone ( $\text{O}_3$ ). Oltmans et al. (1989), using a self-consistent set of ozone soundings from eight stations, indicate that there is more ozone in the Northern Hemisphere than in the Southern Hemisphere. They also report that four geographical monitoring stations for climatic change show increasing ozone concentrations at two Northern Hemisphere stations, while it has decreased considerably at the two Southern Hemisphere stations. The four stations are Barrow, Alaska; Mauna Loa, Hawaii; American Samoa; and South Pole, Antarctica. The mid-latitude troposphere of the Southern Hemisphere generally contains more ozone than does the tropics or high latitudes. One of the possible modes for the higher ozone amounts in the Northern Hemisphere troposphere considered by Komhyr et al. (op. cit.), based in part on the cited models of others, is the greater flow of ozone from the stratosphere. Presumably, this is due to the deep storms greater in number and development previously mentioned. In the Northern Hemisphere, the ratio of land mass to ocean mass is much greater than in the Southern Hemisphere. The land masses are asymmetrically located and some distance from the pole, whereas Antarctica is essentially symmetrically placed at the pole. Interactions between the continents and oceans is much greater in the Northern Hemisphere. Resulting storms then provide mechanisms to induce greater transport in the north than in the south polar regions. Another mode is the greater extent of man's industrial activities. Wuebbles et al. (1989) citing Fishman (1985) indicate that the production of tropospheric ozone may be as great as the injections of ozone from the stratosphere. Thus, there is about 5 percent due to tropospheric reactions, with about 5 percent percolating from the stratosphere, and 90 percent remaining in the stratosphere. Wuebbles et al. (op. cit.) also provide sequences and of the existing reaction sequences which would lead from photooxidation of methane and oxygen,  $\text{CH}_4 + 4\text{O}_2$ , to produce a net  $\text{CH}_2\text{O} + \text{H}_2\text{O} + 2\text{O}_3$ . It would be a tremendous feat to portray fixed precedence of reaction in the entire atmosphere mixture. Presumably, it will be possible to portray potential avenues of such reactions only through a stochastic multimodal-multivariate model. This model would have to provide the probabilities for each reaction.) Wuebbles et al. (op. cit.) is recommended for those interested in such atmospheric constituent reactions and implications for climatic change.

**11.10.5.2 Horizontal Structure.** As indicated previously, Schonbein conjectured that ozone ( $\text{O}_3$ ) was a constituent of the atmosphere. Presumably, this conjecture considered complete mixing. Fabry and Buisson (1913) showed that ozone ( $\text{O}_3$ ) for the most part was located in the upper air in the stratosphere as defined by Tesserenc de Bort (1902, 1908). Estimates now place the amount of ozone in the stratosphere at about 90 percent.

Figure 7 in Gotz (1951) shows isopleths of the annual average ozone amount on a month versus latitude display. An ozone belt is shown at  $60^\circ$ – $80^\circ$  N. latitude with a maximum in March of about 340 DU or  $10^{-3}$  cm. A minimum of 160 DU occurs during the winter at  $80^\circ$  N. latitude and at the equator. For the Southern Hemisphere, at  $60^\circ$  S. latitude, a minimum of 240 DU is shown, while a maximum of 340 DU is shown during the winter. No Southern Hemisphere data are shown at latitudes higher than  $60^\circ$ .

London (1980) presents the observed global variation of total ozone, also presented by London (1985) in his figures 1-1(A) and 1-1(B) and figures 1-6, 1-2(A), and 1-2(B). Respectively, these are reproduced below, with permission.

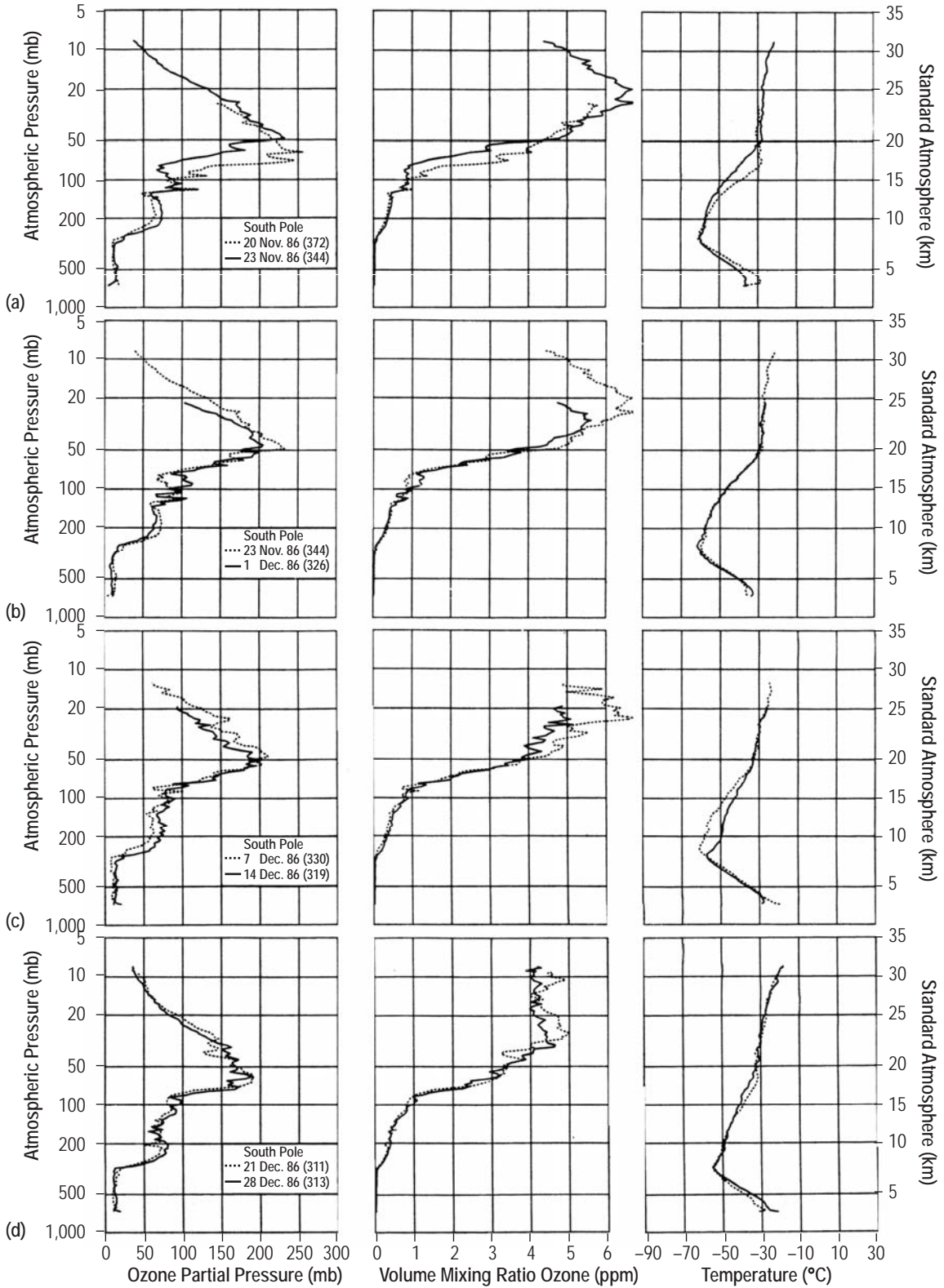


Figure 11-20. Sequentially paired ((a)–(d)) ozone (O<sub>3</sub>) South Pole station soundings through the summer season, November 20 to December 28, 1986. Ozone mixing ratios (ppm) and temperatures (°C) are also shown (courtesy of Komhyr, Oltzman, and Grass (1988)).

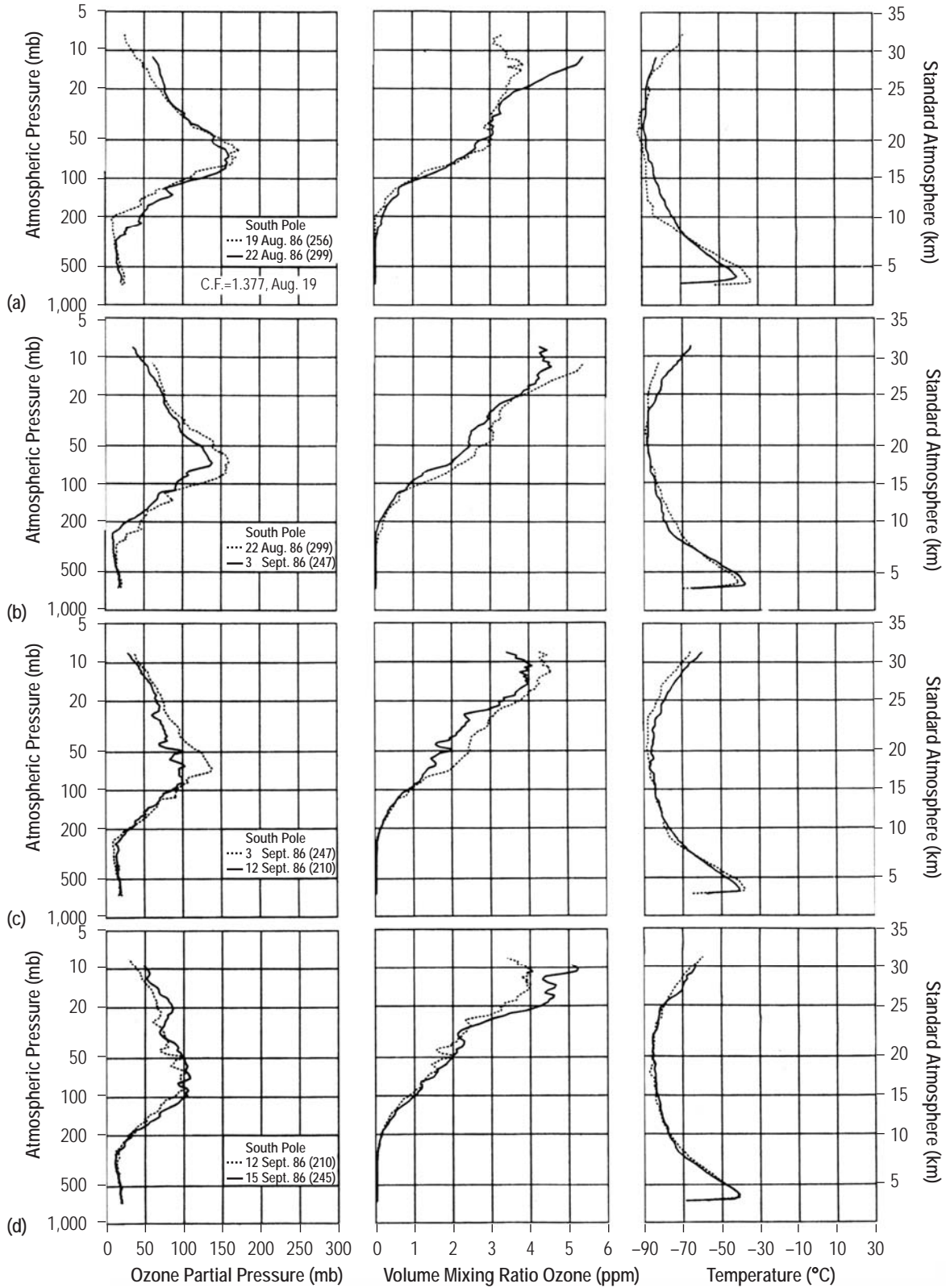


Figure 11-21. Sequentially paired ((a)–(d)) ozone ( $O_3$ ) South Pole station soundings through the winter season, August 19 to September 15, 1986. Ozone mixing ratios (ppm) and temperatures ( $^{\circ}C$ ) are also shown (courtesy of Komhyr, Oltsman, and Grass (1988)).

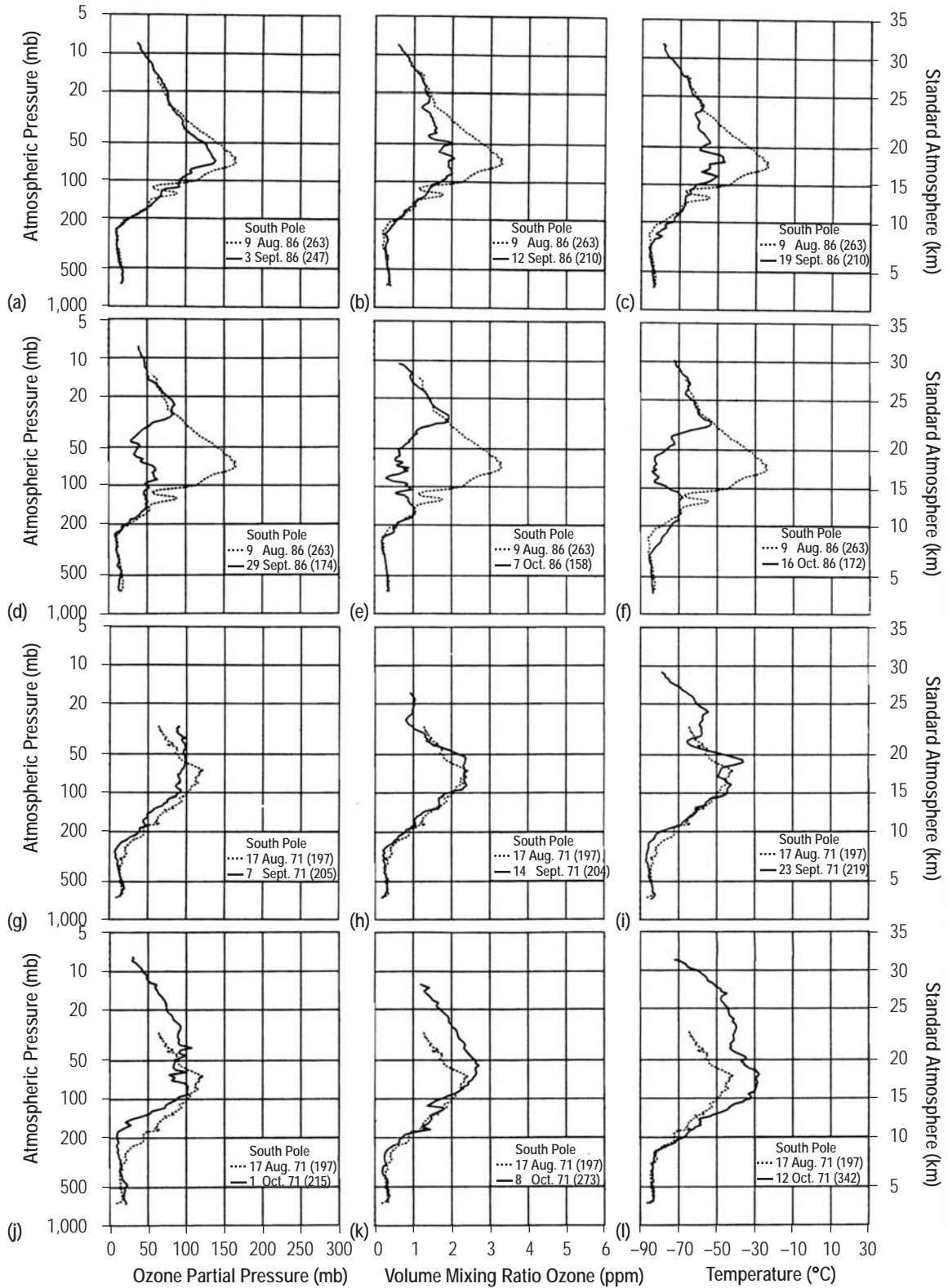


Figure 11-22. Sequentially paired ozone ( $O_3$ ) South Pole station, winter-spring soundings. In (a)–(f), the comparative base sounding is August 9, 1986, while for (g)–(l), the comparative base sounding is August 17, 1971. The dotted lines are the comparative bases (courtesy of American Meteorological Society, with permission Komhyr, Oltsman, and Grass (1988)).

Table 11-5. Trace gas measurements at South Pole, Antarctica, 1977–1987.

	January	Intercept	Slope	December	Intercept
CH <sub>4</sub> (ppbv); methane	1983	1,552	12.5	1987	1602
N <sub>2</sub> O (ppbv); nitrous oxide	1977	299	0.62	1987	305
CCl <sub>2</sub> F <sub>2</sub> (pptv); CFC12	1977	225	15.7	1987	382
CCl <sub>3</sub> (pptv); CFC11	1977	131	9.5	1987	228

Figure 11-23(a) (from London (1985)) shows the long-term annual average distribution of total ozone in m-atm-cm from ground-based Dobson and optical filters from 1958 to 1980. Dashed lines are for regions where there are no data. The equatorial averages are near 260 m-atm-cm (DU) while the Arctic regions are near 380 m-atm-cm and the Antarctic regions are near 340 m-atm-cm. Figure 11-23(b) (from London (1985)) shows the average total ozone for a shorter period (1970–1977) from satellite (BUV) observations. This presentation shows a lower equatorial mean approaching 250 m-atm-cm (DU) while the Arctic and Antarctic values are about 20 m-atm-cm higher, namely 400 and 360. Figure 11-24 (also from London (1985)) represents a measure of global total annual ozone variability, the mean annual range determined from the 1958–1980 ground-based data. The units are m-atm-cm. Additionally, figure 11-25 (from London (1985)) provides a long-term average latitude/season distribution of total ozone, m-atm-cm (DU) from ground-based data (1958–1980). The dashed lines locate the maxima in the poleward regions and the minima in the equatorial regions. The maxima are located poleward in the winter seasons, 460 and 400 m-atm-cm (DU) north and south, respectively.

Latitudinal/seasonal ozone charts shown by London (op. cit.) as reproduced above indicate equatorial minima of  $\approx 240$  m-atm-cm units with mid-latitude maxima of 400–450 units. Minima occur in the latter region during the fall seasons. The variability chart presented by London (1985) is in the form of the annual ranges from  $\approx 25$  m-atm-cm units at the equator and about 200 and 100 in the higher latitudes. If the range is estimated at a 6 $\sigma$  level and if the distribution is a normal (Gaussian) distribution, the equatorial standard deviation is about 5 m-atm-cm units while in the south and north, respectively, the standard deviations are near 10 and 15 units.

Komhyr, Grass, and Leonard (1988) (their fig. 1) show the trend in ozone measurements at the Mauna Loa Observatory for the period 1964–1988. There the trend is not linear. Two linear or one quadratic fit to the data imply a maximum in the period 1972–1976. Linear fits prior to and after the maximum, 1964–1974 and 1974–1987, respectively, have slopes of 0.37 and –0.35 percent per year. The authors note the very evident quasi-biennial oscillation (QBO) in the data presentation. (The period appears to show short oscillation periods ranging from 18 to 30 mo at Mauna Loa as well as at American Samoa.) The present trend at American Samoa, 1976–1988 is 40 percent per year. (By the roughest of conjectures, the maximum and minimum of records go with the minimum and maxima of solar activity. However, this sample is of only one.) There is as yet no complete long wave in the record available. The uncertainties must be large indeed.

### 11.10.6 Recent Extensive Reports

**11.10.6.1 Four Reports.** It is important to bring to the reader’s attention the following reports which have not been previously mentioned. These result, in part, from the increasing interest in the participation of ozone and other trace gases in climate processes. This increasing interest and resultant research accelerated after Farman, Gardiner, and Shanklin (1985) reported the extended loss of ozone in the Antarctic polar stratosphere. Now called the “Ozone Hole,” a companion, less pronounced hole is reported in the Arctic. The implications of these holes to climate and health support the reasons for increased funding and research. In any study of situations which affect

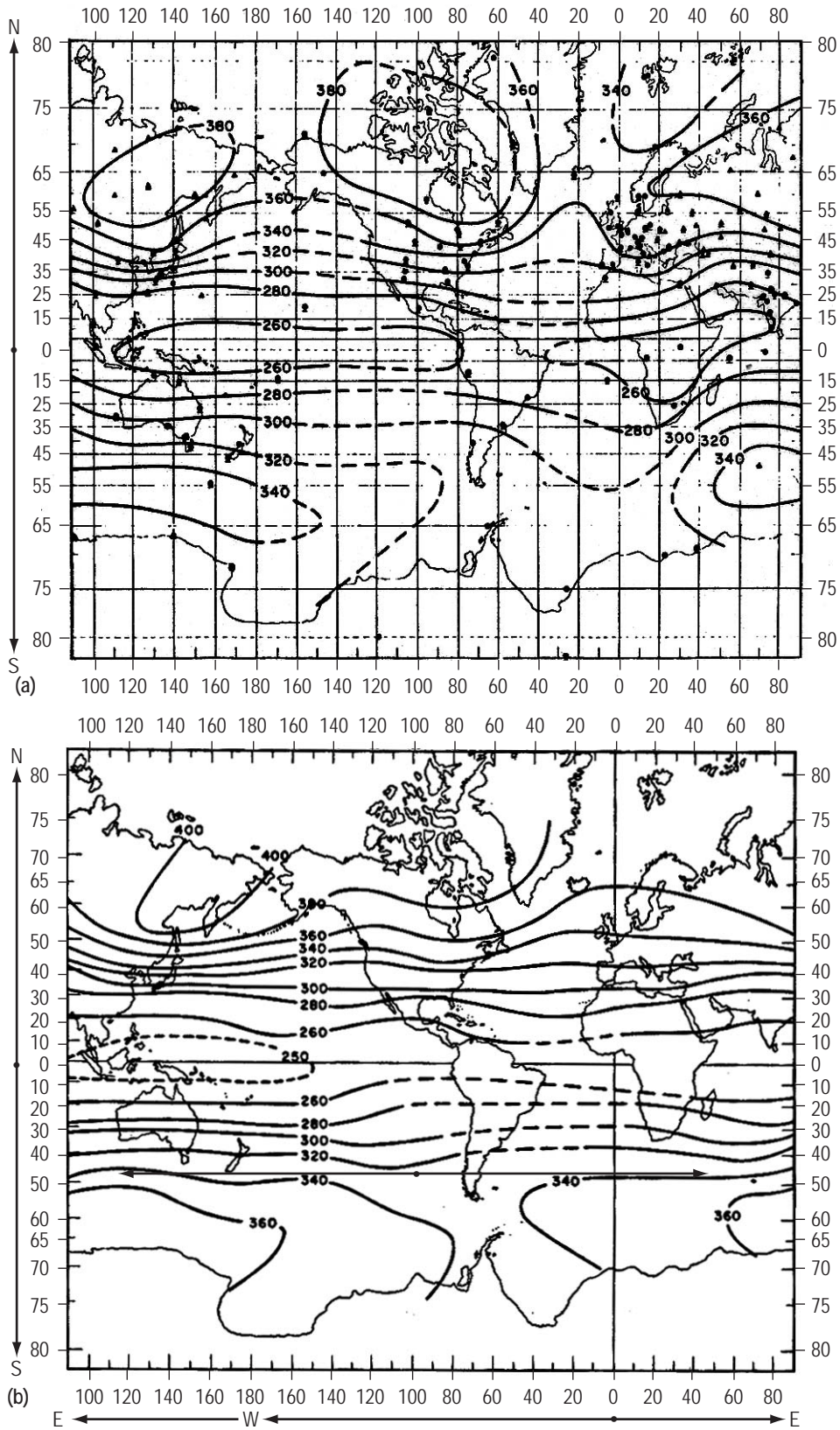


Figure 11-23. Long-term annual average (a) distribution from ground-based Dobson and optical filter locations, 1958–1980, and (b) total ozone from satellite (BUV) observations, April 1970–March 1977. Units are m-atm-cm or Dobson units. Dashed lines for regions where there are no data (with permission, Van Nostrand-Rheinhold, courtesy of London (1985)).

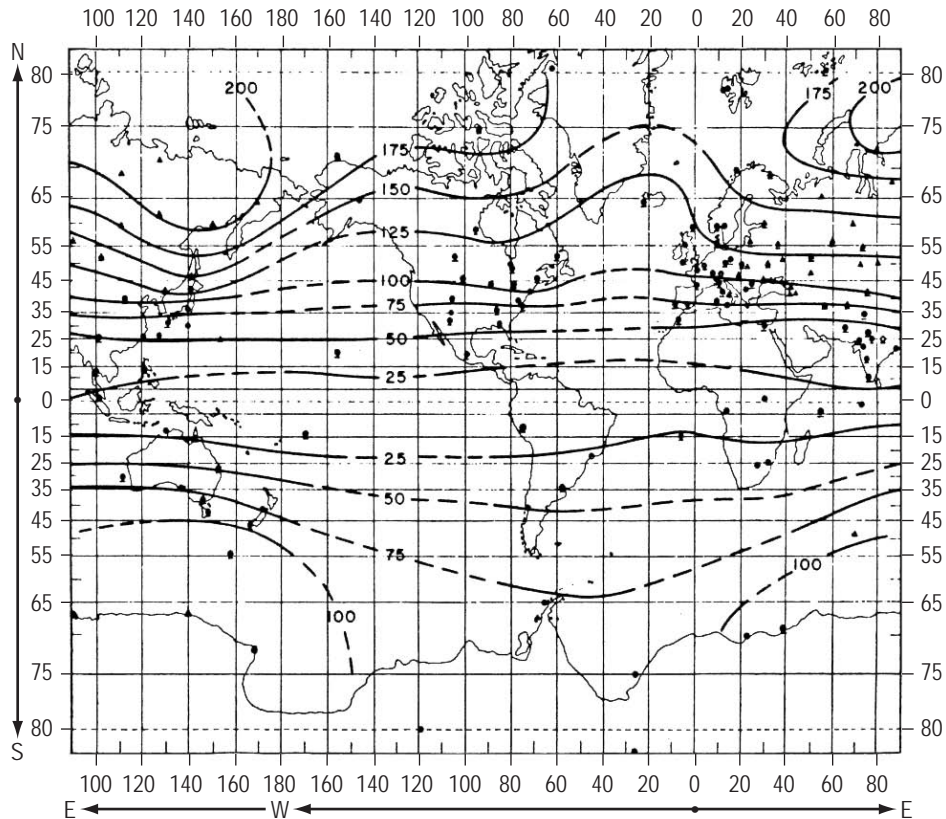


Figure 11-24. Global distribution of mean annual range of total ozone determined from ground-based Dobson observations (1958–1980). Units are m-atm-cm (with permission, Van Nostrand-Rheinhold, courtesy of London (1985)).

or may affect the entire world, many nations and organizations may become involved in joint research and investigative efforts. Supporting groups of some of these studies were the United Nations, World Meteorological Organization, United Nations Environmental Program, National Aeronautics and Space Administration (USA), United Kingdom—Department of the Environment, the National Oceanic and Atmospheric Administration (USA), and the Intergovernmental Panel on Climatic Change. Many scientists are involved and many reports are emerging in the literature.

The following briefly discussed reports reflect the intensive as well as extensive interest, research, and reporting. These are:

(1) The U.S. National Research Council (1989) report. This study was chaired by Anthes and discussed ozone depletion, greenhouse gases, and climate change. Articles on the following are provided:

- Global change and the changing atmosphere.
- Stratospheric ozone depletion; global processes.
- Stratospheric ozone depletion; Antarctic processes.
- Halocarbon role in stratospheric ozone depletion.
- Heterogeneous chemical processes in ozone depletion.
- Free radicals in the Earth's atmosphere; measurements and interpretation.
- Theoretical projections of stratospheric change due to increasing greenhouse gases and changing ozone concentrations.

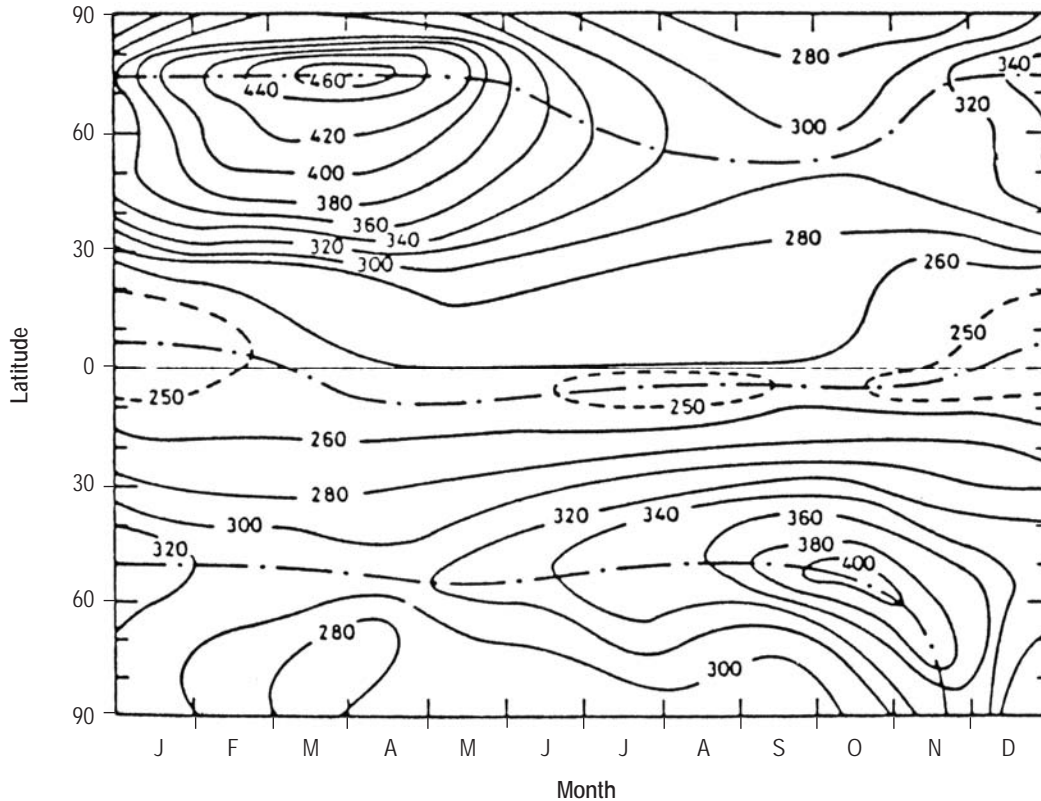


Figure 11-25. Long-term average latitude/season distribution of total ozone from ground-based data (1958–1980). Units are m-atm-cm. Dashed lines connect hemispheric maxima. Dashed lines also connect tropical minima (with permission, Van Nostrand-Rheinhold, courtesy of London (1985)).

- Historical trends in atmospheric methane concentration and the temperature sensitivity of methane outgassing from boreal and polar regions.
- Global temperature trends.
- Use of numerical models to project gas-induced warming in polar regions.

(2) The United Nations World Meteorological Organization Global Ozone Research and Monitoring Project Report No. 20, vols. I and II (1989). Daniel L. Albritton and Robert T. Watson are the assessment co-chairs. There are five chapter coordinators: Solomon (USA), Megie (France), Brasseur (Belgium), R.A. Cox (UK), and Wuebbles (USA). There are 76 listed contributors and reviewers for vol. I and 52 more for vol. II. Volume II is a report on the outcome of the Alternative Fluorocarbon Environmental Acceptability Study (AFEAS). The objective of the AFEAS report, as indicated in its introduction, was to determine the environmental acceptability of the alternative fluorocarbons with special emphasis on:

- The potential of the compounds to affect stratospheric ozone.
- Their potential to affect tropospheric ozone.
- Their potential to contribute to model calculated global warming.
- The atmospheric degradation mechanisms of the compounds in order to determine their products.
- The potential environmental effects of the decomposition products.



The AFEAS was conducted by independent scientists but was organized and sponsored by 15 CFC producers around the world. This was part of a cooperative industry effort to study the safety and environmental acceptability of CFC alternatives. As indicated and discussed in the section on halocarbons, section 11.13, the CFCs are the fully halogenated hydrocarbons while the HFCs are the partially halogenated hydrocarbons; i.e., not all of the hydrogens have been replaced by a halogen.

(3) The U.S. NASA Reference Publication 1242. Watson et al. (1990) author the above report on the "Present State of Knowledge of the Upper Atmosphere 1990: An Assessment to Congress." There is a summary, an executive summary, and a series of scientific summaries. The last includes chapters on polar ozone, global trends, model predictions, halocarbon O<sub>3</sub> depletion, and global warming potentials.

Section B also contains a scientific assessment of stratospheric ozone (AFEAS, vol. II (1989)). There are 12 subsections to this section which is taken from vol. II of the same title mentioned in (2) above. Section C discusses the transient scenarios for the atmospheric halogens. Section D treats chemical kinetics and photochemical data for use in stratospheric modeling. Section E discusses the impact on stratospheric chemistry and ozone caused by the launch of the Space Shuttle and Titan IV. Section F provides the names of the High-Speed Research Program Atmospheric Advisory Committee members as of August 1989. There were 27 members, of which 12 were ex-officio members.

(4) The Intergovernmental Panel on Climate Change (IPCC) reports on climate change sponsored by the United Nations WMO/UNEP (1990). This is the final report of the working group of the IPCC. It is edited by Houghton, Jenkins, and Ephraums. Scientists from over 25 countries participated in the preparation of this report.

All of the above-mentioned reports offer considerable information and detail. These provide a much more extensive base for the reader to base ideas and concepts concerning climate and climate change. As the IPCC report indicates, there is a more secure basis to make scientific and political judgments with respect to climate and its continuance.

**11.10.6.2 Ozone Formation and Depletion.** Ozone formation has been discussed previously and halocarbons are discussed extensively in section 11.13.

Ozone itself absorbs and emits radiation as shown in figures 4-4, 4-5, 11-3, and section 11.9.1.2. Some spectral region lines are located at 14.1, 9.6, 9, 5.75, 4.75, 3.59, 3.27, and 2.7  $\mu$  with other lines in the GHz regions. The remaining atmospheric constituents behave similarly, though not necessarily, at the same frequencies (wavelengths). Thus, in the infrared, they tend towards an equilibrium state. As ozone emits, the atmosphere absorbs. As ozone absorbs, the atmosphere cools. There are many destroyers of ozone. In a sense, this may be a misnomer for the ozone itself may be called an opportunistic seeker and a destroyer. There are many chemical and photochemical reactions of ozone with other atmospheric constituents. Some of these are accorded separate treatment as in section 11.12 and 11.13 for water and the halogens, respectively.

**11.10.6.3 Climatology Outline for the Southern and Northern Hemisphere.** Solomon (1989) in UN, WMO coordinated the work reported for the section on Polar Ozone.

11.10.6.3.1 Outline of the Climatology of the Southern Hemisphere. "During the Southern Hemisphere winter, the coldest temperatures occur in the lower stratosphere over the polar region. A strong westerly vortex covers a large fraction of the Southern Hemisphere, extending through the stratosphere. The vortex is nearly axisymmetric about the South Pole; planetary scale disturbances are weak. After mid-winter, the vortex begins to weaken, at first slowly, because of the evolving field of solar radiative heating. In spring, the weakening is accelerated when planetary scale disturbances develop. Warm air extends towards middle and high latitudes, and the vortex shrinks.

Typically toward the end of September and during October, the vortex becomes highly distorted as a strong, persistent (though fluctuating) planetary scale anticyclone develops in a preferred geographical region, 90° E.–90° W. Mechoso et al. (1988) give a more detailed description. Warm air extends towards middle and high latitudes, and the vortex shrinks quickly. Finally, it breaks down, first in the upper stratosphere, and then later (and more slowly) in the middle stratosphere. As the vortex breaks down during this so-called final warming, warm, ozone-rich air spreads from low latitudes over the polar cap. Notice, however, that in the lower stratosphere, a remnant of the cold core of the vortex lasts throughout October and generally through November. The maximum in the total column of ozone is held off the pole.”

11.10.6.3.2 Outline of the Climatology of the Northern Hemisphere. “The mid-winter circulation of the stratosphere of the Northern Hemisphere is seldom quiescent. Frequent minor warmings occur as planetary scale disturbances grow and decay. Synaptically, these warmings generally involve (1) an intensification of a climatological anticyclone in the stratosphere (called the Aleutian High), (2) a displacement of the polar vortex over Europe, and (3) a rapid warming of air at polar latitudes where air sinks (and warms adiabatically) at the jet entrance between the anticyclone and the westerly vortex. During some winters, there are major stratospheric warmings: the disturbances are so strong that the normal circumpolar westerly flow is completely broken down, to be replaced by easterlies (in the zonal mean) through a large depth of the stratosphere. Synaptically, the warmings involve the development of either one anticyclone (usually the Aleutian High), when the westerly vortex is displaced from the pole. See O’Neill and Taylor (1979), or of a pair of anticyclones, when the vortex splits. See Fairlie and O’Neill, (1988). Air from low latitudes spreads over the polar cap. Polar temperatures rise sharply, often by more than 50 K in a few days. Although rapid radiative cooling in the upper stratosphere can reestablish the westerly flow in a week or two, the longer radiative relaxation times for the lower stratosphere and the persistence of strong disturbances in the upper troposphere may mean that the westerly flow remains weak and polar temperatures high for the rest of the winter and spring. This vertical structure is in marked contrast to the top-down weakening of the westerly vortex in the Southern Hemisphere.

“Final warmings in the Northern Hemisphere show much more interannual variability than in the Southern Hemisphere (Yamazaki (1987)), both in the structure of the flow and in the timing of the final breakdown of the westerly vortex. During some examples, the circulation is highly distorted in the presence of a persistent Aleutian High. The breakdown of the westerlies may happen first in the upper stratosphere, as it does in the Southern Hemisphere, or in the lower stratosphere, the temperature gradient reversal may precede or succeed the wind reversal. Generally, the breakdown of the westerly vortex is almost complete in the stratosphere; ozone-rich air can spread to higher latitudes in spring than in the Southern Hemisphere. Curiously, some final warmings in the Northern Hemisphere, e.g., that of 1981, are quiescent. The weakening of the westerly vortex proceeds slowly, on a radiative time scale, leading to a late final warming. This may happen after the vortex has been largely broken down during an earlier major warming (as in 1981). Planetary scale disturbances of tropospheric origin cannot then penetrate into the stratosphere.”

With the exception of ozone, it is noted that in the above climatology discussion, there is no inclusion of the presence of trace gases. It is these gases and their relationship to radiation that drive the need for and continuance of research efforts. Undeniably, these are elements of climate just as much as are temperatures, pressures, and winds.

11.10.6.3.3 Observed Ozone Amounts in the Two Hemispheres. The dynamical aspects of the QBO and the solar cycle are described with respect to their potential relationship with the ozone holes of the stratospheric polar vortices. The present major chemical theory for the dampening of the usual production and influx of ozone concerns heterogeneous chemical reactions. Heterogeneous chemical reactions are those which develop and proceed in the interphase relation of liquids, solids, and gases. In this case, the polar stratospheric ice cloud crystals form one phase, the solid phase, while the trace gases, the chlorine and nitrogen oxides, form the gas phases. The reactions take place on the ice surface crystals. These will be discussed again later.

#### 11.10.6.3.4 Trends in Total Ozone.

11.10.6.3.4.1 General. The determination of trends in climatological data including ozone and other trace gases is dependent upon (1) the time period involved, (2) the measurement equipment, techniques, and procedures, and (3) the constancy of the processes involved.

In the third case, there are step functions involved as in the case of the production, use, and release of the halogenated hydrocarbons or carbons. Given the precision and accuracy of today's instrumentation and the time of manufacture and use, trends may be estimated. Thus, during the early part of the 20th century a base of essentially zero may be assumed, except in case of the methylated halogens. In the case of ozone, no such zero ground base may be assumed. There was no program to systematically monitor the ozone. Fluctuation in the ozone amounts can be summarized perhaps rather crudely by making assumptions concerning solar radiation variability. But little is known today of the variation of the ultraviolet radiation in connection with solar activity through the centuries and even in the context with this century's solar activity. Observation and real data have been severely limited and hampered by the absorption and emission characteristics of Earth's atmosphere.

Only within the last half century has an observational program with adequate instrumentation and funding begun to develop an appropriate database. The use of satellites outside the buffering atmosphere has opened up a new vista of the available potential. The need for ozone information is not the driving reason for these solar observing satellites, but the general information obtained contains some data which will be extremely useful to the study of ozone. More specifically, the satellites designed to probe the Earth's atmosphere carrying observation systems such as the Total Ozone Mapping System offer great initial and even greater future aid. But a consistent program over decades and centuries is needed. Along with this is the continuance and improvement of the systems discussed in the coordinated works of the Scientific Assessment of Stratospheric Ozone, Report No. 20, United Nations, World Meteorological Organization (1989).

The initiation of an early observation and program by balloon-borne and rocket-deployed ozonsondes along with ground-based observations received some impetus in the late 1950s in preparation for the IQSY in 1964–1968. This followed the solar cycle maximum of the late 1950s. Only the data from about three periods of the solar cycle or 1.5 periods of the Hale cycle are available for the determination of trends in ozone.

11.10.6.3.4.2 Trends. The Ozone Trends Panel (OTP) is a group designed to determine ozone trends. The United Nations Report No. 20 has the objective to:

- (1) Reexamine the data originally used by the OTP by using several statistical techniques.
- (2) Update trends derived from the Dobson network data.
- (3) Examine the regional changes in total ozone using both ground-based and satellite-based measurements.

This study compares the results of five group studies (including the OTP study) over the years 1970–1986 (a 17-yr period) for the Dobson data. The OTP study indicates about a 4-percent change downward over the Northern Hemisphere; the other studies showed a lesser decline, and declines were greater in winter than summer. Trends seem to be less negative with the inclusion of 1987 and 1988 data. The overall trends, though statistically significant, tend towards insignificance on the annual and total overall geographic coverage in the Northern Hemisphere.

For a later period beginning in 1978, an analysis of SBUV and TOMS data includes Dobson information for the Southern Hemisphere. As this period is very short, perhaps less than one solar cycle, the determination of

a long-term trend is very uncertain. The largest ozone decreases during this period occur over the Pacific Ocean mid-latitude range from about 4 to 8 percent (–4.5 to –7.5 percent). The writers indicate that the largest decrease is observed as the polar region is approached. The writers also stress the difficulty in assessing a long-term trend from this short period of record. They provide a rationale for the extraction of the solar cycle effect from the data. They suggest that SBUV and TOMS data are comparable for detecting geographic patterns in ozone change.

**11.10.6.4 Polar Ozone Holes.** From a static point of view, the formation of ozone ( $O_3$ ) occurs with the irradiation and photolytic dissolution of oxygen ( $O_2$ ) and the subsequent three (or more) body collisions. There is no question that this is dependent upon the appropriate high energies of the electromagnetic radiation and that these amounts are dependent upon the solar processes. Also, dependence is assumed with the long period astronomical associations. However, with all of these there will be no ozone ( $O_3$ ) produced in the polar regions during polar nights. This last statement is compromised by the refraction and reflection of solar radiation into these zones, but essentially and in reality the solar radiation production of ozone is a minimum. There will apparently be no disagreement with the above statement and that polar ozone holes exist and will continue to occur for a long time in the future. Presumably, there will be no disagreement with the idea that atmospheric circulation is dynamic and that traveling storm systems will skirt and erode the circumpolar vortices. Ozone will be transported into the regions. Therefore, the problem is both dynamic and static. But what is important in today's world is the extension of the diminution of ozone well into the spring seasons. Thus, there is a resultant change in the polar spring season characteristics. See subsequent discussion on polar stratospheric clouds (PSCs). This implies a change in the biosphere (Luther (1985), Kaminsky (1989), and McCune and Weinstein (1989)).

#### 11.10.6.5 Heterogeneous Chemistry

11.10.6.5.1 Single Compounds. Heterogeneous chemistry is not new but it presents an opportunity to explain some of the processes involved in the atmosphere and hydrosphere. In particular, interest here is in the stratosphere, especially the polar stratospheres.

Material exists in three states—solid, liquid, and gas. A one-compound example is water. In a pressure-temperature restraining region a compound may exist as a solid, a liquid, or a gas. It may also exist as a gas-liquid, gas-solid, or liquid-solid boundary interface. It may also exist in equilibrium at a point of intersection of the three interfaces called the triple point. There is another point called the critical temperature. Above this temperature, no change of phase will be induced by an increase of pressure alone. This pressure at the critical temperature is the critical pressure. At the interfaces between two states, there will be a continual flux between the two states. At the triple point, all three phases will exist in equilibrium; i.e., all three co-exist at that point. Among the many references are Guggenheim (1950) and Chang (1986). See also table A-11-2 for characteristics of a few selected atmospheric gases.

Solids may sublime along the pressure-temperature solid-gaseous interface without going through the liquid phase. Deposition is the reverse change of phase. Water, naphthalene, and carbon dioxide are simple examples. At room temperature, naphthalene and carbon dioxide can sublime only. Water ice sublimates at temperatures above  $0.01^\circ\text{C}$  if the pressure is  $<0.006\text{ atm}$  ( $6.079\text{ kPa}$ ). Thus, water frost, at the surface of the Earth, will be deposited (Chang (1986)) from vapor only after going through the intermediate liquid stage. By the same reasoning, at less than a pressure of  $6\text{ kPa}$  or an altitude over  $3.3\times 10^4\text{ m}$ , these conditions are met (Crutcher (1963) who references Goldie et al. (1957)). Also referenced is Kittinger (1960) who reported clouds at  $102,800\text{ ft}$  (about  $3.1\times 10^4\text{ m}$ ) as he was jumping from a balloon at that altitude over the western plains of the United States. This was reported by *National Geographic*.

11.10.6.5.2 Mixtures of Compounds. The above discussions assume only one isotopic combination of the compounds or substances mentioned. Other isotopic configurations undoubtedly are present and the phase

separation boundaries become more diffuse. Also, the mixtures of different compounds enter and complicate the processes. There are many aerosols—solid, liquid, and gaseous—with their many and varied characteristics. The heterogeneous eutectic mixtures with changing absorption and emission energies and changing pressures and temperatures provide changing amounts of the various phases. Of equal importance are the molecular shapes or configurations of the molecules. The phases are important in inducing selective catalytic actions or reactions. This is especially pertinent in the interfacial regions. Adsorption, absorption, and deposition and sublimation action will vary. An important feature of these potentials is the formation of the PSCs that are discussed next.

11.10.6.5.3 Polar Stratospheric Clouds (PSCs). Toon and Turco (1991) and Toon et al. (1989) provide an excellent concise review of the history and research on the now-emerging importance of the PSCs in the “ozone hole” development mechanism. There are now three proposed cloud types for the polar stratospheres—nacreous clouds, nitric acid hydrate clouds, and water-ice clouds. Though these are now discussed in a sense separately, these can occur and often do in the same regions. Physical chemistry comes into play here just as much as it does in studies of the lithosphere, hydrosphere, and the rest of the atmosphere. Radiation, low temperatures, low pressures, and low vapor are involved among the atmospheric constituents. Some of the participants are water ( $\text{H}_2\text{O}$ ), nitric acid ( $\text{HNO}_3$ ), hydrogen chloride ( $\text{HCl}$ ), chlorine nitrate ( $\text{ClONO}_2$ ), nitrogen oxides ( $\text{NO}_x$ ), and ozone ( $\text{O}_3$ ).

11.10.6.5.3.1 Nacreous Clouds. “Mother of pearl” or nacreous clouds undoubtedly have been seen for ages. These have been noted in the literature since the late 1800s, and are primarily water clouds. Stanford and Davis (1974) present a review.

Lenticular clouds are a familiar sight in the lee of mountain or hill ridges. Laminar atmospheric flow perturbed by the ridge terrain develops standing waves. At the crests of the standing waves the clouds become thicker, while at the bottom of the wave they become thinner. When the amount of moisture is not enough to keep the cloud formation in the base of the wave, the wave form becomes more apparent. Only the clouds at the crest of the wave will be visible.

If the atmospheric laminar flow is sufficiently strong, the standing waves will propagate well into the stratosphere. In many cases, the temperature-pressure-moisture configuration will not be such as to maintain the visible crest formation throughout the atmospheric depth. But these may be sufficient to permit the nacreous clouds to form at the high altitudes under the aforementioned pressure-temperature constraints; these may be 10 to 100 km in length.

Droplets at the leading edge of the windward side of the forming clouds will be small and will also be small at the trailing, dissipating leeward edge. The first is the region of beginning coalescence while the second is the region of dissipation. Larger coalesced droplets will be found in the interior of the clouds. Any ice crystals present will be small due to the rapid drop in temperatures with the dynamic wave action. If there is enough energy present to develop the wave train over large distances, these nacreous clouds will be visible at the wavecrests. When viewed from a moderate angle to the Sun, these droplet sizes will produce a range of iridescent colors which provide the subtle nacreous beauty. Due to their great heights, these will be visible in the sunlight above the dark at the Earth’s surfaces. These are indicators that extremely low temperatures, such as 190 K or less, exist, that water is available, and that standing wave action in the essentially laminar flow exists. These are harbingers for the existence of the other two cloud types.

11.10.6.5.3.2 Water-Ice Clouds. As Toon and Turco (1991) indicate, the slow cooling of the stratosphere and the presence of moisture allows the formation of a water-ice crystalline mixture where the crystals or aggregate can grow to a larger size at warmer temperatures (say 5–10°) than those in the nacreous clouds. The nuclei for these droplets and crystals are provided by nitric acid and sulfuric acid crystals. The first of the interactions may come from gas phase interactions in the stratosphere and may in fact depend on the nitric acid while nuclei of the sulfuric

acid is essentially omnipresent from biota processes and/or from volcanic ejecta. These clouds are diffuse, perhaps a few kilometers thick, layers and may extend over several thousand kilometers. However, as indicated by Toon and Turco (op. cit.), the amount of water in both types of water and water-ice clouds may be equivalent.

McCormick et al. (1982) reported high visible extinction values had been recorded by the stratospheric aerosol measurement II (SAM II) sensors during Arctic and Antarctic winters. These were not necessarily associated with nacreous cloud observations and were perhaps more extensive but thinner and layered. The Nimbus satellite carrying the SAM II instrument was launched in 1978. This instrument detects particles in the atmosphere by examining the sunlight as it grazes the Earth's outer periphery. The temperatures noted were very low (195 K) but not as low as those for the nacreous clouds (190 K). The phenomena associated with these high extinction values created by aerosols were labeled polar stratospheric clouds (PSCs). Two distinct droplet or crystalline sizes were noted. This leads to the suggestion of two different cloud types. Steele et al. (1983), using theoretical and measured extinction trends, concluded that the PSCs were water (H<sub>2</sub>O) crystalline deposition on frozen aerosol nuclei. These nuclei could be water crystals themselves or nitric acid (HNO<sub>3</sub>) or sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) crystals. Sources for the last are biotic as well as volcanic ejecta. A temperature of about 188 K (-85 °C) and 5 ppmv of H<sub>2</sub>O were assumed.

The discovery of an ozone hole in the polar stratosphere by Farman et al. (1985) led to the introduction of several theories of formation. These are discussed in the UNWMO Scientific Assessment of Stratospheric Ozone, Vol. 1, Chapter 1 (Albritton (1989)). As Farman et al. (op. cit.) noted, the marked increase of chlorine over the period in which the ozone hole development was noted led to increased study of the aspect of chlorine effects. Chlorine (halogen) chemistry became more important.

Solomon et al. (1986), Solomon et al. (1989), Solomon (1989, 1990), and McElroy et al. (1986) noted that McCormick et al. (1982) had shown that the extreme cold temperatures of the Antarctic winter and spring led to the increase of PSC occurrences. Suggestions were made that heterogeneous chemistry reactions were involved in PSC formation and subsequent ozone diminution to the extent that an ozone void or hole was formed.

Crystalline complexes of solutes in phase boundaries can form at temperatures above the frost point of the pure solvent phase, in this case, water. See prior discussions and those by O.B. Toon et al. (1986), Crutzen and Arnold (1986), and McElroy et al. (1986). See also discussion by Iwasaka et al. (1985), Poole (1987), and Poole and McCormick (1988) concerning two major types of PSC crystals suggested by the differing backscatter ratios.

The formation of crystalline features above the frost point has been mentioned earlier in the discussion of clathrate formation in the section on methane (CH<sub>4</sub>) (sec. 11.8). In that discussion, though, emphasis was on the clathrate formation in permafrost and ocean sediments, and on clathrates in interplanetary and interstellar space (Lunine and Stevenson (1985)). Such conditions can also be met in the Earth's stratosphere. Regions indicated in figure 11-8 may be extrapolated.

Toon and Turco (1991) indicate that they and their co-workers, along with Crutzen and Arnold, proposed that some PSCs differed from the nacreous clouds. The now proposed cloud types are the water-ice clouds and the nitric acid clouds. Hydrochloric acid clouds may also exist.

In the region of stratospheric low pressure, low temperature, and low water vapor pressure and in the interfacial regions of water, aerosol nuclei, water gas, liquids and solids, a water-ice mixture may form. Water as snow may precipitate, thereby partially dehydrating that portion of the stratosphere.

11.10.6.5.3.3 Nitric Acid Clouds. Auto-oxidation reduction in a mixture of nitrogen dioxide (•NO<sub>2</sub>) and water (H<sub>2</sub>O) will produce nitric acid. The suggested reaction (Sanderson (1960)) is



This reaction both dehydrates the stratosphere and isolates the reactive  $\text{NO}_2$  from potential ozone degradation reactions. The nitric acid readily forms two hydrates which further sequesters water as in  $\text{HNO}_3 \cdot \text{H}_2\text{O}$  and  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$  (the mono- and the trihydrate forms). Phase changes permit the formation of the hydrate crystals. The melting point of the nitric acid itself is 230 K. Precipitation of those crystals further dehydrate the stratosphere. The formation of the nitric acid trihydrate clouds will also deplete the water-ice clouds. In any event, the strata of these clouds represent reservoirs of water, of nitrogen, and of some sulfur, for the sulfuric acid crystals act as deposition nuclei.

#### 11.10.6.5.3.4 Chlorine Reservoirs.

11.10.6.5.3.4.1 Halocarbons. The first major chlorine reservoir of interest here is the reservoir of fully chlorinated carbons. Fully halogenated carbons such as the chlorofluorocarbons (CFCs) also store chlorine. Only the intense ultraviolet radiation will dismember these carbons. In the lower atmosphere, such energies are usually not available but are available in the upper stratosphere. The chlorine reservoir becomes a source in the stratosphere.

11.10.6.5.3.4.2 Hydrogen Chloride. Given a methane source in the stratosphere, free chlorine reacts with the methane to form hydrogen chloride and a methane radical:



The hydrogen chloride (HCl) readily mixes with water to form hydrochloric acid as in



Hydrates, 1–3, readily form all sequestering water. The melting points of  $\text{H}_3\text{OCl}$  and the three hydrates (1–3) are, respectively, 158.4, 257.8, 255.5, and 248.8 K (Weast (1968)) at standard pressure. Thus, as with nitric acid, these could be in crystalline form in the stratosphere. These could also precipitate, thereby removing chlorine from the stratosphere. On the other hand, their sizes may be so small as to inhibit sedimentation.

11.10.6.5.3.4.3 Chlorine Nitrate ( $\text{ClONO}_2$ ). The ozone destructive catalytic reaction as in



and



will continue until the dimer is formed or chlorine nitrate is formed. The dimer  $\text{Cl}_2\text{O}_2$  is formed as in



This weakly stores chlorine for a short time, for with solar radiation the molecule is easily split:



The chlorine is free to destroy ozone:



which can regenerate the temporary  $\text{Cl}_2\text{O}_2$  reservoir. However, the chloroxide (ClO) may react with nitrogen dioxide ( $\cdot\text{NO}_2$ ) as in



The last effectively sequesters both chlorine and nitrogen dioxide, two of the efficient ozone destroyers.

11.10.6.5.3.4.4 Ozone Destroyer Sources. All of the chlorine and nitrate reservoirs developed in the foregoing section are potential destroyer sources. The denitrification, dechlorification, and the dehydration of the stratosphere may be affected by precipitation processes. The dehydration process limits the formation of nitric acid, water-ice, and hydrochloric acid reservoirs. This permits slow, continued ozone destruction.

With the onset of spring season, solar radiation easily decomposes the hydrochloric complex, especially crystalline deposits on water-ice or crystallized complexes. Free atomic chlorine is released in an increasing amount from this reservoir. In addition, gas phase reactions of the intermixing hydrochloric acid and chlorine nitrate reservoirs increase chlorine release to a veritable flood:



Molina et al. (1987) discuss the Antarctic chemistry of chlorine nitrate, hydrogen chloride, and ice—release of active chlorine.

Reactive nitrogen ( $\text{NO}_x$ ) is still suppressed in nitric acid form but molecular chlorine easily changing to atomic chlorine with solar radiation starts its ozone destructive cycles. As long as the supplies of halocarbons continue to be augmented and used, chlorine ozone destruction will continue. As augmentation ceases, the effect is expected to remain yet for another century. See discussion in section 11.13 on halocarbons.

11.10.6.5.4 Mesospheric Clouds.\* Section 11.10.6.5.4 discusses the mesospheric cloud phenomena called (1) noctilucent clouds (NLCs), (2) polar mesospheric clouds (PMCs), and (3) polar mesospheric summer echos (PMSE), which are all similar, if not the same. These mesospheric clouds, which occur in the cold, high-latitude regions (average of 83 km height) surrounding both geographical poles, are the highest clouds on Earth. The clouds occur seasonally between 80–86 km altitude during their respective summer seasons (June–August in the Northern Hemisphere and December–February in the Southern Hemisphere). From the ground, they are seen typically low on the horizon, within the twilight arch near the Sun’s position below the horizon. These clouds are given different names, depending upon their mode of observation. Noctilucent clouds are their ground-based manifestation, visible as bright cloud features seen against the comparatively dark sky during twilight, when the Sun’s rays still strike the clouds and the lower atmosphere is in darkness. At latitudes greater than about 70°, the summer sky never becomes sufficiently dark to view NLCs at any time of the year. At the lower latitude boundary, about 55°, the air is too warm at any season to support water-ice particles. NLCs are most frequent at the center of the NLC zone, around 60° latitude. Occasionally, NLCs are seen outside the “classical” NLC zone. As in June 1999, they were photographed and measured by a lidar as far south as 41° N. (Wickwar et al. (2002)). The occurrence of NLC’s seem to be increasing, while also extending to lower latitudes.

Noctilucent clouds are composed of submicro-sized water-ice particles growing in supersaturated air and occurring in a few-kilometer-thick layer. The NLC season begins and ends earlier than the PMC season, and occurs at significantly lower latitudes than do PMCs. Northern NLC occurrence has been monitored by amateur observers for many decades, and a seasonal pattern has emerged from these data. The behavior for both NLCs and PMCs is roughly defined as a Gaussian, centered on ≈15 days following solstice. (See fig. 11-26). Southern NLC occurrence appears to be quite similar, relative to the summer solstice, although there are too few observations available to perform a statistical analysis. Satellite observations provide a much better north/south comparison. A good historical review of observing NLCs is found in Fogle and Haurwitz (1966). More up-to-date references that include

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\*Much of what has been included in this sub-section was supplied by Dr. Gary E. Thomas (Univ. of Colorado) and Dale L. Johnson (NASA MSFC).



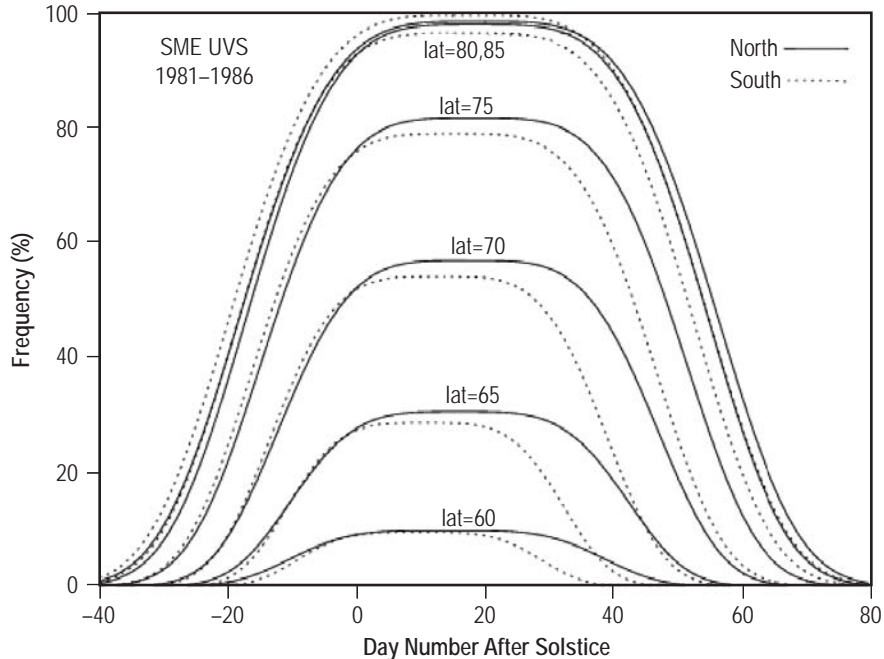


Figure 11-26. Northern and Southern Hemisphere 5-yr average PMC occurrence rate as a function of day number after summer solstice.

knowledge gained from the space era are Gadsden and Schroder (1989), Thomas (1991), and Thomas (1996). A more recent scientific journal that contains numerous scientific papers describing modern developments is Thayer et al. (2003).

11.10.6.5.4.1 Polar Mesospheric Clouds. PMCs are the same clouds as viewed from space. Because it is possible to distinguish clouds from the atmospheric background even during the daytime hours while the atmosphere is fully sunlit, space-based instrumentation allows PMCs to be viewed in their entirety, all the way to the pole. The detectability of these very thin clouds depends upon the geometry of observation. PMCs are very rarely seen from space in the  $40^{\circ}$ – $45^{\circ}$  band, around summer solstice (Merkel (2002)).

It is now established that north-south hemispheric differences in PMC properties occur. In particular, the north has more clouds (by roughly 50 percent), which are inherently brighter than their southern counterparts. Also, lidar observations at the South Pole show that clouds are several kilometers higher than in the north (Chu et al. (2001)). These differences are probably explained by different Earth-Sun distances during the respective summers, and also by the different dynamical states of the lower atmosphere in the Arctic and Antarctic. Because of different topographies in the two hemispheres, the tropospheric and stratospheric winds are distinctly different in the two hemispheres. Since these lower atmospheric regions are the sites of wave generation, and are also the medium through which the waves must propagate, mesospheric dynamics has a different morphology in north versus south (Dowdy (2001)).

As far as is known, there are no inherent differences in PMCs and NLCs, although there are not enough simultaneous space and ground-based observations to definitely rule out physical differences. Because PMCs are generally observed poleward of the NLC zone, PMCs are located closer to the cold source regions where the temperature approaches 100 K. It has been suggested that dynamical transport of particles from their point of origin to where they are ultimately observed might account for the fact that NLCs are much more variable, and are seen about  $5^{\circ}$ – $10^{\circ}$  equatorward of PMCs in a latitude zone where the temperature is considerably warmer ( $\approx 150$  K).

Summertime temperatures at mesopause heights are colder than in winter, which accounts for the distinct seasonality of mesospheric clouds. Although seemingly paradoxical, this phenomenon is now well understood as an indirect dynamical effect of atmospheric wave forcing. Summertime upwelling of air causes both expansional cooling and advective transport of water vapor from the lower mesosphere and stratosphere, thus explaining the existence of water-ice supersaturation during the 3-mo cloud period. Maximum frequency of PMCs/NLCs occurs 2 to 3 wk following summer solstice. Cloud composition is water-ice, at least this has been empirically verified for very bright clouds. The particles are expected to be essentially pure ice, with moderately nonspherical shapes. Very small dust cores of silicate matter may exist since these tiny dust particles seem to be necessary to begin the nucleation process.

11.10.6.5.4.2 Polar Mesospheric Summer Echos. Polar mesospheric summer echos (PMSE) are very strong radar echoes which appear during the NLC season, closely related to charged ice particles which reduce the diffusivity of electrons such that very small spatial scale structures in the electron gas can exist. They may be caused by highly structured plasma density fluctuations, concentrated in thin layers, thought to be controlled by the breakup of upward propagating gravity waves. Some of the morphology of PMSEs is similar to that of NLCs.

11.10.6.5.5 Mesospheric Cloud Formation. Mesospheric clouds are believed to form (nucleate) on preexisting aerosol particles, most likely produced by meteoric ablation and recondensation ('meteor smoke'). It cannot be ruled out that, under certain conditions, they also could form on large proton-hydrate ions, which are stable to large sizes (containing dozens of water molecules) at very low temperatures. Another possibility for nucleation is condensed sulfuric acid which is carried upward during summer from the stratosphere. The formation rate of new ice particles is largest near the temperature minimum ( $\approx 88$  km altitude). They grow slowly at this altitude, and despite their number density being quite high (perhaps  $1,000 \text{ cm}^{-3}$ ), they are not optically visible, due to their small cross sections. In order for the particles to scatter light efficiently, they need to grow many hours to reach optically-efficient sizes ( $>20$  nm radius). However, the small nanoparticles make their presence known through ground-based radar. The small (1–10 nm radius) particles are readily charged in even the weakly ionized mesopause region. By causing highly structured layers of differing electrical properties, these subvisible particles thus have a very large affect on the radar reflectance of the region at UHF and VHF frequencies. This radar phenomenon is known as polar mesospheric summertime echoes, as mentioned above (Rapp et al. (2002)).

As the newly-formed subvisible particles acquire water by sublimation in the supersaturated region of the mesopause, their increasing mass accelerates their downward sedimentation we ignore for now the effects of upward winds. They eventually fall out of the region of saturation and are destroyed, near 83 km. It is at this point where the air becomes unsaturated that the particles are largest, and because of the very steep dependence of the scattering cross section on particle size, this is where they are visible to optical measurement techniques, either passive scattering of sunlight, or active scattering by lidars. This size dependence of the scattering also accounts for the thinness of the optically-visible layers, which are often  $<1$  km thick. In fact, the particles apparently occupy the thicker region between about 82 km and 90 km, but their altitude-dependent sizes greatly affect what is observed optically. The relative thinness of the layers also make it possible to view wave structure. Atmospheric waves, e.g., gravity waves or tidal waves, perturb the heights of the layers by a few kilometers. Even this small excursion from the mean height causes the line-of-sight opacity to vary strongly over the sky, depending upon whether one is viewing the layers tangentially (along a surface, in which case, they appear bright), or viewing them at a steeper angle. This effect is not present for nadir viewing from space, or viewing of NLCs at the zenith (which occurs rarely). The presence of a vertical wind, which on the average is upward during summertime at these heights, changes the properties of the clouds in several ways. Because the upward drag on the particles can exceed the downward pull of gravity, there is a tendency for the levitated particles to remain in the saturated region for a longer period of time, and thus grow larger and hence become brighter than in a static atmosphere. On the other hand, for sufficiently high upward wind speeds ( $>5$  cm/s), the particles can be "blown" upward, into the warmer and subsaturated region of the lower thermosphere (90 km and above). There are many aspects of cloud microphysics that are not well understood. The difficulties of

measurement in this inaccessible region explain our relative ignorance of many of the cloud processes. However, cloud nucleation processes are notoriously difficult to study, even for tropospheric ice clouds (cirrus).

11.10.6.5.6 Physical Properties of Mesospheric Clouds. Although the chemical composition of the cloud particles has been established to be water-ice, their size distribution is not well known. However, numerous experiments over the past several decades have determined that the effective spherical radii range between 20 nm and 100 nm, with a typical size near 50–60 nm. It is fairly well established that much smaller ice particles are ubiquitous in the supersaturated regions of the summertime polar region (von Zahn and Berger (2002)). Although invisible by optical means, their presence is inferred from the existence of PMSE, mentioned earlier. Lidar experiments have determined from backscattered depolarization measurements that in parts of the cloud, the particles can be aspherical, with moderate asymmetries (but not similar to the long, hexagonal needles present in tropospheric cirrus clouds). The smallness of the particle size, relative to the wavelength of light, causes them to have a bluish color (Ostdiek and Thomas (1993)). However, the bluish-white coloration of NLCs is determined more from the extinction of light through the ozone layer, which removes yellow light. In addition, in the part of the NLCs where the Earth’s shadow can be identified, the borders of NLCs are often reddish. This is because the solar extinction becomes very large for these light rays. The lower atmosphere removes the blue and yellow light, leaving only the longer wavelengths to reach the clouds. The particles are too small to exhibit haloes, sundogs, and the various optical phenomena associated with lower atmosphere ice and water particles. The clouds are too thin to have any perceptible effects on starlight. However, as noted earlier, the small extinction (a few percent at most) of sunlight by PMCs can be detected by sensitive instruments in space when the light is attenuated at the Earth’s limb. Starlight extinction as seen from the ground is, in principle, detectable with sufficiently sensitive instrumentation, but has not been attempted.

Summarized in table 11-6 are estimates of physical properties of mesospheric clouds and their environment. All quantities refer to the NLC zone and the summertime polar mesosphere. The seasonal climatology for NLCs/PMCs is given in table 11-7.

Table 11-6. Typical estimates of the physical properties and characteristics of mesospheric clouds (Source: Fogle and Haurwitz (1966), Thomas and Olivero (1989), Kaufman (1989), and Toon and Farlow (1981)).

• Cloud heights	81–86 km, with the most common height being at 83 km
• Ice particle size	20–100 nm, with most in the 35- to 70-nm range
• Ice particle concentration	100–200 cm <sup>-3</sup> (5- to 500-cm <sup>-3</sup> range)
• Ice particle column number	10 <sup>6</sup> - to 10 <sup>8</sup> -cm <sup>-2</sup> range
• Water mixing ratio (w)	1–4 ppmv (up to 10–15 ppmv during cloud processing)
• Temperature at cloud heights	<150 K
• Temperature at mesopause height (88 km)	100–140 K
• Cloud thickness	0.5–2.5 km
• Cloud extent:	100's to 1,000's of kilometers, and small-scale structure down to meters
• Latitude of observations	50° to 80°; best about 60°
• Season of observation	Northern Hemisphere: March through October (best June through August) Southern Hemisphere: December through February
• Spatial extent	10 <sup>4</sup> to more than 4 × 10 <sup>7</sup> km <sup>2</sup> (within latitudes north of 45°)
• Duration	Several minutes to more than 5 hr
• Average velocity	40 m s <sup>-1</sup> towards the southwest*
• Thickness in the vertical	0.5 to 2 km
• Vertical wave amplitude	1.5 to 3 km

\*Individual bands often move in different directions and at speeds differing from the NLC display as a whole. Apparent motions of NLCs across the sky are not necessarily indicative of wind speeds, because wave patterns move with their own specific phase speeds, even at times, moving against the mean wind vector.

Table 11-7. Mesospheric cloud seasonal climatology. Comparison of PMC seasonal properties for 1981–1985 with NLCs (1885–1972). Times are given in days after summer solstice (Thomas and Olivero (1989) and Thomas, private communications (2004)).

	South PMCs	North PMCs	North NLCs
Beginning date <sup>1</sup>	–32	–23	–38
Ending date	61	64	50
Time of maximum	7–16	16–22	16–20
Duration of season (days)	93	87	88
Lower latitude boundary	55°	55°	50°
Months observed	Dec.–Feb.	June–Aug.	June–Aug.
Interannual variability	±20 percent	±20 percent	Factors up to 4
Altitude (km)	83.2±1.5	85±1.5	

<sup>1</sup>Begins at high latitude 10 to 20 days before lower latitude observation. South season begins somewhat earlier and ends earlier than North season (fig. 11-26).

11.10.6.5.7 Mesospheric Cloud Frequency, Climatology and Probabilities. PMC occurrence rate, defined as the number of clouds viewed in a time interval, divided by the total number of observations, may be thought of as a probability of viewing a cloud from space. The daily occurrence rate is rarely 100 percent, meaning that the cloud distribution is “patchy,” undoubtedly due to wave perturbations on a variety of spatial and temporal scales. The experience of the Ultraviolet Spectrometer Experiment onboard the SME spacecraft is summarized in figure 11-26, where the 5-yr (1981–1986) average PMC occurrence rate is plotted against day measured from summer solstice (Shettle et al. (2002)). Each solid curve refers to a 5°-wide bin of north latitude. The dashed curves refer to the southern PMC seasons (6 mo separated in actual time). The curves are analytic functions which are fitted to the actual 5-yr average frequencies, accumulated into 5-day time bins. The actual behavior is much more complicated, and on any given year, can vary by as much as 20 percent from the smoothed function shown in figure 11-26. A comparison between NLCs and PMCs is useful because it shows that the seasonal run of activity of both PMCs and NLCs are similar, even peaking at nearly the same day relative to solstice. It should be mentioned that NLC sightings can be relatively rare during some seasons, particularly around the times of solar maximum activity. For example, during the previous solar maximum period (1992), the number of NLC nights reported by the Canadian-Alaskan network of observers was 12. In contrast, some seasons provide a large bounty of cloud sightings. The same network (NLC CAN AM) reported the largest number of NLC nights (53) in their 15-yr history during the summer of 2003 (Zalcik (2004)). This is despite the fact that the preceding year coincided with the last solar maximum.

Even though the solar cycle seems to be an important factor in determining overall cloud activity, there are other important sources of interannual variability that are not at all understood. Recently, the PMC database verifies an inverse relationship between PMC occurrence frequency and solar activity; i.e., they are less often seen at solar maximum throughout the 11-yr solar cycle. Stronger anticorrelation values are observed in the Northern Hemisphere; i.e.,  $R_{\text{solar}} = -0.87$  (DeLand et al. (2003)).

11.10.6.5.8 Noctilucent Cloud Types. Fogle and Haurwitz (1966) have classified noctilucent clouds as follows:

- Type I. Veils—These are the simplest. They are very tenuous with no well-defined structure, and are often present as a background for other categories or forms. They are somewhat like cirrus clouds of uncertain shape; however, occasionally they exhibit a faintly visible fibrous structure. They often flicker.

- Type II. Bands—These are long streaks with diffuse edges (type IIa) or sharply defined edges (type IIb). They are sometimes hundreds of kilometers long and often occur in groups arranged roughly parallel to each other or interwoven at small angles (perhaps visible evidence of the gravity waves propagating through the region). Occasionally an isolated band is observed. Bands change very little with time and blurred bands with little movement are often the predominant structure in the noctilucent cloud field. When they do move, it is often in a direction and with a speed that is different than that of the display as a whole. Very closely spaced thin streaks, called serrations, are occasionally seen in the veil background. They look like a continuous cloud mass since the serrations are separated by only a few kilometers.
- Type III. Billows—These are groups of closely spaced short bands which sometime consist of straight and narrow, sharply outlined parallel short bands (type IIIa). Sometimes they exhibit a wave-like structure (type IIIb). The distance separating pairs of billows is  $\approx 10$  km. Billows sometimes lie across the direction of the long bands and their alignment usually differs noticeably in close portions of the sky. Unlike the long bands, billows may change their form and arrangement or even appear and disappear within a few minutes.
- Type IV. Whirls—Whirls of varying degrees of curvature are also observed in veils, bands, and billows; infrequently, complete rings with dark centers are formed. Whirls of small curvature ( $< 1^\circ$ ) are classified as type IVa while whirls having a single simple band or several bands with a radius of  $3^\circ$  to  $5^\circ$  are classified as type IVb. Larger scale whirls are classified as type IVc.
- Type V. Amorphous—These are similar to veils in that they have no well-defined structure but they are brighter and more readily visible than the veil type NLCs.

11.10.6.5.9 PMCs From Shuttle Exhaust? It has been determined by the Naval Research Laboratory (Stevens (2003)) that the exhaust plume from NASA's Space Shuttle (which is  $\approx 97$  percent water vapor) can travel to the Arctic thermosphere where it descends to form ice in creating PMCs. NRL's MAHRSI satellite instrument launched on STS-85 in August 1997 was allowed to follow the Shuttle plume's rapid poleward transport and then to observe a discrete region of ice clouds as they appeared in the Arctic mesosphere near the end of the mission. Water contained in these clouds was consistent with the amount injected into the thermosphere during the Shuttle's east coast ascent. About half of the Shuttle's water vapor exhaust is injected into the thermosphere between 103 km and 114 km altitude and was determined to be transported to the Arctic in a little over a day. Ground-based measurements also supported this. As the water vapor moves to the Arctic, solar ultraviolet destroys some of the plume. The remaining plume falls from the warmer thermosphere down to the colder (down to  $-40^\circ\text{C}$ ) mesospheric regions where the water vapor condenses into ice particles and the clouds (PMC) form.

This section on mesospheric clouds is an abridged version taken from NASA-HDBK-1001 edited by D.L. Johnson, with key contributions by Dr. Gary Thomas (University of Colorado).

**11.10.6.6 Quasi-Biennial Oscillation.** Quasi-biennial oscillation (QBO) has previously been discussed briefly in the sections on temperatures and winds. Some of the material here may be repetitive. With respect to ozone ( $\text{O}_3$ ), Funk and Garnham (1962) reported a 24-mo cycle using data from Aspendale and Brisbane. Much work has been done since and the reader is referred to London (1985).

The average timespan of the QBO is about 27 mo, varying from 18 to 36 mo. Zerefos (1983) indicates that the QBO maximum is associated with maximum temperatures at the 50-mb level. It seems to be in phase with the QBO. The warmest temperatures occurred with westerly winds at 30 mb (Crutcher and Joiner (1977b)). These occur at higher altitudes than do the cooler, stronger easterly winds. There is a latitude dependence for ozone as

indicated by London (1985). In the Northern Hemisphere, a possible maximum occurs at about 25° N., a minimum between 40°–50° N., and then a poleward increase. In the Southern Hemisphere, a minimum occurs at 10°–15° S. according to Hilsenrath and Schlesinger (1981) and Tolson (1981) (as cited by London (1985)). As London (1985) further indicates, poleward of the QBO amplitude minimum there seems to be a 13- to 14-mo phase retardation. This is about one-half of the QBO cycle. Latitudinal variation of the ozone QBO amplitude and phase needs further research in order to arrive at a viable explanation.

With respect to the QBO in extra-tropical stratospheric region winds, use of radiosondes or pilot balloons is difficult. Presumably, there is an inverse relationship of tropospheric winds to stratospheric winds. With slow tropospheric winds, balloons can rise into the stratosphere where fast stratospheric winds can be measured. With fast tropospheric winds, balloon tracking becomes impossible except in relay operations where “handing off” from an upwind station to a downwind station can be affected. These are relay station configurations. The recorded data for the 40°–60° N. latitude stations are biased in that stratospheric slow wind speeds are lost. With the potential advent of accurate sequential and extensive satellite real wind observations, considerable progress in this field of research will be made.

## 11.11 Chlorine

### 11.11.1 General

The physical relationships of chlorine ( $\bullet\text{Cl}$ ) or ( $\text{Cl}_2$ ) with other chemical elements may be seen, in part, by reference to tables A-11-1 through A-11-3. Gas is vented from the lithosphere through fissures, rifts, and volcanoes. The amount in the atmosphere is so small that it is in the trace gas category. In its ionic, liquid, or solid complexes, it is present in oceanic and lithospheric (crustal) sinks as salts of sodium, potassium, etc. In the oceans, these complexes are a part of the density development. See the discussion on the hydrosphere. In the Earth’s crust, these form the great salt beds. It exists in hydrogen, oxygen, or nitrogen components such as  $\text{ClH}$ ,  $\text{Cl}_y\text{O}_x$ , and  $\text{Cl}_y\text{N}_y$ . The first is hydrogen chloride, which in water, forms hydrochloric acid.

This section is short since many reactions are covered in prior sections and in later sections, which simply emphasizes the importance of chlorine in atmospheric gas reactions.

The stable but reactive chlorine ( $\text{Cl}_2$ ) molecule may be dissociated into two chlorine atoms or radicals, thermally, by chemical reaction or by a supply of sufficient energy from the electromagnetic (photoelectric) energy supply. The energy required is  $243 \text{ kJ mol}^{-1}$ . Such photoelectric energies are available at 492 nm or less. The spectrum extends from the lower part of the visible spectrum through the ultraviolet and below.

Chlorine ( $\text{Cl}_2$ ) is used in many ways in industrial processes due to its availability and to its chemical reactivity. It is precisely this activity as a mobile unit of the atmosphere which makes it important as an element of climate.

Due to many possibilities for reactions among various atmospheric molecules, ions, groups, neutral or radical, there are many avenues to reach any one specific result. Some are theoretically possible but practically unattainable, and there may be many blockings and diversions in the avenues.

### 11.11.2 Oxides of Chlorine

Molina and Rowland (1974), Rowland and Molina (1975), Wuebbles et al. (1989), and Rowland (1991) discuss trace gas problems associated with halogenated hydrocarbons.

Any neutral fragment of a molecule containing an unpaired electron is called a free radical (Chang (1986)). Free radicals are indicated in some texts with a prior or post dot, by parentheses, or simply with no special identification.

Wuebbles et al. (1989) indicate, based on the initial work of Molina and Rowland (1974), an especially efficient catalytic chain mechanism that involves the chlorine free radical as



These chains will proceed, say 100,000 times, until the chlorine (Cl) enters a sink reaction.

The net result is two even oxygen molecules but the chlorine atom is regenerated to enter another cycle, destroying another set of odd oxygens. Thus, the reaction is catalytic. This cycle will continue until some other molecule or atom reacts with the chlorine. There are other oxides not discussed here. A free oxygen (O) atom, instead of reacting with chlorine oxide (ClO), may react with ozone (O<sub>3</sub>) as shown in section 11.11.3:



Here again, the result is the neutralization or destruction of the two odd oxygens,  $\bullet\text{O}_1$  and O<sub>3</sub>. There are many avenues for atmospheric chemical reactions to proceed. In lieu of direct receipt of electromagnetic energy, molecular encounters may be involved in energy exchanges. For example, in radical form,



where M is any third body involved in the collision and the exchanges of energy and (or) momentum. Then, in a subsequent reaction,



which may be followed by



Thus, there are many opportunities for the oxides of chlorine to provide radical chlorines, which are just as reactive (voracious) as the (OH) radical in destroying, modifying, or consuming ozone (O<sub>3</sub>). This is not the only activity of chlorine radicals.

There must be, of course, a supply of chlorine for these reactions to occur. Totally halogenated hydrocarbons are chemically nonreactive and were not considered to be a chlorine source in the troposphere. But they are physically sensitive to high electromagnetic energies which become available in the stratosphere disbond. (This feature is discussed in more detail in section 11.13, Halocarbons.)

### 11.11.3 Nitrate of Chlorine

Rowland et al. (1986) discuss hydrolysis of chlorine nitrate. This will be involved in many other aspects of the polar night stratospheric problem. Nitric acid clouds and ices must be considered.

## 11.12 Hydrogen, Water, and Hydroxyl

### 11.12.1 Molecular Hydrogen

Previous material included discussions of the importance of hydrogen ( $H_2$ ) in atomic, molecular, and isotopic forms. Section 14 on nucleogenesis continues this discussion in more detail.

As a basic unit in atomic development and within the Earth, the solar system, galaxy, and universe, hydrogen is an integral part, component, or element of our climate. Chlorination of methane to methyl chloride ( $CH_3Cl$ ) releases an atomic hydrogen. This may pair with another to form molecular hydrogen ( $H_2$ ). Hydrogen ions or hydrogen radicals may be developed. The latter may be formed in chemical reactions, such as indicated above, or by the absorption of the correct quanta of electromagnetic energy. Weast (1979) indicates that about  $435 \text{ kJ mol}^{-1}$  of energy are involved.

Previously noted was the tendency of hydrogen to escape from planets. This is particularly true of those planets of lesser mass, such as the inner planets, including the tellurian planet Earth. The intense solar radiation and temperature play their part in keeping hydrogen in ionized or radicalized form. These permit formation and escape of the atomic forms from the gravitational attraction of the tellurian planets. Conversely, the mass of the so-called gas giants and less quantity of radiation tend to keep losses to a minimum. Today the gas giants are thought to be formed of liquids and ices as well as gases. Thermodynamic considerations support the idea of liquid and essentially solid hydrogen in the outer planets. Pluto is small but certainly not warm.

In the Earth's atmosphere, hydrogen is continually lost to outer space, yet there is a compensating resupply. This resupply comes from within the crust as well as in the dissolution of compounds, such as water. The mantle is yet a speculative source. Hydrogen sulfide is another outgassing compound as are the hydrocarbons—alkanes, alkenes, and alkynes. Methane is the simplest alkane. With respect to the vertical distribution of hydrogen, Good (1985) indicates that there is little variation latitudinally. Between the latitudes of  $40^\circ$  to  $60^\circ$  N. latitude, there is a decrease from the tropopause to an altitude of about 35 km, from about 0.55 ppm to 0.45 ppm. See Ehhalt (1978), Fabian et al. (1981), and Ehhalt and Tonnissen (1980).

Table A-11-8 provides bonding energies for a few selected gases. These energies and their associated wavelengths are only for simple dissociation of the gases. Other bonds may be ruptured if energy and the opportunities exist. For example, methane ( $CH_4$ ) may photodissociate into the radical methyl ( $\bullet CH_3$ ) molecule and the single hydrogen radical ( $\bullet H$ ). Energy ( $421 \text{ kJ mol}^{-1}$ ) is required and such is available at a wavelength of 284 nm in the electromagnetic spectrum. The radical ( $\bullet H$ ) will engage actively in reactions, one being joining with another hydrogen radical ( $\bullet H$ ). Yet, as Wayne (1988) points out, hydrogen ( $H_2$ ) may be split from the methane molecule; i.e., sufficient energy may be available, at the same time, to split two hydrogen atoms from a methane molecule ( $CH_4$ ), producing in an ensuing immediate reaction the methylene radical ion ( $\bullet CH_2$ ) and the hydrogen molecule ( $H_2$ ). Equation (11.63) depicts this:



From table A-11-8, the energy required to rupture the two bonds separately is the sum of 421 and 469 or  $890 \text{ kJ mol}^{-1}$ . Such energy is available at 135 nm (quite close to the above statement of  $<144 \text{ nm}$ ). Nowhere in this section are the energies involved to produce excited atoms discussed. See the Rydberg constant and the associated series.

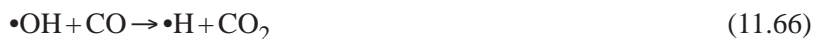
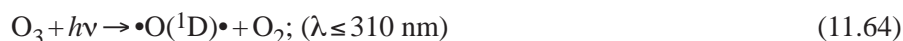
Biogenic sources are very important. Already the sources of methane ( $CH_4$ ) have been mentioned in section 11.9. But bacteria play a role in conversion of hydrocarbons and hydrogen sulfides and possibly other



hydrogen-bearing components. Wherever seeps or sources of such materials are available to bacteria, hydrogen will be produced as a byproduct. Recently, attention has been focused on mussels and tube worms near such sources. Both organisms employ bacteria in their tissues to absorb; i.e., methane (CH<sub>4</sub>) to provide life-maintaining energy. Hydrogen (H<sub>2</sub>) is a byproduct released to the environment. Later, this hydrogen escapes from the hydrosphere into the atmosphere. Thus, above such seeps, in both the hydrosphere and atmosphere, more than normal amounts of hydrospheric and atmospheric hydrogen should be detected. Conversely, any anomaly in hydrogen amounts could indicate the presence on the ocean floors of hydrocarbon sources, animal life of the dark oceanic or lake depths, as well as necessary bacteria.

### 11.12.2 Oxides of Hydrogen

There are several oxides of hydrogen (H<sub>y</sub>O<sub>x</sub>). The oxide water (H<sub>2</sub>O) was discussed extensively in the introduction, a separate subsection, and will be discussed again in other detail in the next subsection. The oxide hydroxyl radical (•OH) now is treated briefly, though it deserves more. Photolysis of ozone (O<sub>3</sub>) as a first step leads to the hydroxyl radical (•OH) formation as shown through equations (11.64) and (11.65). Equation (11.64) repeats equation (11.37):



or



As indicated previously, in the liquid form of water, there is some formation of the (•H) and (•OH) units but the percentage amount is very small. These tend to leave the water itself. Electrolytic decomposition will introduce some (•OH) to the atmosphere yet the main products will be (H<sub>2</sub>) and (•O•). The hydroxyl free radical (•OH) and its variations were the first to be identified in the search for interstellar gases in the 1960s (Zeilik (1982)). A source among still others is the photolytic decomposition of the water molecule itself.

The reader is referred to the Stanford Research Institute Report (1961) and to Wuebbles et al. (1989) for further reactions of the hydroxyl radical and other atmospheric trace gas constituents. The above equation cycling for water (H<sub>2</sub>O) also can produce carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>), both of which are better absorbers and radiators of infrared radiation. These reactions indicate an ozone (O<sub>3</sub>) sink. Please note the oxidation of methane in the upper atmosphere to produce water. Ellsaesser (1974, 1977, and 1983) discusses stratospheric water vapor and indicates that oxidation of methane will add <2 ppm of water (H<sub>2</sub>O) to stratospheric air. He conjectures that the increase of water (H<sub>2</sub>O) with altitude in the stratosphere must come through some other mechanism.

The oxide of hydrogen, the hydroxyl free radical (•OH), so quickly enters many reactions that it must be considered as one of the more important scavenging gases of the atmosphere. For that reason, its mass contribution to atmospheric constituency can never be great.

As Chang (1986) points out, hydrogen ions (H<sub>x</sub><sup>+</sup>) may be hydrated. As such, they may be associated with more than one water molecule as H<sub>3</sub>O<sup>+</sup>, H<sub>7</sub>O<sub>3</sub><sup>+</sup>, or H<sub>9</sub>O<sub>4</sub><sup>+</sup>. The usual form used is H<sub>3</sub>O<sup>+</sup> (the hydronium ion). Two other oxides, following the general formula H<sub>y</sub>O<sub>x</sub><sup>+</sup>, will be •HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>. Both of these and the (•OH) group are active in atmospheric gas reactions, such as oxidation of methane or carbon monoxide.

But with all the above, gaseous, liquid, and solid forms of water ( $H_2O$ ) are extremely important elements or components of Earth's climate(s). These are discussed in sections on the hydrosphere, the cryosphere, clouds, and drought. Thus, gaseous water, deriving from the solid and liquid stages coupled with electromagnetic radiation and chemical reactions, provide a base source for hydrogen, hydroxyl, and oxygen ions and radicals. All of these enter into many different reactions and are pervasive, ubiquitous participants in climate(s).

### 11.12.3 Water

Water ( $H_2O$ ) is the subject of several sections of this publication. Here, it is discussed from the viewpoint of a trace gas. Even though the relative amounts available in the atmosphere place it in the trace category, its physical and chemical characteristics place it in a qualitative way of comparative equality with the major gases.

Hydroxyl ( $\bullet OH$ ) as a free radical, ion, or neutral group is an active agent in the atmosphere. This is apart from the fact that it is found as a participant in many different molecules. Vinogradov and Linnell (1971) present considerable discussion on the isotopes (O-H) and (O-O). Presumably, the hydroxyl radical ( $\bullet OH$ ) is a precursor of water because it is a simpler molecule. Water then is the most natural source for the hydroxyl radical.

Liquid water covers about three-quarters of the globe. During glaciation periods, liquid water will recede from continents but reappear in solid crystalline form. Elsewhere it exists in soils of the continents and in vapor form.

Previous discussions reveal these and many molecular forms that water may take in the gas, liquid, and solid states, the three isotopes of hydrogen where  $\bullet^2H$  (D, deuterium) and  $\bullet^3H$  (T, tritium) are twice and three times as massive as  $\bullet^1H$ . The seven isotopes of oxygen provide the basis for these many forms. A water molecule containing two tritium atoms and one oxygen 20 ( $\bullet^{20}O\bullet$ ) will evaporate later and precipitate sooner than any other water molecule isotope, all other things being equal. In the same fashion, ordinary hydrogen ( $\bullet^1H$ ), the lightest, and oxygen 14 ( $\bullet^{14}O\bullet$ ), the lightest, will make the lightest molecule. These are the extremes. In the discussion on isotopic ratios (sec. 11.8.3.4), it is clearly evident that the above indicated extremes have only a small chance to exist. The relative percentages of the hydrogens ( $\bullet^1H$ ), ( $\bullet^2H$ ), and ( $\bullet^3H$ ), respectively, are 98.985, 0.015, and (—); the (—) indicates that percent is somewhere within the rounding error. Respective percentages for the three oxygens ( $\bullet^{16}O\bullet$ ,  $\bullet^{17}O\bullet$ , and  $\bullet^{18}O\bullet$ ) are 99.759, 0.037, and 0.204, while those for ( $\bullet^{14}O\bullet$ ,  $\bullet^{15}O\bullet$ ,  $\bullet^{19}O\bullet$ , and  $\bullet^{20}O\bullet$ ) also are somewhere in the rounding error for all oxygen isotopes. Another aspect is that  $\bullet^3H$  and  $\bullet^{14}O\bullet$ ,  $\bullet^{15}O\bullet$ ,  $\bullet^{19}O\bullet$ , and  $\bullet^{20}O\bullet$  are radioactive and for practical purposes and in the long terms, transmute. Tritium ( $^3H$ ) has a half-life of 12.26 yr. It is aperiodically supplied or created by high-energy reactions in the upper atmosphere. The half-lives of  $\bullet^{14}O\bullet$ ,  $\bullet^{15}O\bullet$ ,  $\bullet^{19}O\bullet$ , and  $\bullet^{20}O\bullet$ , respectively, are 73 s, 2.03 min, 29.4 s, and 14 s. Therefore, though there may be a minuscule error involved in neglect, the molecules involving T( $^3H$ ),  $\bullet^{14}O\bullet$ ,  $\bullet^{15}O\bullet$ ,  $\bullet^{19}O\bullet$ , and  $\bullet^{20}O\bullet$  are neglected for the remainder of this discussion.

Water is an indispensable element of climate and life. It is difficult to envisage a better one. In its isotopic configurations, alone or with those of other elements, it holds one of the keys to Earth's climate. How could a better environmental laboratory recording mechanism be developed? There are others but none better. Measures of water and its constituents therefore provide a readable record in isotopic ratios. This record is in skeletal remains of animals, plants, cryosphere, and icefields and glaciers as their isotopic ratios retain the imprint of climate through the ages. There are, of course, problems and difficulties encountered. Some aspects of these are discussed in other sections.

**11.12.3.1 Constituents.** Water, dihydrogen monoxide ( $H_2O$ ), consists of the atoms of hydrogen and oxygen in any of their isotopic configurations. Consider ( $^1H_2^{16}O_1$ ), the molecule of water, most prevalent. It, like other water molecules, is a planar dipolar bent molecule. Three points determine a plane. The three atoms do not lie on a straight line. The two hydrogen atoms are bonded to the oxygen atom but not to each other. One bond is weaker than the other. Its bonds are subject to the stresses which result from the absorption and emission of energy.

Collisions represent or induce energy exchanges. The atoms can be excited or damped by the absorption or emission of energy. In excitation, the electronic cloud changes due to the electrons rising to higher orbitals. When the electrons fall inward towards the nuclei, either one step at a time, in a continuous cascade, or in one step, the excitation is removed and energy is emitted. The entire width of the electromagnetic spectrum is involved but only at those discrete (quantum) levels to which a molecule or atom is responsive. The activation of only one electron to a higher level changes the energy absorption and emission stance of the atom (molecule).

Bonds themselves may absorb and utilize energy from the entire spectrum, yet as in the case of electrons, only a discrete responsive wavelength (wave number) is involved. These may change with the isotopic structures (Mitton (1977)). Bonds may be disrupted (broken), bonds may stretch or compress (vibrate), molecules may increase or decrease rotation (spin), molecules may change their bending (flexing) and/or their translation (movement from one spot to another). Each of these occurs with exchange of energy from or to the energy stream. Interchanges may be made without exchange of energy to and from the main stream. In the neighborhood of the responsive line spectra, vibration, rotations, flexing, and translation broaden the spectra and produce wings to the lines.

The water molecule, as indicated above, is planar and polar. One atom is more closely bound to the oxygen atom than the other. At 235 nm, an energy packet (quantum, photon) can supply energy to a mole of water,  $502 \text{ kJ mol}^{-1}$ , sufficient to sever the weakest bond between the oxygen ( $\bullet\text{O}\bullet$ ) atom and a hydrogen ( $\bullet\text{H}$ ) atom of each molecule. If a similar hydrogen atom returns to the severed molecule, a proportionate amount of energy is returned to the energy stream. With the removal of an ( $\bullet\text{H}$ ) from  $\text{H}_2\text{O}$ , a resulting ( $\bullet\text{OH}$ ) hydroxyl unit or radical is created which is very reactive. It, in turn, can be decomposed or composed with the absorption or emission of a quantum of electromagnetic energy of  $\approx 459 \text{ kJ mol}^{-1}$  available at  $\approx 261 \text{ nm}$  or less. These wavelengths are in the ultraviolet, and these energies can also be provided by thermal means or in chemical reactions.

**11.12.3.2 Spectra.** Figure 11-3 (Howard (1960)) provides comparison spectra for several molecules. Figure 11-27 (derived from figure 11-3) permits easier comparison of the simulated solar spectrum with that of ordinary water ( $\text{H}_2\text{O}$ ) and with a heavier water (HDO), also called deuterated water due to the presence of  $^2\text{H}(\text{D})$  or deuterium. These spectra are in the infrared. Water ( $\text{H}_2\text{O}$ ) absorbs and emits electromagnetic radiation strongly in the  $6,000, 5,000\text{--}3,000, 2,000\text{--}1,400 \text{ cm}^{-1}$ , less strongly from  $1,400$  to  $700 \text{ cm}^{-1}$ . Beyond, in the microwave and radiowave portions of the spectrum, it absorbs strongly.

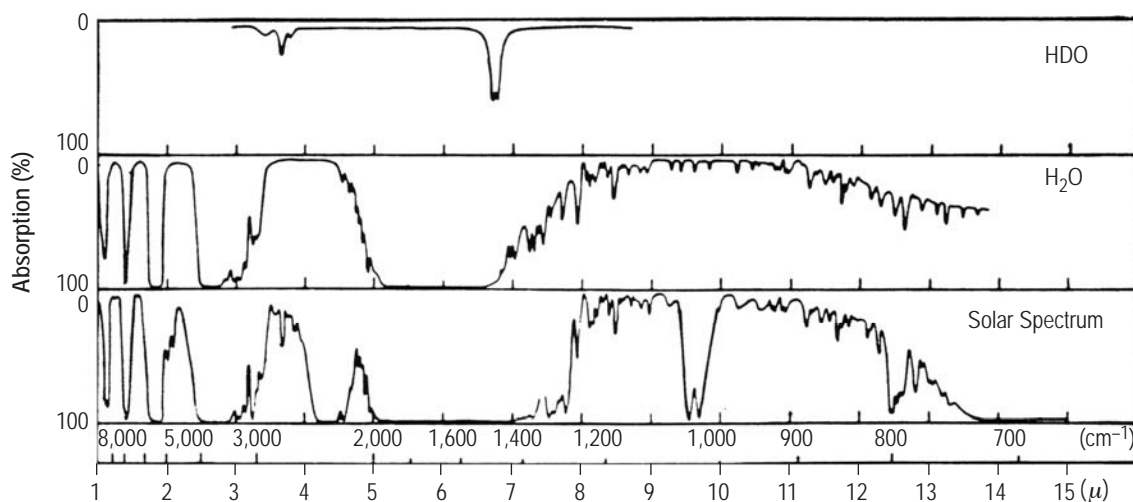


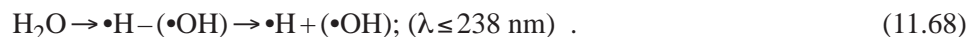
Figure 11-27. Comparison of the infrared absorption of solar radiation by (HDO) and ( $\text{H}_2\text{O}$ ) with the total simulated infrared absorption of solar radiation at the Earth's surface. The latter includes the absorption shown in the upper two curves (courtesy of Howard (1960)).

On the other hand, HDO absorbs or emits little radiation except slightly in narrow bands at 3,000 and 1,400  $\text{cm}^{-1}$ . Goody and Yung (1989) show absorption at 3,000  $\text{cm}^{-1}$ . Chantry (1984) indicates that the hydroxyl ion absorbs and emits energy at peaks near 0.725, 0.875, and 0.95  $\mu\text{m}$  (above the visible in the near infrared portion of the spectrum). Goody and Yung (1989) indicate that the  $\bullet\text{OH}$  is active at 8.49 lines from the second part of the AFGL listings. Similar to water ( $\text{H}_2\text{O}$ ) in its absorption and emission of energy in the microwave region, ( $\bullet\text{OH}$ ) strongly emits at a wavelength of 18 cm (Henbest (1979)). Hydrogen ( $\text{H}_2$ ) absorbs and emits energy at 21-cm wavelengths ( $21 \times 10^7$  nm) while water ( $\text{H}_2\text{O}$ ) absorbs and emits energy at a 1.35-cm wavelength. These are some of the vibration-rotational energy characteristics. The ( $\bullet\text{OH}$ ) group hydroxyl ion was the first interstellar gas to be identified. The reader also may be interested in the discussion of ( $\bullet\text{OH}$ ) in interstellar intergalactic situations and also in star formation (Shklovskii (1978)). Shklovskii (op. cit.) also gives the frequencies of 1,665; 1,612; 1,667; and 1,720 MHz associated with the ( $\bullet\text{OH}$ ) ion. These bracket the 18-cm wavelength which is well beyond the far infrared and in the radiowave region. These cannot be expected to extract or furnish large amounts of energy in the microwave region but furnish some in the near infrared for the “greenhouse” effect. Water, on the other hand, is pervasive and is active in the ultraviolet, the visible, the infrared, the microwave, and the radio wavelengths. The next most active and pervasive trace gas is carbon dioxide which was discussed in section 11.9.

#### 11.12.4 Hydroxyl Sources

The following indicates only a few paths for hydroxyl group formations. The hydroxyl group—ion, neutral, or radical—derives in climate mainly from water. Water itself is available from the spheres—lithosphere, hydrosphere, cryosphere, and atmosphere. Main immediate sources are the hydrosphere and cryosphere. As indicated above, the water molecule is responsive to selected quanta of the entire electromagnetic spectrum; so too is the hydroxyl.

Water ( $\text{H}_2\text{O}$ ) may be decomposed to obtain the hydroxyl. Weast (1968) credits thermochemistry D(O-H) and Foner and Hudson (1962) the bond strength (energy) of about 120 k cal  $\text{mol}^{-1}$  (502 kJ  $\text{mol}^{-1}$ ). Dissociation of water to hydroxyl is represented in reaction



The hydroxyl free radical ( $\bullet\text{OH}$ ) can be produced by the reaction of excited oxygen  $\bullet\text{O}(^1\text{D})\bullet$  with water:



Here, energy is supplied sufficient to raise the oxygen atom from the ground state to the excited state ( $^1\text{D}$ ). After absorption of energy from the electromagnetic spectrum by a molecule, there are 10 pathways by which this energy may be utilized (Wayne (1988)). The two processes above show dissociation and reaction. These pathways have been indicated in section 11.1. Excitation of atoms or molecules indicates a possible change of chemistry along there with a reaction speed change.

Solar radiation is strongly depleted in its passage through the atmosphere, particularly in the ultraviolet. See section 11.15. However, a small portion does succeed in reaching the Earth’s surface. One of the increasing sources of depletion or blocking is the ozone layer discussed in section 11.10. The very thin surfaces of the spheres are sometimes termed skins. Some radiation can penetrate these skins and provide energy for subsequent changes or reactions.

In the case of water surfaces, such as on oceans, rivers, lakes, etc., water molecules may be affected as indicated in reaction equation (11.68). The two radical particles ( $\bullet\text{H}$ ) and ( $\bullet\text{OH}$ ) are free to reunite or to react with other bodies. Each is lighter than the water molecule and will tend to rise. Each begins its upward journey through

the atmosphere, but neither exists alone for a long time. For example, the hydrogen atom released in reaction equation (11.68) may interact with an oxygen (O<sub>2</sub>) molecule to form another hydrogen oxide (HO<sub>2</sub>) as in reaction equation (11.70):

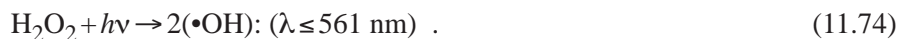
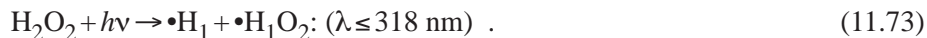


A third body, M, is utilized to absorb the energy of collision. The third body can be any other molecule, even another oxygen molecule. Its momentum is changed in the process and there may be internal intramolecular exchanges of energy without emission or absorption of electromagnetic energy. See Wayne (1988) for discussion on radiationless internal redistribution of energies. This is pertinent to any molecule, not just the hydroxyl radical. This reaction, in turn, provides a source for formation of hydroxyl groups. Warneck (1988) presents information on the vertical distribution of (•OH) radicals in the stratosphere. A number density maximum of about 10<sup>7.3</sup> is indicated between 30- and 50-km altitude. Mixing ratios increase from 10<sup>-10.8</sup> to 10<sup>-9.4</sup> from 30- to 70-km altitude. Attribution is made to Anderson (1971, 1976, and 1980) and to Heaps and McGee (1982). Additionally, it should be noted again that the hydroxyl group (•OH) is involved in many other chemical reactions. It is a characteristic group of the alcohols.

It participates also as shown in the following reactions:



Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), with an appropriate quantum, then may be transformed to produce a free radical of hydrogen or to produce two hydroxyls. Different photons are involved:



The •HO<sub>2</sub> of reaction equation (11.70) also is available for other reactions such as

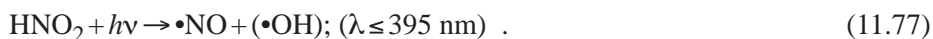


The resulting hydrogen of reaction equation (11.68) is available for a reaction (Wayne (1988)) such as

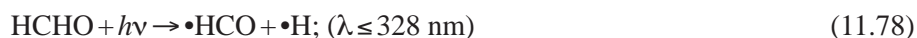


This also is discussed in section 11.9 (on ozone). Infrared chemiluminescence displayed by this (•OH) emission extends from the infrared into the long wavelength of the spectrum. Wayne (1988) further makes the point, which is also made in other parts of this section, that chemical reaction excitation of species after electrochemical proceeds in the same fashion as after absorption of light (electromagnetic radiation). See also the discussion of Foner and Hudson (1986a,b) on the mass spectrometry of the •HO<sub>2</sub> free radical and the dissociation of H<sub>2</sub>O by electron impact.

Photolysis of HNO<sub>2</sub>, nitrous acid, is a source of hydroxyl radicals and is discussed by Goody and Yung (1989). The reaction is



Goody and Yung (1989) discuss the existence of  $\text{HNO}_2$  in pathways to the ( $\bullet\text{OH}$ ) free radical. (They attribute data sources as Platt and Perner (1980), Platt et al. (1980), and Pitts et al. (1984)). The Riverside, California, community is the data source. From personal experience, Riverside rarely was besieged by smog prior to 1950, though the problem is inherent in the Los Angeles area due to hydrocarbons. Borne on the sea breeze, it threatened Riverside. In the last three decades, the problem is not sporadic but almost continual. The following reactions are diurnal in magnitude, just as the  $\text{NO}_x$  and  $\text{O}_3$  distributions are diurnal (Rhodes (1980) and Crutcher et al. (1986)). The diurnal generation of one provides a destroyer of the other. It is essential to note that other climatological variates are involved—winds, both direction, moisture and speed, and the time of day:



Goody and Yung (1989) also point out that the reaction equation (11.76) is a more efficient producer of ( $\bullet\text{OH}$ ) in the mornings than that of the decomposition route of formaldehyde ( $\text{HCHO}$ ) shown in reaction equations (11.78) through (11.81). Again, it is the idea behind the third body that M serves to modify the energies of the collision of three bodies. Thus, M is not quite the same as it was before. The molecule may be more energetic; i.e., vibrating more. It may be rotating faster, flexing more, the electronic levels are higher than before, it itself may enter a subsequent reaction more easily and/or its translation may be greater, but more likely, both its direction and speed velocity are different with its speed much reduced. This is not indicated by the reaction. But chemically speaking, it is still the same third body but physically, its motion and momentum are changed. Oxidation of the many hydrocarbons is a process whereby the ( $\bullet\text{OH}$ ) radical initiates a step reaction where the ( $\bullet\text{OH}$ ) radical is later regenerated (Goody and Yung (1989)).

**11.12.4.1 Hydroxyl Sinks and Sources.** The hydroxyl free radical is reactive and there will be many sinks, of which only a few can be indicated here. See Warneck (1974, 1975). Oxidation of the many hydrocarbons is one large sink. Alkanes, alkenes, and alkynes are some of the many hydrocarbons. The simple alkane, methane ( $\text{CH}_4$ ) is chosen as an example. Methane ( $\text{CH}_4$ ) can be represented by (RH) where R is that part of a molecule which becomes a radical upon the extraction of a hydrogen. Thus ( $\text{CH}_4$ ) becomes ( $\text{CH}_3\text{H}$ ), where  $\bullet\text{CH}_3$  is the methyl free radical. In a similar fashion, ethane ( $\text{C}_2\text{H}_6$ ) may be written (RH) or  $\bullet\text{C}_2\text{H}_5\text{H}$ , where  $\text{C}_2\text{H}_5$  is the ethyl free radical. The extraction of the single H can occur thermally or photochemically. Table A-11-8 indicates that the bonds in  $\text{CH}_3\text{-H}$  can be broken by the absorption of  $435 \text{ kJ mol}^{-1}$  which may be available thermally in combustion processes or in the electromagnetic spectrum at wavelengths of 275 nm or less. Note that  $502 \text{ kJ mol}^{-1}$  of energy will split the water molecule ( $\text{H}_2\text{O}$ ) to furnish both hydrogen and hydroxyl free radicals. One pathway in which the oxidation of methane may proceed follows. Both Warneck (1988) and Wayne (1988) provide the basis for the following sequences. Warneck (1988) attributes prior discussions by Levy (1971) and McConnell et al. (1971).



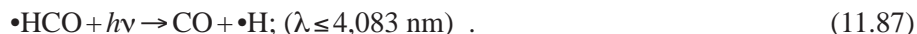
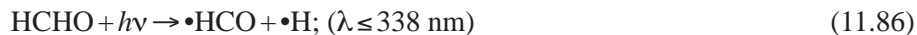
This reaction is a source of water, particularly in the stratosphere. A methyl radical remains for actions:



Here, the three-way meeting of the methyl radical, an oxygen molecule, and a third body serves to let the third body, M, absorb excess energies released in the association of  $\bullet\text{CH}_3$  and  $\text{O}_2$  into  $\bullet\text{CH}_3\text{O}_2$ . This molecule with excess energies removed tends to remain relatively quiet and not fly apart. These energies may be redistributed within M:



$\text{CH}_2\text{O}$  or  $\text{HCHO}$  is formaldehyde. Its bonding strength is about  $354 \text{ kJ mol}^{-1}$ , which energy is available at 338 nm or less:



Bonding in  $\text{HCHO}$  involves a double bond between carbon (C) and oxygen ( $\bullet\text{O}\bullet$ ) and single bonds between each hydrogen ( $\bullet\text{H}$ ) and carbon. Thus, the reaction equation (11.88) presumably occurs in two steps in photodissociation in reaction equations (11.86) and (11.87). Weast (1968) provides a value of  $7 \text{ k cal mol}^{-1}$  for  $\bullet\text{HCO}$  and  $87 \text{ k cal mol}^{-1}$  for  $\text{HCHO}$ . The latter is equivalent to energy at a wavelength of 329 nm. As stated before, uncertainties given by Weast (1968) are about  $\pm 1$  in  $\text{k cal mol}^{-1}$ . The value of 338 is provided in Wayne (1988). This is equivalent to  $\approx 85 \text{ k cal mol}^{-1}$  as compared with 87 given above. These uncertainties do not seem to be out of order. Energies for the above reactions would be available in wavelengths  $< 338 \text{ nm}$ . Note that the wavelength for the reaction equation (11.87) is in the infrared at  $4 \mu$ .

Formaldehyde can also be attacked by ( $\bullet\text{OH}$ ) as in



and the  $\bullet\text{HCO}$  can react with oxygen ( $\text{O}_2$ ):



while the hydrogens also may react with oxygen and a third body:



In both reaction equations (11.87) and (11.89), carbon monoxide ( $\text{CO}$ ) results.

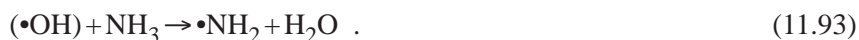
A hydroxyl radical ( $\bullet\text{OH}$ ) will react with the carbon monoxide output of equation (11.89) in reaction equation (11.91):



The  $\bullet\text{HO}_2$  radical produced in equation (11.89) or (11.90) also consume ( $\bullet\text{OH}$ ) as follows:

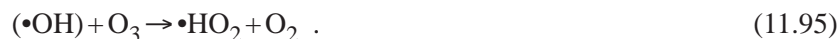


Warneck (1988) also provides a 13-step sequence for the oxidation of methane. This procedure is also covered in section 11.8, methane, of this publication. However, here it is viewed from the viewpoint of an ( $\bullet\text{OH}$ ) sink:



Warneck (1988) indicates that this sink is not important, yet it is a sink:





This last reaction is important as it will remove ozone ( $\text{O}_3$ ) in the stratosphere and, at the same time, provide a molecule for reaction (as in eqn. (11.92)), which will remove another hydroxyl radical ( $\bullet\text{OH}$ ). The reaction of ( $\bullet\text{OH}$ ) with  $\text{H}_2$  also is a sink for ( $\bullet\text{OH}$ ) with the production of water ( $\text{H}_2\text{O}$ ) and a free hydrogen ( $\bullet\text{H}$ ):



The reaction of the hydroxyl ( $\bullet\text{OH}$ ) with hydrogen chloride ( $\text{HCl}$ ) represents a sink and the product is water ( $\text{H}_2\text{O}$ ) and a free halogen, such as chlorine ( $\bullet\text{Cl}$ ), as follows:



For those who are interested in the rapidity of reactions and the relative importance of the sources and sinks of the hydroxyl radical ( $\bullet\text{OH}$ ), reference may be made to Warneck (1988) and to Wayne (1988). In the above discussions, the oxidation of the hydrocarbons was discussed as an ( $\bullet\text{OH}$ ) sink. Methane ( $\text{CH}_4$ ), the simplest hydrocarbon, was used as an example where  $\text{RH}$  represents methane with the  $\bullet\text{R}$  radical and  $\bullet\text{H}$  as constituents.  $\bullet\text{R}$  can be any hydrocarbon radical with ( $\bullet\text{OH}$ ) extracting the  $\bullet\text{H}$  of the molecule. See Warneck (1988) for a fuller discussion.

Figure 11-28 (courtesy of Wayne (1990)) schematically illustrates some processes which both create and destroy the hydrogen oxides ( $\bullet\text{OH}$ ) and ( $\bullet\text{HO}_2$ ). These are crucial groups in oxidation processes within the troposphere. These are all trace gases with the exception of oxygen ( $\text{O}_2$ ) and are key elements in climate. These pass general scrutiny because they are, though ubiquitous, small in amount for their creation and destruction, so fast, essentially balance. There is no great accumulation, such that in their amount, they would be classed as major gases. Yet their effect is real, effective, and consequential. Heavier arrows on the left-hand side of the diagram indicate steps that can occur in the absences of  $\bullet\text{NO}_x$ . With  $\bullet\text{NO}_x$  present, the processes on the right-hand side can close a loop, with regeneration of ( $\bullet\text{OH}$ ) and oxidation of  $\bullet\text{NO}$  to  $\bullet\text{NO}_2$ . This is from a diagram devised by M.G. Jenkins; see Wayne (1990).

Figure 11-29 (courtesy of Warneck (1988)) provides the vertical distribution of ( $\bullet\text{OH}$ ) radicals in the stratosphere. On the left are number densities in molecules  $\text{cm}^{-3}$ . On the right are averages from balloon and rocket measurements of Anderson (1971, 1976, 1980) and Heaps and McGee (1982). The envelope indicates the ranges of the observed data. The ( $\bullet\text{OH}$ ) mixing ratio is controlled by a great number of chemical reactions. As indicated previously, the ubiquitous radical ( $\bullet\text{OH}$ ) is extremely reactive. Its activity is so great that it will not cumulate to any great extent in Earth's atmosphere. As Warneck (1988) indicates, the radical  $\bullet\text{OH}$  participates in a chain reaction exemplified in the following reactions:



These reactions shuttle the odd hydrogen ( $\bullet\text{H}_1$ ) or ( $\bullet\text{H}$ ) between the two oxides, the hydroxyl ( $\bullet\text{OH}$ ) and the hydroperoxide ( $\bullet\text{HO}_2$ ). Note the sink for  $\bullet\text{OH}$  in reaction equation (11.98) and sources in reaction equations (11.99)–(11.101). Yet note also the destruction of odd oxygens  $\bullet\text{O}_1$  and  $\text{O}_3$  on the left in the generation



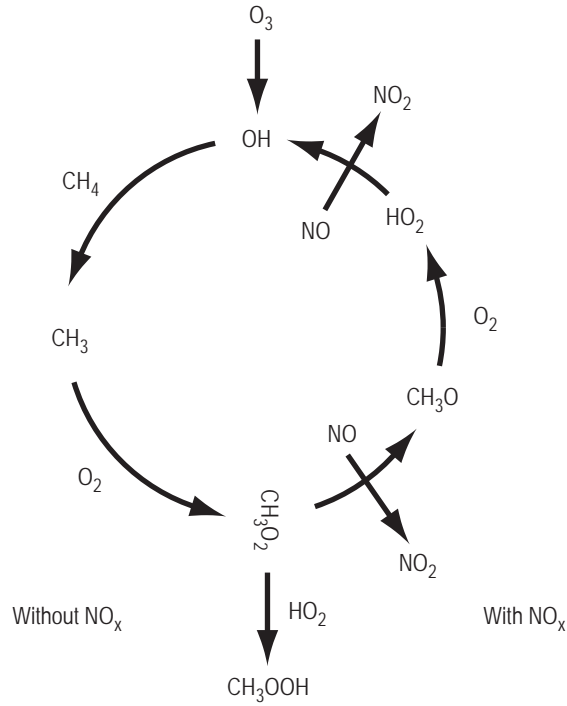


Figure 11-28. Schematic of some processes which both create and destroy the oxides (OH) and ( $HO_2$ ) (courtesy of Wayne (1990), personal communication).

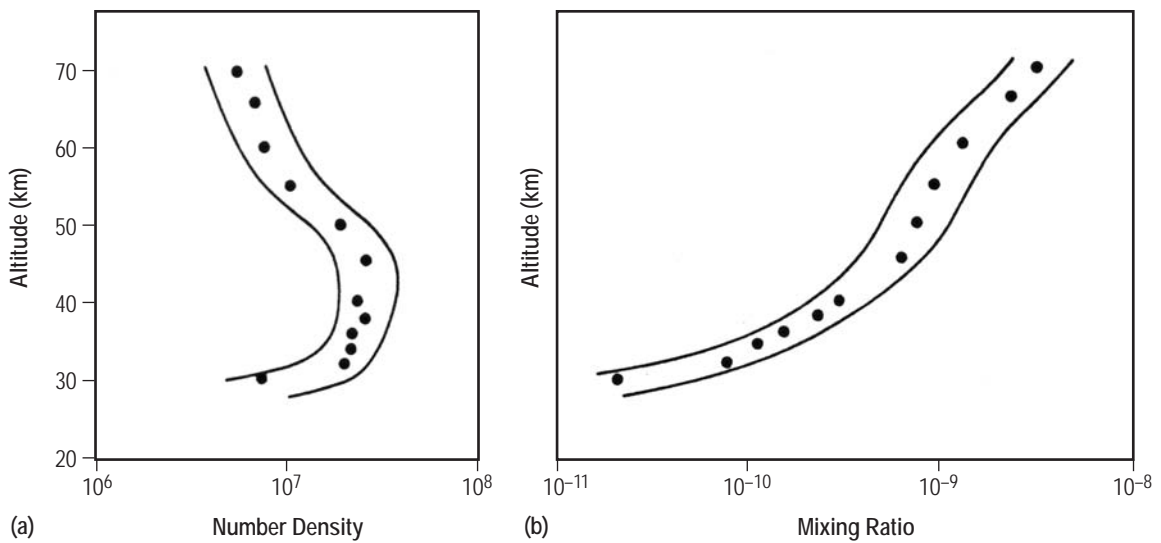


Figure 11-29. Vertical distribution of (OH) radicals in the stratosphere for (a) number density and (b) mixing ratios (with permission, Academic Press, and courtesy of Warneck (1988)).

of even oxygen on the right. (The latter is discussed in section 11.9.) Wayne (1988) notes that reaction equation (11.96) is exothermic ( $335 \text{ kJ mol}^{-1}$ ). Reactivity of the hydrogen oxides  $\bullet\text{OH}$  or  $(\bullet\text{HO})$  and  $\bullet\text{HO}_2$  as well as  $\text{H}_2\text{O}_2$  is illustrated by Wayne (1990) in figure 11-30. (This also shows the many potential reactions among a few other trace gases. This figure could have been used in almost any subsection of section 11.)

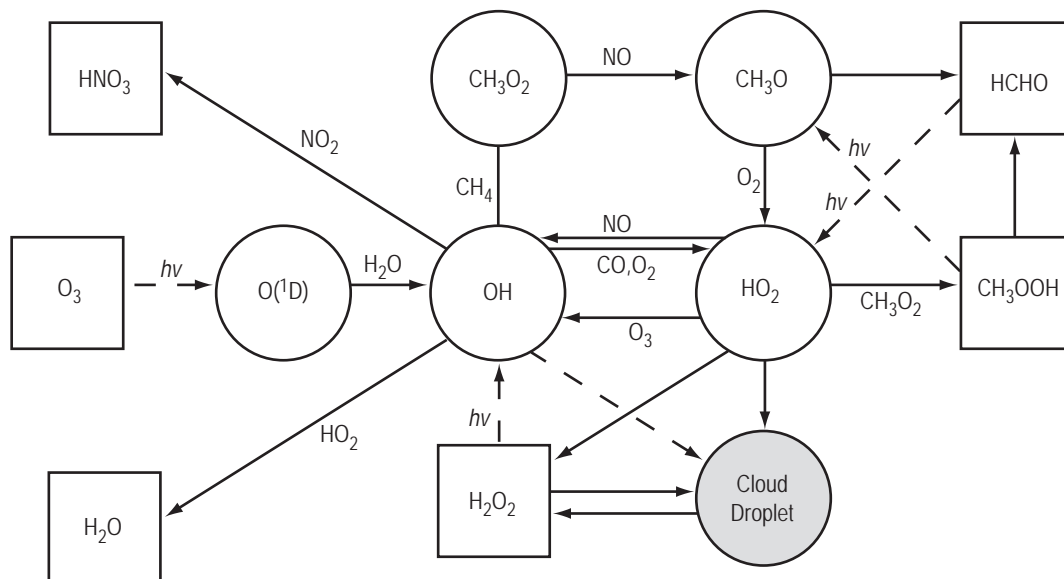


Figure 11-30. Reactivity of  $(\text{HO})$ ,  $(\text{H}_2)$ , and  $(\text{H}_2\text{O}_2)$  illustration (courtesy of Wayne (1990), personal communication).

## 11.13 Halocarbons

### 11.13.1 General (1)

Halocarbons, from a climate point of view, are important for at least two reasons: (1) They can serve as a source of halogen radicals, which are potential destroyers of stratospheric ozone, and (2) they, in the troposphere, can also act as a greenhouse gas as does carbon dioxide ( $\text{CO}_2$ ).

The halocarbons and haloalkanes have been mentioned or discussed briefly in prior sections. The halocarbons, under conditions of the troposphere, chemically are essentially stable and unreactive. This is a characteristic which has led to their use in industrial applications, such as refrigeration equipment and in aerosol sprays. Released and escaping the confines of their applications, they tend to slowly diffuse through the troposphere. Eventually, they will reach the tropopause and enter the stratosphere through ruptures in the tropopause, such as produced by violent convective thunderstorms and the augering action of the great storm systems. From there, as they diffuse upwards through the stratosphere, they become physically subject to more and more intense short wave radiation. The haloalkanes (HFCs) are chemically reactive throughout the atmosphere. Warneck (1988) in his table 2-6, pp. 78–81, provides information on the photochemical behavior of selected trace gases, including the halocarbons, in the atmosphere. That table contains the absorption spectrum for each respective gas, the type, and approximate long wavelength limit and the dissociation limits. The photochemistry is provided in a main primary process and the quantum yield is also shown. Their significance in the atmosphere is indicated, but these statements may be revised as more information, particularly in marine environments, becomes available. The dissociation upper limit for halocarbons, with few exceptions, is 400 nm or less, which is below the visible spectrum.  $\text{CFCl}_3$

(known in the commercial trade as F11),  $\text{CF}_2\text{Cl}_2$  (known as F12), methyl chloride ( $\text{CH}_3\text{Cl}$ ), carbon tetrachloride ( $\text{CCl}_4$ ), and methyl chloroform ( $\text{CH}_3\text{CCl}_3$ ) are a few of the many halocarbons. Seemingly, the methyl halides are natural in origin. The amount of methyl chloride in the air produced by natural means seem to be in larger amount than that manufactured by man.

Those halocarbon (the halohydrocarbons) species that contain hydrogen (the halohydrocarbons) react with ( $\bullet\text{OH}$ ) radicals and  $\bullet\text{O}_1(^1\text{D})$  (the excited oxygen) produced by photolysis (as indicated previously in reactions (11.64) and (11.65)). The others undergo photolytic and chain reactions (as indicated by reactions (11.102) and (11.103):



These may be followed by the catalytic chain reactions, which were previously shown as reaction equations (11.43) and (11.44) in section 11.10.3 on ozone ( $\text{O}_3$ ):



As Warneck (op. cit.) indicates, the nitrogen oxides enter into reactions with chlorine, chlorine oxides, and ozone. The catalytic chains which can reach 100,000 reactions in length will be stopped or blocked by reactions with methane ( $\text{CH}_4$ ) or  $\bullet\text{NO}_x$ . Temporarily, chlorine ( $\text{Cl}_2$ ) compounds are formed, such as  $\text{HCl}$  or  $\text{ClONO}_2$ . See Molina and Rowland (1974), Rowland and Molina (1975), and Rowland and Sherwood (1991). In any event, halocarbons and nitrogen oxides represent sink reactions with ozone, but this generally occurs at the high altitudes with ultraviolet radiation usually  $< 200 \text{ nm}$ . Wuebbles et al. (1983, 1989) present chlorocarbon emission scenarios with their potential impact on stratospheric ozone and on climate change, respectively. Thompson, Komhyr, and Dutton (1985) present chlorofluorocarbon -11, -12, and nitrous oxide measurements at NOAA/GMCC baseline stations (September 16, 1973, to December 31, 1979). These improved data sets should be useful in studies of atmospheric trichlorofluoromethane ( $\text{CCl}_3\text{F}$ ;  $\text{F}_{11}$ ), dichlorodifluoromethane ( $\text{CCl}_2\text{F}_2$ ;  $\text{F}_{12}$ ), and  $\text{N}_2\text{O}$  meridional distributions, mixing ratios, global abundances, growth rates, interhemispheric exchange rates, and tropospheric residence times. It should be pointed out that the halocarbons are potentially capable of influencing the thermal structure of the atmosphere as some of them possess strong absorption and emission bands. Intense interest in these is in their potential absorption of short wave radiation and subsequent physical release of halogens to participate in ordinary chemical reactions and catalytic reactions. These points will be discussed again briefly. Many of the halogenated hydrocarbons are known as freons.

### 11.13.2 General (2)

Reading of basic organic texts as well as general chemistry texts is suggested. See Huheey (1978), Chang (1986), and others.

Halocarbons may be good or bad. Whether these are good (CFCs; or HFCs) or bad depends upon the viewpoint of the reader and of those who may be affected. Their use and application must be compared with their potential atmospheric activity associated with the biosphere. In general, the term "halocarbon" signifies association of any one carbon with any halogen atom. There are four halogens in molecular form: (1) fluorine ( $\text{F}_2$ ), (2) chlorine ( $\text{Cl}_2$ ), (3) bromine ( $\text{Br}_2$ ), and (4) iodine ( $\text{I}_2$ ). A halohydrocarbon may also be called a halocarbon; however, there seems to be no firm definition and the terms are used indiscriminately in most texts. The reader must ascertain through

context just what is meant. Here, the term halohydrocarbon will be preferred for the general feature. The term halo-carbon implies that all hydrogen peripheral atoms have been replaced by a halogen. For example, methane (CH<sub>4</sub>) has four hydrogen atoms, each of which may serve as an extraction and/or substitution base. The general formula for the linear chain hydrocarbon carbon compounds is C<sub>n</sub>H<sub>2(n+i)</sub>. The range of *i* is 1, 0, -1. For *i* = 1 the range of *n* is “1” upwards while for otherwise *n* ranges from “2” upwards. These are, respectively, the alkanes, alkenes, or alkynes. Then there are the carbon ring compounds such as benzene and other aromatics. If one hydrogen is removed from any molecule, the remaining group is an alkyl or aryl (if aromatic) group. This group may be a radical.

The methyl halides—CH<sub>3</sub>F, CH<sub>3</sub>Cl, CH<sub>3</sub>Br, and CH<sub>3</sub>I—are presumably natural products. Probably these are of marine origin. See Chang (1986) and Warneck (1988) for discussion on CH<sub>3</sub>Cl and CH<sub>3</sub>Br. Presumably, ethyl halides; e.g., ethane with hydrogen (H) replacement by the halogens also could be of natural origin, but this is uncertain.

Full halogenation of alkanes, alkenes, alkynes, alkyls, etc., is believed to be done only by man’s deliberate synthesis. But a caveat is given that some could be of natural origin; i.e., synthesized in the universe’s physical and chemical reaction processes. As far as is known by the author, minimal amounts of natural origin detected are negligible with comparison to manufactured products.

The compounds CHCl<sub>3</sub> and CCl<sub>4</sub>, respectively, chloroform and carbon tetrachloride, have been used as an anesthetic and as degreasing and cleaning compounds. But both have been shown to be toxic and potentially carcinogenic. The same should hold true for other similar halogen compounds. Some are extremely toxic to both plants and animals, and their uses are being curtailed.

Another point to be made is that care must be exercised with the ordinary uses of any of these compounds. Methane (CH<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), propane (C<sub>3</sub>H<sub>8</sub>), butane (C<sub>4</sub>H<sub>10</sub>), and others are known to be explosive (in gas form) in confined spaces if an oxidant such as oxygen (O<sub>2</sub>) is available. As more hydrogens in any molecule are replaced by halogens, explosiveness will decrease but never to zero. Fluorine organic compounds are extremely reactive and generally exothermic. Fully halogenated compounds are used as fire suppressants. Because these, as they reach the upper atmosphere, represent a possible potential source of fluorine radicals for destruction of the ozone (O<sub>3</sub>) layer, replacements are being sought. Thus, CFCs are being replaced by HFCs, hydrofluorocarbons, in industry and commerce.

### 11.13.3 Combinations and Permutations

Combinations and permutations of the hydrocarbons are many. This is true even though the atoms’ electronic fields may be considered to be in the ground state and isotopes are disregarded. Perhaps the lowest count goes to ethyne (acetylene), C<sub>2</sub>H<sub>2</sub>. With four different halogens replacing hydrogens one at a time, the matrix of potential combinations would be C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>HF, C<sub>2</sub>F<sub>2</sub>, C<sub>2</sub>HCl, C<sub>2</sub>Cl<sub>2</sub>, C<sub>2</sub>HBr, C<sub>2</sub>Br<sub>2</sub>, C<sub>2</sub>HI, C<sub>2</sub>I<sub>2</sub>, C<sub>2</sub>FCl, C<sub>2</sub>FBr, C<sub>2</sub>FI, C<sub>2</sub>ClBr, C<sub>2</sub>ClI, and C<sub>2</sub>BrI. With C<sub>2</sub>H<sub>4</sub>, ethylene, the permutations and combinations increase rapidly. The reader may want to employ the usual mathematical formula (Beyer (1966)) for permutations:

$$P(n,m) = n!/(n-m)! = n(n-1)\dots(n-m+1) \quad (11.106)$$

or combinations

$$C(n,m) = n!/(m!(n-m)!) = (P(n,r))/m! \quad (11.107)$$

The above equations and their summations give the number of permutations or of combinations of “*n*” distinct things taken “*m*” at a time. To the climatologist, it is only necessary to realize that there are many possible

halohydrocarbons, each with its chemical reactivity and each with its own electromagnetic energy absorption, distribution, and emission characteristics.

### 11.13.4 Electromagnetic Spectrum Energies

**11.13.4.1 General.** The electromagnetic solar spectrum is a continuum. It emits energy over the entire spectral range as  $0 < \lambda < \infty$ . In essence, energy is emitted and, in turn, may be absorbed by the Sun. It is emitted in quanta (photons) which may be written as  $h\nu$ . Interstellar media absorb and emit photonic energies, as do the planets and the spheres of Earth—the hydrosphere, lithosphere, and atmosphere. Even the internal spheres and cores of the Earth obtain and transmit energies. Each atom and molecule have their individual absorption and emission characteristics. In general, these are very selective and unique, yet the energies must be received and released in those specific little package forms called quanta.

**11.13.4.2 Electronic Features.** Aurorae may be explained in part by application of the Rydberg series and the Ritz combination principle (Chantry (1984) and Chang (1986)). The Rydberg ( $R_H$ ) constant is  $1.09737317(83) \times 10^7 \text{ m}^{-1}$  or  $2.18 \times 10^{-18} \text{ J}$ . The formula is here given as equation (11.108),

$$E = R_H (n_i^{-2} - n_f^{-2}) \quad , \quad (11.108)$$

where  $i$  and  $f$  represent the initial and final orbitals (states) through which energy photons rise or fall. As indicated by Chang (1986), the various series in atomic hydrogen emission or absorption spectrum are adapted as follows in table 11-8 (from Chang's table 8.1).

Table 11-8. Atomic spectrum absorption and emission regions (after Chang (1986)).

Series	$n_i(n_f)$	$n_f(n_i)$	Spectrum Region
Lyman	1	2,3,4...	Ultraviolet
Balmer	2	3,4,5...	Ultraviolet and visible
Paschen	3	4,5,6...	Visible and infrared
Brackett	4	5,6,7...	Infrared

#### 11.13.4.3 Ultraviolet and Infrared.

**11.13.4.3.1 Ultraviolet.** The ultraviolet spectrum extends from the lower wavelength portion of the visible spectrum ( $\approx 420 \text{ nm}$ ) down to  $\approx 1 \text{ nm}$ . Figure 4-4 theoretically indicates solar energy output in all regions of the spectrum, including the ultraviolet portion. High-energy quanta (photons) ( $h\nu$ 's) of the solar energy output are involved in this spectrum region. Table A-11-8 provides bonding (disbonding) energies for several molecules including some of the halohydrocarbons. For example, oxygen ( $\text{O}_2$ ) will be permitted to separate (or join) with the absorption (or emission) of a photon (quantum) ( $h\nu$ ) containing equal energy packets amounting to  $499 \text{ k J mol}^{-1}$  at a wavelength of  $240 \text{ nm}$  ( $\approx 41,711 \text{ cm}^{-1}$ ). Conversion factors are available in table A-4-3. Methyl chloride ( $\text{CH}_3\text{Cl}$ ) may release chlorine ( $\text{Cl}$ ) with absorption of energy at about  $347 \text{ nm}$  ( $337 \text{ k J mol}^{-1}$ ) (Warneck (1988)). (Table A-11-8 shows  $\approx 341 \text{ nm}$  ( $350 \text{ k J mol}^{-1}$ .) This simply illustrates that any of these values need to be used with a little caution. As more research is conducted, the figures published will be presumably a little better in agreement. Coupled with this is the fact that in a molecular complex, a molecule may absorb larger quanta at shorter wavelengths. The excess energy may be used to increase the internal energy of the remaining group in increasing the translation, vibration, rotation spin, and/or flexing aspects. These will be noted particularly in the infrared activities of the molecule or group.

As noted in table 11-5, electrons moving from orbitals 1 or 2 to higher orbitals will be supplied energy from the ultraviolet. Electrons moving to either levels 1 or 2 from higher orbitals will emit ultraviolet quanta (photons). Atoms of a molecule may be excited, as above; i.e., they may absorb energy and move an electron to a higher orbital. An isolated atom may be excited. Thus, for example, an oxygen ( $\bullet\text{O}_1\bullet$ ) in an  $\text{O}_2$  molecule may be excited which causes the entire  $\text{O}_2$  molecule to be excited. Excitation may be so great as to lift electrons to orbitals outside the influence of the nucleus. The complex would then be termed an ion. Such ionization energies would be those where the final state is essentially infinite and the second term of equation (11.108) is zero.

As the stream of solar radiation progresses downward through the atmosphere, more and more radiation is absorbed by the atmosphere, particularly in the ultraviolet. Only a small portion of the radiation reaches the surfaces of the lithosphere and hydrosphere, but that which reaches the surfaces is absorbed. Some radiation may be reflected in its downward passage, such as from ice or snow surfaces.

A look at any solar spectrum record at the surface of the Earth indicates that not all ultraviolet radiation from the Sun reaches the Earth. There is a deficit in the ultraviolet region, implying that much of it has been absorbed by atmospheric atoms and molecules. That these atoms and molecules should be in higher energy states than before the onslaught of solar radiation becomes an assumption. Potentially, energy absorption occurs over the total spectrum, principally in the ultraviolet, visible, and infrared.

11.13.4.3.2 Infrared. Equation (11.108) and table 11-5 show the energies involved in the electronic level changes. Table A-11-8 shows the energies involved for a few selected simple molecular bonding (association) atoms. Absorption of a specific photon does not imply that that specific energy packet is held unchanged. It may serve to increase the total internal energy. Quanta of a different energy amount may be further absorbed or emitted. Conditions may be such that a quantum will not drop all the way to the lowest level possible. Generally, in the photoelectric reaction mechanism indicated, greater energy may be absorbed than is required for bond dissociation. This excess energy may be used to increase the translation (motion) of the molecule, the vibration-stretching of the molecular bonds, rotation and spinning of the molecule, and/or bending-flexing of the molecule. A change in situation or environment may permit loss of any of these energies. The sensible energies will decrease so that a former warming effect becomes a cooling effect. In addition to the above resulting infrared heating and cooling, there is actual contribution of visible and infrared energies to and from the solar radiation stream. Absorption of these energies from the infrared further increases the internal activities of the molecules as indicated above.

## 11.13.5 Halocarbons and the Spectrum

**11.13.5.1 Ultraviolet Spectrum.** Noted before was the fact that not all ultraviolet radiation from the Sun is absorbed before hitting the lands and seas, but most of it is absorbed. A small portion of the small amount that does penetrate the atmospheric boundary layer can and may be absorbed by the halocarbons. (Please refer to table A-11-8 on bonding energies.) Already discussed are the catalytic chain reactions of the chlorine radical with respect to oxygen, ozone, and other elements. The same goes for other halogen radicals. However, fluorine is so reactive that it apparently will not cycle long, and iodine is comparatively so large and heavy that even if some is able to reach the upper atmosphere, it will not be a serious factor. Energies to dissociate halogen molecules exist in the visible spectrum while energies necessary for the fully halogenated carbons exist only in the ultraviolet spectrum from  $\approx 450$  nm down to 1 nm. For example, Weast (1988) gives  $71 \text{ kcal mol}^{-1}$  dissociation energy for  $\text{C}_6\text{H}_5\text{Br}$ ,  $81 \text{ kcal mol}^{-1}$  for  $\text{C}_2\text{H}_5\text{Cl}$ ,  $100 \text{ kcal mol}^{-1}$  for  $\text{HCF}_3$ , and  $73 \text{ kcal mol}^{-1}$  for  $\text{CCl}_4$ .

The ultraviolet spectrum extends from the lower edge of the visible spectrum,  $\approx 420$  nm down to  $\approx 1$  nm. (Please note the radiation curves exhibited in figure 4-4). Also note the sharp drop in the absorption where the ultraviolet is expected to be found. The implication is that the atmosphere absorbs most of that energy. Only a small part reaches the Earth's surface, land, and sea. But, that surface-absorbed radiation serves to produce some of the hydroxyl ( $\bullet\text{OH}$ ) radicals. In fact, these are produced throughout the atmosphere from water vapor in the

atmosphere. Oxidation of methane ( $\text{CH}_4$ ) to carbon dioxide ( $\text{CO}_2$ ) with many intermediate products returns, in the first step, water to the atmosphere. Also, there may be sufficient package energy such that, if absorbed by the fully halogenated carbons, it may serve to lift a halogen from a molecule, leaving a radicalized halogen and the remaining portion of the molecule. That is, a bond will be severed. (See table A-11-8 for some selected appropriate bond energies of dissociation or of association.) Thus, halogenated carbons anywhere in the atmosphere will absorb and emit energies in the infrared if those energies are available for absorption. Except for a few instances, bond dissociation energies will not be available in any great amount until the stratosphere is reached and molecules reach much higher altitudes.

Iterating the above, fully halogenated carbons (known also as CFCs) will absorb and emit infrared radiation throughout the entire passage from the surfaces of the Earth to the high stratosphere. Energies sufficient to break molecular bonds will be minimal at the Earth's surfaces but will be greatly increased as regions of ultraviolet radiation are entered. These regions increase in size and depth with altitude. (See again table A-11-8.) Bonding energies are given in  $\text{kJ mol}^{-1}$ . The reader may divide these energies by Avagadro's number,  $6.02486 \times 10^{23}$ , to obtain energy in kJ per molecule.

On the other hand, partially halogenated carbons, such as the halohydrocarbons, are both chemically and physically reactive throughout the atmosphere. The fewer the hydrogen atoms have been replaced by a halogen atom, the more the chemical reactivity will be. Thus,  $\text{CH}_3\text{Cl}$  may be expected to be more reactive than  $\text{CHCl}_3$ . The omnipresent free hydroxyl radical, ( $\bullet\text{OH}$ ), actively engages the ( $\bullet\text{H}$ ) hydrogen atom of the halohydrocarbon, leaving a radicalized group. The word omnipresent does not mean that the individuals of a swarm of ( $\bullet\text{OH}$ ) hydroxyls are present for a long time. Quite the contrary. The individuals are so active (reactive) that their individual lifetime is small. But enough other ( $\bullet\text{OH}$ ) free radicals are being generated such that the swarm as an entity seems to continue. There are other reactants which will remove a hydrogen from a halohydrocarbon. Thus, reactant halohydrocarbons will not last too long in the atmosphere. (These are known as HFCs.) The letter F implies that fluorine (F) atoms must be involved. This is a general acronym and is used here to imply a halogen. Thus, HFCs do not have longer lifetimes than CFCs and therefore are not as available to the extent CFCs might be in the ozone ( $\text{O}_3$ ) layer. In that layer or in the region of ozone ( $\text{O}_3$ ) generation, absorption of an appropriate quantum of energy (photon) will disbond halogen so that it is available for immediate reaction.

Fully halogenated hydrocarbons, which are chemically unreactive, will eventually reach the upper atmosphere. There, sufficient energies are available to strip one or more halogens from the molecules, leaving radicals. These radicals are then free to cycle to produce long chain lengths. That is, these radical atoms or groups will cycle, destroy a molecule, say ozone ( $\text{O}_3$ ), and be ejected to start another destructive cycle. This may occur many times before the radical is trapped in another reaction. Lovelock (1961, 1971) has been an avid investigator of and builder of instrumentation to detect atmospheric halocarbons. Molina and Rowland (1974) proposed degradation of ozone ( $\text{O}_3$ ) by marauding chlorine radicals. The proposed source of these radicals was photodissociation of the halocarbons. Warneck (1988) provides charts showing mixing ratios in their vertical distribution based on the work of several investigators.

**11.13.5.2 Infrared Spectrum.** In an energy stream such as to or from the Earth or in a laboratory, halocarbon (haloalkane) molecules, or any other atmospheric molecules, absorb and emit energy from and to that stream. The net change depends on whether the stream is one of relative surplus or deficit. As indicated previously, molecules and associated atoms have their own characteristic responses to an energy stream. That is, each one responds with unique quanta absorption or emission associated with unique wavelengths or wave numbers (frequencies) of the electromagnetic spectrum.

The discussions which follow are not restricted to only halohydrocarbons; they apply to any molecule. Figure 11-1 is a schematic illustration of the energy relationships over a large part of the spectrum. Table A-11-8 provides selected energy requirements for association or dissociation of a few molecules. These values indicate

that the infrared portion of the spectrum cannot supply the necessary single quantum energies for association or dissociation. Part of the visible spectrum does. As most ultraviolet radiation is absorbed by the atmosphere during passage of the stream through the atmosphere, the amount reaching the surface of the Earth will be minimal. Dissociation will be inhibited in the troposphere. However, a large portion of infrared energy will penetrate the atmosphere. Of course, atmospheric molecules will be receptive to and will emit energy (quanta) in the infrared portion of the electromagnetic spectrum. Absorption of appropriate quanta from the infrared will increase translation, vibration, rotation, bending, and flexing of the molecules themselves and will raise electrons to higher orbitals as in the Paschen and Brackett series. Excitation of electrons to higher orbitals results in an excited atom, and because of this, an excited molecule. In a deficit stream, energies will be emitted; i.e., returned to the stream. Translation, vibration, rotation, and flexing of molecules will decrease and electrons will drop to lower orbitals in the atoms. The radiation will not be visible but will be sensible; i.e., will be felt by the body. The atmosphere will warm or cool with this absorption or emission.

Figure 11-3, courtesy of Howard (1960), and adapted from Howard, Burch, and Williams (1956), shows a simulated solar spectrum absorption pattern and spectral absorptions in the infrared for seven selected gases. Note the nonabsorption or full transmissions, except for that of ozone (O<sub>3</sub>), carbon dioxide (CO<sub>2</sub>), and some water (H<sub>2</sub>O) in the 8- to 14-μ range (1,200 to 700 cm<sup>-1</sup>). A window is partially open.

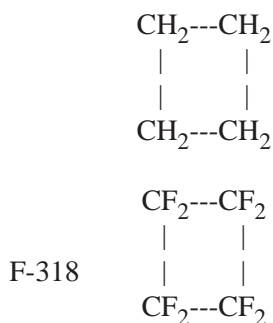
The known production of halogenated carbons and their eventual release or escape to the atmosphere is estimated to be less than 1 × 10<sup>-9</sup> by volume.

Goody and Yung (1989) estimate that F11 and F12 (CFCl<sub>3</sub> and CF<sub>2</sub>Cl<sub>2</sub>) amounts are a 1–2 × 10<sup>-10</sup> part of the atmosphere. MacCracken and Luther (1985) and Mitchell (1989) indicate energy absorption and emission by CFCl<sub>3</sub> and CF<sub>2</sub>Cl<sub>2</sub> in the neighborhood of 850 cm<sup>-1</sup>. Fessenden and Fessenden (1986) show the strong absorption by chloroform (the trihaloalkane, CHCl<sub>3</sub>) at about 750 cm<sup>-1</sup>. (See fig. 4-5.)

Trade names may be associated with specific halocarbons such as freon, genetron, and ucon. See Routh, Eyman, and Burton (1969). The main identifying atom here is fluorine (F), but any hydrocarbon may be used. Following are some examples where F in the designator stands for freon, and not necessarily fluorine as it does in the formulae:

F11; C Cl <sub>1</sub> F <sub>1</sub> :	F21; C H Cl <sub>2</sub> F:	F110; C <sub>2</sub> Cl <sub>6</sub>
F12; C Cl <sub>2</sub> F <sub>2</sub> :	F22; C H Cl F <sub>2</sub> :	F111; C <sub>2</sub> Cl <sub>5</sub> F
F13; C Cl <sub>3</sub> F <sub>3</sub> :	F23; C H F <sub>3</sub> :	F112; C <sub>2</sub> Cl <sub>4</sub> F <sub>2</sub>
F14; C	F <sub>4</sub> :	F113; C <sub>2</sub> Cl <sub>3</sub> F <sub>3</sub>
		F114; C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub>
		F115; C <sub>2</sub> Cl F <sub>5</sub>
		F116; C <sub>2</sub> F <sub>6</sub>

and cyclobutane base, C<sub>4</sub>H<sub>8</sub>,





In the above, the F coding is as follows: The units number gives the number of fluorine atoms in the molecule. The tens digit is the number of hydrogen atoms, plus one in the molecule. The hundreds digit gives the number of carbon atoms less one in the molecule (Rowland (1989)).

These halocarbons find use in refrigeration, aerosols, lubricants, electrical insulators, and in industrial plastics. Teflon, a remarkable compound, is a fluorinated and polymerized ethylene,  $C_2H_4$  ( $H_2C=CH_2$ ) as  $(CF_2=CF_2)_n$ , where  $n$  is a large number. It is a polymer of tetrafluoroethene. It is inert to most chemical reagents, has excellent insulating properties, maintains its lubricating properties over a wide temperature range ( $-50$  to  $300$  °C), and does not stick to most materials. Presumably this molecule will be sensitive to ultraviolet radiation.

Reference again is now made to figure 11-1 (Howard (1960)). No halocarbon spectrum is shown in that figure. This is not surprising, for increased production of halocarbons had not as yet reached present-day accumulations and importance. Note the partially open “window” from about  $1,000$  to  $700$   $cm^{-1}$ . Chloroform, the trihalomethane, absorbs and emits energy at about  $750$   $cm^{-1}$  (Fessenden and Fessenden (1986)). MacCracken and Luther (1985) and Mitchell (1989) indicate absorption and emission close to that of chloroform. Goody and Yung (1989) indicate absorption and emission for  $CCl_3F$  and  $CCl_2F_2$  (F11 and F12) at  $8.7$ ,  $9.1$ ,  $9.2$ ,  $10.9$ , and  $11.8$   $\mu$  ( $\approx 1,150$  to  $850$   $cm^{-1}$ ). The absorption of these three halocarbons further close the window partially closed by ozone ( $O_3$ ), carbon dioxide ( $CO_2$ ), and water vapor ( $H_2O$ ). A considerable part of the window still remains open; however, increasing halocarbon types and amounts may close this infrared window still more. (See fig. 4-5.)

The following point is stressed by Rowland (1991) and others. Carbon dioxide ( $CO_2$ ) fairly well saturates those frequencies of the infrared spectrum with which it is associated. The addition of another carbon dioxide ( $CO_2$ ) molecule does not add as much to the absorption and emission potential in the overall sense as does a molecule of methane ( $CH_4$ ) or a halocarbon (halohydrocarbon), CFC or HFC. The incremental absorption or emission in a transparent window of a methane ( $CH_4$ ) or a CFC (HFC) molecule will be, respectively, 20 or 10,000 times as effective as a carbon dioxide ( $CO_2$ ) molecule (Ramanathan et al. (1985) and Rowland (1989, 1990)). Since these will be effective in the present partially open window, this window will close a little more. Loss of infrared radiation from the atmosphere will be further reduced. The frequencies are those associated with vibration (stretching) frequencies of the molecules.

Energies associated with translation rotation, spin, and flexing will not be as noticeable in longer wavelengths of the microwave and radio regions. Water absorption and emission dominate these regions.

### 11.13.6 Montreal Protocol

The Montreal protocol includes the following:

(1) The Conference of Plenipotentiaries on the Protocol on Chlorofluorocarbons to the Vienna Convention for the Protection of the Ozone Layer was convened by the Executive Director of the United Nations Environment Program (UNEP) pursuant to the decision 13/18 adopted by the Governing Council of UNEP May 1985.

(2) The conference met at the Headquarters of the Civil Aviation Organization, Montreal with the kind support of the Government of Canada, from September 14–16, 1987.

(3) All States were invited to participate in the conference; fifty-five states were represented. Six observers also attended, as well as representatives of the European community. Observers from other units of the United Nations attended also. The protocol was adopted by the committee of the whole. The protocol was available and at the United Nations for signature from September 1987 to September 1988—1 year.

(4) In essence, the protocol attempts to decrease the production, sale, and use of the halocarbons and to develop suitable alternatives. The halocarbons under discussion were  $\text{CFCl}_3$  (CFC-11),  $\text{CF}_2\text{Cl}_2$  (CFC-12),  $\text{C}_2\text{F}_3\text{Cl}_3$  (CFC-113),  $\text{C}_2\text{F}_4\text{Cl}_2$  (CFC-114),  $\text{C}_2\text{F}_5\text{Cl}$  (CFC-115), and the group  $\text{CF}_2\text{BrCl}$ ,  $\text{CF}_3\text{Br}$ , and  $\text{C}_2\text{F}_4\text{Br}_2$  (halon-2402).

### 11.13.7 Alternative Fluorocarbon Environmental Acceptability Study

**11.13.7.1 General.** The last paragraph of subsection 11.13.6 indicates a need to study potential alternatives to the fully halogenated hydrocarbons. Under the United Nations, a scientific assessment of stratospheric ozone was initiated. One report in two volumes in 1989, volume II, is an appendix of this assessment. It is the Alternative Fluorocarbon Environmental Acceptability Study (AFEAS) already mentioned in section 11.10 on ozone. This assessment is extensive.

The AFEAS evaluates all relevant current scientific information to help determine the environmental acceptability of alternative fluorocarbons with special emphasis on the following:

- The potential of the compounds to affect stratospheric ozone.
- Their potential to affect tropospheric ozone.
- Their potential to contribute to model calculated global warming.
- The atmospheric degradation mechanism of the compounds, in order to identify their products and hence potential environmental effects of the decomposition products.

The halocarbons (fully halogenated carbons), CFCs, are the most stable gases introduced into the atmosphere. Partially halogenated carbons are less stable and are the subjects of the study; these are the HCFCs which were elected for study because they are produced and are available commercially by essentially the same techniques used to produce the CFCs.

It is important to state here that there may be other compounds which could replace CFCs and HCFCs. But this requires research, expenditure of time and funds, and testing to ascertain their environmental acceptance. Thus, decisions were made to study HCFCs as these were available.

Briefly, the study emphasized the evaluation of the following HFCs:

HCFC 123	$\text{CCl}_2\text{HCF}_3$
HCFC 141b	$\text{CCl}_2\text{FCH}_3$
HCFC 142b	$\text{CClF}_2\text{CH}_3$
HCFC 22	$\text{CClF}_2\text{H}$
HCFC 124	$\text{CClFHCFC}_3$
HCFC 134a	$\text{CF}_3\text{CFH}_2$
HCFC 152a	$\text{CF}_2\text{HCH}_3$
HFC 125	$\text{CF}_3\text{CF}_2\text{H}$

The AFEAS was conducted by interested and independent scientists. It was organized and sponsored by 15 CFC producers around the world as a part of cooperative industry efforts to study the safety and environmental acceptability of the CFC alternatives.

In general, the study gives information on the following subjects which form the various sections:

- The physical property alternatives to fully halogenated carbons.
- Reaction rate constants.

- Absorption cross sections.
- Tropospheric (OH) and HCFC/HFC lifetimes.
- Degradation mechanisms.
- Liquid phase processes.
- Ozone depletion potentials.
- Halocarbon warming potentials.
- Impact of photochemical oxidants including tropospheric ozone.
- Natural sources.
- Biological and health effects.

This AFEAS is recommended reading for those interested in the potential environmental acceptability of products designed to replace fully halogenated carbons. This study may also be found in section B of NASA Reference Publication 1242 by Watson et al. (1990). See also Prather (1989) for more information on the halocarbon half-lives.

**11.13.7.2 Executive Summary of the Scientific Assessment of Stratospheric Ozone: 1989.** The Executive Summary of the Scientific Assessment of Stratospheric Ozone, 1989, is quoted below:

*“Recent Findings: The past few years have been remarkable insofar as stratospheric ozone science is concerned. There have been highly significant advances in the understanding of the impact of human activities on the Earth’s protective ozone layer. Since the last international scientific review (1985), there are four major findings that each heighten the concern that chlorine- and bromine-containing chemicals can lead to a significant depletion of stratospheric ozone:*

- *Antarctic Ozone Hole: The weight of scientific evidence strongly indicates that chlorinated (largely man-made) and brominated chemicals are primarily responsible for the recently discovered substantial decreases of stratospheric ozone over Antarctica in springtime.*
- *Perturbed Arctic Chemistry: While at present there is no ozone loss over the Arctic comparable to that over the Antarctic, the same potentially ozone-destroying processes have been identified in the Arctic stratosphere. The degree of any future ozone depletion will likely depend on the particular meteorology of each Arctic winter and future atmospheric levels of chlorine and bromine.*
- *Long-Term Ozone Decreases: The analysis of the total-column ozone data from ground-based Dobson instruments show measurable downward trends from 1969 to 1988 of 3 to 5% (i.e., 1.8–2.7% per decade) in the Northern Hemisphere (30–64 °N Latitudes) in the winter months that cannot be attributed to known natural processes.*
- *Model Limitations: These findings have led to the recognition of major gaps in theoretical models used for assessment studies. Assessment models do not simulate adequately polar stratospheric cloud (PSC) chemistry or polar meteorology. The impact of these shortcomings for the prediction of ozone depletion at lower latitudes is uncertain.*

*Supporting Evidence and Other Results:*

- *Polar Ozone:*
  - *There has been a large, rapid, and unexpected decrease in the abundance of springtime Antarctic ozone over the last decade.*

- *The weight of scientific evidence strongly indicates that man-made chlorine and bromine compounds are primarily responsible for the ozone loss in Antarctica.*
- *While the onset of the Antarctic ozone hole is linked to the recent growth in the atmospheric abundance of chlorofluorocarbons (CFCs) and to a lesser extent bromine compounds, many of its features are influenced by meteorological conditions.*
- *The chemical composition of the Arctic stratosphere was found to be highly perturbed.*
- *Global Trends:*
  - *Several recent analyses of total column ozone data support the conclusion of the 1988 International Ozone Trends Panel (OTP) that there is a downward trend in ozone during winter at mid-to-high latitudes in the Northern Hemisphere over the past two decades.*
  - *Substantial uncertainties remain in defining changes in the vertical distribution of ozone.*
  - *Recent measurements suggest that the rate of growth in atmospheric methane has slowed somewhat.*
- *Theoretical Predictions:*
  - *Theoretical models do explain many of the general features of the atmosphere, but new limitations have been recognized.*
  - *Current understanding predicts that, if substantial emissions of halocarbons continue, the atmospheric abundances of chlorine and bromine will increase and, as a result, significant ozone decreases, even outside of Antarctica, are highly likely in the future.*
- *Halocarbon Ozone Depletion and Global Warming Potentials (ODPs and GWPs):*
  - *The impact on stratospheric ozone of the halocarbons (HCFCs and HFCs) that are proposed as substitutes for the CFCs depends upon their chemical removal processes in the lower atmosphere (troposphere).*

*Because they contain hydrogen atoms, the HCFCs and HFCs are primarily removed in the troposphere by reaction with the hydroxyl radicals ( $\bullet\text{OH}$ ). Although the photochemical theory of tropospheric  $\bullet\text{OH}$  is well developed, it has not been validated experimentally, and the global OH distributions are based on models. Furthermore, the global abundance of OH is influenced by tropospheric composition, which is changing.*

*The various estimates of the lifetimes of HCFCs and HFCs in the troposphere have an uncertainty of  $\pm 50\%$ . This contributes an important source of uncertainty in the prediction of the ODPs and GWPs of the HCFCs and HFCs. The fate of the degradation products of the HCFCs and HFCs and their environmental consequences are inferred from data on analogous compounds and hence the specific degradation processes require further study.*

- *The values of the ODPs for the HCFCs are significantly lower than those for the CFCs.*

*Theoretical predictions performed by different groups using a variety of models have calculated similar, but not identical, values for the ODPs of the HCFCs, as indicated in Table 1 below.*

*None of the models used for calculating the ODPs are able to simulate the chemical and dynamical processes causing the Antarctic ozone hole. However, relative to CFC 11, the local Antarctic ODPs of HCFCs 22, 142b, and 124 will be larger, perhaps as much as a factor of two or three times greater than those derived from model calculations that do not include heterogeneous chemistry and that cannot simulate polar dynamical processes. The ramifications of polar ozone depletion for ODPs is not currently clear.*

*– The steady-state values of the halocarbon GWPs of the HCFCs and HFCs are lower than those of the CFCs.”*

### 11.13.8 Atmospheric Halocarbon Lifetimes

Lifetimes of halocarbons in the atmosphere are dependent upon:

- Thermal decomposition.
- Photolysis.
- Bimolecular reactions with atmospheric species. The hydroxyl free radicals ( $\bullet\text{OH}$ ) are important here.

Derwent, Volz-Thomas, and Prather (1989) are authors of Tropospheric (OH) and HCFC/HFC lifetimes.

As indicated by gas-phase chemical lifetimes of the troposphere, thermal decomposition is important for the peroxy nitrates,  $\text{ROONO}_2$ , and  $\text{RC(O)OONO}_2$ . In colder regions of the troposphere, the acylperoxy nitrates,  $\text{RC(O)OONO}_2$ , have longer lifetimes than 1 yr. These are considered to be stable. On the other hand, haloalkylperoxy nitrates ( $\text{ROONO}_2$ ) are short lived, usually <1 day. The estimated lifetimes vary considerably and the reader is referred to this assessment for details.

Lifetimes of hydrocarbon are directly proportional to the number of hydrogen atoms that have been replaced by halogens. The more free radicals ( $\bullet\text{OH}$ ) are available, the greater is the number of reactions and the degradation of the molecules. The estimated lifetime of methane ( $\text{CH}_4$ ) is 10 yr. In this report, the estimated lifetime is 9.4 yr. No estimate of the expected lifetime of the ( $\bullet\text{OH}$ ) radical is presented. It is short, very short.

Table 11-9 provides the maximum relative chlorine loading potential (CLP) for examined CFCs, HCFCs, HFCs, and other chlorinated halocarbon-based reference species lifetimes chosen to be compatible with available atmospheric measurements and modeling studies. (This is taken with permission from the WMO Report No. 20, Vol. 1, Chapter 4, “Halocarbon Ozone Depletion and Global Warming Potentials.” Coordinators were Cox (U.K.) and Wuebbles (U.S.A.) with 16 other contributors.) These lifetimes are not measured in totality, of course, and are based on scenarios developed in chapter 3 of the document “Scientific Assessment of Stratospheric Ozone–1989.” See bibliography under United Nations.

Chlorine loading potentials are defined in the above assessment study as the maximum chlorine transported across the tropopause per mass emitted relative to the same for CFC-11. Note that the values (CLP) for CFC-11 is 1 as it is also in  $\text{CCl}_4$ . It is proportional to lifetime and the number of chlorine atoms per molecule. It is inversely proportional to molecular weight. See table A-11-1 for atomic weights which can be used to assess the molecular weights.

Table 11-9. Maximum relative CLP for examined CFCs, HCFCs, HFCs, and other chlorinated halocarbons based on reference species lifetimes chosen to be compatible with available atmospheric measurements and modeling studies (Cox and Wuebbles (1989b)).

Species	Reference* Lifetime (yr)	Chlorine Loading Potentials**
CFC-11	60	1
CFC-12	120	1.5
CFC-113	90	1.11
CFC-114	200	1.8
CFC-115	400	2
HCFC-22	15.3	0.14
HCFC-123	1.6	0.016
HCFC-124	6.6	0.04
HFC-125	28.1	0
HFC-134a	15.5	0
HCFC-141b	7.8	0.1
HCFC-142b	19.1	0.14
HFC-143a	41	0
HFC-152a	1.7	0
CCl <sub>4</sub>	50	1
CH <sub>3</sub> CCl <sub>3</sub>	6.3	0.11

\* Lifetimes (e-folding time) are based on estimates used in scenario development in chapter 3 summary for the CFCs and from the analysis in Ozone Depletion section for the HCFCs and HFCs.

\*\*CLP is defined as the maximum chlorine transported across the tropopause per mass emitted relative to the same for CFC-11. It is proportional to lifetime and the number of chlorine atoms per molecule. It is inversely proportional to molecular weight.

CLPs chosen as chlorine seems to undergo special processing and dynamics within the polar winter vortex. These specialties are discussed in section 11.10 (the section on ozone), in part in the subjects of heterogenous chemistry and the polar stratospheric clouds (PSCs).

### 11.13.9 Production

Chemical and Engineering News (C&EN) of the American Chemical Society (ACS) publishes facts and figures in worldwide chemical production. The June 24, 1991, issue shows a worldwide production of the chlorofluorocarbons (formulae F-22, F-12, and F-11) over the past 10 yr. Their source is the International Trade Commission, and 1990 figures are given as preliminary. The letters "na" indicate "not available." Units have been changed from millions of pounds to metric tons, where a million pounds is set equal to 453.6 metric or long tons. Table 11-10 shows the results. Results indicate that for the decade 1980–1990 overall production change in percent has been 3, –3, and –2 percent, respectively. Production changes in 1989–1990 show a production drop of 11, 47, and 30 percent respectively. The compounds F-22, F-12, and F-11 are, respectively, chlorodifluoromethane (ClF<sub>2</sub>CH) (F-22), dichlorodifluoromethane (Cl<sub>2</sub>F<sub>2</sub>C) (F-12), and trichlorofluoromethane (Cl<sub>3</sub>FC) (F-11). All other fluorinated hydrocarbon production is not available for 1980–1989. Presumably, the protocol limiting production is beginning to be effective. Manzer (1990) estimates 1 metric ton consumption in 1988 while C&EN tables below indicate 0.6 metric ton. Information sources apparently differ. Manzer (op. cit.) provides a concise review of the

Table 11-10. Chlorofluorocarbon production to the nearest k t (modified from ACS, C&EN (1991)).

	1990*	1989	1988	1987	1986	1985	1984	1983
F-22	138	148	150	125	123	107	115	107
F-12	95	178	188	152	146	137	153	132
F-11	66	88	113	90	92	80	84	98
Other**	na	175	172	161	156	139	153	127
Total	na	596	624	528	517	463	505	464

	1982	1981	1980	Percent Annual Change		
				1989-1990	1980-1990	1979-1989
F-22	79	114	103	-11	3	4
F-12	117	147	134	-47	-3	3
F-11	64	74	72	-30	-2	1
Other	na	na	na	na	na	na
Total	na	na	na	na	na	na

\* Preliminary

\*\* Includes all other fluorohalogenated hydrocarbons

NA: Not Available. (Source: C&EN, June 24, 1991, with attribution to International Trade Commission.)

halocarbons, CFCs, and HCFCs, and the proposed Montreal protocol for a reduction of 50 percent in their commercial production. He then describes the work being done to replace the decreased production with alternatives. As Manzer indicates, issues in preparing these alternatives are those of toxicity, flammability and explosiveness, cost, environmental impact, and physical properties.

Inevitably, it seems that more of these alternative gases will be released to the atmosphere. These may have other effects than just the initial catalytic destruction of ozone. They will also affect radiation characteristics of the atmosphere, particularly in the infrared spectral region.

## 11.14 Radon

### 11.14.1 Radon—Continental

Israel (1951) discusses radon in his paper on atmospheric radioactivity. His table 1 presents symbols, ray type emanation, half-lives, and disintegration constants for 15 radioactive substances in the atmosphere. One of these is radon. He indicates that 1 L of air over continents and over oceans contain  $\approx$ 2,000 atoms and 30 atoms, respectively. He deduces that continental regions are the primary source.

Radon ( $^{222}\text{Rn}$ ) evolves as a gaseous emanation from the radioactive uranium decay. All resulting isotopes are radioactive, except the final stage isotope. Radon becomes extremely dangerous in its disintegration products; the alpha rays damage cells by living cell ionization and the solid polonium ( $^{210}\text{Po}$ ) remains for further disintegration. Radon's half-life of 3.825 days allows it to be fairly well detected and measured. The gaseous emanations radon (Rn), thoron (Tn), and actinon (An) are continuously emitted from rocks and soil into air entrapped in the spaces among the soil particles or into the air at the Earth's surface. Falling surface pressures will allow the exhalation of soil air, including these gaseous radioactive elements. The semidiurnal and principally the diurnal pressure changes pump these and other gases from the Earth except when the Earth is frozen. Likewise, warm and cold front passages can exert pump action. There, these gases will be further transported throughout the troposphere. Some will dispute the effectiveness of the pumping action. The half-lives of Tn and An of 54.5 and 3.92 s, respectively,

almost assures that these will not reach very far. As the half-life of Rn is 3.825 days, it can reach the tropopause before disintegrating. Emanations from any radioactive gas in the atmosphere can ionize other gases and induce formation of aerosols.

Though man has evolved in this environment, Rn poses a real threat to human life wherever man works in partially closed environments, such as in mines or in closed, unventilated spaces, such as may be found in offices and homes in single floor or double floor buildings. Emanations from soil may enter basements through cracks in floors or walls, or even from the floors or walls themselves. Wherever the uranium series exists in sediment, a continuous radon source exists. The closer this layer is to the Earth's surface, the more readily radon percolates upwards through the soil. It is one of the largest and heaviest elements in the molecular sense and is relatively inactive chemically. See Sanderson (1960).

Radon exhibits a diurnal curve showing a single period with a maximum in the early morning, according to Israel (op. cit.), citing the work of other investigators. Landsberg (1976) was an early writer on home climates. Cohen and Gromicko (1988) describe the variation of Rn levels in U.S. homes with various factors. Though no amounts are specified in their abstract, the following is the abstract used with permission:

*“A program combining 70,000 purchased and 3,500 random selection-no charge measurements with extensive questionnaires is described. Methods for reducing biases in purchased measurements have been reasonably successful. Distributions are roughly lognormal with  $\mu=3.0$  but with an excess of very high measurements. Winter and spring-fall measurements average about 60 percent and 40 percent, respectively, higher than summer measurements. Basements average 2.5 times higher radon levels than upper floors. Tightening of homes since 1974 has increased radon levels by less than 10 percent, but well-weatherized houses have ~40 percent higher levels than poorly weatherized houses. Open windows reduce levels by a factor of about 2.5. Low-cost newer houses have much lower levels than more expensive newer houses, but among older houses this is reversed. Low income families have substantially lower radon levels than average. There is little variation with education level. Nonsmokers have higher radon levels than smokers, but this seems to apply mainly to living rooms and dining rooms. Suburban houses have higher levels than urban, and rural houses have still higher levels. Owner-occupied houses have much higher levels than rented houses. Variations of radon levels with weatherization do not seem to be due to cost factors. A strategy for locating areas with high mean radon levels is described.”*

The measuring unit of radiation of this type is the Curie (Ci) and the usual amounts are measured in picocuries per liter (pCi/L). Since the 1950s, the University of Chicago's Argonne National Laboratory has recorded radon amounts at various height levels. Annual reports on the National and International situation are issued by the U.S. Department of Energy. Three of these are recent publications in 1987, 1988, and 1990 entitled “Radon.” These are published by the Office of Health and Environmental Research in their Technical Report Series. Diminution of radon with height from the surface indicates turbulent mixing processes.

Warneck (1988) (citing Wexler et al. (1956)), Machta (1974), and Wilkening (1970) display radon activity in nCi m<sup>-3</sup> against altitude. The graph indicates a gradual but irregular decrease of activity from a surface value of ≈0.1 nCi m<sup>-3</sup> to a value near 0.01 nCi m<sup>-3</sup> at ≈8 km. The impact of such research requires that all house or building engineering and construction should consider the problem of adequate ventilation to keep radon from accumulating in homes and work places. In most cases, homeowners can seal all cracks in basement floors and walls below ground level. Additionally, homeowners can ventilate their homes by opening doors and windows.

Marks (1988) authors “Radon Epidemiology” as a guide to the literature on radon. This is an up-to-date survey. Population clusters generally considered by research are those deemed most likely to be affected. Two



main groups emerge—miners and home dwellers. Both involve nearness to source and confinement. Both exist worldwide and no particular nation or state is excepted. However, there are locales which are nearer than others to sources. Survey and research can help to locate such troublesome areas. Known regions of radioactive subsurface materials certainly have a high potential for radon production. The two best procedures to attenuate the dangers are isolation procedures and better than normal ventilation. The first procedure provides protective shields while the second reduces the radioactive gas concentrations. In homes with concrete slabs, it is necessary to have adequate ventilation and maintenance. In isolation procedures such as the use of concrete slabs, concrete or cement brick walls, or even clay brick, it would be wise to determine the makeup of concrete, clay, or tailings from mining areas. These could be excessive radon producers. Phosphate rock is often a radon producer, for portions of the uranium series may be mixed in prior to rock formation. Such radioactive materials should not be used, but if used, other adequate isolation measures should be applied and adequate ventilation should be supplied. In mines, more than adequate forced ventilation is suggested and the use of masks and other protective devices are necessary. Use of the continual forced ventilation also will attenuate deadly carbon gases, such as CO and CO<sub>2</sub>, and alkanes, such as methane and ethane. In sufficient quantity, all four will asphyxiate by reducing oxygen uptake in the lungs while alkanes are explosive. Marks (op. cit.) provides many references and definitions used in this particular discipline.

Problems associated with radon have not elicited much action in the past. It is low in physical amounts though quite pervasive in all regions. Radon's effect, slow in appearance, is increased by its tendency, and the tendency of its ionized daughter products, to gather on dust and smoke particles. Greatly increased cigarette use provides a multitude of such condensation nuclei in gases and smoke inhaled and exhaled. These particles with their charges of radon and its progeny will collect on clothing, drapery, and furniture and to some extent on the walls of homes, offices, and manufacturing plants. These are probably reasons why the gas amount is a minimum in smokers' homes; i.e., deposition has occurred. These deposits readily adhere to the walls of respiratory organs. But the development of related respiratory organ cancer is so slow in appearance in the lungs that little thought has been given to this problem. It has taken a period of three human generations for the significance to become unmistakable. Puskin and Nelson (1989) discuss the Environmental Protection Agency (EPA) of the U.S. Government present perspective on risks from residential radon exposure.

Table 11-11 duplicates table 1 of Puskin and Nelson (op. cit.). This table provides estimates and uncertainties of these estimates of radon risk determined from epidemiological studies of underground miners. WLMs are "working level months." Their reference numbers 2 through 8 apply to (2) Thomas, McNeill, and Dougherty (1988), (3) U.S. NRC, National Academy of Sciences (1988), (4) Sevc, Kunz, Tomasek, et al. (1988), (5) Muller (1984), (6) Howe, Nair, Newcombe, et al. (1986), (7) Radford and Renard (1984), and (8) Morrison, Semenciw, Mao, and Wigle (1988).

Table 11-12, table II (distribution I) of Puskin and Nelson (op. cit.), presents on a national (U.S.A.) basis a distribution of houses and radon-induced cancer risk with respect to radon concentration. These data are based on the log normal distribution of radon levels estimated by Nero et al. (1986). The geometric mean (GM) = 0.9 pCi/L, while the geometric standard deviation (GSD) = 2.8 pCi/L). To use these last two measures the reader must first determine bounds in the logarithmic field and then transform these into actual pCi/L measures. Puskin and Nelson (op. cit.) in their table III (distribution II), shown here as table 11-13, indicate a somewhat higher risk; the GM is the same, 0.9 pCi/L, but the GSD is 3.2 pCi/L. This broadened distribution implies a lowering of measurements on the low side, but the portion of houses above the U.S. EPA-recommended level of 4 pCi/L for remedial action is greater. Additional research work is expected to develop a broader and more secure basis for action. For the moment, the last columns of tables 11-12 and 11-13 may be compared. In table 11-13, assuming that risk of radon-induced lung cancer ranges downward from 100 for any amount of radon, 86 percent of that risk is attributed to houses with a radon level >1 pCi/L. Exceeding the 4 pCi/L level, the portion of houses with this level is  $1 \times 10^{-1}$  (10 percent), the average radon level is 8 pCi/L, and the percent of risk is 44. This does not mean that the risk is less but that while

Table 11-11. Estimates of radon risk determined from epidemiological studies of underground miners (with permission, Air Poll. Control Assoc., presently Air and Waste Management Association, courtesy of Puskin and Nelson (1989)).

Study Population	Exposure (WLM)	Average Coefficient (%/WLM)	Relative Risk Reference
U.S. uranium miners	1,180	0.45	2
		0.6	3
Czech uranium miners	313	1.92	2
		1.5	4
Ontario uranium miners	40-90	0.15-1.3	5
		1.4	3
Saskatchewan uranium miners	20.2	3.28	6
		2.6	3
Malmberget iron miners	81.4	3.6	7
		1.4	3
Newfoundland fluorspar miners	382.8	0.9	8

Table 11-12. Distribution of houses and radon-induced lung cancer risk with respect to radon concentration—distribution I (with permission, Air Poll. Control Assoc., presently Air and Waste Management Association, courtesy of Puskin and Nelson (1989)).

Radon Level X (pCi/L)	Portion of Houses Above X*	Average Radon Level in Houses Above X* (pCi/L)	Percent of Risk Associated With Houses Above X*
0	$1.0 \times 10^0$	1.5	100
1	$4.6 \times 10^{-1}$	2.7	82
2	$2.2 \times 10^{-1}$	4.2	60
4	$7.4 \times 10^{-2}$	7.0	33
10	$9.7 \times 10^{-3}$	15	9
20	$1.3 \times 10^{-3}$	28	2
50	$4.8 \times 10^{-5}$	65	0.2
100	$2.4 \times 10^{-6}$	130	0.01

\*Based on lognormal distribution of radon levels estimated by Nero et al. (GM = 0.9 pCi/L, GSD = 2.8).

the amount of radon has increased by four, the number of houses has decreased down to 10 percent, and the percent risk in the total picture has decreased to 44. Similarly, few houses have a radon level >100 pCi/L. The average for this group is 130 pCi/L. Though, with a high individual risk, the national percent risk is 0.1. Problems always exist in measurements of any object or material. Estimates of characteristics of the objects are made either or both qualitatively and quantitatively. These are influenced directly by the measurement modes.

The Environmental Protection Agency in “A Citizen’s Guide to Radon” (1986) recommends screening tests and techniques. There are several companies which make and sell radon detection kits. Some of these are charcoal absorption devices which are exposed from 2 to 7 days. Others may be alpha track detectors where the time exposure is several weeks. Companies will process the returned kits and provide estimates of radon amounts detected. Bierma, Croke, and Swartzman (1989) study and report on the accuracy and precision of current (1989) home radon

Table 11-13. Distribution of houses and radon-induced lung cancer risk with respect to radon concentration—distribution II (with permission, Air Poll. Control Assoc., presently Air and Waste Management Association, courtesy of Puskin and Nelson (1989)).

Radon Level X (pCi/L)	Portion of Houses Above X*	Average Radon Level in Houses Above X* (pCi/L)	Percent of Risk Associated With Houses Above X*
0	$1.0 \times 10^0$	1.8	100
1	$4.6 \times 10^{-1}$	3.3	86
2	$2.5 \times 10^{-1}$	4.9	68
4	$1.0 \times 10^{-1}$	8	44
10	$1.9 \times 10^{-2}$	17	17
20	$3.8 \times 10^{-3}$	31	6
50	$2.8 \times 10^{-4}$	70	0.9
100	$2.6 \times 10^{-5}$	130	0.1

\*Based on lognormal distribution of radon levels characterized by GM = 0.9 pCi/L, GSD = 3.2.

monitoring and the effectiveness of the U.S. EPA monitoring guidelines. At the time of publication, their assessment is that about one-third of the homes with low amounts will indicate too low amounts while few homes with large amounts will be incorrectly classified as having lower amounts. See also Nazaroff and Nero (1988).

Puskin and Nelson (op. cit.), using risk equations, provide information on the costs to reduce the radon (Rn) loads to  $\approx 1.5$  pCi/h. As radon is pervasive, costs to lower loads below 1.5 pCi/h would be prohibitive. The EPA suggests mitigation procedures when the loads exceed 4 pCi/h. The higher the initial radon loads the greater is the cost of reduction to the 1.5 pCi/L level. But the saving of lives (the reduction of lung cancer) is considerable. Apparently, there is a synergism with smoking and radon. Puskin and Nelson (op. cit.) indicate that  $\approx 85$  percent of all lung cancer deaths attributed to radon may be associated with smoking. So even if the radon loads in homes and offices can be lessened, cessation of smoking would be quite helpful.

The discussion above establishes the premise that smoking and the incidence of radon (Rn) contribute strongly to lung cancer inducement. As in any discipline, even if the facts seem to require no further support, premises such as this are subjected to severe scrutiny. This scrutiny is not intended to deny the premise but to establish its validity. Hypotheses are established and tested. In the statistical sense, hypotheses always can be rejected or not rejected.

A hypothesis never accepted for continual attempts will be made to reject. Thus, any protocol or protocols developed must provide for adequate testing of the premise. Quality assurance and control procedures should be an overall integral part of protocols design, the protocols themselves, and the implementation of the protocols. This includes management. Now follows the summary of a meeting (US DOE (1989)) to attempt, on an international scale, an epidemiological study of the important interaction among climates, the atmospheric trace gas, radon (Rn), smoking, and people. This is limited to residential dwellings, but the procedure is applicable elsewhere.

*“Under the auspices of the U.S. Department of Energy (DOE) and the Commission on the European Community (CEC) a Workshop was convened of all investigators with active projects on residential radon epidemiology known to the organizers. The meeting was held in Alexandria, VA, from July 24–26, 1989 and it was attended by 18 active participants from 10 countries representing epidemiological studies recently completed, currently on-going, or planned for the immediate*

*future. The studies reported on are located in the United States, Canada, Norway, Sweden, Finland, the United Kingdom, Belgium, the Federal Republic of Germany, France, and the Peoples' Republic of China. The meeting was also attended by 17 observers from the U.S. DOE, the CEC, the U.S. Environmental Protection Agency (EPA), the U.S. Public Health Service, representatives from the Health Agencies of the States of California, Minnesota and New Jersey, the International Atomic Energy Agency (IAEA) and the International Agency for Cancer Research (IARC). The discussions were focused on issues of lifetime radon exposure assessment, design considerations for epidemiological studies, problems of statistical power and analysis of study data, including the possibility of pooling data from different studies for increased power. Another issue which was discussed was the relationship between the needs of policy makers and the capacity of epidemiological investigations to satisfy these needs.*

*The participants agreed on several specific recommendations concerning the measurement of exposures to residential radon and to cigarette smoking. The interaction between cigarette smoking and radon exposure is important to assess. It was also agreed that epidemiological studies should be designed to obtain exposure-effect relationships. Such studies will need to be based on large populations for adequate power. It was concluded that pooling of the results of different studies was essential, and that coordination of study designs and facilitation of mechanisms for pooling of individual data should be pursued. Both the public and public policy makers would benefit from a greater consensus on radon science and on the magnitude of the risk to public health of current radon exposures. Public information documents and radon mitigation guidelines are improved by careful review by scientists and by state and local officials and others who respond to the public.*

*The participants in the Workshop agreed that a future Workshop should be devoted to an aggregation or even a formal quality-weighted meta-analysis of residential radon epidemiology studies published so far. A consensus evaluation of this type would tend to reduce the uncertainty about the magnitude of the lung cancer risk associated with residential radon exposures. It was also recommended that a mechanism be set up to facilitate and encourage pooling of data from different studies now on-going or planned. This mechanism should address the development of rules and protocol requirements.”*

#### **11.14.2 Radon—Compounds**

Radon is the largest in physical size of the noble or essentially inert gases. See Sanderson (1960). The other five in terms of structure and size are neon (Ne), argon (Ar), helium (He), krypton (Kr), and xenon (Xe). Only radon is naturally radioactive, but radioactive isotopes of the others may exist or be synthesized. Compounds with krypton (Kr), xenon (Xe), and radon (Rn) have been synthesized with the halogens F, Cl, Br, and I. Intermediate halogenated compounds are often used in this process. See Bartlett's 1962 work published in the *Proc. of the Chem. Soc.* (Fields, Stein, and Zirin (1962) and Stein (1984)). Stein (1984) indicates that xenon (Xe) forms the oxide  $\text{XeO}_3$ , attributing this to works of Malm and Appleman (1967) and Bartlett and Sladky (1973). He also indicates that Avrorin et al. (1974, 1981) synthesized radon fluorides and water-soluble radon oxide ( $\text{RnO}_3$ ). Radon can be released to the atmosphere upon dissolution of halides and oxides. Whether these fluorides and oxides exist naturally is not known by the writer but there is no reason to say they do not.

#### **11.14.3 Radon—Hydrospheric**

In the very first paragraph of this subsection, reference was made to Israel (1951). He indicates that more radon (Rn) is measured over continents than over water. Presumably this is so because radon (Rn) and other noble

gases, as well as many other gases, are soluble in water. Hydration occurs and even formation of respective gas clathrates may ensue. Either of these hydration phenomena would tend to isolate or hold the gas(es). Thus, though the same processes release radon (Rn) through lake bottoms, water aquifers, and oceanic lithospheric or sediment covers, retention of the gas by water will keep the atmospheric content of radon (Rn) lower over water and wet soil than over dry land.

However, the larger amounts of radon (Rn) in well and aquifer waters may present health problems in drinking water. According to Stein (1984), there seems to be no reason that radon (Rn) forms compounds held in water as Avrorin et al. (1974) assumed but that the radon is trapped in precipitates, suspended solids, and sediments. Another factor, from a climatic point of view, is that as with all physical and chemical processes, trapping and release of gases is, in part, temperature dependent. Stein (1984) further provides a reaction of a noble gas fluoride with water to release the gas as oxygen and hydrogen fluoride as exemplified by



To cover one more point for the reader, radon (Rn), with a half-life of 3.85 days, in any compound will, upon disintegration, release alpha radiation and change the compound. Subsequent changes with release of radiation will eventually lead to a stable isotope such as lead. The impression of the author is that the radon content of water may be six times more than that in air. To this extent, some steps may be taken to filter the radon from air as well as from water.

As a radiative gas (as compared to a radioactive gas), Rn (radon) may not participate very much in radiation features of the atmosphere, except in a secondary role of creating situations conducive to aerosol formation which will have their effects on infrared absorption, retention, and emission. As a trace gas, however, this gas is necessarily discussed.

The discussion above is not meant to produce panic alarm for people. Rather, the pervasive danger is pointed out.

#### 11.14.4 Summary

Nero et al. (1990) present a current update on indoor radon, on its decay products, its concentrations, causes, and control strategies. They review the past 15 yr of meetings and research. Some of the problems are those in providing reliable estimates of average indoor concentrations. This report is suggested reading for those needing more detail than is provided in this section.

### 11.15 Trifluoromethyl Sulfur Pentafluoride

Sturgess, Walington, Hurley, et al. (2000) report on the detection of a compound previously unreported in the atmosphere—trifluoromethyl sulfur pentafluoride ( $\text{SF}_5\text{CF}_3$ ). They report that measurements of the infrared absorption cross section show  $\text{SF}_5\text{CF}_3$  to have a radiative forcing of 0.57 with per square meter per parts per billion. This forcing is larger than that of any other gas found in the atmosphere to date. Apparently it has increased from a zero amount in the 1960s to  $\approx 0.12$  parts per billion in 1998. It is increasing at  $\approx 0.008$  parts per trillion per year. Apparently it has a 1,000-yr life in the atmosphere. Also, it appears to have GWP of 22,000 relative to  $\text{O}_2$  over a 100-yr time horizon. This is a new entrant into the known trace gas ensemble of the atmosphere. It needs to be watched and studied.



## 12. AEROSOLS

### 12.1 Introduction

Graham (1861) distinguished between two classes of solutes which he named crystalloids and colloids (Getman and Daniels (1931)). In a mixture or solution there are the solvent and the solute where the solvent is simply the greater in amount. To the first of the solutes, the crystalloids, belonged generally the acids, bases, and salts. Colloids were generally amorphous, such as albumin, starch, etc. By 1931, the terms changed in concept. They now encompass more the idea of subdivision rather than class. Getman and Daniels (1931) indicate that in a two-component system, if the particle size of one of the components is reduced more and more, a disperse system is developed. For example, a cube 1 cm on a side has a surface area of 6 cm<sup>2</sup> (a centimeter equals 10<sup>7</sup> nm). If this cube is cut into cubes 1 nm on an edge, there will be 10<sup>21</sup> cubes whose total surface area is 6,000 m<sup>2</sup>. Surface effects nondetectable for the first small cube will be detectable where the surface area is several m<sup>2</sup>. Graham (op. cit.) also made other points of distinction. Where the colloid resembled a liquid, the solute was termed a sol and where it resembled a solid or gel, the solute was termed a gel.

Schmauss and Wigand (1929) originated the idea of air as a colloid and the term aerosol for air containing an ensemble of suspended particles (Warneck (1988)). Thus, terms such as aerosol and aerogel would be available for use. Hydrosols and hydrogel (Getman and Daniels (op. cit.)) are terms applied to colloid systems which have one component of water. All particles are subject to impact with other particles due to molecular movement or translation. When the particle sizes are small, the kinetic energies impacts are so effective in the three-dimensional sense that the particles are kept in suspension. These do not tend to settle out by sedimentation. The velocities are Maxwellian or Rayleighian in distribution. The motion of the particles is Brownian after the English Botanist in 1827, Robert Brown (Getman and Daniels (op. cit.)). These motions can be watched under an ultramicroscope. Such motion can also be viewed in a two-dimensional surface such as an otherwise quiet water or other liquid surface. The motion can also be observed in the well known Tyndall phenomenon. In a quiet room or in a pool of quiet water or other liquid, the reflected motion of the suspended particles may be seen when a narrow beam of light, such as sunlight traverses the air or water. A true solution will be optically void; i.e., no particles will be present to be seen. In an evolutionary sense, the original ideas of Graham and others have changed. The demarcations or classes of aerosols now are differentiated by size alone. Getman and Daniels (op. cit.) choose size and classes as follows: (1) 1 nm and smaller—true solution of molecular and ionic dispersoids, (2) 1–100 nm—colloid solutions, and (3) 100 nm or greater—coarse dispersions. As indicated above, the terms are more closely allied with the different subdivision states rather than different classes of substances: (1) the range of the Aitken nuclei, (2) the range of large particles, and (3) the range of the giant particles (Warneck (1988)).

### 12.2 Atmospheric Nuclei

Only with time have the terms aerosol and particulates come into general use. Early investigators, in general, with the atmosphere as the medium have concerned themselves with nuclei counts.

As implied previously, the individual aerosol particles may be solid, liquid, or a mixture. All types are found in the atmosphere. Solid particles, with the exception of the frozen form of water, are called dust. These are dispersed throughout the atmosphere by the winds of convection and circulation, even though the sources are the Earth's surface. The large cyclonic vortices, the frontal actions, the hurricanes, like tornadoes and water spouts, and the deep dust devils play their part. Volcanic injection is also a source. These dust particles may be silicate, granitic, clay, or chemical compounds such as the sulphur or halide salts. These serve as condensation nuclei. In addition

to sea spray action, bubble action ejects droplets into the atmosphere which are carried aloft. These most often evaporate, leaving concentrated salt droplets on the nuclei which later serve as nuclei for condensation of water vapor as the solid salts. The vivid colors of sunrise and sunset and the increasing opaqueness of the overhead sky are evidence of dust or the condensates of organic vapors produced by burning smoke particles carried aloft. The different colors may provide an indication of particle size. Estimated radii of the particles often is used in particle size descriptions. The crystalloids of the desiccation of sea spray (salt crystals), bubble collapse, and droplet injection into the atmosphere and the ejecta of volcanoes may be absorbent or wettable. In either case, the forming shape will be spherical. Where the particle is not wettable but is of preferred shape for water absorption, such as a silicate crystal (sand), a spherical shape of the resultant particle will result. Additionally, just as an appropriate central circle will enclose an equivalent area of an associated ellipse, so will an appropriate sphere enclose an equivalent volume of an associated ellipsoid. In many instances, as in winds or targetings, circular forms are used for elliptical estimates. Thus, the circular normal error distribution is often used in lieu of the elliptical. The error is not great. Though these particles cannot be seen, the number count in a given volume can be determined by counters, then comparable volumes can be estimated, and the radii of the associated spheres can be assessed. Though Aitken's (1923) type counts may be used to determine the number of particles by the scintillation of light, neither the size nor shape can be determined. This type of detector is suitable for sizes <100 nm. Instruments to determine these and larger particle sizes now are available (Warneck (1988)). Warneck (op. cit.) also provides the integrable equation to determine surfaces, volumes, and mass. There is no single instrument available to span the size range of all particles from Aitken to giant particles. Information collectives then are composites of data produced by many investigators and instruments.

Table 12-1, after Warneck (1988), provides some typical mass and particle concentrations for different tropospheric aerosols near the Earth's surface. Included are the corresponding mean particle radii assuming spherical particles and a mean density of  $1.8 \text{ kg/dm}^3$ . Table 12-2 compares mass concentrations of several trace gases with that of natural aerosols (Warneck (1988)). Table 12-3 shows the international standard classification system for size ranges of soil particles (Weast (1988) and Warneck (1988)). Table 12-4, after Landsberg (1958), shows the variation in the number of suspended particles with elevation. Table 12-5, after Landsberg (1958), indicates the average number of particles in various Earth environments. Without question, the increase of population and human activities since 1948 directly affects these numbers. Deposition of these aerosols and particulates have created the great depths of fertile soils of the western plains of the United States, those of Argentina, Russia, Africa, and China. Roll (1965) divides aerosols into two main classes—condensation and freezing nuclei. The condensation nuclei are necessary for the formation of cloud droplets from water vapor. The air must be saturated or supersaturated with water vapor. In the case of the large insoluble particles, supersaturation should be considerable. Freezing nuclei are active in ice nucleation in supercooled clouds. These, in turn, serve as nuclei for production of precipitation. Warm clouds can be induced to precipitate without the freezing mechanism through surface turbulence or in air wave action over small obstacles such as islands or cliffs. The nucleating agents are presumed to be the nuclei derived from ocean spray or bubble ejection and the collision of small droplets to form the larger, heavier precipitating drops.

Junge (1951) discusses the process of coagulation wherein mixed intermediate types develop. The droplet radii of most interest are those ranging from 4 to 200 nm. These he designates as Aitken Nuclei. Landsberg (1938) and Burckhardt and Flohn (1939) provide two excellent monographs. Landsberg shows two-thirds of observed concentrations to be  $<400 \text{ cm}^{-3}$ . These are for oceanic areas and were collected during various cruises of the U.S. Research Vessel Carnegie. Other research projects mentioned by Roll (op. cit.) show low cumulative counts with 30 percent  $<400 \text{ cm}^{-3}$  and 71 percent  $<800 \text{ cm}^{-3}$ . Junge has contributed much to the study and understanding of atmospheric condensation nuclei. Roll (op. cit.) provides references to seven additional works of Junge, while Warneck (1988) provides about eighteen more. Not all deal with condensation nuclei but all deal with atmospheric chemistry and physics. The timeframe of work spans 1935 to 1979. Roll's (op. cit.) discussions concern the marine environment. The continental environments and urban localities have much larger nuclei counts. As mentioned previously, the nuclei are spread throughout the troposphere. The stratosphere is not unaffected but the amount of moisture is low, as are the temperatures.



Table 12-1. Typical mass and particle concentrations for different tropospheric aerosols near the Earth's surface and the corresponding mean particle radius, assuming a mean density of 1.8 kg/dm<sup>3</sup> and spherical particles (with permission of Academic Press, courtesy of Warneck (1988)).

Location	Mass Concentration (µg/m <sup>3</sup> )	Particle Concentration (particles/cm <sup>3</sup> )	Mean Radius (nm)
Urban	100	10 <sup>5</sup> -10 <sup>6</sup>	30
Rural continental	30-50	15,000	70
Maritime background	10*	300-600	100
Arctic (summer)	1	25	170

\*Includes 8 µg/m<sup>3</sup> sea salt.

Table 12-2. Comparison of mass concentration of several trace gases with those of natural aerosols (with permission of Academic Press, courtesy of Warneck (1988)).

Trace Constituent	Concentration (µg/m <sup>3</sup> )
Hydrogen (0.5 ppmv)	40
Ozone (30 ppbv)	64
NO <sub>2</sub> (0.03-10 ppbv)	0.06-20
CH <sub>3</sub> Cl (0.5 ppbv)	1
Ethane (0.5-2 ppbv)	0.8-3.2
Aerosol	1-100

Table 12-3. International standard classification for size ranges of soil particles\* (adapted from Stanford Research Journal, courtesy of Lapple (1961)).

Diameter (µm)	Nomenclature
<2	Clay**
2-20	Silt
20-200	Fine sand
200-2,000	Coarse sand
>2000	Gravel

\*Also in "Handbook of Chemistry and Physics" characteristics of particles and particle dispersoids (Weast (1988), with attribution to C.E. Lapple (1961); also used by Warneck (1988)). Other classifications use slightly different ranges.

\*\*The term clay is used here to indicate a size class, not a type of mineral.

Table 12-4. Variations in the number of suspended particles with elevation (courtesy of Landsberg (1958), with attribution to Gray Publishing).

Height Above Sea Level (m)	Average Number of Particles	
	Per cc.	Per in <sup>3</sup>
0-500	25,000	435,000
500-1000	12,000	209,000
1,000-2,000	2,000	34,800
2,000-3,000	800	14,000
3,000-4,000	350	6,100
4,000-5,000	170	3,000
5,000-6,000	80	1,400

Table 12-5. Average number of particles in various Earth atmospheric environments (courtesy of Landsberg (1958), with attribution to Gray Publishing).

Type of Locality	Average Number of Particles	
	Per cc.	Per in <sup>3</sup>
City	150,000	2,600,000
Town	35,000	610,000
Countryside	10,000	174,000
Mountain <1,000 m	6,000	105,000
Mountain 1,000-2,000 m	2,100	36,000
Mountain >2,000 m	1,000	17,400
Open ocean	1,000	17,400

### 12.3 Aerosol Chemical Constitution

The available nuclei in the atmosphere are many and as varied as their sources. Warneck (1988) suggests three broad categories: (1) Water-soluble inorganic salts (electrolytes), (2) water insoluble minerals of crustal origin, and (3) organic compounds, both soluble and insoluble in water. For water-soluble inorganic salts, wet chemical analyses establish the presence of sulfate, nitrate, and the halides such as chloride. For the cations, there is ammonium and the ions for alkali and the alkaline earths. In a tabular presentation, concentrations are indicated for silicon, aluminum, and iron, the major crustal elements. The oxidized forms are prevalent. While sulfate is the greatest constituent usually treated in tabular presentations, sodium chloride dominates the marine environment aerosols. The following elements in order of abundance (in ppmw from 330,000 to 8) are Si, Al, Fe, Ca, Mg, Na, K, Ti, Mn, Cr, V, and Co (Warneck (1988)). See table A-11-1. As Warneck (1988) indicates, Wood (1974) and Ridley et al. (1977) have pointed out that trace metals such as As, Se, S, Pd, Tl, Pb, Pt, Au, Sn, and Hg serve as acceptors of methyl (CH<sub>3</sub>) groups in microbiological processes. This leads to the emission of metal alkyls into the hydrosphere and the atmosphere. Some of these gas fractions are deleterious in the food chains and respiratory processes. In addition, oxidation forms oxides which serve as condensation nuclei.

Attention is drawn to the work of Hanson, Conway, Steele, et al. (1989). The increasing amounts of carbon combustion effluents in a formerly assumed pristine air on the north slope of Alaska and neighboring Canada is of

concern. This simply reflects the increased use of carbon fuels and increasing aerosol production. See also Turco et al. (1980, 1981a,b) on OCS, carbonyl sulfide, OH, hydroxyl radicals and gaseous and particulate sulfur with respect to climate.

Further discussion of the organic components is beyond the present scope of this publication and the reader is referred to Warneck (1988). Residence times of all aerosols in the atmosphere are of interest. Sedimentation rates are important. Turbulent diffusion represents opposition to settling so the real sedimentation is a balance of these two. In addition, contact with the surface, trees, and grasses with short roughness lengths, and with the aerosols either sticking to these or nullifying the turbulent diffusion processes, permits faster removal of aerosols from the atmosphere. Additionally, the cleansing effect or sweeping of the atmosphere by rain drops and snow crystals reduces the aerosols and keeps their residence lives low. Without question, aerosols constitute one of the elements of climate. They affect the radiation characteristics of the atmospheric reception of and distribution of solar and terrestrial radiation. In particular, the ingestion of the sulfur and nitrogen compounds into the atmosphere's tropospheric shells are effective climate influences. These will effectively absorb, block, and reflect solar radiation. Global temperatures in the average may be expected to become cooler by a small amount. This, presumably, was the case with the El Chichon eruption and is expected to be so for the Unzen, Japan, and Mt. Pinatubo, Philippines, of 1991. See Ellsaesser (1986). Precipitated out of the atmosphere, the aerosols and colloids form change agents of the Earth's surfaces and vegetation.



## 13. EXTREMES

### 13.1 General

Extremes of climatic elements can exert great stresses. Studies of extremes are important as they provide practical information on climatic element boundaries.

Actual extremes at places and times for which measurements were not available may exceed those recorded. Therefore, extremes described here generally are documented values that have been recorded; extremes are those of record. Where proxy data are used, these will be identified. Sources of proxy data would be tree rings, ice cores, varves, weathering processes, flood stage marks and debris, damage, etc. Isotopic abundance, isotopic ratios, and radio-carbon dating may be used to determine time scales.

In general, when making extreme value distribution studies, only one datum should be used per time unit for the study so that the deductions will be in that timeframe. More observations than one will introduce uncertainties in the results due to the potential internal correlation. The resulting statements cannot then be applied to inferences for a future time unit.

Intriguing and important as the general precipitation patterns are to present day life forms, food production, and river flow maintenance, the extreme events or eras with their shock effects of drought Rosenberg (1978) and floods merit consideration. These merit consideration due to their providing concepts of climate limits. In addition to the usual study of only deleterious effects, extreme periods of helpful and productive features will provide other useful guidelines.

The chances of an estimated or recorded extreme being exceeded when the period upon which the extreme is based is short are great. As the period of record increases, the frequency of breaking records generally can be expected to decrease for any one particular location. Gumbel (1953) discusses statistical models to represent distributions of extremes of one element. In particular, he discusses the Fisher-Tippet (1928) models. Essenwanger (1976, 1986) provides a good discussion of the extreme value models. Such models are used to provide some procedures to extrapolate or forecast occurrences of specified values or intervals. Most data sets available in climatology are censored or truncated and inherently contain varying oscillations, lumps, or trends in the data set. For these reasons, extrapolation much beyond the period of information must be viewed with care. Mooley and Crutcher (1968), using 139 yr of Indian annual rainfall data, determined that stability in the estimates of the gamma distribution function was reached in about 80 yr. If stability has not been reached in any data set, this author feels that a forecast (climatological) becomes rather uncertain at 1.5 times the length of record. Beyond that length of time, the confidence (uncertainty) in forecast values is exponentially decreased (increased) with increasing time. Return periods, for example, from a period of record of 50 yr, are relatively good for the next 25 yr. Longer extrapolation periods can be used, but error bars will widen. All extreme value analyses ideally should be accompanied by risk assessments in the form of probable range of errors. Estimates of 100-yr return periods, 500-yr return periods, and 1,000-yr return periods are used in engineering design problems. The risk assessments accompanying these estimates informs the designers and engineers of the expected accuracy of the estimates. Table 13-1 and figure 13-1, World Weather Extremes, are strongly dependent on and have the same title as the excellent work of Riordan and Bourget (1985) which is, in turn, an update of their 1974 report. Their reports consist of a global map of weather extremes and a separate map for the United States and Canada. Here, no maps of the United States and Canada are presented. Included are highest and lowest temperatures, largest temperature variations, greatest and least amounts

Table 13-1. World weather extremes (Note: Numbers 1–64, excepting 50, refer to fig. 13-1. Numbers above 64 are additional data through 1988).

1. World's greatest point (a) average yearly precipitation and (b) U.S. greatest rainfall in twelve months, respectively, during a 32-year period:		9. U.S. largest two-minute temperature rise:	
(a) 1168 cm	Mt. Waialeale, Kauai, HI, USA, during a 32-year period US DOC ESSA NOAA, 1977	27°C from –20°C	Spearfish, SD, USA, 22 Jan. 1913 US DOC NOAA EDIS, 1979
(b) 1878 cm	Kukui, Maui, HI, USA, Dec. 1981 - Dec. 1982 US DOC ESSA NOAA, 1977	10. U.S. largest hailstone, circumference:	
		44.5 cm	Coffeyville, KA, USA, 3 Sept. 1977 Anon., 1971
2. U.S. Largest 24-hour temperature fall:		11. North America's greatest 24-hour snowfall:	
6.7°C to –49°C	Browning, MT, USA, 23–24 Jan., 1916 US DOC ESSA EDIS, 1967	192.5 cm	Silver Lake, CO, USA, 14–15 April 1921 Schmidli, 1983
3. North America's greatest average yearly precipitation during a 14-year period:		12. South America's greatest average yearly precipitation:	
647.7 cm	Henderson Lake, B.C., Canada US DOC ESSA EDS, 1968 Newark, 1984 - Chinook, 6(3): 76–78 Manning, 1983	899 cm	Quibdo, Columbia, during a 10–16 year period Arkin, 1969
4. North America's greatest snowfall in one storm:		13. World's lowest average yearly precipitation:	
480 cm	Mt. Shasta, Ski Bowl, CA, USA, 13–19 Feb. 1959 Schmidli, 1983	0.08 cm and no rain for more than 14 years	Arica, Chile, Oct. 1903 to Jan. 1918 Schmidli, 1983
5. (a) Western Hemisphere's highest temperature, (b) hottest summer average, (c) highest annual mean, and (d) lowest average precipitation during a 42-year period 1941–1971:		14. Average days per year with rain:	
(a) 57°C, 10 July 1913	Death Valley, CA, USA	325 days	Bahia Felix, Chile Seamon and Bartlett, 1956
(b) 37°C	Schmidli, 1983	15. Thule, Greenland, Denmark:	
(c) 26°C		(a) peak gust and (b) mean wind speed for a month:	
(d) 4.1 cm		(a) 93 m/s	Thule Air Base, Greenland, Denmark, 8 March 1972
6. North America's lowest average yearly precipitation:		(b) 31 m/s	Stansfield, 1972
3 cm	Bataques, Mexico US DOC ESSA EDS, 1968	16. Mt. Washington's, NH, USA, highest (a) peak gust, (b) five-minute wind, (c) 24-hour mean, (d) monthly mean, (e) annual mean:	
7. North America's lowest temperature (excluding Greenland):		(a) 103 m/s	12 April 1934 US DOC NOAA EDIS NCDC, 1982
–63°C	Snag, Yukon Territory, Canada, 3 Feb. 1947 Schmidli, 1983	(b) 84 m/s	12 April 1934 Schmidli, 1983
8. North America's greatest snowfall in one season:		(c) 57 m/s	11–12 April 1934 Pagliuca, 1934
2850 cm	Mt. Ranier, Paradise Ranger Station, WA, USA, 1971–1972 Anon., 1972	(d) 31 m/s	Feb. 1939 Anon., 1943
		(e) 15.8 m/s	1971–2000 Mt. Washington, 2006

Table 13-1. World weather extremes (Note: Numbers 1–64, excepting 50, refer to fig. 13-1. Numbers above 64 are additional data through 1988) (Continued).

17. World's greatest 42-minute rainfall:  30.5 cm  Holt, MO, USA, 22 June 1947 Paulhus, 1965	26. Possibly the world's highest annual mean temperature:  35°C  Dallol, Ethiopia Pedgely, 1967
18. World's greatest 1-minute rainfall:  3.1 cm  Unionville, MD, USA, 4 July, 1956  The 3.8 cm quoted in recent literature for Barrot, Guadeloupe, 26 Nov., 1970 is in error, according to the letter from the Director, French Meteorological Service, which gives 2.25 cm. Director, French Meteorological Service	27. Highest solar radiation in one hour:  113 Lys  Malange, Angola, Africa, 7 Nov., 1961 Anon., 1961
19. South America's highest temperature:  49°C  Rivadavia, Argentina, 21 Dec. 1905 US DOC ESSA, 1968	28. Average daily insolation in December (summer):  955 Lys  South Pole, Antarctica, 1958–1966 US DOC ESSA, 1962 and 1968
20. South America's lowest temperature:  –33°C  Sarmiento, Argentina, 1 June 1907 US DOC ESSA, 1968	29. Instantaneous temperature rise:  12°C  Edinburgh, Scotland, 8 April, 1969 Chuter, 1970
21. Antarctica's highest temperature:  15°C  Esperanza, 20 Oct., 1956 Ties with Vanda, 5 Jan. 1974. N.Z. Ant. Soc. US DOC ESSA, 1968	30. Greatest snowfall in 19 hours:  172 cm  Bessans, France, 5–6 April 1969 Jail, 1969
22. Greenland's lowest temperature:  –66°C  Northice, Greenland, Denmark, 9 Jan. 1954 Schmidli, 1983	31. Europe's greatest average yearly precipitation during a 22-year period:  465 cm  Orkvice, Yugoslavia US DOC ESSA, 1968
23. Europe's highest temperature:  50°C  Seville, Spain, 4 August 1881 US DOC ESSA, 1968	32. World's highest surface temperature:  58°C  El Azizia, Libya, 13 Sept. 1922 Schmidli, 1983
24. Africa's lowest temperature:  –24°C  Ifrane, Morocco, 11 Feb. 1935 US DOC ESSA, 1968	33. Africa's lowest average yearly precipitation during a 39-year period:  Less than 0.25 cm  Wadi Halfa, Sudan US DOC ESSA, 1968
25. Africa's (a) greatest average yearly precipitation and (b) average annual precipitation variability during a 32-year period:  (a) 1,029 cm (b) 191 cm  Debundscha, Cameroon US DOC ESSA, 1968	34. Highest annual average number of thunderstorms during a ten-year period:  242 days  Kampala, Uganda UN WMO, 1953
	35. (a) Lowest July mean temperature; (b) annual mean temperature:  (a) –73°C (b) –57°C  Plateau Station, Antarctica (a) July 1968 (b) 1966–1969 Dalrymple, personal communication

Table 13-1. World weather extremes (Note: Numbers 1–64, excepting 50, refer to fig. 13-1. Numbers above 64 are additional data through 1988) (Continued).

36. Europe's lowest temperature:  –55°C  lowest in 15-year period, date unknown. Ust Schuger, USSR US DOC ESSA, 1968	46. Mean annual temperature range:  8°C, –47°C to 34°C  Eastern Sayan Region, USSR Suslov, 1961
37. World's greatest twenty-minute rainfall:  20.5 cm  Curtea-de Arges, Romania, 7 July 1889 Paulhus, 1965	47. Highest sea surface temperature:  36°C  Persian Gulf, 5 Aug. 1924 US DOC ESSA EDS, 1961
38. Europe's lowest average yearly precipitation during a 25-year period:  16 cm  Astrakan, USSR US DOC ESSA, 1968	48. Greatest 24-hour rainfall:  100 cm 108 cm  formerly Dharampuri, India, and now Alvin, TX, USA possibly the world's greatest on flat terrain Schmidli, 1983
39. Annual relative variability of precipitation:  94%  Themed, Israel, 1921–1947 Katznelson and Kotz, 1958	49. Average thunderstorm days per year (five-year period):  322 days  Bogor, Indonesia, 1916–1920 Arabadzhi, 1966
40. Asia's highest temperature:  54°C  Tirat Tsvi, Israel, 21 June 1942 US DOC ESSA, 1977	50. World's greatest rainfalls for approximately one day to fifteen days:
41. Asia's lowest average annual precipitation during a fifty-year period:  4.6 cm  Aden, South Yemen US DOC ESSA, 1968	50.1 a. 24 hours: 1825 mm Foc Foc, La Reunion I, 7–8 January 1966 b. 48 hours: 2500 mm Cilaos, La Reunion I, 15–16 March 1952 c. 72 hours: 3240 mm Grand Ilet, La Reunion I, 24–27 January 1980 d. 4-day: 3551 mm Commerson, La Reunion I, 23–26 January 1980 e. 5-day: 3951 mm Commerson, La Reunion I, 23–27 January 1980 f. 7-day: 4653 mm Commerson, La Reunion I, 21–27 January 1980 g. 10-day: 5678 mm Commerson, La Reunion I, 18–27 January 1980 h. 15-day: 6078.5 mm Commerson, La Reunion I, 13–27 January 1980
42. Average afternoon low point in June:  29°C  Assab, Ethiopia Dodd, 1969	Director, French Meteorological Service, Letter 27 April 1987
43. World's greatest twelve-hour rainfall:  135 cm  Belouve, La Reunion I, 28–29 Feb. 1964. See also 50. Paulhus, 1965	50.2 24-hour: 174.2 cm Grand-Ilet, 14–28 January 1980. Compare with 1.a above. This is not the record. The region is the same.
44. World's lowest temperature:  –89°C  Vostok, Antarctica, 21 July 1983 Schmidli, 1983	51. Consecutive days temperature at or above 38°C:  162 days  Marble Bar, W. Australia, 30 Oct. 1923 to 4 April 1924 Ashton and Maher, 1960
45. (a) Northern Hemisphere's lowest temperature; (b) overall range between highest and lowest temperatures:  (a) –68°C (b) 105°C  Verkhoyansk, USSR, 5–7 Feb. 1892 and Oymekon, USSR, 6 Feb. 1933 Suslov, 1961 Schmidli, 1983	



Table 13-1. World weather extremes (Note: Numbers 1–64, excepting 50, refer to fig. 13-1. Numbers above 64 are additional data through 1988) (Continued).

52. Australia's lowest average yearly precipitation during a 34-year updated to a 42-year period: Troudaninna, S. Australia	60. World's lowest sea level pressure:
10 cm	87 kPa
Mulka, S. Australia J. de la Lande, Bureau of Meteorol.; Correspondence with U.S. Corps of Eng., Riordan and Bourget, July 5, 1985.	Typhoon Tip, 17 N 138 E, 12 Oct. 1979 Estimated by aerial reconnaissance dropsonde Schmidli, 1983
53. World's highest sea level pressure:	61. Australia's greatest average yearly precipitation:
108.38 kPa	455 cm
Agata, USSR, 31 Dec. 1968 Anon., 1971	Tully, Queensland, Australia, 31-year period 425 cm 59-year period de la Lande, 1985
54. Relative variability of annual precipitation:	62. Australia's greatest 24-hour rainfall:
108%	91 cm
Lhasa, Tibet, 1935–1939 Lu, 1939	Crohamburst, Queensland, Australia, 3 Feb., 1893 114 cm Bellender Ker, Queensland, Australia, 4 Jan., 1979 de la Lande, 1985
55. Australia's highest temperature:	63. Australia's lowest temperature:
53°C	–22°C
Cloncurry, Queensland, Australia, 16 Jan. 1889 US DOC ESSA, 1975	Charlotte Pass, N.S.W., Australia, 14 June, 1945 and 22 July, 1947 US DOC ESSA EDS, 1968
56. World's greatest (a) 24-hour mean wind speed and (b) mean wind speed for a month:	64. Northern Hemisphere's greatest 24-hour rainfall:
(a) 48 m/sec	125 cm
Mt. Washington, NH, USA, April 11–12, 1934	Paishih, Taiwan, 10–11 September, 1963 Paulhus, 1965
(b) 31 m/sec	65. North America's greatest depth of snow on the ground:
Thule Air Base, Greenland, Denmark, Paglioca et al., 1934 Stansfield, 1972	1,146 cm
57. Northern Hemisphere's lowest temperature:	Tamarack, CA, U.S.A. Schmidli, 1983
–68°C	66. Maximum temperature (possibly) Antarctica's highest, tying Esperanza:
Oymyakon, USSR (tied with Verkhoyansk, USSR), 6 Feb. 1933 Schmidli, 1983	15°C
58. Asia's greatest average yearly precipitation during a 74-year period:	Vanda Station, Antarctica, 5 Jan., 1974 New Zealand, Antarctic Soc., Inc., 1974
1,143 cm	67. Highest temperature, South Pole:
Cherrapunji, India, during a 74-year period. Paulhus, 1965 US DOC ESSA, 1968	–14°C
59. Peak gust:	South Pole, Antarctica, 27 Dec., 1978 US NSF, 1979
85 m/sec	
Miyakojima I, Ryukyu Islands, 5 Sept. 1966 See Mt. Washington, NH, USA, for world Mituta and Yoshizumi, 1968	

Table 13-1. World weather extremes (Note: Numbers 1–64, excepting 50, refer to fig. 13-1. Numbers above 64 are additional data through 1988) (Continued).

68. Greatest 24-hour rainfall on flat terrain (possibly the world's greatest). See also No. 48, Dharampuri, India:	73. Lowest U.S. average winter temperature:
108 cm Alvin, Texas, U.S.A., 25–27 July, 1979 Schmidli, 1983	–29.8°C Umiat, Alaska
69. Variability—three temperature rises and two falls or more during a period of three hours and ten minutes:	74. Lowest pressure: North Atlantic
22°C Rapid City, SD, U.S.A., 22 Jan., 1943 Hamann, 1943	92 kPa 61.5 N 30.5 W, 14–15 Dec. 1987 Burt, 1987
70. World's greatest rainfall in 42 minutes:	75. Lowest pressure: Caribbean-Gulf of Mexico-Yucatan, Mexico
30.5 cm Holt, MO, U.S.A., 22 June, 1947 Paulhus, 1965	88.5 kPa Hadeen, 1988
71. Canada's highest average frequency of days with precipitation:	NOTE: Main sources of information are:
242 days Langara, Queen Charlotte Islands, British Columbia, Canada Newark, 1984	1. Paulhus, J.L.N., <i>Monthly Weather Review</i> , Vol. 93, No. 5 pp. 331–335, 1965. 2. Riordan and Bourget, <i>World Weather Extremes</i> , 1985. 3. Manning, F.D., <i>Climatic Extremes for Canada</i> , 1983. 4. Schmidli, R.J., <i>Weather Extremes</i> , NOAA, 1983. 5. US, DOC, NOAA. 6. Director, French Meteorological Service, 1987. 7. Director, Australian Meteorol. Service, 1987. 8. Director, New Zealand Meteorol. Service, 1987.
72. Antarctica's highest (a) 24-hour mean wind speed and (b) one-month mean wind speed:	
(a) 48 m/sec (b) 29 m/sec	Port Martin, Antarctica, March 1951 Loewe, 1972

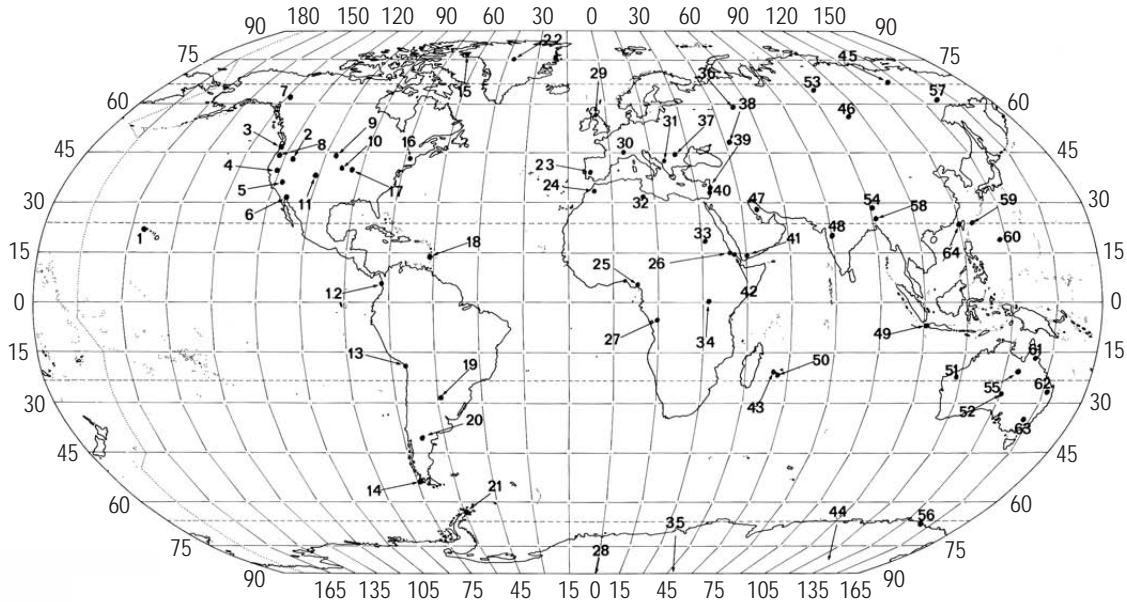


Figure 13-1. Locations of recorded extremes corresponding to the first 64 data of table 13-1.

of precipitation for various durations, maximum precipitation variabilities, greatest thunderstorm frequencies, highest and lowest atmospheric pressures, highest solar radiation, largest and heaviest hailstones, greatest snowfalls, highest wind speeds, high dewpoint, and most frequent occurrence of fog. Table 13-1 is organized generally with a start in the Western Hemisphere for all items listed and continues eastward through Australia and Japan. Some documentation is provided. Figure 13-1 presents many of the locations of data origins of table 13-1 in the same fashion, with the same respective numbers, ranging from 1 through 64. The following subsections present material on a few of the extreme features associated with climate.

The extremes shown may have been exceeded but, if so, no record or verification of them could be found. Conversion of scales, including rounding, introduces problems. Scales used previously have been changed when necessary to present the information in terms of presently accepted scales. Usually, the appropriate National Weather Service organization examines extreme value data and the conditions under which these were observed. A decision then is made to publish or not to publish these data. All of the above extremes may have been previously exceeded, but the writer has no verified information.

### 13.2 Temperatures

For many applications, it is important to perform studies of distributions of extreme values for a point, an area, or a region. Figures 13-2(a) and (b) show the fit of an extreme value distribution, the Gumbel (1954), Lieblein (1954), and the Gumbel and Lieblein (1954) models, respectively, for annual maximum and minimum temperatures for Cincinnati, OH. The closely spaced vertical lines show the one standard deviation confidence band regions. While the fit to the maximum temperature seems to be adequate, the fit to the minimum temperature is not adequate. Either a different model is required or this set of data is composed of two or more different groups; i.e., it is heterogeneous. As an example of using these two diagrams, it might be said that at Cincinnati, OH, there are about two chances in a thousand that the maximum temperature of 44 °C will be exceeded. There are about two chances in a thousand that the minimum temperature will fall below -37 °C. Fair confidence for the maximum temperature may be held. The confidence is not so high for the minimum temperature statement. The models and the various estimators of the required statistical parameters are discussed by Essenwanger (1976, 1986).

Nicodemus and Guttman (1980) provide probability estimates of temperature extremes for the contiguous United States.

### 13.3 Precipitation

Table 13-2 provides the world's greatest observed point rainfalls. It represents an update of the tables provided by Paulhus (1965) and Linsley, Kohler, and Paulhus (1949, 1975). By means of linear regression, with table 13-2 data, where both scales are logarithmic, figure 13-3 provides a good representation of the time distribution of global extreme precipitation data. The linear expression

$$R = \text{EXP}(3.828 + 0.495 * \text{LOG}(T)) \quad (13.1)$$

appears to provide an adequate data fit. Here,  $R$  is precipitation in millimeters and  $T$  is time in minutes. A general impression is that there are periods in which new extreme records may be expected. One of these is in the periods shorter than 3 hr. Also, records may be broken in the extremely long period. There may be no physical reason that this empirical distribution should be expected to hold over wifetime and space scales.

Therefore, if the above presumed fit is not the best, new records for the short periods and for, say, 3 or 4 yr will create a noticeable tendency for points below the linear best fit shown in figure 13-3. If so, then a better fit will be obtained with a quadratic (parabolic) fit. In July 1979, from the third tropical storm of the season, Claudette,

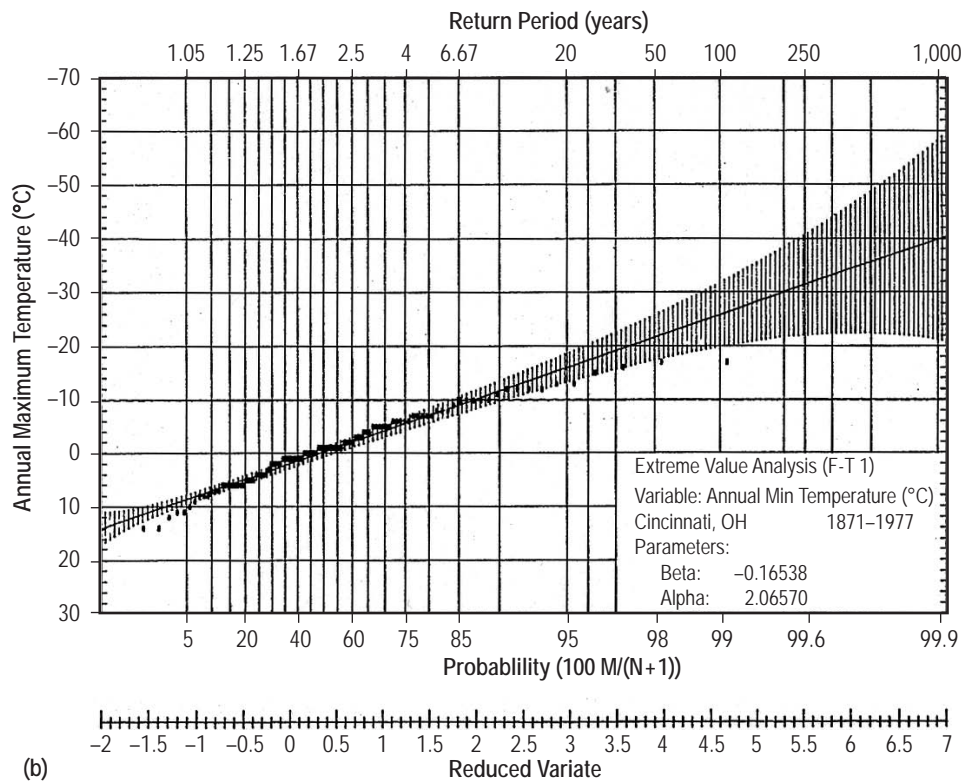
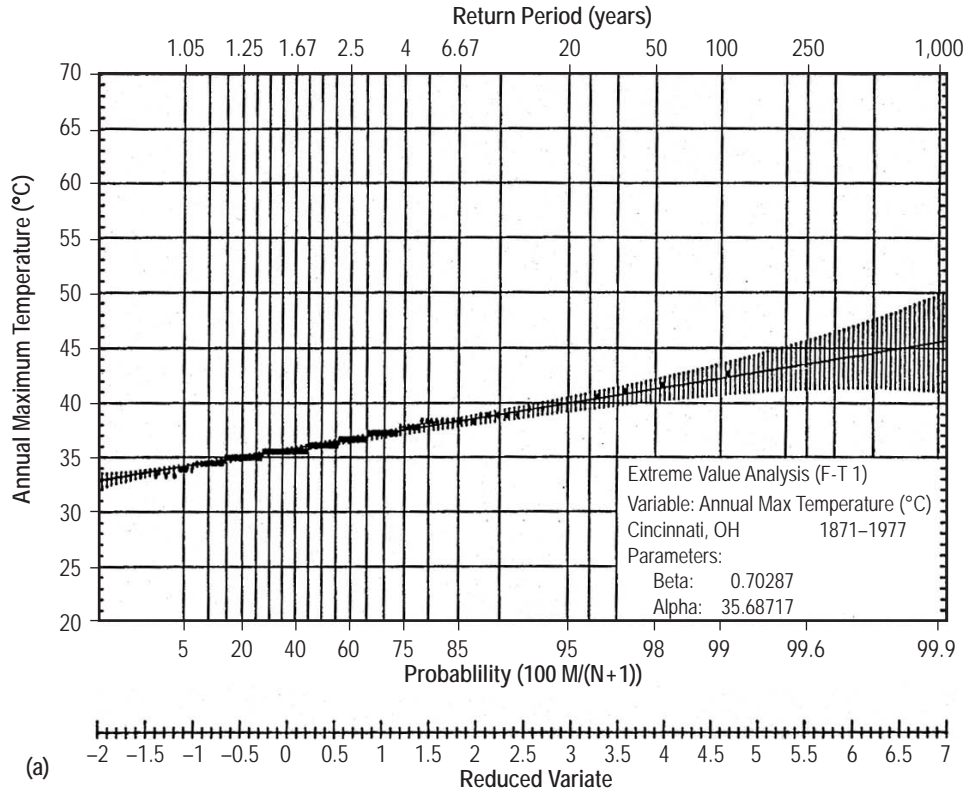


Figure 13-2. Extreme value distribution fit for (a) maximum temperatures and (b) minimum temperatures at Cincinnati, OH, 1871-1977 (Gumbel-Lieblein (1954)).

Table 13-2. World's greatest observed point rainfalls.

Duration	Depth (mm)	Source	Location	Date
1 min	31	1	Unionville, MY	July 4, 1956
8 min	126	1	Fussen, Bavaria	May 25, 1920
15 min	198	1	Plumb Point, Jamaica	May 12, 1916
20 min	206	1	Curtea-de-Arges, Roumania	July 7, 1889
42 min	305	1	Holt, MO	June 22, 1947
2 h 10 min	483	1	Rockport, WV	July 18, 1889
2 h 45 min	559	1	D'Hanis, TX (17 mi NNW)	May 31, 1935
4 h 30 min	782+	1	Smethport, PA	July 18, 1942
9 h	1,087	2	Belouve, La Reunion	Feb. 28, 1964
12 h	1,144	2	Foc Foc, La Reunion	Jan. 7-8, 1966
18 h	1,589	2	Foc Foc, La Reunion	Jan. 7-8, 1966
24 h	1,825	2	Foc Foc, La Reunion	Jan. 7-8, 1966
2 d	2,500	2	Cilaos, La Reunion	March 15-17, 1966
3 d	3,240	2	Grand Ilet, La Reunion	March 24-27, 1980
4 d	3,551	2	Commerson, La Reunion	Jan. 23-26, 1980
5 d	3,951	2	Commerson, La Reunion	Jan. 23-27, 1980
6 d	4,303	2	Commerson, La Reunion	Jan. 22-27, 1980
7 d	4,653	2	Commerson, La Reunion	Jan. 21-27, 1980
8 d	4,936	2	Commerson, La Reunion	Jan. 20-27, 1980
15 d	6,078	2	Commerson, La Reunion	Jan. 13-27, 1980
31 d	9,300	1	Cherrapunji, India	July 1861
2 mo	12,767	1	Cherrapunji, India	June-July 1861
3 mo	16,369	1	Cherrapunji, India	May-July 1861
4 mo	18,738	1	Cherrapunji, India	Apr.-July 1861
5 mo	20,412	1	Cherrapunji, India	Apr.-Aug. 1861
6 mo	22,454	1	Cherrapunji, India	Apr.-Sept. 1861
11 mo	22,990	1	Cherrapunji, India	Jan.-Nov. 1861
1 y	26,461	1	Cherrapunji, India	Aug. 1860-July 1861
2 y	40,768	1	Cherrapunji, India	1860-1861

a new U.S. record 24-hr precipitation of 1,082 mm fell at Alvin, TX, between noon on the 25th and noon on the 26th. This does not exceed the world record of 1,245 mm at Paisha, Taiwan. See figure 13-1.

Extremes in the free atmosphere and for the surface for the elements previously mentioned, and for some other elements, except for the Antarctic region, are presented by Sissenwine and Cormier (1974). Tattleman and Grantham (1983) provide Northern and Southern Hemispheric charts of 1-min rainfall rates.

Haggard, Bilton, and Crutcher (1973) used the gamma distribution to study the maximum rainfall from tropical cyclones which cross the Appalachian 330-m-altitude contour. The gamma distribution was used as it is zero bound.

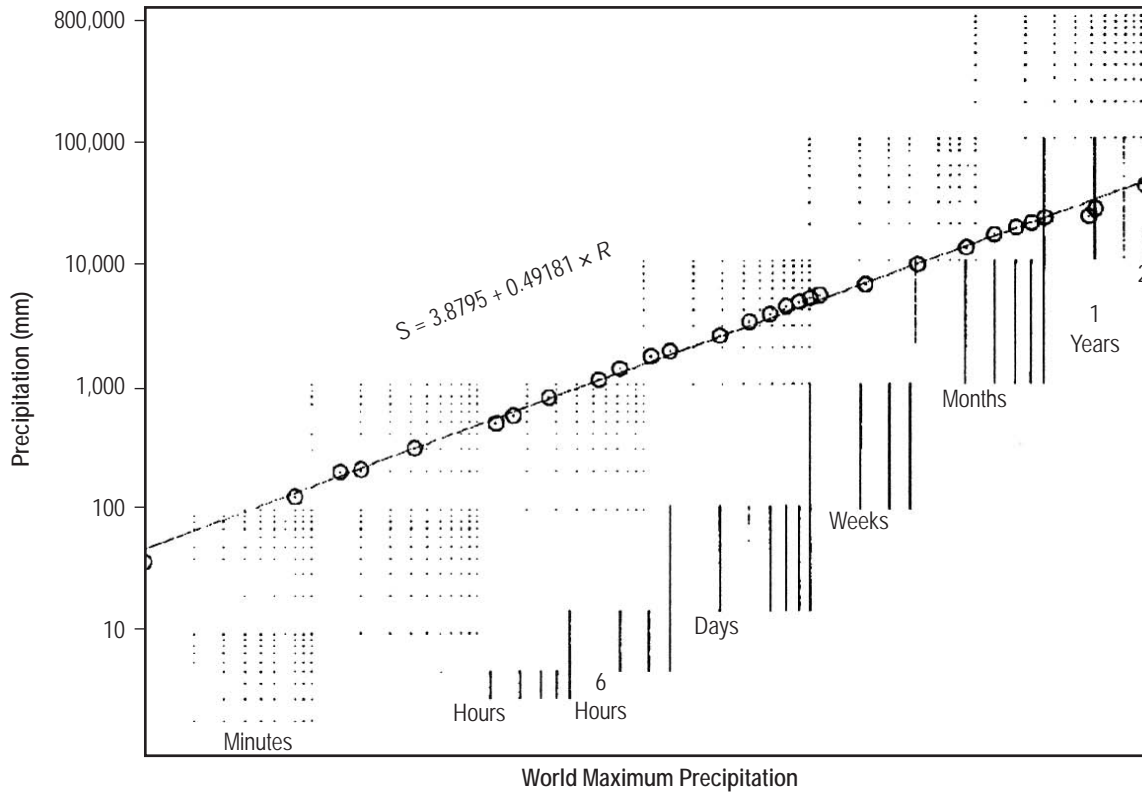


Figure 13-3. World's greatest observed point rainfalls; an update of Paulhus (1965) and Linsley, Kohler, and Paulhus (1975), *Hydrology for Engineers*.

### 13.4 Wind

Court (1948, 1952, 1969, 1970), and in his Doctoral Dissertation (1956), examines the winds and the structures of their distributions. Instrumental in applications of the circular normal distribution, Court also has been active in the study of extreme value data. Fisher and Tippett (1928) provide three basic statistical models for extreme values for any element, including winds. Three models are given. Gumbel (1958) uses the Fisher-Tippett type I model. Thom (1968) has also worked in this field as have Simiu and Scanlan (1978), and Simiu, Changery, and Filliben (1979). In the light of history, the extremes of surface winds in tornadoes, speculatively estimated not many years ago as high as  $400 \text{ ms}^{-1}$ , are now estimated to be  $125\text{--}150 \text{ ms}^{-1}$  (Fujita (1987)). Until more data become available,  $160 \text{ ms}^{-1}$  is the speed used for planning massive structures. The fastest winds at levels of the jet stream are east-southeast of Tokyo at an altitude of 15 km in February where winds reach mean speeds of  $75 \text{ ms}^{-1}$  and recorded individual values of  $\approx 150 \text{ ms}^{-1}$  (Crutcher (1961)). Their forces are not the same at this height as for winds at the ground surface. The ratios of densities at 10 and 15 km to surface densities, respectively, range from about 0.33 to 0.16. The momenta are correspondingly decreased. Wind speeds that are not as fast are indicated for the upper air in the band from Marion to Kerguelen to Heard Island in the Southern Hemisphere. But, in general, these are not as fast as the fastest winds in the Northern Hemisphere (Taljaard et al. (1969)).

Figures 13-4 and 13-5 illustrate various tornadoes. Figure 13-4 is provided by the Department of Commerce, NOAA and figure 13-5 by Oklahoma University and used with permission of the American Meteorological Society and Professor Bluestein. Figure 13-5 illustrates an ongoing program of research using doppler techniques. Figure 13-5 appeared on the cover of the *Bulletin of the American Meteorological Society* in December 1989.

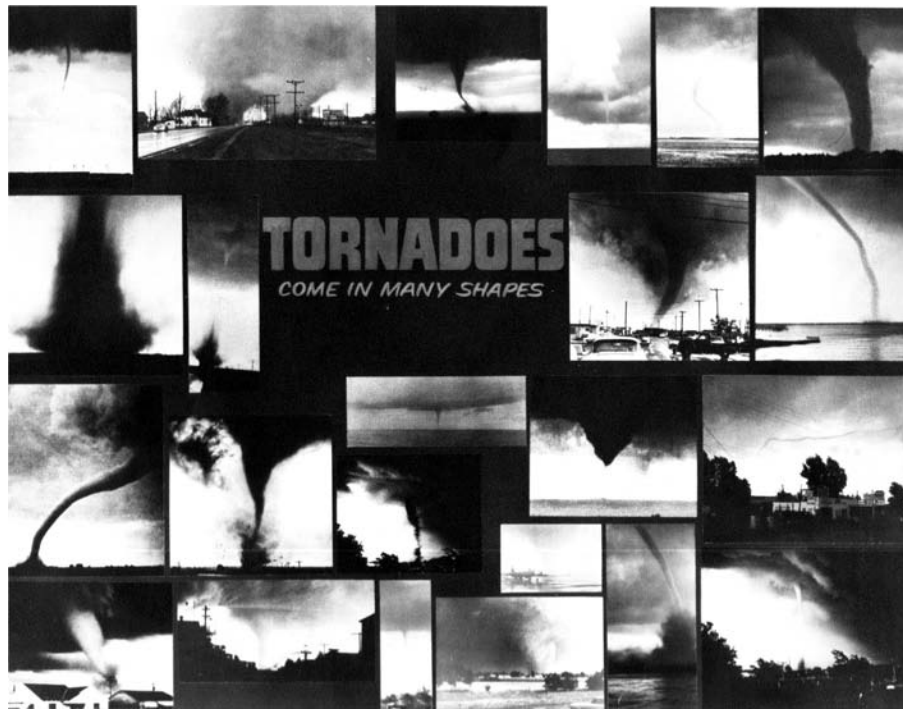


Figure 13-4. Ensemble of pictures of various tornadoes (courtesy of NOAA).



Figure 13-5. A tornado being observed at close range with doppler equipment (with permission, American Meteorological Society, and courtesy of Prof. Bluestein, Oklahoma State University).

Tornadoes usually are associated with strong thunderstorms with extensive vertical development, with frontal activity, or with areas of extreme instability. Vortices, such as tornadoes over land, waterspouts over water, and the giant whirlwinds of the arid regions occur worldwide. Tornadoes and waterspouts often occur in conjunction with tropical cyclones, hurricanes, or typhoons in which strong thunderstorms are embedded. Flora (1954) provides good examples of early studies of tornadoes in the United States. Fujita (1987) has been a foremost investigator in these phenomena. His presentation is excellent and is an extensive and amplified report on tornadoes in the United States. In 1971, he developed a classification system known as the Fujita scale, or F-scale, to better delineate the destructive power of tornadoes. Figure 13-6 (used with permission of the University of Chicago, courtesy of Fujita (1987)) presents the windspeeds of the Fujita scale with comparison to the Beaufort scale and the Mach number. Note that the F1 scale starts with the Beaufort Force 11 and continues upward to Mach 1, the speed of sound. Figure 13-7 (also used with permission of the University of Chicago, courtesy of Fujita (1987)) shows a three-dimensional diagram relating the chronological aggregation of tornadoes 1905–1985, by 10-yr periods. Additionally, these are classified according to the F-scale and their associated frequencies. Improved reporting of the weaker tornadoes resulted in the higher frequencies noted in scales F0 and F1.

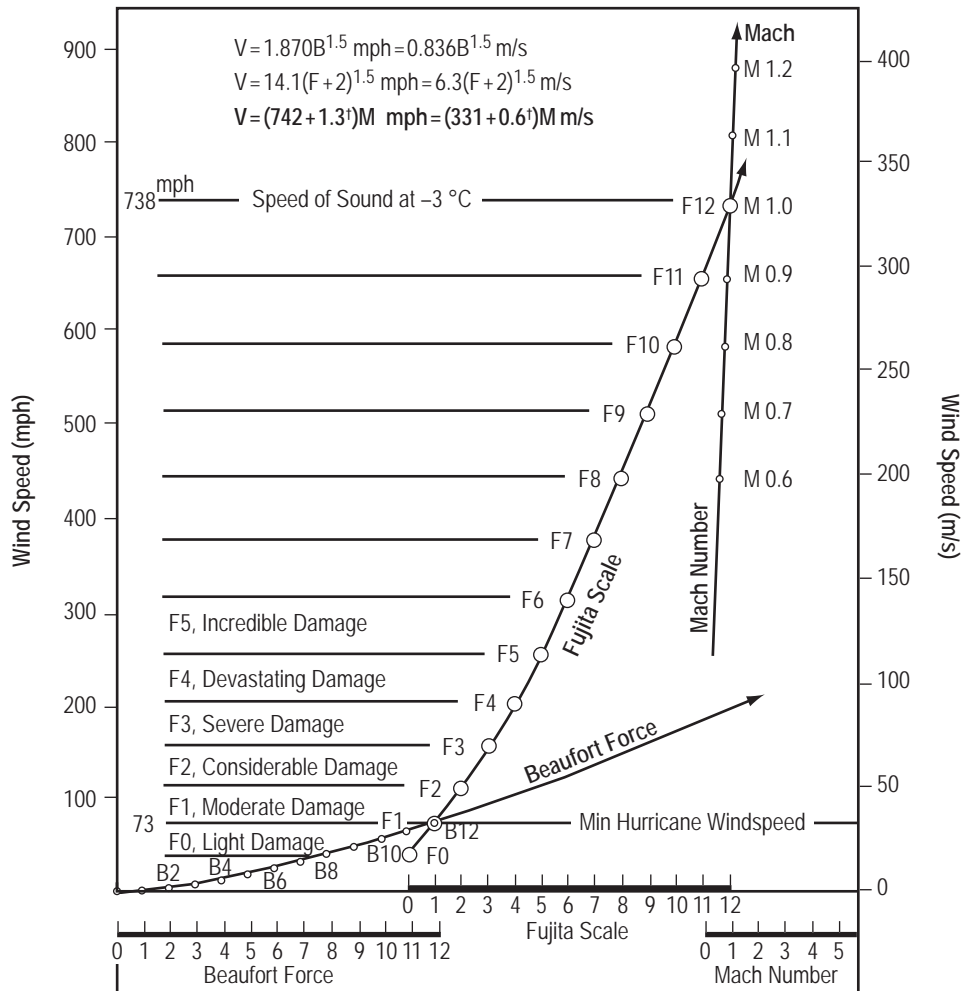


Figure 13-6. Comparison of wind speeds of the Fujita scale with the Beaufort and Mach scales.



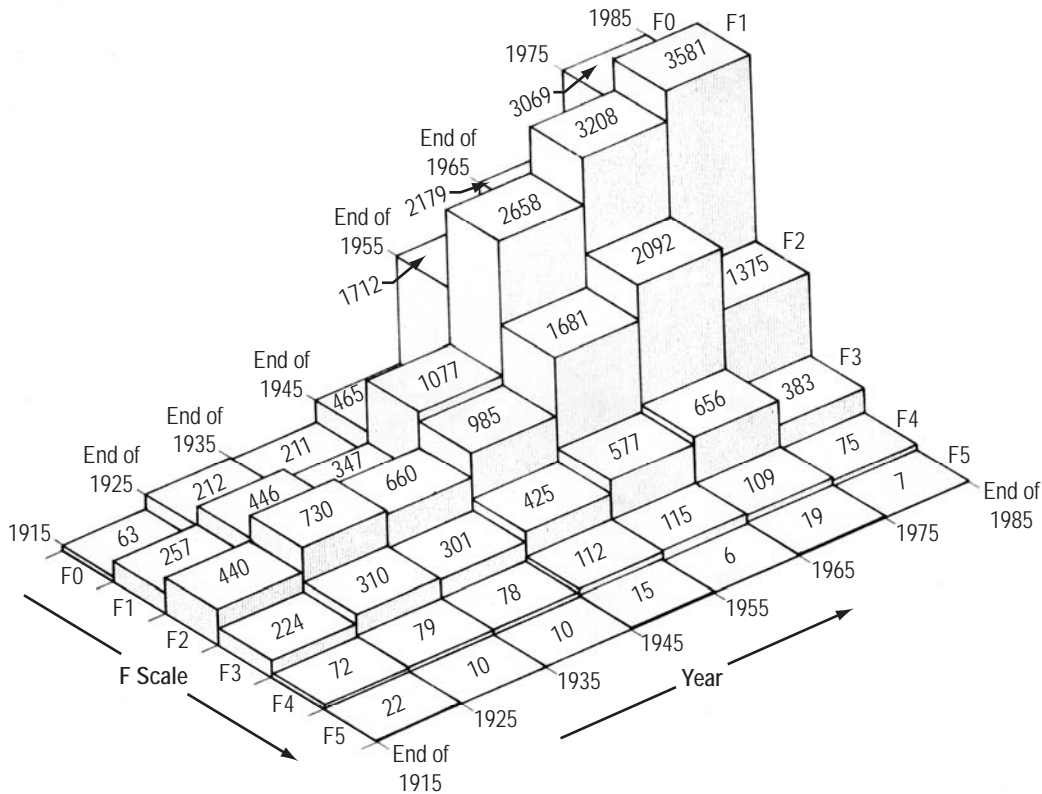


Figure 13-7. Three-dimensional aggregate of tornadoes by 10-yr periods (1905–1985) (with permission of the University of Chicago, courtesy of Fujita (1987)).

There are many specialized applications of extreme wind information. Often, in construction, in assessment of wind power, of protection or danger, the item of interest is an extreme. Sometimes, the direction of the wind is of no concern. At other times, the direction is of vital concern. The latter requires the extraction of the direction of the wind associated with an extreme wind speed or the extremes of wind from a specified direction or sector. This necessitates, of course, much more data preparation. See the discussion by Newton, Nicodemus, and Guttman (1983). Their article concerns the Tennessee Valley extreme wind speed climatology. Figure 13-8(a) and (b) illustrates the extreme value analysis (Lieblein (1954)) of the Chattanooga, TN, annual 30-min winds in  $\text{ms}^{-1}$  from all directions and then only from north specifically. The period of record is 1948–1974. The hachuring is a measure of the variability of the estimates in terms of the variances. These areas portray the 16th and 84th percentile confidence limits on the straight line of best fit. Studies such as these may be required where there is a large body of water and the direction and length of fetch may present a potential hazard to a dam or other installation, both from the wind, water, and wave considerations. Overtopping of the spillway(s) may occur. The fit of the Lieblein model to the data appears to be good. For any direction, this value is  $\approx 16 \text{ ms}^{-1}$ . The 100-yr return period (average) value for north winds is  $\approx 12.5 \text{ ms}^{-1}$ . That is, an annual extreme 30-min north wind of  $12.5 \text{ ms}^{-1}$  occurs at varying time intervals (in terms of years) and the average of these time intervals is 100 yr. Because of the asymmetric distribution of extreme value data, there is approximately a 70 percent probability that a return period value or less wind will occur in 100 yr. Gumbel (1958) discusses return periods as do many others such as Linsley, Kohler, and Paulhus (1975) and Essenwanger (1959). There is an estimated probability of 67 percent that this return period value lies between 10 and about  $14 \text{ ms}^{-1}$ .

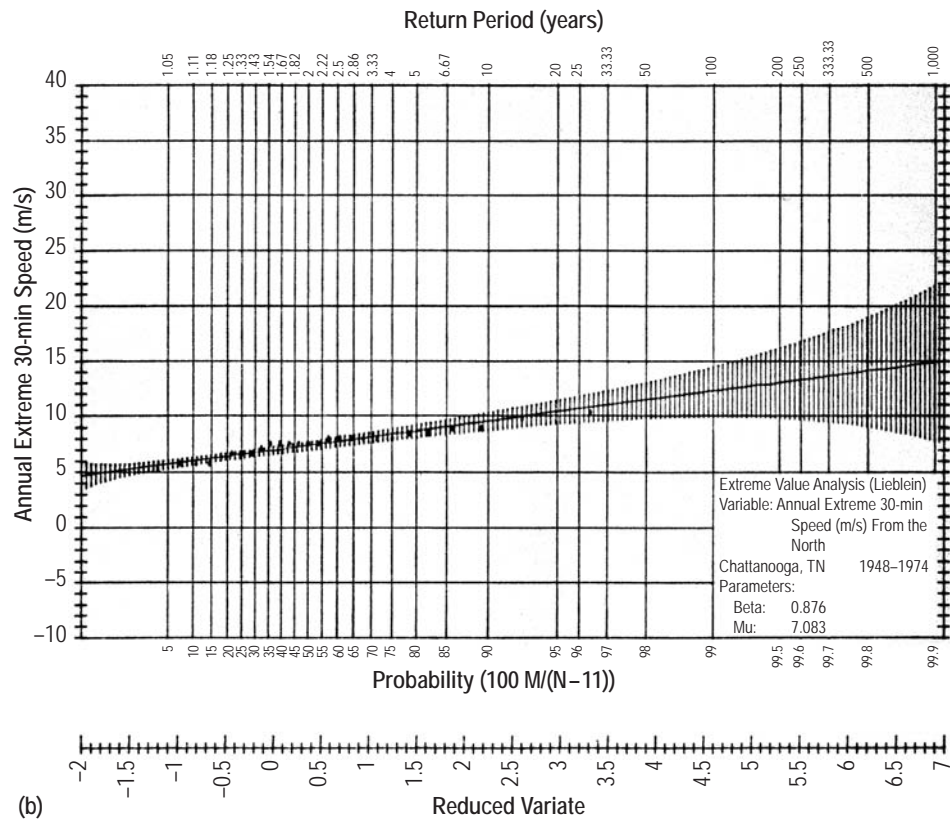
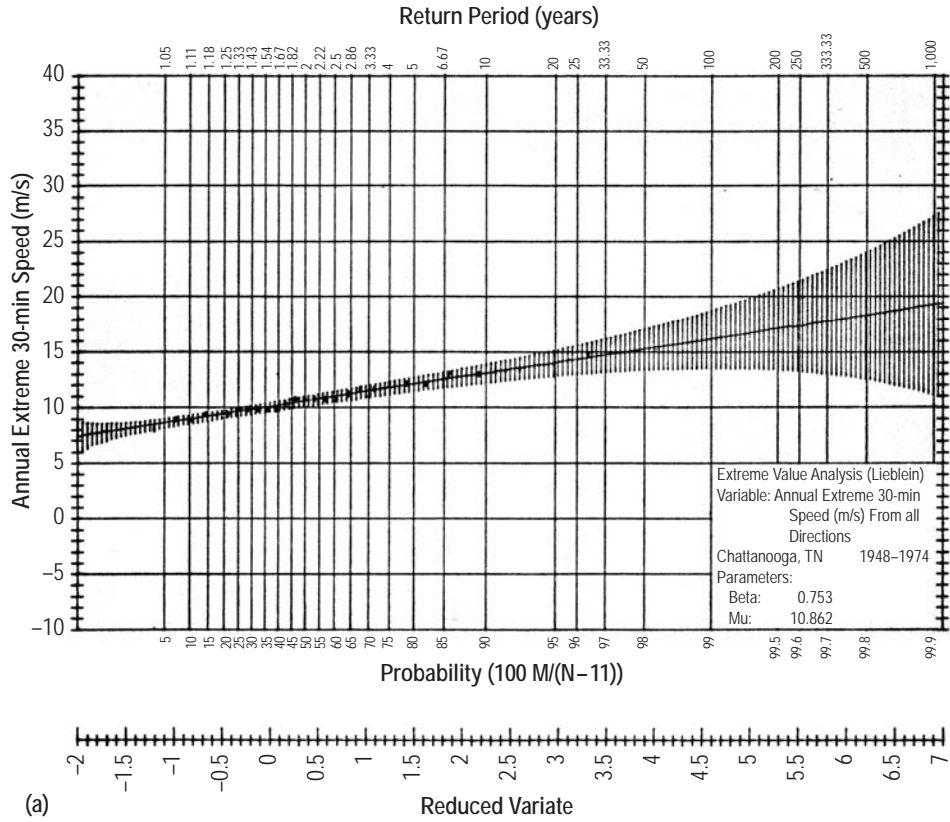


Figure 13-8. Extreme value analysis of Chattanooga, TN, annual 30-min winds in  $\text{ms}^{-1}$  from (a) all directions and (b) north winds (1948–1974). Confidence bands are shown.

Waves are incredibly complex (Lamb (1932), Neumann and Pierson (1966), Menzel (1959), and Shklovskii (1978)). As components of motion, they may be longitudinal, transverse, or vertical. They may be gravity waves. They may travel in packets.

### 13.5 Waves

Waves exist in or on all interfaces of the Earth, its lithosphere, its hydrosphere, and its atmosphere. Evidence of these waves and their effects may be seen from the tiniest of ripples on the bottom of water bodies, to the ripples in the soil, dust, and the sand to the great sand dunes, to the visibly moving waves on the oceans, lakes, bays, rivers, ponds, and creeks, to the undulations of the Earth in tremors and earthquakes, and to waves in the atmosphere made visible by clouds. Some of the longest ocean waves are the tidal waves but their heights are small except in shoaling areas near coastlines and in bays, which are progressively restricted perpendicular to the wave travel. Waves may be generated by seismic shock, such as the earthquake tsunami waves of the ocean. Waves may exist along the water interfaces separating different density regions. Waves are generated by the motion of one medium, such as air, against another medium, such as water. From the smallest to the largest, the waves tend to erode boundaries, such as the coastline. The eroded material is transported by currents in the media. These materials often are deposited in the average form of the wave of the media which do the transporting. Large waves understandably do great damage to coastlines and to shipping. The shipping industries and coastal industries are affected vitally by the winds, currents, and waves of the atmosphere and hydrosphere. Equally damaging are the waves generated in the terrain and buildings by tremors and earthquakes.

Here, we take a look at the heights of ocean waves generated by winds. Sverdrup, Johnson, and Fleming (1942), Neumann and Pierson (1966), Pierson, Neumann, and James (1955), and Longuet-Higgins and Stewart (1963), as do many others, discuss waves. The significant wave height is defined as the average of the heights of the one-third highest waves in a long sequence of waves observed at a point. It is generally identified as  $\bar{H}_{1/3}$ .

Figure 13-9, after Crutcher and Quayle (1974), shows an empirically derived envelope curve of sustained wind speed versus wave height for both increasing and decreasing wind speeds. Hundreds of ship reports were used. The broad data scatter below the envelope is not shown. The scatter thins out as the envelope is approached. The inertia of the wave height phenomenon is evident in the right-hand curve. The wave heights reported were the significant wave heights. The broad scatter of data is created in part by the observer's experience, by training, and by the differing physical and reactive characteristics of the many ships involved. Few observations were made and recorded near the peak of the curve which may represent the top of the envelope. One of the difficulties lies in the early coding used to report observations. Until about 1960, detailed coding was restricted to 10 m ( $\approx 33$  ft) or less. However, in many cases, notes or remarks in the ships' logs by the quartermasters or observers provided additional information.

With reference to figure 13-9, two special observations are made. In 1933, the U.S. Navy oiler, RAMAPO, in the Pacific reported a 112-ft ( $\approx 34$ -m) series of waves, crest to trough (Whitemarsh (1934)). The report is believable to this author from the descriptions provided in the ship's log as reported in the *Proceedings of the U.S. Naval Institute of 1934*. These waves were not rogues which are to be described later. The ship, RAMAPO, was able to maintain headway and to ride these immense "rollers," if these can be termed "rollers." Brown (1989) also cites that report. Deep water, sustained strong winds of long duration, and straightline fetch of long distance are necessary conditions for growth of extreme properties. The period of stormy weather was more than 7 days. Presumably, the waves experienced by the RAMAPO were created under these conditions with winds of  $\approx 60$  kt persisting and with some 60-kt winds. A similar situation was noted by the present author in the North Atlantic area east-southeast of the Davis Strait in winter of 1941 or 1942. A 3-day similar situation produced estimated wave heights of 110–120 ft ( $\approx 33$ – $36$  m). The ship was quite manageable during this storm but food was necessarily sandwiches and soup served in usual two-handled cups but only one-third to one-half full. Triangulation served to estimate the wave heights as

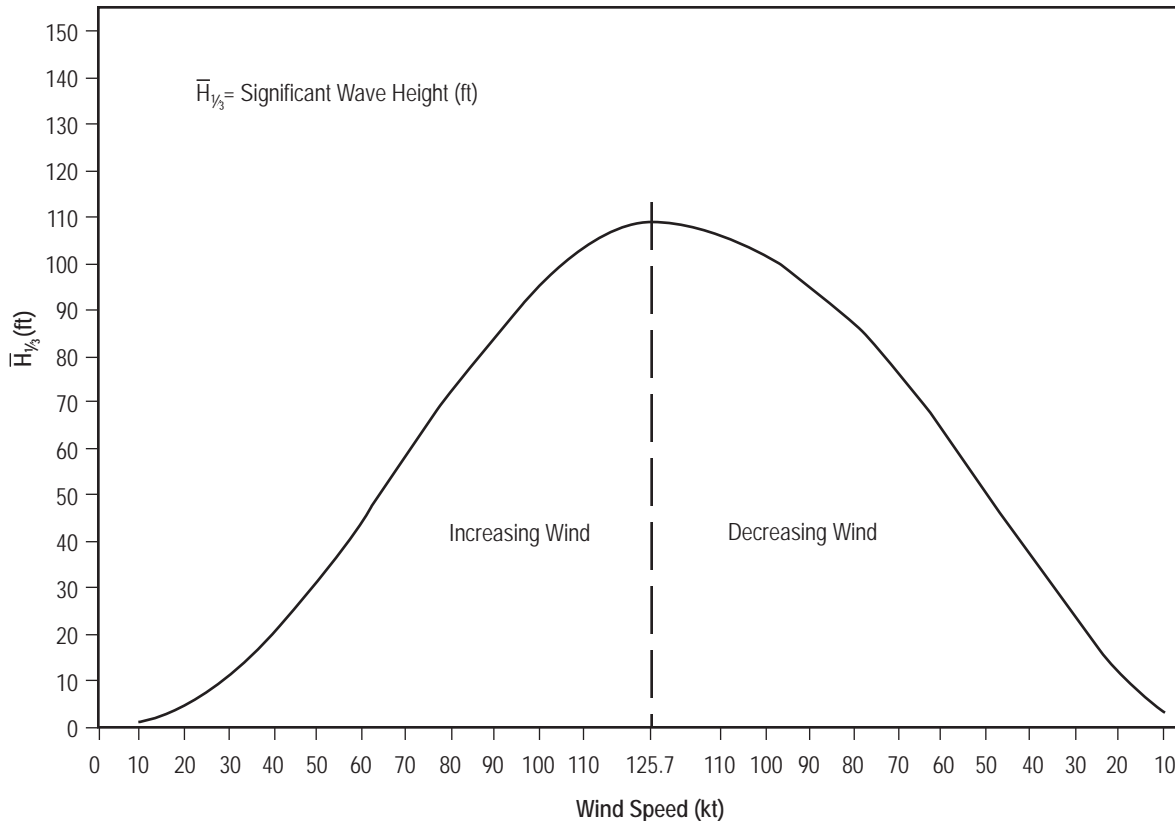


Figure 13-9. Empirically derived envelope curve of sustained wind speed versus wave height both for increasing and decreasing winds (Crutcher and Quayle (1974)).

was done for the RAMAPO. In both cases, the ships were able to maintain headway. The winds presumably were not extremely excessive, but they were estimated to be  $\approx 80$  kt and were sustained for 2 days or more. The anemometer remained pegged even though the winds were gusting. A plot of 85 kt and a wave height of 112 ft ( $\approx 34$  m) is somewhat below the envelope shown in figure 13-9. Documentation has been lost for the North Atlantic case but the similarities are remarkable. Remarkable is the fact that the highest waves are not necessarily produced by the highest winds. Other conditions influence the situation. February, the month of the RAMAPO's experience, is one of the stormiest months in the North Pacific and the North Atlantic.

Bretschneider et al. (1962) reported on a study of high wave conditions observed by the OWS Weather Reporter in December 1959. The highest wave group height reported was  $\approx 14$  m ( $\approx 46$  ft). The location of this ship during the period December 15–19, 1959, was position "J" near  $53^\circ$  N.  $18^\circ$  W. However, this is not the region of highest waves in the world. There are others, such as those off the southwest coast of South Africa where very strong current opposing or cross flows intermix.

Quayle (1974) discusses the Cape rollers of the South African coast. Quayle and Elms (1979) discuss the high waves of the Benguela current. The Agulhas current flowing southward between Southeast Africa and Madagascar splits when reaching the region of the southern tip of Africa. One branch turns eastward while the other branch turns westward and enters the region of the north-flowing Benguela with its attendant cool upwelling water masses. Here, the winds are channeled by the southwest African coast and its shelf and the South Atlantic high atmospheric pressure cell and the associated gyre. The wind and water flowing towards the coast and forming the coast rollers, interact with the Benguela current. The result is a highly perturbed sea surface. The interacting wave

structures when in synchronism produce the isolated giant peaks and deep holes or crests and troughs so dangerous to shipping. These “loners” or “rogues” can devastate a ship without warning before corrective action can be taken. Occurring at night and without radar or other aids, the ship may essentially just broach or disintegrate and disappear. Interacting counter or cross currents are not required. Traveling in the same direction, wave packets may be effective. Seen during the day as a wave train, the peak may appear to be a hill moving through the water as another ship for some distance before simply sinking back into the wave system. Conversely, traveling holes or deep pockets will appear, and after some distance, disappear as they fill. But some may travel as waves with long crests and troughs, be slow in building, and slow in decay, but nevertheless very dangerous at every stage. Brown (1989) discusses the rogue waves and makes attribution to work by others in this field.

Interacting situations also can be induced by reflections and refractions from coastlines or by shoals or islands. The incessant pounding by large waves can create dangerous conditions for shipping and industry.

Towers constructed in shallow waters for any purpose must be designed for construction, maintenance, and damage control. Many disciplines are involved for the structures must withstand the slow erosion process of both mechanical (physical) and chemical processes. The first includes the wind, temperature (radiation), and wave action as well as the physical work that is done. Towers have collapsed in storms with loss of life.

One of the problems associated with manning towers and drilling platforms is the necessity to guard the worker’s lives. If the platforms must be abandoned, such abandonment should occur sometimes 3 days before the onslaught of heavy seas. Prior fog, drizzle, rain, and rough seas may preclude evacuation by ship and/or helicopter. This requires an extensive forecast protection program.

Mobile drilling units are also vulnerable to storm and high wave action. An example is the capsizing and sinking of the Mobile Offshore Drilling Unit (MODU) Ocean Ranger, O.N. 615641 (Department of Transportation, U.S. Coast Guard Marine Casualty Report of 20 May 1983). During a severe storm, about 1 a.m., February 15, 1982, the Ocean Ranger indicated in distress calls that the crew was abandoning ship. About 2 hr later, the Ocean Ranger, about 166 mi (260 km) east of St. John’s, Newfoundland, capsized and sank in  $\approx 260$  ft ( $\approx 80$  m). The entire crew of 84 perished. Whether a rogue wave was involved is not known, but rogues are known to occur in the region east of Newfoundland, also southeast of Nova Scotia and Sable Island. The cold Labrador current flowing southward encounters the northeastward flowing periphery of the Gulf Stream. Here, there are ideal conditions for rogues. There are many such regions. A review of available wind current and wave charts of present atlases will indicate potential troublesome regions.

Extreme wave height distributions have been studied by Thom (1971). Figure 13-10 for ocean weather station “India” at  $59^\circ$  N. and  $18^\circ$  W. almost due north of ocean weather station “J” above shows the probability of exceeding specified significant wave heights at that location. For example, the probability of exceeding, in any one year, the curve maximum height of figure 13-9, 65 m (126 ft), is 0.03 or three chances in 100. The probability of exceeding, in any one year, a height of 18 m (60 ft) is about 85 percent. In the model used for this determination, only one observation per year was used. Experience would indicate that the probabilities of exceedance would be much lower in the summer months. As this is an extreme example of extremes, there may be those who question this particular figure. However, this is accepted here until a longer period of record for that location is examined, a new fit made, and confidence bounds placed on the curve. Examples of such confidence bounds have already been shown in figures 13-8.

### 13.6 Tropical Cyclones

Dunn and Miller (1960) write about the tropical cyclones of the Atlantic. The word “cyclone” (Dunn and Miller (1960)), in general, is the name given to any atmospheric system which has decreasing pressure from

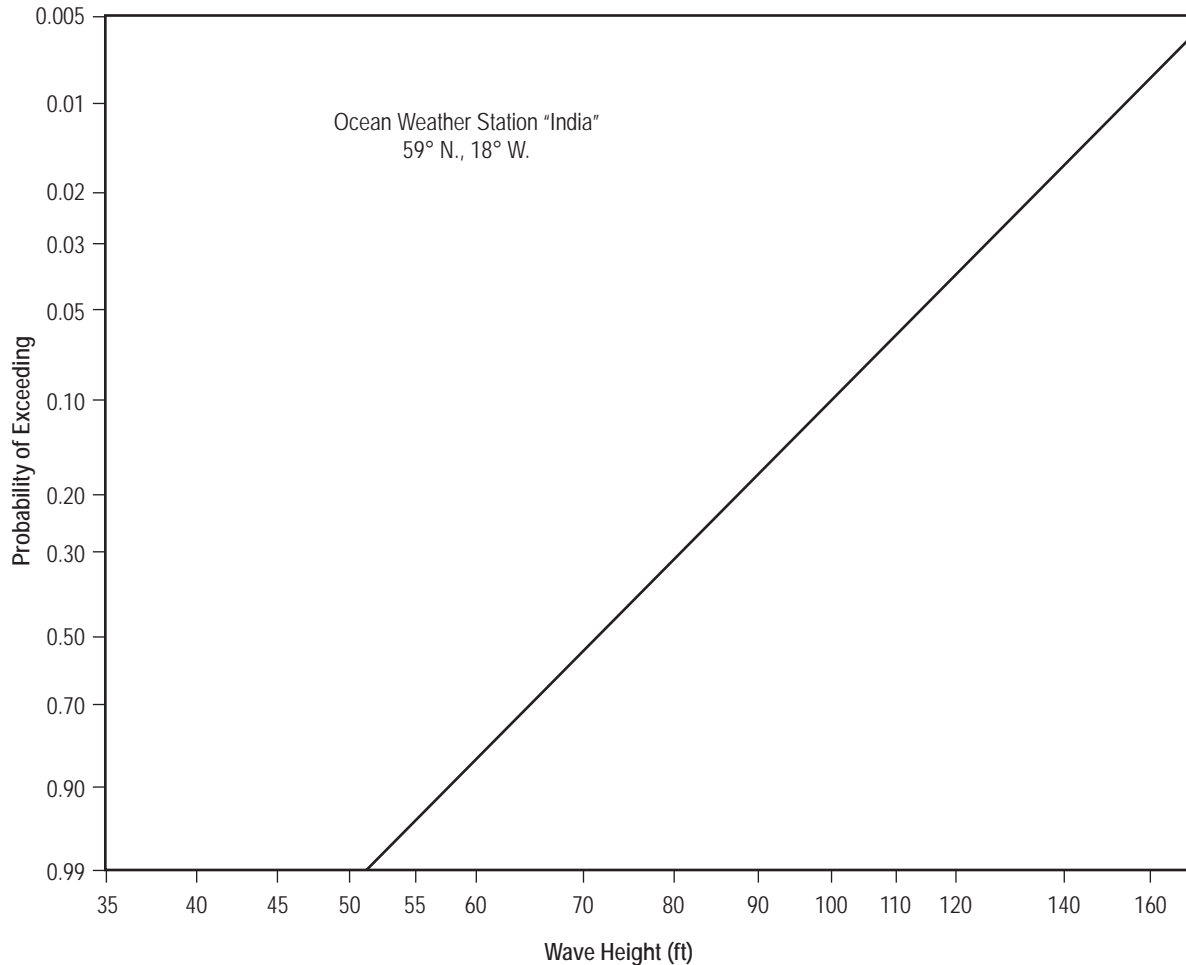


Figure 13-10. Extreme wave height analysis for ocean weather station "India" at 59° N. and 18° W. (Thom (1971)).

a periphery to a center of minimum pressure into which winds inwardly spiral. This definition covers many types of rotating storms, including extratropical cyclones, tropical cyclones, and tornadoes. The size of the tropical cyclone is between that of the extratropical cyclone and the tornado. As an entity, the tropical cyclone is perhaps the most destructive of all cyclones in the accompanying winds, rains, waves, storm surges, and floods. In general, tropical cyclones are not characterized by fronts, yet they can entrain and consume frontal systems of nearby extratropical systems. Tornadoes may develop within the extensive thunderstorm systems of the tropical cyclones. Inward-spiralling rainbands typify the tropical cyclone. In the center of the tropical cyclone, there often is an "eye" or cloudfree region encircled by a towering wall of clouds. In some cases where considerable relatively dry air moves downward from high levels in the eye, the adiabatic compression of that air warms the air and helps to maintain the cloudfree character. Such a characteristic, along with many others, can be used to describe tropical cyclones and to help predict the future position of such a storm. But even with all of the information available today, such forecasting is difficult. However, the availability of satellite weather surveillance on a global scale provides a good base for early warning.

Tropical cyclones have specialized regional names usually based on early languages. The word cyclone is used in the Indian Ocean region and the Arabian Sea, the willy-willy of Australia, the typhoon of the western

Pacific, and the hurricane of the Atlantic and eastern Pacific. In 1976, the World Meteorological Organization (WMO) published the quantitative evaluation of the risk of disaster from tropical cyclones.

Several organizations today maintain computer files of tropical storm and cyclone information. Copies are maintained and updated each year by NOAA of the U.S. Department of Commerce. Such copies exist at the National Hurricane Center, Miami, FL, and the National Climatic Data Center, Asheville, NC.

Crutcher and Quayle (1974) prepared a global climatology of tropical cyclones, an issue of the U.S. Navy Mariners Worldwide Climatic Guide to Tropical Storms at Sea. This includes frequency presentations by month and ocean areas, and an annual summary. Figure 13-11 shows a global annual presentation of the seemingly preferred tracks with isogon isopleths of travel direction. The wider the arrows, the greater the frequency of tropical storms, including hurricanes.

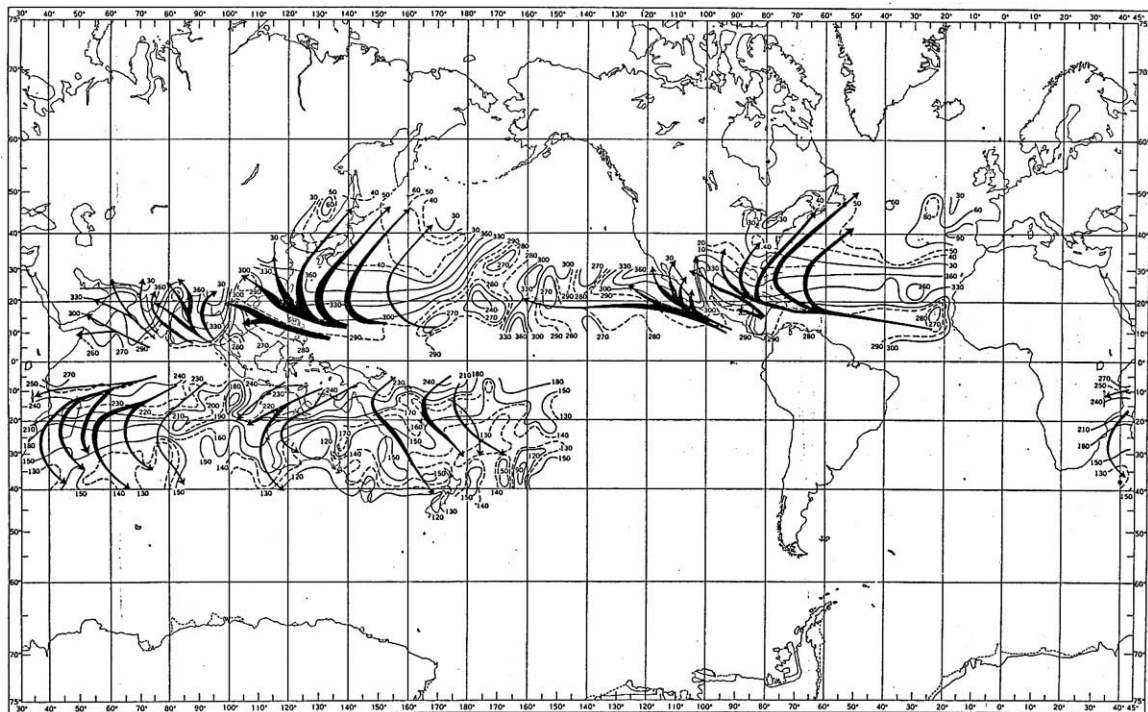


Figure 13-11. Tropical cyclone preferred tracks with isogons (dotted lines) of travel direction. The wider the solid arrows, the greater the percent frequency (Crutcher and Quayle (1974)).

Hurricanes create extremes of many elements; hence, they could have been discussed in many sections of this publication. They have been mentioned briefly in prior sections but your attention is now drawn to the section on clouds, Section 9. There you will see in figures 9-5 through 9-7 and 9-10 through 9-12 several different cloud structures associated with hurricanes.

Crutcher, Neumann, and Pelissier (1982) present a breakout of the North Atlantic, Caribbean, and Gulf of Mexico hurricanes. Without specifying the precise functional form, the general multimodal, multivariate distribution may be written as

$$f(x,y,\dots,m) = \sum a_i f_i(x,y,\dots,m)$$

$$\sum a_i = 1; i = 1, 2, \dots, k . \quad (13.2)$$

In the bivariate form used with the east-west and north-south hurricane movements, the above reduces to the marginal bivariate form:

$$f(x,y) = \sum a_i f_i(x,y)$$

$$\sum a_i = 1 . \quad (13.3)$$

Either actual movements or errors of forecasts may be used in these expressions. When errors are studied, it is shown that Atlantic tropical cyclone forecast errors are essentially of two types—easy forecast situations and difficult forecast situations.

The easy forecast group has one-half the standard error or about one-fourth the variance of the difficult forecast group. The so-called easy forecast situations are mainly those initially located in the Gulf of Mexico, Caribbean, or in the North Atlantic Ocean south of 18° N. latitude. Error distributions of these forecasts are essentially circular with component standard deviations of ≈70 nmi (≈130 km) or a vector standard deviation of 100 nmi (185 km).

The so-called difficult forecast situations refer to storms over the Atlantic, north of 18° N. latitude. These distributions are elliptical with standard deviations about twice those of the easy group.

### 13.7 Return Periods

See discussions by Linsley, Kohler, and Paulhus (1949), Lieblein (1954), Gumbel (1954, 1958), Thom (1959), Mann, Shafer, and Singpurwalla (1974), and Essenwanger (1986). Linsley, Kohler, and Paulhus (1949), citing Thomas (1947), present their table 20-1 of the average return periods for various levels of probability. They include the distributions of the highest to the fifth highest values on record in selected time intervals. In general, in this particular type of study with climatic data, only one value per year is used. However, for other uses, shorter or longer time periods may be of interest. For example, if January data are being used, only one value per January should be used. For example, take the tabular values of table 20-1 of Linsley, Kohler, and Paulhus (op. cit.). Select the maximum value (say, a flood) for a period of 20 yr. The tabular values indicate that the return period for that flood amount, whatever it is, has the following probabilistic characteristics. Only one datum per year was used. As shown by Linsley, Kohler, and Paulhus (op. cit.) after Thomas (1947), the return periods are given as chances in 100 of less than or equal to a certain number of years such as (1, ≤4.86), (25, ≤14.9), (50, ≤29.4), (75, ≤70), and (99, ≤1990).

The first may be read as there is one chance in 100 (0.01 percent probability) that the return period is less than or equal to about 5 yr.

The uncertainty (imprecision) or the certainty (precision) of these statements is a function of the number of years (one datum per time period) available and the assumption that the climatic process is or the conditions are stationary. The latter statement assumes that the process is not subject to oscillation, trends, or jumps (shifts). There is a tendency for many persons to view the return period as fixed, because of the idea that the terms, a 30-yr or a 100-yr flood engenders, i.e., a 30-yr flood must occur in a 30-yr period. As Gumbel (op. cit.) and Linsley, Kohler, and Paulhus (op. cit.) clearly indicate, it is not certain that the 20-yr flood will occur again in the next 20 yr, as indicated above. There is one chance in 100 (100–99) that it will not occur again in 1990 yr or less.



A 100-yr flood does not occur once in 100 yr nor mean that once a 100-yr flood occurs, it will be 100 yr before such a flood occurs again. Given  $F(x)$  as the cumulative probability of the nonoccurrence of ( $x$ ).  $F(x)$  may be derived from any model pertinent to the representation of the data set. Once the  $F(x)$  has been determined, or accepted, then as Gumbel (1954, 1958) does, define the return period as

$$T(x) = 1/(1 - F(x)) \quad . \quad (13.4)$$



## 14. CLIMATOLOGICAL DATA PUBLICATIONS

### 14.1 Comments on Future Aspects of Climate

It is important at this point to make a few comments.

This entire survey has included trace gases along with the more common aspects of climate. The development of these features is noticeable in the past few years of survey. The following references among the many available mirror this development. These are Boldirev (1992), Obasi (1995), (Houghton et al. (1995), and Houghton et al. (1996).

These references among others discuss the monitoring of the global climate system. These treat the global climate system prior to and including 1995. It must be mentioned that the extremes of climate discussed here will, in time, be exceeded and already may have been exceeded. Other aspects of weather and climate may be chosen to represent what is important to our understanding of climate. The disciplines of astronomy, volcanology, tectonophysics, interplanetary features of chemistry, physics, and geology, etc., may in time come under the purview and umbrella of climate. The door is wide open to those who wish to explore these and other fields.

Climatological data, in general, are available in every nation. The respective National Services may be contacted. Here, in the United States, the main service is the National Climatic Data Service (NCDS). The address is: National Climatic Data Center (NCDC), Federal Building, 151 Patton Avenue, Asheville, NC 28801. A service charge and an explanation of how they charge will be added to each order. Write to the above address or call 828-CLI-MATE or 828-271-4800 for current prices. VISA, Mastercard, or American Express credit cards may be used.

Section 2 discussed data primarily from the viewpoint of quality; once data have been collected, edited, and marked for outlying or impossible errors, these are available for use. There are many organizations that collect archive and service data. They may not have their data in the same format, particularly if the data have been prepared for computer use and are on some medium other than written or printed on paper. The purchaser or user generally must pay for data in whatever format specified or obtainable. Even the international forms may change and the data formats may not be the same from one period to another.

### 14.2 Example—Local Climatological Data

Current serial publications are available at the U.S. NCDC Local Climatological Data (LCD) issued monthly and annually for each of the approximately 280 National Weather Service stations. These are available separately or by subscription. See figure 14-1.

The monthly issue includes daily and monthly temperatures, dewpoint temperatures, heating and cooling degree days (base 65 °F), weather, precipitation, snowfall, pressure, wind, sunshine, and sky cover. Three-hour weather observations and hourly precipitation data are also presented for most stations.

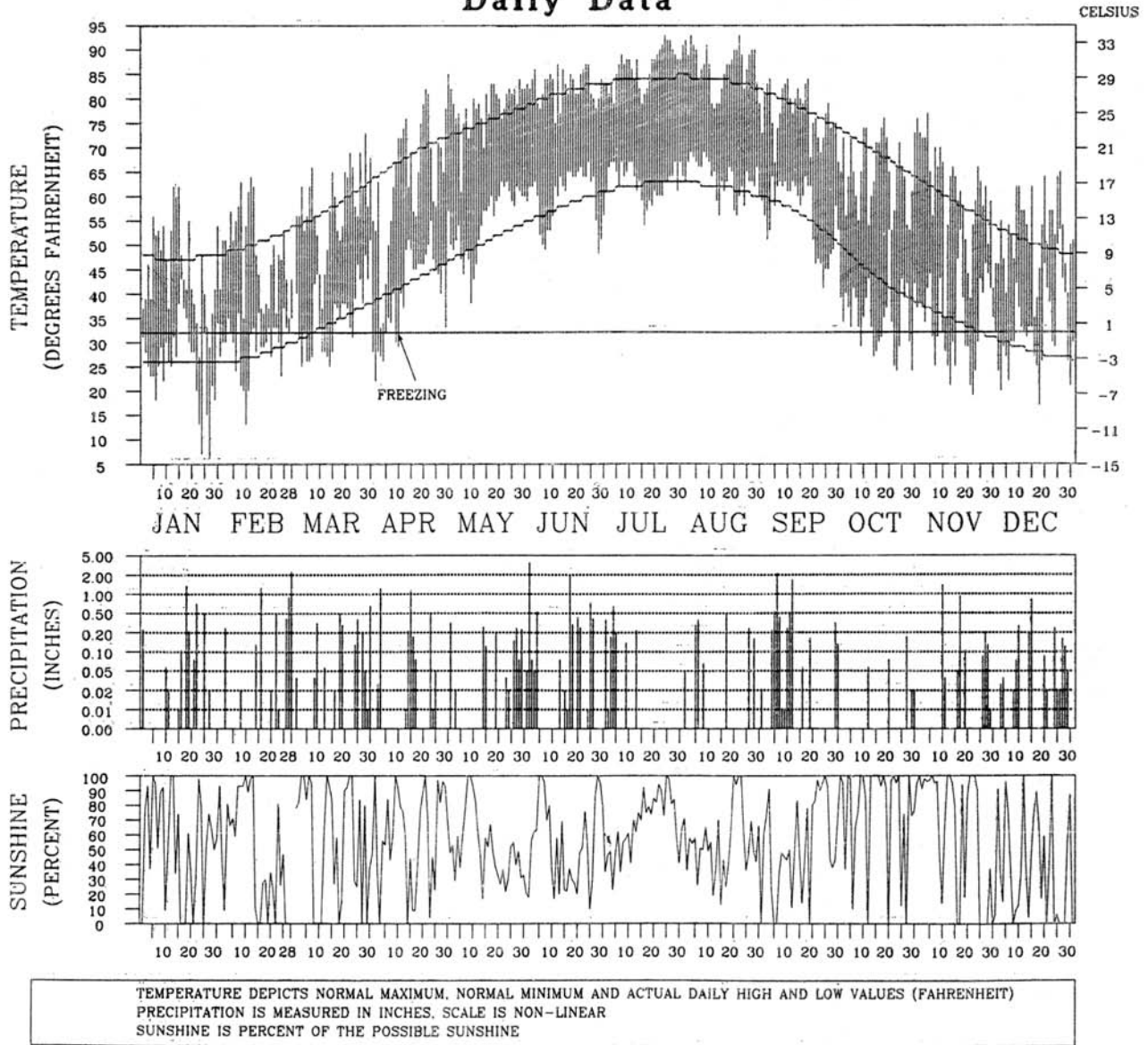
The annual issue summarizes monthly and annual data for the current year for most of the same stations. A climatological narrative, a “Normals, Means, and Extremes” table, and tables listing by month, year, or season the average temperatures, total precipitation, total snowfall, and heating and cooling degree days for approximately the last 30 yr is also presented.

# 1987 LOCAL CLIMATOLOGICAL DATA ANNUAL SUMMARY WITH COMPARATIVE DATA



ASHEVILLE,  
NORTH CAROLINA

## Daily Data



TEMPERATURE DEPICTS NORMAL MAXIMUM, NORMAL MINIMUM AND ACTUAL DAILY HIGH AND LOW VALUES (FAHRENHEIT)  
 PRECIPITATION IS MEASURED IN INCHES. SCALE IS NON-LINEAR  
 SUNSHINE IS PERCENT OF THE POSSIBLE SUNSHINE

I CERTIFY THAT THIS IS AN OFFICIAL PUBLICATION OF THE NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION, AND IS COMPILED FROM RECORDS ON FILE AT THE NATIONAL CLIMATIC DATA CENTER, ASHEVILLE, NORTH CAROLINA, 28801

**noaa**

NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION

NATIONAL ENVIRONMENTAL SATELLITE, DATA AND INFORMATION SERVICE

NATIONAL CLIMATIC DATA CENTER ASHEVILLE NORTH CAROLINA

*Kenneth D. Halpern*  
 DIRECTOR  
 NATIONAL CLIMATIC DATA CENTER

Figure 14-1. Frontispiece illustration of a set of 1991 climatological data, annual summary with comparative data, Asheville, NC (National Climatic Data Center, Asheville, NC).

# METEOROLOGICAL DATA FOR 1987

ASHEVILLE, NORTH CAROLINA

LATITUDE: 35°26' N LONGITUDE: 82°33' W ELEVATION: FT. GRND 2140 BARO 2161 TIME ZONE: EASTERN WBAN: 03812

	JAN	FEB	MAR	APR	MAY	JUNE	JULY	AUG	SEP	OCT	NOV	DEC	YEAR
<b>TEMPERATURE °F:</b>													
Averages													
-Daily Maximum	45.0	48.3	57.9	64.5	78.5	82.6	86.6	86.1	77.1	65.2	59.8	52.1	67.0
-Daily Minimum	25.6	29.4	35.0	40.7	54.8	59.7	62.8	63.3	55.8	35.0	34.2	32.2	44.0
-Monthly	35.3	38.9	46.5	52.6	66.7	71.2	74.7	74.7	66.5	50.1	47.0	42.2	55.5
-Monthly Dewpt.	26.0	26.8	32.3	38.8	57.0	63.0	64.7	64.6	58.0	36.0	34.5	31.3	44.4
Extremes													
-Highest	62	64	73	85	84	87	93	93	84	76	77	65	93
-Date	15	12	28	30	28	24	24	22	18	31	4	26	AUG 22
-Lowest	6	13	25	22	38	48	54	56	41	24	19	17	6
-Date	27	10	14	1	9	28	16	21	24	29	22	18	JAN 27
<b>DEGREE DAYS BASE 65 °F:</b>													
Heating	913	725	567	369	40	1	0	0	47	452	532	702	4348
Cooling	0	0	0	7	97	192	310	309	97	0	0	0	1012
<b>% OF POSSIBLE SUNSHINE</b>													
	55	45	57	60	50	54	66	53	54	77	64	38	56
<b>AVG. SKY COVER (tenths)</b>													
Sunrise - Sunset	6.3	7.4	6.2	5.4	6.4	6.0	5.2	5.9	5.8	3.0	4.7	6.8	5.8
Midnight - Midnight	6.2	7.3	6.0	5.6	6.6	6.0	5.0	5.6	5.8	2.8	4.5	6.4	5.7
<b>NUMBER OF DAYS:</b>													
Sunrise to Sunset													
-Clear	8	7	11	9	3	8	9	5	9	21	14	6	110
-Partly Cloudy	10	2	4	9	17	10	16	18	10	5	6	10	117
-Cloudy	13	19	16	12	11	12	6	8	11	5	10	15	138
Precipitation													
.01 inches or more	11	10	13	10	12	14	7	8	13	5	9	15	127
Snow, Ice pellets													
1.0 inches or more	3	1	0	1	0	0	0	0	0	0	0	0	5
Thunderstorms													
	0	1	1	3	6	9	8	9	4	0	1	2	44
Heavy Fog, visibility													
1/4 mile or less	0	2	2	0	14	8	6	10	12	5	4	4	67
Temperature °F													
-Maximum	0	0	0	0	0	0	7	10	0	0	0	0	17
90° and above	2	0	0	0	0	0	0	0	0	0	0	0	2
32° and below	26	18	13	7	0	0	0	0	0	10	15	19	108
-Minimum	0	0	0	0	0	0	0	0	0	0	0	0	0
32° and below													
0° and below													
<b>AVG. STATION PRESS. (mb)</b>													
	938.0	940.7	940.1	936.8	944.1	942.4	944.0	943.1	942.1	944.8	944.5	941.4	941.8
<b>RELATIVE HUMIDITY (%)</b>													
Hour 01	83	76	79	77	91	96	93	93	94	82	80	77	85
Hour 07	85	84	84	79	94	94	94	94	97	87	84	83	88
Hour 13 (Local Time)	59	54	47	47	55	59	55	55	59	40	50	62	54
Hour 19	65	62	57	57	73	74	66	73	77	56	63	69	66
<b>PRECIPITATION (inches):</b>													
Water Equivalent													
-Total	3.49	6.17	2.85	3.67	1.87	8.94	1.86	1.79	6.79	0.36	3.09	2.33	43.21
-Greatest (24 hrs)	1.44	2.52	2.53	1.46	0.35	3.93	0.76	0.65	2.28	0.18	1.48	1.07	3.93
-Date	18	28	PM-1	14-15	1-2	PM-1	3-4	5-6	6	27	10	14-15	JUN PM-1
Snow, Ice pellets													
-Total	15.0	2.7	0.3	11.5	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.5	30.3
-Greatest (24 hrs)	9.6	2.4	0.3	11.5	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.5	11.5
-Date	21-22	16	11-12	3							11	29	APR 3
<b>WIND:</b>													
Resultant													
-Direction (!!!)	341	333	345	342	175	326	339	347	352	347	342	316	340
-Speed (mph)	5.6	2.1	1.8	6.1	0.7	1.2	2.5	1.0	2.1	3.5	2.7	2.0	2.5
Average Speed (mph)	10.2	8.1	8.5	9.9	5.4	5.9	6.4	5.8	5.9	7.4	8.4	9.5	7.6
Fastest Obs. 1 Min.													
-Direction (!!!)	36	33	34	34	34	34	34	34	35	36	35	34	33
-Speed (mph)	32	40	25	28	20	20	20	20	21	24	29	30	40
-Date	31	8	2	24	8	4	12	23	30	3	11	29	FEB 8
Peak Gust													
-Direction (!!!)	NW	NW	N	NW	N	N	S	W	N	N	N	N	NW
-Speed (mph)	46	54	36	48	26	52	31	32	30	38	41	46	54
-Date	19	8	31	4	8	1	30	26	30	3	11	29	FEB 8

(!!!) See Reference Notes on Page 6B  
Page 2

Figure 14-1. Frontispiece illustration of a set of 1991 climatological data, annual summary with comparative data, Asheville, NC (National Climatic Data Center, Asheville, NC) (Continued).

# NORMALS, MEANS, AND EXTREMES

ASHEVILLE, NORTH CAROLINA

LATITUDE: 35°26'N	LONGITUDE: 82°33'W	ELEVATION: FT. GRND 2140 BARO 2161												TIME ZONE: EASTERN	WBAN: 03812
	(a)	JAN	FEB	MAR	APR	MAY	JUNE	JULY	AUG	SEP	OCT	NOV	DEC	YEAR	
<b>TEMPERATURE °F:</b>															
Normals															
-Daily Maximum		47.5	50.6	58.4	68.6	75.6	81.4	84.0	83.5	77.9	68.7	58.6	50.3	67.1	
-Daily Minimum		26.0	27.6	34.4	42.7	51.0	58.2	62.4	61.6	55.8	43.3	34.2	26.2	43.8	
-Monthly		36.8	39.1	46.4	55.7	63.3	69.8	73.2	72.6	66.9	56.0	46.4	39.3	55.5	
Extremes															
-Record Highest	23	78	77	83	89	91	96	96	100	92	86	81	78	100	
-Year		1975	1986	1985	1972	1969	1969	1983	1983	1975	1986	1974	1971	AUG 1983	
-Record Lowest	23	-16	-2	9	22	29	35	46	42	30	21	8	-7	-16	
-Year		1985	1967	1980	1987	1986	1966	1967	1986	1967	1976	1970	1983	JAN 1985	
<b>NORMAL DEGREE DAYS:</b>															
Heating (base 65°F)		874	725	577	283	114	23	0	0	57	286	558	797	4294	
Cooling (base 65°F)		0	0	0	0	61	167	254	239	114	7	0	0	842	
<b>% OF POSSIBLE SUNSHINE</b>	23	56	60	62	66	60	64	59	54	55	60	58	57	59	
<b>MEAN SKY COVER (tenths)</b>															
Sunrise - Sunset	23	6.0	5.9	5.9	5.5	6.2	6.1	6.4	6.3	6.2	5.2	5.5	5.8	5.9	
<b>MEAN NUMBER OF DAYS:</b>															
Sunrise to Sunset															
-Clear	23	9.9	9.1	9.3	10.2	7.6	6.5	5.2	5.0	7.0	12.2	10.5	10.2	102.5	
-Partly Cloudy	23	7.2	6.2	8.4	8.6	9.7	12.2	13.5	13.9	10.5	7.7	7.2	7.1	112.2	
-Cloudy	23	14.0	13.0	13.3	11.2	13.7	11.3	12.3	12.2	12.6	11.0	12.3	13.7	150.5	
Precipitation															
.01 inches or more	23	10.1	9.3	11.2	9.1	11.9	11.2	11.9	12.1	9.4	8.2	9.4	9.7	123.7	
Snow, ice pellets															
1.0 inches or more	23	1.6	1.4	0.8	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.5	4.6	
Thunderstorms	23	0.4	0.8	2.2	3.0	7.3	7.9	9.1	9.0	3.4	1.0	0.7	0.4	45.2	
Heavy Fog Visibility															
1/4 mile or less	23	3.7	3.0	2.3	2.4	5.8	8.1	9.9	14.3	12.1	8.4	4.6	4.8	79.4	
Temperature of															
-Maximum															
30° and above	23	0.0	0.0	0.0	0.0	0.0*	1.7	4.4	2.5	0.3	0.0	0.0	0.0	9.0	
32° and below	23	3.6	1.5	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.8	6.3	
-Minimum															
32° and below	23	24.3	20.9	13.8	4.2	0.3	0.0	0.0	0.0	0.0*	4.0	13.1	20.7	101.3	
0° and below	23	0.6	0.0*	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.8	
<b>AVG. STATION PRESS. (mb)</b>	15	940.9	940.8	940.1	940.2	940.7	942.3	943.4	944.1	943.8	944.2	943.3	942.4	942.2	
<b>RELATIVE HUMIDITY (%)</b>															
Hour 01	23	81	78	79	78	90	94	95	96	96	91	86	83	87	
Hour 07 (Local Time)	23	85	84	85	85	92	95	96	98	97	94	89	86	91	
Hour 13	23	59	56	53	50	58	60	64	64	64	58	57	59	59	
Hour 19	23	68	63	60	56	67	70	74	79	81	75	70	70	69	
<b>PRECIPITATION (inches):</b>															
Water Equivalent															
-Normal		3.48	3.60	5.13	3.84	4.19	4.20	4.43	4.79	3.96	3.29	3.29	3.51	47.71	
-Maximum Monthly	23	7.47	7.02	9.86	7.26	8.83	8.94	9.92	11.28	9.12	7.05	7.76	8.48	11.28	
-Year		1978	1982	1975	1979	1973	1987	1982	1967	1977	1971	1979	1973	AUG 1967	
-Minimum Monthly	23	0.45	0.44	0.77	0.25	1.59	1.28	0.46	0.52	0.16	0.30	1.19	0.16	0.16	
-Year		1981	1978	1985	1976	1985	1986	1986	1981	1984	1978	1981	1965	SEP 1984	
-Maximum in 24 hrs	23	2.95	3.47	5.13	3.06	4.95	3.93	4.02	4.12	3.41	2.95	4.03	2.66	5.13	
-Year		1978	1982	1968	1973	1973	1987	1969	1967	1975	1977	1977	1973	MAR 1968	
Snow, ice pellets															
-Maximum Monthly	23	17.6	25.5	13.0	11.5	T	T	T	T	T	9.6	16.3	25.5	25.5	
-Year		1966	1969	1969	1987	1979	1979	1979	1979	1977	1968	1971	FEB 1969	FEB 1969	
-Maximum in 24 hrs	23	9.6	11.7	10.9	11.5	T	T	T	T	T	5.7	16.3	16.3	16.3	
-Year		1987	1969	1969	1987	1979	1979	1979	1979	1977	1968	1971	DEC 1971	DEC 1971	
<b>WIND:</b>															
Mean Speed (mph)	23	9.8	9.5	9.4	8.9	7.0	6.1	5.8	5.4	5.6	6.7	8.2	8.9	7.6	
Prevailing Direction															
Fastest Obs. 1 Min.															
-Direction (!!!)	23	34	34	35	22	34	36	35	34	32	33	32	34	34	
-Speed (MPH)	23	40	60	46	44	40	40	43	40	35	35	40	44	60	
-Year		1975	1972	1969	1970	1971	1977	1966	1973	1980	1972	1974	1965	FEB 1972	
Peak Gust															
-Direction (!!!)	4	NW	NW	SW	NW	N	N	SW	NW	SW	N	N	N	NW	
-Speed (mph)	4	49	54	45	48	37	52	36	36	37	38	41	46	54	
-Date		1984	1987	1984	1987	1984	1987	1985	1985	1985	1987	1987	1987	FEB 1987	

(!!!) See Reference Notes on Page 6B.  
Page 3

Figure 14-1. Frontispiece illustration of a set of 1991 climatological data, annual summary with comparative data, Asheville, NC (National Climatic Data Center, Asheville, NC) (Continued).

PRECIPITATION (inches)

ASHEVILLE, NORTH CAROLINA

YEAR	JAN	FEB	MAR	APR	MAY	JUNE	JULY	AUG	SEP	OCT	NOV	DEC	ANNUAL
1958	2.89	3.03	3.05	4.04	4.02	1.15	3.91	1.56	1.94	1.83	1.88	3.93	33.23
1959	2.96	1.51	3.37	4.70	7.33	1.53	3.38	3.41	8.33	5.09	1.01	1.97	44.59
1960	2.79	4.19	3.97	2.76	2.11	3.05	2.85	7.24	2.21	4.26	0.68	1.49	37.60
1961	1.45	5.18	3.19	2.98	3.04	4.44	2.54	8.13	1.07	2.36	4.85	6.09	45.32
1962	4.46	3.58	4.13	3.25	2.83	6.20	3.24	3.47	2.40	2.40		1.66	40.02
1963	1.73	1.76	7.66	3.02	2.53	2.71	2.93	3.83	3.64	T	4.42	2.44	36.67
#1964	2.83	3.58	5.13	5.21	0.94	0.80	3.29	8.88	5.37	8.46	2.51	2.88	49.88
1965	2.16	4.60	5.10	2.62	3.33	4.12	4.47	4.03	4.69	2.92	1.30	0.16	39.50
1966	3.37	6.56	2.59	5.47	4.73	2.46	3.24	7.73	4.55	5.37	3.32	2.36	51.75
1967	2.02	2.20	2.86	1.11	6.79	4.45	6.90	11.28	2.53	3.30	2.54	6.13	52.11
1968	2.93	0.62	6.65	2.37	2.92	5.06	7.18	3.31	2.64	5.02	2.98	3.10	44.78
1969	2.64	5.08	4.01	3.53	3.32	3.82	7.53	6.47	3.04	2.63	1.91	4.63	48.61
1970	1.75	2.42	2.62	2.96	1.72	2.72	5.02	2.46	1.17	5.55	1.83	2.72	32.94
1971	2.53	4.93	3.48	2.06	3.54	5.00	5.47	3.03	3.80	7.05	2.84	4.32	48.05
1972	3.57	2.02	3.19	1.49	6.63	6.54	4.66	1.88	5.29	4.44	4.42	3.89	48.02
1973	4.26	4.23	8.91	5.71	8.83	3.87	6.95	4.57	3.12	2.41	3.57	8.48	64.91
1974	3.44	4.24	3.18	4.99	5.58	3.73	3.93	7.34	4.13	1.28	4.22	2.38	48.44
1975	3.86	4.56	9.86	0.61	8.17	2.12	3.31	3.63	7.53	3.94	4.89	4.44	56.92
1976	3.51	2.20	4.96	0.25	8.67	5.51	3.18	4.23	3.50	5.59	1.58	4.05	47.23
1977	2.09	1.02	7.29	4.05	3.96	5.11	1.03	3.68	9.12	3.79	6.88	2.43	50.45
1978	7.47	0.44	5.22	2.97	4.65	2.29	0.63	6.91	2.57	0.30	2.49	4.32	40.26
1979	6.81	5.14	5.72	7.26	5.35	2.20	5.52	3.63	5.60	1.40	7.76	1.05	57.44
1980	2.85	0.53	8.26	4.77	4.54	4.68	2.21	2.38	4.36	2.62	3.04	0.59	40.83
1981	0.45	4.80	3.24	2.07	7.50	4.41	2.06	0.52	1.36	2.19	1.19	4.79	34.58
1982	5.41	7.02	1.92	3.62	3.78	3.98	9.92	1.73	1.33	3.48	4.59	4.04	50.82
1983	3.39	5.63	6.27	5.27	3.48	3.71	1.06	0.95	5.66	4.43	4.77	8.30	52.92
1984	2.36	6.43	4.82	4.05	6.62	3.69	5.88	5.02	0.16	2.73	2.61	1.34	45.71
1985	2.95	4.74	0.77	2.74	1.59	1.47	4.37	7.04	1.25	3.41	4.91	0.70	35.94
1986	1.11	1.85	2.75	0.57	3.55	1.28	0.46	6.10	3.15	4.19	5.28	4.28	34.57
1987	3.49	6.17	2.85	3.67	1.87	8.94	1.86	1.79	6.79	0.36	3.09	2.33	43.21
Record Mean	3.24	3.80	4.63	3.23	4.83	3.96	4.21	4.34	3.80	3.41	3.57	3.51	46.52

See Reference Notes on Page 6B.  
Page 4A

AVERAGE TEMPERATURE (deg. F)

ASHEVILLE, NORTH CAROLINA

YEAR	JAN	FEB	MAR	APR	MAY	JUNE	JULY	AUG	SEP	OCT	NOV	DEC	ANNUAL
1958	32.2	29.7	42.9	55.5	64.8	71.2	74.4	73.4	66.4	55.5	50.1	37.0	54.4
1959	36.5	42.1	44.6	57.3	66.5	69.9	74.4	75.4	67.6	59.9	45.1	40.7	56.7
1960	39.0	36.6	33.5	58.2	61.1	71.1	73.4	74.1	68.1	58.9	47.4	34.7	54.7
1961	33.5	44.1	50.1	50.4	60.0	68.6	72.5	72.0	68.4	55.3	50.4	39.7	56.5
1962	37.4	45.8	43.4	52.9	69.4	70.2	73.7	72.3	65.4	58.3	46.0	34.4	55.7
1963	34.4	34.2	51.0	57.6	63.6	69.2	71.4	72.0	66.2	59.6	47.8	31.4	54.8
#1964	38.1	34.7	46.3	57.3	65.3	72.8	72.9	71.7	66.0	53.0	51.4	42.9	56.1
1965	37.0	37.9	42.4	57.4	65.8	66.8	72.2	71.1	66.8	53.8	46.4	40.3	54.8
1966	30.1	36.2	43.5	52.0	60.1	66.1	71.1	69.9	62.9	51.7	45.0	37.6	52.2
1967	38.7	35.0	49.8	57.6	59.7	66.8	68.7	68.5	60.2	53.5	42.7	41.8	53.6
1968	34.3	32.4	46.6	54.8	61.0	69.5	73.1	74.1	64.1	56.7	46.0	36.2	54.0
1969	36.7	37.8	41.3	56.7	65.2	73.1	75.9	70.7	65.8	56.2	44.0	36.5	55.0
1970	30.9	39.1	46.8	57.6	63.7	70.1	74.4	73.1	70.7	59.0	46.0	42.8	56.2
1971	36.5	39.5	43.1	55.2	61.1	72.4	72.5	72.2	69.5	61.8	45.8	47.7	56.5
1972	42.1	37.6	46.5	55.8	61.2	66.5	72.3	72.5	69.0	55.0	45.5	45.2	55.7
1973	37.5	38.5	52.7	52.8	60.3	71.0	74.1	74.2	70.0	58.8	49.1	39.8	56.5
1974	48.2	40.5	51.1	54.9	64.2	66.7	72.9	72.3	65.7	54.6	47.4	40.3	56.6
1975	41.7	42.5	44.8	54.1	66.0	68.8	72.4	72.9	65.2	57.3	48.2	38.6	56.1
1976	33.6	45.3	50.6	54.9	59.5	68.1	71.2	70.2	63.1	51.5	41.2	36.2	53.8
1977	24.8	37.4	50.7	58.2	64.6	69.7	75.7	73.8	69.1	54.3	49.3	36.8	55.3
1978	29.3	33.4	45.9	56.8	62.0	71.1	73.4	74.1	70.0	55.7	51.8	41.0	55.4
1979	34.2	35.8	50.0	55.9	64.3	68.8	72.2	73.2	66.5	55.3	49.2	42.0	55.6
1980	40.5	35.1	46.2	56.5	64.8	71.7	77.5	74.8	70.2	54.7	47.1	39.6	56.5
1981	33.3	39.9	44.9	60.1	60.7	74.3	75.0	71.7	66.1	54.5	48.2	35.8	55.4
1982	32.3	41.2	50.0	53.6	67.3	71.5	74.6	71.7	64.5	56.3	47.1	44.9	56.3
1983	36.7	38.8	46.7	51.1	61.6	69.0	75.7	76.5	66.6	57.5	47.3	36.4	55.3
1984	34.0	40.5	44.8	51.7	59.9	70.0	70.6	71.6	62.8	62.7	43.1	46.3	54.8
1985	30.5	38.3	48.1	56.6	62.6	69.8	72.2	70.9	64.2	60.5	56.0	34.7	55.4
1986	35.0	42.2	46.0	56.0	63.3	71.7	76.1	70.9	68.0	57.4	50.7	39.8	56.4
1987	35.3	38.9	46.5	52.6	66.7	71.2	74.7	74.7	66.5	50.1	47.0	42.2	55.5
Record Mean	35.3	38.4	46.8	55.3	62.9	69.8	73.4	72.4	66.3	56.0	47.1	40.0	55.3
Max	46.1	49.8	59.1	68.3	75.0	81.2	83.9	82.8	77.2	68.3	58.8	51.0	66.8
Min	24.6	27.0	34.6	42.3	50.7	58.3	62.9	61.9	55.5	43.7	35.4	29.1	43.8

See Reference Notes on Page 6B.  
Page 4B

Figure 14-1. Frontispiece illustration of a set of 1991 climatological data, annual summary with comparative data, Asheville, NC (National Climatic Data Center, Asheville, NC) (Continued).

HEATING DEGREE DAYS Base 65 deg. F

ASHEVILLE, NORTH CAROLINA

SEASON	JULY	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUNE	TOTAL
1958-59	0	0	41	292	449	860	877	635	624	249	58	3	4088
1959-60	0	0	21	204	591	747	800	818	969	226	181	2	4559
1960-61	0	0	32	194	522	931	971	582	453	444	169	18	4316
1961-62	0	0	49	295	433	778	851	531	664	371	27	1	4002
1962-63	0	0	91	224	565	941	943	857	426	241	98	6	4392
1963-64	4	0	51	164	513	1038	826	873	572	251	59	8	4359
# 1964-65	0	20	46	372	399	679	863	751	691	232	23	27	4103
1965-66	0	7	39	344	550	759	1075	800	660	383	149	42	4808
1966-67	1	1	87	405	593	838	810	834	465	226	185	51	4496
1967-68	7	2	158	351	660	713	947	939	566	306	150	7	4806
1968-69	0	20	42	258	563	884	873	755	729	246	70	9	4449
1969-70	0	8	59	280	623	875	1050	720	557	236	86	3	4497
1970-71	0	0	29	194	565	682	875	707	672	290	137	0	4151
1971-72	0	0	6	129	576	530	704	790	569	294	116	39	3749
1972-73	3	0	8	304	578	605	846	737	374	362	158	0	3975
1973-74	0	0	7	205	473	772	516	680	423	299	83	24	3482
1974-75	0	0	65	316	519	760	715	624	619	331	46	7	4002
1975-76	0	0	77	232	498	812	966	566	439	296	168	33	4087
1976-77	2	3	83	411	706	884	1239	768	437	198	66	25	4822
1977-78	0	0	14	331	466	868	1101	878	586	241	139	0	4624
1978-79	0	0	12	283	390	741	951	810	457	268	71	18	4001
1979-80	9	0	44	299	468	707	753	861	573	258	65	2	4035
1980-81	0	0	37	315	533	778	978	696	615	152	152	0	4256
1981-82	0	1	57	326	499	897	1006	659	458	333	38	0	4274
1982-83	0	0	74	274	531	616	872	725	562	410	127	13	4204
1983-84	0	0	84	229	527	882	955	706	618	391	176	9	4577
1984-85	1	0	107	91	648	576	1064	737	520	249	109	19	4121
1985-86	0	6	111	156	266	932	923	633	581	273	91	2	3974
1986-87	0	32	16	268	419	774	913	725	567	369	40	1	4124
1987-88	0	0	47	452	532	702							

See Reference Notes on Page 6B.  
Page 5A

COOLING DEGREE DAYS Base 65 deg. F

ASHEVILLE, NORTH CAROLINA

YEAR	JAN	FEB	MAR	APR	MAY	JUNE	JULY	AUG	SEP	OCT	NOV	DEC	TOTAL
1969	0	0	0	4	85	262	343	196	92	15	0	0	997
1970	0	0	0	22	52	159	296	259	206	17	0	0	1011
1971	0	0	0	3	25	232	238	231	149	37	8	0	923
1972	0	0	0	24	6	84	236	237	134	0	1	0	722
1973	0	0	0	1	16	190	288	292	163	19	0	0	969
1974	0	0	0	3	65	82	254	234	92	1	0	0	731
1975	0	0	0	11	82	124	237	252	89	0	0	0	795
1976	0	0	0	0	5	135	198	170	35	2	0	0	545
1977	0	0	0	2	59	173	340	279	146	7	1	0	1007
1978	0	0	0	2	53	188	266	292	168	4	0	0	973
1979	0	0	0	1	55	141	234	261	96	4	0	0	792
1980	0	0	0	8	64	210	396	311	198	7	0	0	1191
1981	0	0	0	10	25	286	316	212	98	4	0	0	955
1982	0	0	0	0	117	206	305	215	64	16	0	0	923
1983	0	0	0	0	25	139	335	362	141	5	0	0	1007
1984	0	0	0	0	25	165	180	211	49	27	0	0	657
1985	0	0	5	2	43	170	229	194	90	25	4	0	762
1986	0	0	0	8	43	209	353	222	112	38	0	0	985
1987	0	0	0	7	97	192	310	309	97	0	0	0	1012

See Reference Notes on Page 6B.  
Page 5B

Figure 14-1. Frontispiece illustration of a set of 1991 climatological data, annual summary with comparative data, Asheville, NC (National Climatic Data Center, Asheville, NC) (Continued).



SNOWFALL (inches)

ASHEVILLE, NORTH CAROLINA

SEASON	JULY	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUNE	TOTAL
1958-59	0.0	0.0	0.0	0.0	T	2.3	1.5	T	T	0.3	0.0	0.0	4.1
1959-60	0.0	0.0	0.0	0.0	T	1.0	2.0	8.5	28.9	0.2	T	0.0	40.6
1960-61	0.0	0.0	0.0	0.0	T	0.2	0.8	3.0	T	T	0.0	0.0	4.0
1961-62	0.0	0.0	0.0	T	T	1.2	13.3	T	8.3	T	0.0	0.0	22.8
1962-63	0.0	0.0	0.0	0.0	0.3	4.2	T	4.5	T	0.0	0.0	0.0	9.0
1963-64	0.0	0.0	0.0	0.0	1.2	8.9	1.7	13.9	0.1	0.0	0.0	0.0	25.8
#1964-65	0.0	0.0	0.0	0.0	T	T	5.5	4.3	5.0	0.0	0.0	0.0	14.8
1965-66	0.0	0.0	0.0	0.0	T	T	17.6	6.2	0.2	T	0.0	0.0	24.0
1966-67	0.0	0.0	0.0	0.0	1.3	0.8	1.5	4.2	T	0.0	0.0	0.0	7.8
1967-68	0.0	0.0	0.0	0.0	0.0	1.9	7.2	6.0	0.1	0.0	0.0	0.0	15.2
1968-69	0.0	0.0	0.0	0.0	9.6	T	0.1	25.5	13.0	0.0	0.0	0.0	48.2
1969-70	0.0	0.0	0.0	0.0	T	10.9	4.8	1.1	0.5	0.0	0.0	0.0	17.3
1970-71	0.0	0.0	0.0	0.0	T	6.1	0.1	0.1	8.9	0.2	0.0	0.0	15.4
1971-72	0.0	0.0	0.0	0.0	0.6	16.3	T	7.4	7.4	0.0	0.0	0.0	31.7
1972-73	0.0	0.0	0.0	0.0	0.6	T	7.1	0.5	1.0	T	0.0	0.0	9.2
1973-74	0.0	0.0	0.0	0.0	0.0	3.0	T	0.3	1.1	T	0.0	0.0	4.4
1974-75	0.0	0.0	0.0	0.0	3.1	3.0	0.4	4.3	3.7	T	0.0	0.0	14.5
1975-76	0.0	0.0	0.0	0.0	5.0	0.4	1.6	3.5	T	0.0	0.0	0.0	10.5
1976-77	0.0	0.0	0.0	0.0	0.1	0.3	11.9	0.7	0.0	0.0	0.0	0.0	13.0
1977-78	0.0	0.0	0.0	T	T	1.5	9.7	5.3	5.3	T	0.0	0.0	21.8
1978-79	0.0	0.0	0.0	0.0	0.0	T	5.2	17.8	T	0.0	T	0.0	23.0
1979-80	0.0	0.0	0.0	0.0	T	T	2.1	6.3	5.4	T	0.0	0.0	13.8
1980-81	0.0	0.0	0.0	0.0	T	T	4.7	T	9.9	0.0	0.0	0.0	14.6
1981-82	0.0	0.0	0.0	0.0	T	2.0	8.6	8.1	0.1	3.0	0.0	0.0	21.8
1982-83	0.0	0.0	0.0	0.0	0.0	0.4	10.5	9.3	4.5	2.0	0.0	0.0	26.7
1983-84	0.0	0.0	0.0	0.0	T	T	0.2	2.9	T	0.0	0.0	0.0	3.1
1984-85	0.0	0.0	0.0	0.0	0.0	T	4.5	3.1	0.1	0.4	0.0	0.0	8.1
1985-86	0.0	0.0	0.0	0.0	0.0	0.4	0.8	3.7	0.1	T	0.0	0.0	5.0
1986-87	0.0	0.0	0.0	0.0	T	T	15.0	2.7	0.3	11.5	0.0	0.0	29.5
1987-88	0.0	0.0	0.0	0.0	0.3	0.5							
Record Mean	0.0	0.0	0.0	T	0.9	2.1	5.2	5.4	2.9	0.7	0.0	0.0	17.1

See Reference Notes on Page 6B  
Page 6A

REFERENCE NOTES

ASHEVILLE, NORTH CAROLINA

GENERAL

T - TRACE AMOUNT.  
BLANK ENTRIES DENOTE MISSING/UNREPORTED DATA.  
# INDICATES A STATION OR INSTRUMENT RELOCATION.  
SEE STATION LOCATION TABLE ON PAGE 8.

SPECIFIC

PAGE 2

PM - INCLUDES LAST DAY OF PREVIOUS MONTH

PAGE 3

(a) - LENGTH OF RECORD IN YEARS, ALTHOUGH INDIVIDUAL MONTHS MAY BE MISSING.

\* LESS THAN .05

NORMALS - BASED ON THE 1951-1980 RECORD PERIOD.

EXTREMES - DATES ARE THE MOST RECENT OCCURRENCE

WIND DIR. - NUMERALS SHOW TENS OF DEGREES CLOCKWISE

FROM TRUE NORTH. "00" INDICATES CALM.

RESULTANT DIRECTIONS ARE GIVEN TO WHOLE DEGREES.

PAGE 4B

MAX AND MIN ARE LONG TERM MEAN DAILY MAXIMUM AND MEAN DAILY MINIMUM TEMPERATURES.

EXCEPTIONS

PAGES 4A, 4B, 6A  
RECORD MEANS ARE THROUGH THE CURRENT YEAR,  
BEGINNING IN 1965 FOR TEMPERATURE  
1965 FOR PRECIPITATION  
1965 FOR SNOWFALL

Figure 14-1. Frontispiece illustration of a set of 1991 climatological data, annual summary with comparative data, Asheville, NC (National Climatic Data Center, Asheville, NC) (Continued).

## ASHEVILLE, NORTH CAROLINA

The city of Asheville is located on both banks of the French Broad River, near the center of the French Broad Basin. Upstream from Asheville, the valley runs south for 18 miles and then curves toward the south-southwest. Downstream from the city, the valley is oriented toward the north-northwest. Two miles upstream from the principal section of Asheville, the Swannanoa River joins the French Broad from the east. The entire valley is known as the Asheville Plateau, having an average elevation near 2,200 feet above sea level, and is flanked by mountain ridges to the east and west, whose peaks range from 2,000 to 4,400 feet above the valley floor. At the Carolina-Tennessee border, about 25 miles north-northwest of Asheville, a relatively high ridge of mountains blocks the northern end of the valley. Thirty miles south, the Blue Ridge Mountains form an escarpment, having a general elevation of about 2,700 feet above sea level. The tallest peaks near Asheville are Mt. Mitchell, 6,684 feet above sea level, 20 miles northeast of the city, and Big Pisgah Mountain, 5,721 feet above sea level, 16 miles to the southwest.

Asheville has a temperate, but invigorating, climate. Considerable variation in temperature often occurs from day to day in summer, as well as during the other seasons.

While the office was located in the city, the combination of roof exposure conditions and a smoke blanket, caused by inversions in temperature in the valley on quiet nights, resulted in higher early morning temperatures at City Office sites than were experienced nearer ground level in nearby rural areas. The growing season in this area is of sufficient length for commercial crops, the average length of freeze-free period being about 195 days. The average last occurrence in spring of a temperature 32 degrees or lower is mid-April and the average first occurrence in fall of 32 degrees is late October.

The orientation of the French Broad Valley appears to have a pronounced influence on the wind direction. Prevailing winds are from the northwest during all months of the year. Also, the shielding effect of the nearby mountain barriers apparently has a direct bearing on the annual amount of precipitation received in this vicinity. In an area northwest of Asheville, the average annual precipitation is the lowest in North Carolina. Precipitation increases sharply in all other directions, especially to the south and southwest.

Destructive events caused directly by meteorological conditions are infrequent. The most frequent, occurring at approximately 12-year intervals, are floods on the French Broad River. These floods are usually associated with heavy rains caused by storms moving out of the Gulf of Mexico. Snowstorms which have seriously disrupted normal life in this community are infrequent. Hailstorms that cause property damage are extremely rare.

Figure 14-1. Frontispiece illustration of a set of 1991 climatological data, annual summary with comparative data, Asheville, NC (National Climatic Data Center, Asheville, NC) (Continued).

STATION LOCATION

ASHEVILLE, NORTH CAROLINA

Location	Occupied from	Occupied to	Airline distance and direction from previous location	Latitude North	Longitude West	Elevation above								Automatic Observing Equipment	* Type M = AMOS T = AUTOB  Remarks	
						See level	Ground									Hygrothermometer
							Ground at temperature site	Wind instruments	Extreme thermometers	Psychrometer	Sunshine Switch	Tipping bucket rain gage	Weighting rain gage			
<u>COOPERATIVE</u>	1857	1902	NA												Smithsonian Institute and Army Signal Corps observers. Records almost continuous, but exact locations and details as to exposure are not available.	
<u>CITY</u>																
Drumor Building Patton Avenue and Church Street	8/22/02	5/22/03	NA	35° 36'	82° 32'	2207	106	75	73		**			62	** - Elevation not on record. Notes indicate same exposure as 8-inch gage.	
Library Building South Pack Square	5/22/03	7/1/10	600 ft. ENE	35° 36'	82° 32'	2218	75	55	53		**			46		
Legal Building South Pack Square	7/1/10	1/1/31	60 ft. ENE	35° 36'	82° 32'	2218	84	72	70			61		61		
U. S. Post Office and Court House Building Otis and Post Streets	1/1/31	8/31/64 (X)	2000 ft. WSW	35° 36'	82° 32'	2203	b92	78	77			75 a75	77 b	75	a - Effective 9/1/52. (X) - Office moved to airport. Climatological observations continued at City site through May 1967. b - Removed 9/1/64.	
<u>COOPERATIVE</u>																
Federal Building	6/1/67	Present	500 ft. NE	35° 36'	82° 32'	2242		110					108	108	Elevations above ground are approximate values with reference to point opposite shelter on west side of building.	
<u>AIRPORT</u>																
Administration Building Asheville Airport†	9/1/64	Present	12 mi. S of Post Office	35° 26'	82° 32' c82° 33'	2140	20	NA d4 g4	3 g3 e21	57 e21	NA	4 g4	3 g3	4 f4	NA c - Resurveyed effective 6/20/75. d - Installed 12/15/77. e - Lowered 10/5/84. f - Type change 10/18/84. g - Moved 30-35' N 3/4/87.	
† Asheville Regional AP (Effective 7/1/80)																

SUBSCRIPTION: Price and ordering information available through: National Climatic Data Center, Federal Building, Asheville, North Carolina 28801

USCOMM-NOAA-ASHEVILLE, N.C. - 480

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FIRST CLASS

Figure 14-1. Frontispiece illustration of a set of 1991 climatological data, annual summary with comparative data, Asheville, NC (National Climatic Data Center, Asheville, NC) (Continued).

Due to the modernization program of the National Weather Service, the format of the LCD is revised from time to time to accommodate the new technologies implemented. However, much of the basic data currently presented in the LCD will continue.

Summarization and publication of data may take many forms. One example is given here. This is the publication of 1987 Local Climatological Data, Annual Summary with comparative data at Asheville, NC. Only the frontispiece is illustrated. This type of summary, one of many, is published for each First Order Station of the U.S. National Oceanic and Atmospheric Administration, Department of Commerce, National Weather Service stations. Once the data have been cleared for publication, electronic computers produce the formatted data on microform. Forwarded immediately to the printing facilities, the microforms are used to prepare the printing plates and printing then is done. Mailing and distribution follow immediately.

Page number 1 contains a daily maximum-minimum temperature (fahrenheit) bar for the year. The freezing temperature (fahrenheit) line is presented as a guide here and for comparison with summaries of other similar station publications. An annual fitted curve is presented for the maximum temperatures (fahrenheit) and another is presented for the minimum temperatures (fahrenheit). Daily vertical bars provide a precipitation measure in inches throughout the year. The scale is arbitrary, nonlinear, and cannot be interpreted precisely. A logarithmic scale might have been used. The artifice used is to conserve time, space, and money, yet present the main features for rough comparison. On a daily basis, percent of sunshine is also shown.

Page No. 2 provides first the year of summary, by months (not days), the location (Asheville, NC), the latitude, the longitude, the elevation of the station above sea level (in feet), the elevation of the barometer, the time zone, Eastern, and the Weather Bureau Army and Navy (WBAN) identification number 03812. In an international format, the metric system would be used and the WMO identification number would be used.

The monthly averages of temperatures ( $^{\circ}\text{F}$ ) are shown for the daily maxima, daily minima, and daily averages. In addition, the dates and values for the extremes, both maximum and minimum, are shown.

The tabular presentation includes normal degree days to the heating and cooling base of  $65^{\circ}\text{F}$  ( $18.3^{\circ}\text{C}$ ).

The monthly average percent sunshine is also shown.

Monthly average sky cover sunrise to sunset and sunset to sunrise is shown. The number of days of clear, partly cloudy, and cloudy are indicated. The tables present the number of days with 0.01 in (0.25 mm) precipitation and the number of days with frozen precipitation with more than 1 in (25.4 mm).

The table reveals the number of days in each month with thunderstorms and the number of days with heavy fog with the visibility  $\leq 0.25$  mi (0.4 km). Also seen are the number of days when the maxima were above  $90^{\circ}\text{F}$  ( $32.2^{\circ}\text{C}$ ) and below  $32^{\circ}\text{F}$  ( $0^{\circ}\text{C}$ ), presented as the number of days in each month when the minima were below  $32^{\circ}\text{F}$  ( $0^{\circ}\text{C}$ ) and  $0^{\circ}\text{F}$  ( $-17.7^{\circ}\text{C}$ ).

The average pressure in millibars is shown for each month.

Relative humidities in percent are shown for the hours of 01, 07, 13, and 19 local (EDT) time which are 06, 12, 18, and 24 (00) Greenwich.

For the precipitation, the monthly water equivalents in inches appear in total, the date, and the greatest amount. In addition, that part of the water equivalent of frozen precipitation shows.

The last section, on page 2, gives the speed (mph) and the direction of the resultant wind, the average speed (mph) the fastest 1-min scale, direction, speed, and date, and the peak gust, direction, speed, and date.

Page 3 provides the normal values for all items shown on page 2, based on the 1951 to 1980 database. Where this base is not available for other locations, the period used is indicated. Comparison of these normals then may be made with the data on page 2.

For those interested in the last 30 years of data, the length of the WMO approved normal period, pages 4A and 4B, provide the comparative information, month by month through the 30-yr period 1958–1987. The monthly means, the maxima, and the minima are shown. The precipitation is in inches while the temperatures are in Fahrenheit.

In similar fashion, on pages 5A and 5B, the heating and cooling degree days (base 65 °F) are given. Where data are not available for any reason, blank spaces occur. No means or averages or maxima or minima are computed or shown.

On page 6A, the monthly snowfall depths are shown, along with the computed monthly means. On page 6B, explanatory remarks pertaining to the data appear.

Page 7 (our p. 14-8) presents a description of Asheville and the location of the observation station. This description is extended to page 8 where the details appear for the entire history of the station location.

Included on page 8 (our p. 14-9) is information for those who want to subscribe for this particular location summary. The prices are subject to change. It will be noted that this particular publication is a unit in itself, and can be mailed as a unit.

### **14.3 Publications of 1961–1990 Climatic Normals**

*Climatology of the United States No. 85*, Divisional Normals and Standard Deviations of Temperature, Precipitation, Heating and Cooling Degree Days, 1931–1990 (1931–1960, 1941–1970, 1951–1980, and 1961–1990). Only the frontispiece page is shown (fig. 14-2).

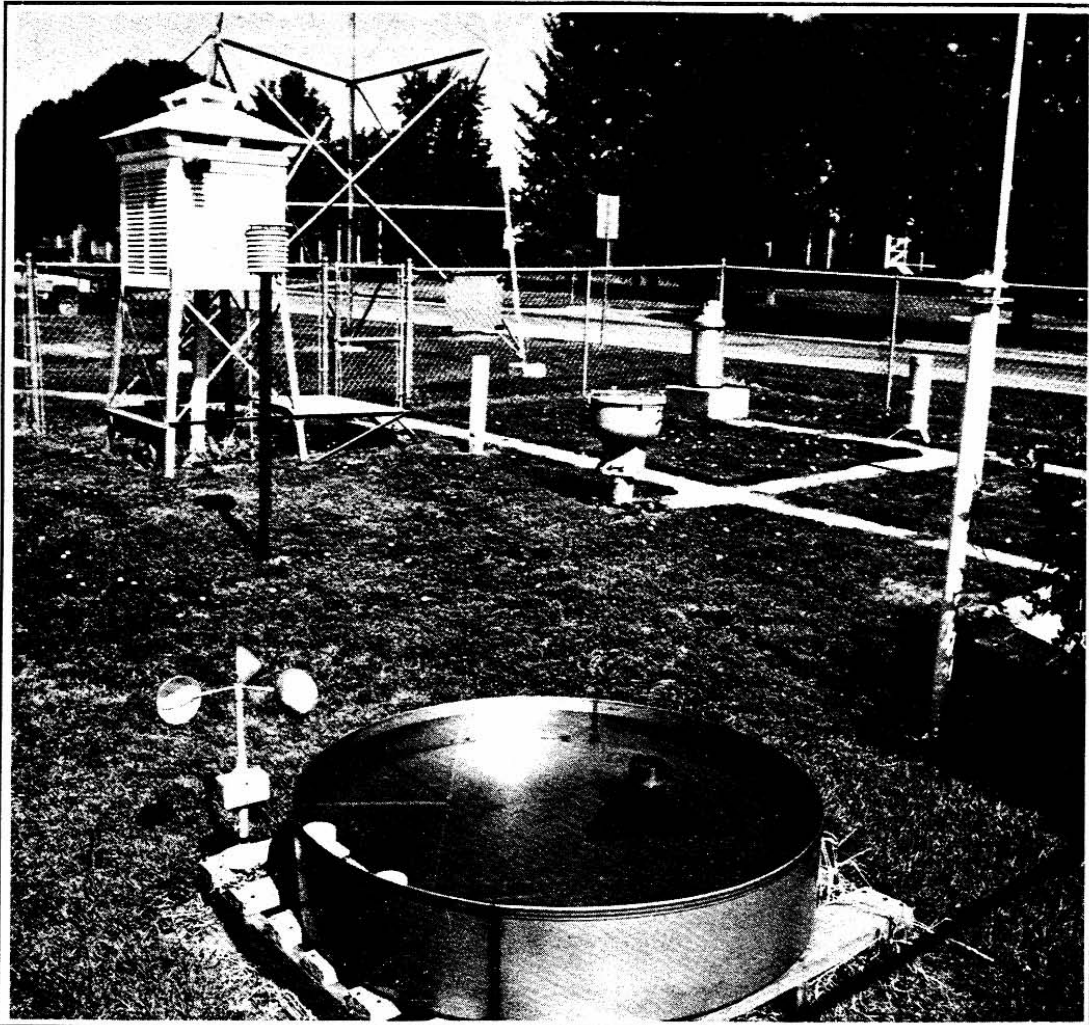
This publication presents normals and standard deviations for the four 30-yr periods and the 60-yr period between 1931–1990 for each division in a state. A division represents a region within a state that is, as nearly as possible, climatically homogeneous. Some areas, however, may experience rather extreme variations within a division (e.g., the Rocky Mountain states). The divisions have been established to satisfy researchers in hydrology, agriculture, energy supply, etc., who require data averaged over an area of a state rather than for a point (station).

The divisional data are displayed by name and number for a state or island. The states and islands include the contiguous United States, Alaska, Puerto Rico, and the Virgin Islands, and are arranged alphabetically. Hawaii is not included because the varied topography and locations of the observing stations do not allow for the establishment of homogeneous divisions. The data include monthly and annual values of mean temperature, precipitation, heating degree days (base 65 °F), and cooling degree days (base 65 °F). Standard deviations of these values are also provided.

The divisional normals as well as the 60-yr sequential monthly and annual data are also available on microfiche and magnetic tape. See figure 14-2.



# Divisional Normals and Standard Deviations of Temperature ( $^{\circ}\text{F}$ ) and Precipitation (Inches) 1931-1990



**noaa** NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION / NATIONAL ENVIRONMENTAL SATELLITE, DATA, AND INFORMATION SERVICE / NATIONAL CLIMATIC DATA CENTER ASHEVILLE, N.C.

Figure 14-2. Frontispiece illustration of the 1931–1990 divisional temperatures ( $^{\circ}\text{F}$ ) and precipitation (inches) normals and standard deviation, *Climatology of the United States, No. 85* (National Climatic Center, Asheville, NC).

## 14.4 Climatic Normals 1961–1990

Climate is an important factor in agriculture, commerce, industry, and transportation. It is a natural resource that affects many human activities such as farming, fuel consumption, structural design, building site location, trade, analysis of market fluctuations, and the utilization of other natural resources. The influence of climate on our lives is continual. The NCDC inherited the U.S. Weather Bureau's responsibility to fulfill the mandate of Congress "... to establish and record the climatic conditions of the United States," an important provision of the Organic Act of October 1, 1890, which established the Weather Bureau as a civilian agency (15 U.S.C. 311).

The mandate to describe the climate was combined with guidelines established through international agreement. The end of a decade has been set by the WMO as the desirable term for a 30-yr period from which to calculate climatic conditions. The average value of a meteorological element over the 30 yr is defined as a climatological normal. The normal climate helps in describing the climate and in determining climatic time trends by comparing the current 30-yr period with earlier periods.

### 14.4.1 *Climatology of the United States No. 81 (by State), Monthly Station Normals of Temperature, Precipitation, and Heating and Cooling Degree Days, 1961–1990*

This publication presents normals of average monthly and annual maximum, minimum, and mean temperature, monthly and annual total precipitation, and heating and cooling degree days (base 65 °F) for individual locations for the 1961–1990 period. There are temperature and degree day data for 4,775 stations and precipitation data for 6,662 stations. The locations represent cooperative weather observer sites, National Weather Service offices, and principal climatological stations in the 50 states, Puerto Rico, Virgin Islands, and Pacific Islands.

The monthly normals are published by state. The data are arranged in four tables representing temperature, precipitation, heating degree days, and cooling degree days. The locations are listed alphabetically within each table. A station locator map and cross reference index providing station name, number, type, location, and elevation are included in the publication for each state.

The monthly normals as well as the 30-yr sequential temperature and precipitation data are available on microfiche and magnetic tape. The cross reference index is also available on magnetic tape and is designated as the "monthly 1961–1990 normals name tape." See figure 14-3, monthly precipitation probabilities.

## 14.5 Other Climate Normals and Information

### 14.5.1 Climatological Data

A monthly and annual publication are issued for each state—separate volumes are issued for New England, Maryland, and Delaware, Hawaii and Pacific Islands, and Puerto Rico and Virgin Islands.

The monthly issue contains station daily maximum and minimum temperatures and precipitation. Some stations provide daily snowfall and snow depth, evaporation, and soil temperature data. A monthly summary of these data and heating and cooling degree days (base 65 °F) is also presented. In addition, the July issue contains a recap of monthly heating degree days and snow data for the past season (July through June). The annual issue contains monthly and annual average temperatures, total precipitation, temperature extremes, freeze data, soil temperatures, evaporation, and a recap of monthly total cooling degree days.



**Monthly Station Normals  
of Temperature, Precipitation,  
and Heating and Cooling  
Degree Days  
1961 - 1990**

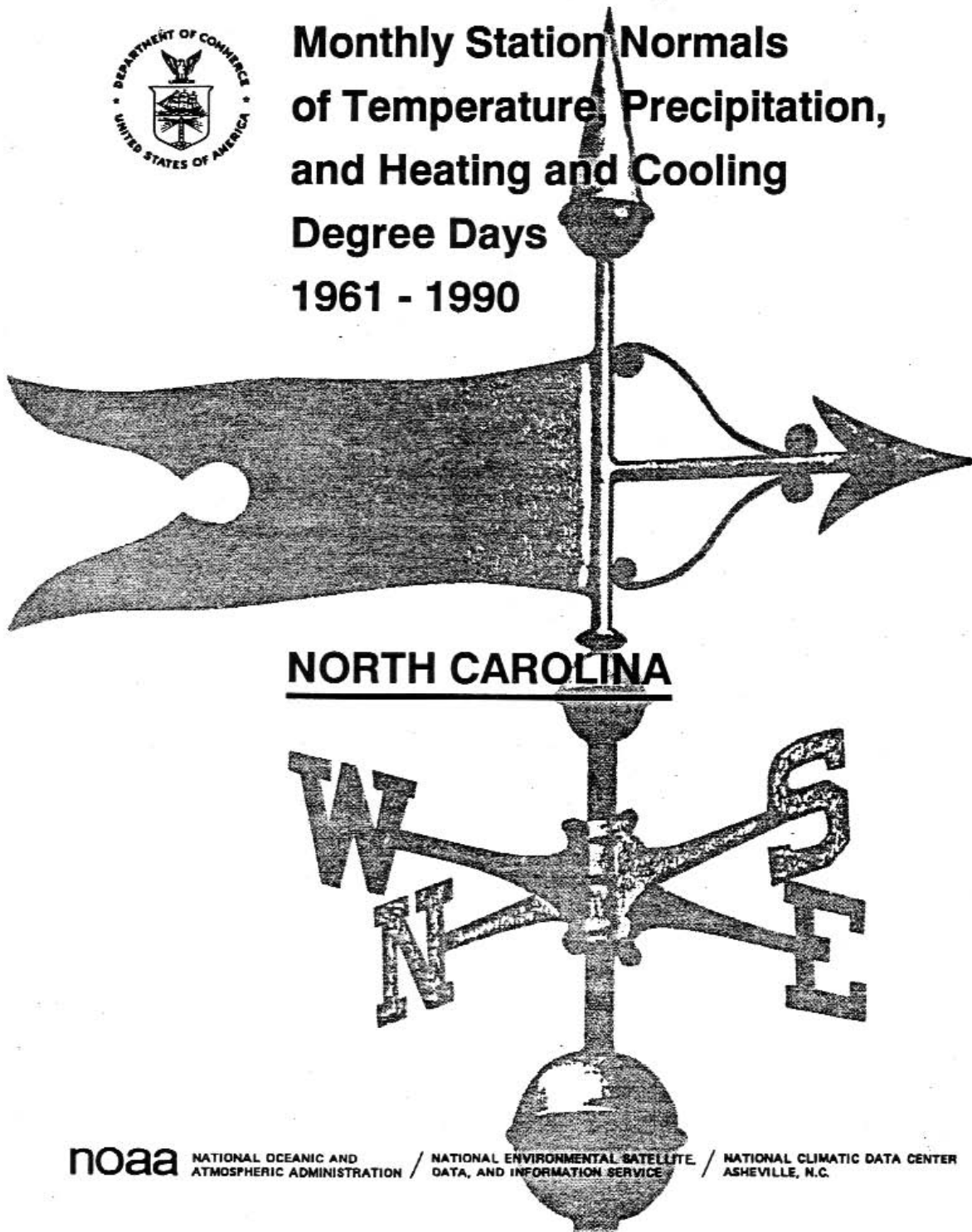


Figure 14-3 Frontispiece illustration of the monthly precipitation levels of the 1961–1990 normals, *Climatology of the United States, No. 81-Supplement No. 1*, Asheville, NC.



### **14.5.2 Storm Data**

*Storm Data* is issued monthly and includes data for each of the 50 states. This publication presents the place, time, character, and estimated damage (by broad categories) of all reported severe storms or unusual weather phenomena. The number of deaths and injuries are also shown for each event. Data are divided chronologically by states, and place within the state. A short narrative of each storm is included. Also included are special articles on “Outstanding Storms of the Month,” descriptive photographs, storm track maps, and a table summarizing storm statistics by states. No annual summary is issued. The December issue contains a General Summary of Tornadoes and Lightning for the year, and a Summary of North Atlantic and Pacific Tropical Cyclones.

### **14.5.3 Hourly Precipitation Data**

The *Hourly Precipitation Data* is issued monthly for each state; separate volumes are issued for New England, Maryland, and Delaware, Hawaii and Pacific Islands, and Puerto Rico and Virgin Islands. Alaska is not published. Hourly and daily precipitation values and monthly maximum amount of precipitation for select time categories are presented for stations equipped with recording gauges. No annual summary is issued. The December issue contains monthly and annual totals of precipitation for that year.

### **14.5.4 Monthly Climatic Data for the World**

The *Monthly Climatic Data for the World* contains monthly mean values of surface and upper air measurements from a large number of selected stations throughout the world. The surface elements included are pressure, temperature, vapor pressure, precipitation, and percent of long-term averaged sunshine. The upper air data consist of height, temperature, dewpoint depression, and mean vector wind at standard constant pressure levels. No annual summary is issued.

### **14.5.5 State, Regional, and National Monthly and Annual Temperatures Weighted by Area (January 1931–December 1985)—Historical Climatology Series 4-1 and State, Regional, and National Monthly and Annual Total Precipitation Weighted by Area (January 1931–December 1985)—Historical Climatology Series 4-2**

These two publications present temperature or precipitation averages by month and annually for the entire period 1931 through 1985. All states are included except Hawaii and Alaska. The mean and standard deviation of each element are provided for the 50-yr record. Weighting procedures are included. Monthly updates are available.

### **14.5.6 State, Regional, and National Monthly and Seasonal Heating Degree Days Weighted by Population (1980 Census) (July 1931–June 1987)—Historical Climatology Series 5-1 and State, Regional, and National Monthly and Seasonal Cooling Degree Days Weighted by Population (1980 Census) (January 1941–December 1986)—Historical Climatology Series 5-2**

These two publications present these data by month and season for the entire period. Data for all states are included except for Hawaii and Alaska. The mean and standard deviation of each element are provided for the 50-yr record. Weighting procedures are included. Monthly updates are available.

### **14.5.7 Climate Variations Bulletin—Historical Climatology Series No. 4-7**

*Climate Variations Bulletin—Historical Climatology Series No. 4-7* is a preliminary report that puts current monthly climate anomalies into historical perspective. When appropriate, supplemental sections are included which address seasonal and annual perspectives. These preliminary data are useful for estimating how current anomalies compare to the historical record; however, the actual values and rankings for the current year will change as the

final data are compiled. Issued monthly, the bulletin presents a narrative summary, tables, and graphs that compare current temperature, precipitation, drought conditions, and hurricane/tornado activity to the long-term mean.

## **14.6 Unscheduled Publications (Available Upon Request Only)**

### **14.6.1 Climates of the World**

Climates of the World is a 28-page brochure which presents average temperature and precipitation data for ≈800 stations throughout the world. It also includes brief narrative descriptions of the climate of each continent and maps depict the annual average worldwide distribution of temperature and precipitation.

### **14.6.2 Climatic Atlas of the United States**

This is an 80-page, large format (16-in×22-in) collection of 231 maps, 21 graphs, and 13 tabulations depicting the climate of the United States in terms of the distribution and variation of temperature, precipitation, wind, barometric pressure, relative humidity, dewpoint temperature, sunshine, sky cover, heating degree days, solar radiation, and evaporation.

### **14.6.3 Selected Climatic Maps of the United States**

This is an abbreviated version (8-in×10 1/2-in) of the Climatic Atlas consisting of 32 maps. Designed primarily for quick reference, it includes climatic information on temperature, precipitation, sunshine, solar radiation, heating and cooling degree days, freeze data, and other selected data. Most maps are annual or for the months of January and July only.

### **14.6.4 Climatological Summaries—*Climatology of the United States No. 20***

Climatological Summaries are prepared for over 2,000 cooperative stations and are similar to the annual issues of the Local Climatological Data publications. Most summaries present only average temperature, precipitation, and snowfall data. Those developed and published after 1974 also present tables on freeze and precipitation probabilities. Those published after 1980 also present tables on growing degree units.

### **14.6.5 Freeze/Frost Data—*Climatology of the United States No. 20, Supplement No. 1***

This 186-page publication presents tables of freeze/frost-related information for 3,106 observation sites within the United States. Also included are six freeze/frost occurrence data maps for the entire United States. The main contents are probability tables for each station, listed by state. Given are dates of probable first and last occurrence, during the year beginning August 1 and ending July 31, of freeze-related temperatures; probable durations (in days) where temperature exceeds certain freeze-related values; and the probability of experiencing a given temperature, or less, during the year. For the fall and spring dates of occurrence, and freeze-free period, probabilities are given for three temperatures (36, 32, and 28 °F) at three probability levels (10, 50, and 90 percent).

### **14.6.6 Climates of the States—*Climatology of the United States No. 60***

Published for every state, each issue contains a narrative summary describing the principal climatological features of the State; “Normals, Means, and Extremes” tables excerpted from the annual LCDs published for the state; and a Climatological Summary for select locations in that state. Issues previous to 1976 (available by photocopy or microfiche) also contained average monthly temperature and precipitation data for many locations, freeze data, and selected mean temperature and precipitation maps.

#### **14.6.7 *Summary of Hourly Observations—Climatology of the United States No. 82***

These summaries were published for 138 National Weather Service stations, mainly for the 10-yr period 1951–1960. Three tables present monthly and annual percentage frequencies of wind direction and speed; ceiling and visibility; and hourly sky cover, wind speed, and relative humidity. Two additional tables show frequency of hourly and daily occurrences of precipitation amounts by category, and total occurrences of various ranges of temperature, relative humidity, and wind speed.

#### **14.6.8 *Climatological Summary of the U.S., 1951–1960—Climatology of the United States No. 86***

This publication is the last in a series published separately for each state. Presented are sequential tables of precipitation; snowfall; mean temperature; monthly and annual averages of maximum, minimum, and mean temperature, precipitation, snowfall, and evaporation; monthly and annual highest and lowest temperature, mean number of days with precipitation  $\geq 0.1$  and 0.5 in, and mean number of days with temperature  $\geq 90$  °F or  $\leq 32$  °F.

#### **14.6.9 *Airport Climatological Summary—Climatology of the United States No. 90***

These summaries contain monthly and annual tables of percent frequency of selected flying weather conditions, wind direction versus wind speed (IFR and VFR), and mean number of days occurrence of various weather conditions. Also presented are means and extremes and sequential tables of monthly maximum, minimum, and average temperatures, total snowfall, total precipitation, heating degree days, and cooling degree days.

#### **14.6.10 *Comparative Climatic Data***

*Comparative Climatic Data* contains 16 tables of long-term monthly and annual climatological elements. Temperature, precipitation, wind, sunshine, cloudiness, and relative humidity data are presented for about 280 stations. The stations are listed alphabetically by state so that values for the same element may be easily compared for different stations by use of a single table—issued annually.

#### **14.6.11 *Tropical Cyclones of the North Atlantic Ocean 1871–1986 (with storm track maps updated through 1989)—Historical Climatology Series 6-2***

This publication consists of a narrative of characteristics, classifications, frequencies, etc. of tropical cyclones. The maps present the “best-track” storm positions at 7 a.m. and 7 p.m. E.S.T., one map per year, 1871 through the most recent year completed. (Also see Storm Data in sec. 1.) Also included are maps of all tropical storms or hurricanes for each month, May through November, 1886–1986.

#### **14.6.12 *Climatic Averages and Extremes for U.S. Cities—Historical Climatology Series No. 6-3***

First produced for the 1990 data year, this publication contains normals, long-term averages, and extremes for the principal ( $\approx 280$ ) climatological stations of the National Weather Service. The source of the information is the “Normals, Means, and Extremes” page of Local Climatological Data Bulletin: Annual Summary (see sec. 1) compiled into one booklet. All available digitized data, from the beginning of station operations through December 1990 were used in establishing the long-term averages and extremes. The Normals in the 1990 edition are based on data from the 1951–1980 period. This publication will be updated annually beginning in September 1993—no 1991 data update—with data for the most recent year. The 1961–1990 normals will be incorporated into the publication with the September 1994 edition (1993 data year).

### **14.6.13 *Daily Normals of Temperature, Precipitation, and Heating and Cooling Degree Days, 1961–1990— Climatology of the United States No. 84***

This publication presents daily 1961–1990 normal maximum, minimum, and mean temperature, heating and cooling degree days (base 65 °F), and precipitation for 422 National Weather Service offices and principal climatological stations. Monthly, seasonal, and annual normals of these elements are also presented. Monthly and annual precipitation probabilities and quintiles are included in the back of the publication. The data are published in a separate pamphlet for each location.

The daily normals were derived by statistically fitting smooth curves through monthly values; daily data were not used to compute daily normals. As a result, the published values reflect smooth transitions between seasons. The typical daily random patterns usually associated with precipitation are not exhibited; however, the precipitation normals may be used to compute average amounts accumulated over time intervals.

The published data are also available on microfiche and magnetic tape.

## **14.7 Computational Procedures**

### **14.7.1 Divisional Normals**

Climatic divisions are regions within each state that have been determined to be reasonably climatically homogeneous. The maximum number of divisions in each state is 10. Monthly divisional average temperature and total precipitation data were derived using data from all stations reporting both temperature and precipitation within a climatological division. The number of reporting stations within a division varies from month to month and year to year. This variation was ignored in the computation of the normals.

Monthly temperature normals and 60-yr averages for a division were computed by adding the yearly values for a given month and then dividing by the number of years in the period. The annual normal and 60-yr average were computed by adding all the monthly normal or long-term average values and then dividing by 12. Consequently, if an annual normal were computed by averaging annual values obtained for each year in the period (by adding the corresponding 12 monthly values and then dividing by 12), it may be slightly different from the average of the 12 monthly normals because of rounding differences. Precipitation normals and 60-yr averages were computed in a similar manner, except that the annual values are the totals of the 12 monthly values.

Sequential monthly degree days were derived using procedures developed by Thom (1954, 1966). This technique utilizes the historical monthly average temperature and its corresponding standard deviation (over some “standardizing period”) to compute degree days. The procedure for the computation of the divisional degree day normals involved the following three steps: (1) Calculate the standard deviations of the temperatures for each of the 12 calendar months over the standardizing period, (2) use the Thom technique to compute the heating and cooling degree days for every month for every year in the period 1931–1990, and (3) calculate the 30-yr normals and 60-yr (1931–1990) averages of the degree days using the procedure discussed in the preceding paragraph.

### **14.7.2 Monthly Normals for First Order and Cooperative Stations**

Monthly normals were computed for as many stations as practical. In order to be included, the station had to have at least 10 yr of monthly temperature data and 10 yr of monthly precipitation data from the period 1961–1990.

As noted earlier, a normal is the arithmetic mean of a climatological element computed over three consecutive decades (Guttman (1989)). The data record should be consistent (have no changes in location, instruments, observation practices, etc.; these are identified here as “exposure changes”) and have no missing values so a normal will reflect the actual average climatic conditions. If any significant exposure changes have occurred, the data record is said to be “inhomogeneous” and the normal may not reflect a true climatic average. Such data need to be adjusted to remove the nonclimatic inhomogeneities. The resulting (adjusted) record is then said to be “homogeneous.” If no exposure changes have occurred at a station, the normal was calculated simply by averaging the appropriate 30 values from the 1961–1990 record.

To address the inhomogeneity problem, the normals methodology involved the following four steps: (1) Estimating missing data, (2) adjusting first order stations with inhomogeneous records, (3) calculating the average monthly values, then (4) converting the temperature averages to the station’s official normal, which is valid for the current (as of 1990) observation time. NOTE: This Environmental Information Summary corrects some minor inaccuracies in the narrative of some copies of the *Climatography of the United States No. 81* publication. The estimation of missing data and inhomogeneity adjustments made to the first order stations were done as indicated in this summary.

Neighboring stations were used to estimate missing data. For precipitation, missing values were estimated by averaging the precipitation values from the four nearest neighbors having data for the month in question. The neighboring stations included first order and cooperative stations that were within a 30-mi radius of the station being estimated.

For temperature, the nearest 40 neighboring stations were examined and their temperature variations were compared to the temperature variations at the station for which the normals were being calculated (the candidate station). Of these, a pool of 20 neighbors that had the highest correlation with the candidate station were used to estimate the candidate station’s missing temperature value. The estimate was calculated using a weighted average of the values from these neighboring stations. The neighboring stations included stations that were part of the Historical Climatology Network (HCN). (See Karl et al. (1990)).

The method used to adjust for inhomogeneities is based on the HCN methodology outlined by Karl and Williams (1987). This technique involves comparing the record of the candidate station to the records of neighboring stations. A neighboring station was not used if its record did not cover the same time period as the candidate station. ‘The underlying assumption behind such a methodology is that variations in average weather have similar tendencies over a region. For example, cold winters at a candidate station usually occur simultaneously at its neighboring stations. If this assumption is violated, then there will be a systematic difference between the stations which will show up as temperature differences (or precipitation ratios) that do not follow the expected statistical pattern. Acceptance of this methodology allows the use of certain well-defined statistical techniques to make the adjustments.

Inhomogeneities in the candidate station’s record were determined by examining the location, instrument, and observation history of the station.

After the periods of inhomogeneity were determined, adjustments were applied to remove the biases. The adjustments were determined using the following criteria. Neighboring stations were found that had homogeneous data records, covering the time period of the candidate station’s inhomogeneous period. If the candidate station and a neighbor had a reasonably high correlation ( $r^2 > 0.6$ ) of monthly anomalies for the period in question, then the established homogeneous neighboring station was used to assess the impact of the candidate station’s discontinuity; the part of the data record before the discontinuity was statistically compared to the part after the discontinuity. The student’s t-test was used for the temperature differences, while the nonparametric Wilcoxon rank-sum test was used

for the precipitation ratios. If the statistical test indicated that the two parts of the candidate station's record were significantly different, then the earlier part of the record was adjusted. (Further details, with examples, can be found in Karl and Williams (1987)). After all exposure changes at the candidate station were corrected, the normal was estimated by averaging the appropriate 30 values from the 1961–1990 adjusted record. If none of the neighboring stations had a sufficiently high correlation, then no adjustment was made. The climatological elements (maximum temperature, minimum temperature, and precipitation) were adjusted separately.

Exposure change adjustments were made to first order stations in the lower 48 states, but not to the stations in Alaska, Hawaii, or U.S. possessions because of the lack of a sufficient number of neighboring stations. The neighboring stations used in the adjusting procedure included stations from the Cooperation Station Network. No exposure change adjustments were made to the cooperative stations due partly to a lack of adequate computerized station history information, but also because a cooperative station's identity changes (according to National Weather Service standards) when significant moves occur (generally at least 5 mi horizontally or 100 ft in elevation, subject to the judgement of the National Weather Service Cooperative Program Manager).

Due to the adjustment techniques employed, the normals published in the *Climatology of the United States No. 81* publication will not necessarily agree with values calculated by simply averaging the monthly observed values from 1961–1990.

Comparison of temperature data between stations works best if all of the stations involved have the same observational schedule. This is generally true for first order stations which use the calendar day (midnight) observation time. Unfortunately, some cooperative stations have an observation time in the morning, some in the afternoon, some in the evening, and some at midnight, and this introduces a nonclimatic bias into the record. For an explanation of this bias, see Karl et al. (1986). To make the data reflect a consistent observational schedule, the adjustment technique developed by Karl et al. (op. cit.) was used to determine midnight observation time adjustment factors to convert the maximum and minimum temperature data for all appropriate stations to a midnight-to-midnight schedule, thus removing the time of observation bias. No adjustments were made to stations in Alaska, Hawaii, or U.S. possessions because of the lack of a sufficient number of neighboring stations.

It should be emphasized that the official normal temperature values printed in the Series No. 81 publication are for the current (as of 1990) observation time. The station's observation time and the adjustment necessary to convert the temperature values to a midnight-to-midnight observation time are also shown in the tables. The adjustment factors should be added to the official normals to approximate a "midnight observation time average." This helps a user determine if temperature differences between nearby stations are true climate differences or if they may be caused by different observing schedules. The precipitation data were not adjusted for observation time.

The monthly normals for maximum and minimum temperature were computed as described above. The monthly average temperature normals were computed by averaging the corresponding maximum and minimum normals. The annual temperature normals were calculated by taking the average of the 12 monthly normals. The annual precipitation normals were calculated by adding the 12 monthly normals.

Simple arithmetic procedures were not applied to obtain the heating and cooling degree day normals. Instead, the rational conversion formulae developed by Thom (1954, 1966) were used. These formulae allow the adjusted mean temperature normals and their standard deviations to be converted to degree day normals with uniform consistency. In some cases, this procedure will yield a small number of degree days for months when degree days may not otherwise be expected. This results from statistical considerations of the formulae. The annual degree day normals were calculated by adding the corresponding monthly degree day normals.

### 14.7.3 Daily Normals

Daily normals of maximum, minimum, and mean temperatures, heating and cooling degree days, and precipitation were prepared for 422 stations by interpolating between the monthly normal values. The interpolation scheme was a cubic spline fit through the monthly values. Each element was interpolated independently from the other elements. The procedure is described by Greville (1967).

The series of daily values of an element resulting from the cubic spline yields a smooth curve throughout the year without requiring the use of daily data. Another property of this technique is that the average of the daily temperatures in a month equals the monthly normal and that the total of the daily precipitation or degree days in a month equals the monthly normal. In order to eliminate discontinuities between December 31 and January 1, the spline interpolation was performed on a series of 24 monthly values. This extended series was created by appending July–December normals before January and January–June normals after December.

Since each element was interpolated independently, the daily series of temperatures and degree days were edited to remove spurious inflection points caused by rounding and to ensure adherence to functional relationships among the elements. Specifically,

- All inflection points were examined for climatological reasonableness.
- One-half of the sum of a daily maximum and minimum temperature, after rounding, was checked for equivalence with the daily mean temperature.
- The relationship between a daily mean temperature ( $T$ ) and the heating ( $H$ ) and cooling ( $C$ ) degree days for the day was checked to ensure that

$$|T - 65 + H - C| = 0 \quad . \quad (14.1)$$

Daily precipitation normals were published as generated by the cubic spline interpolation. The smooth curve through a month does not represent a climatologically reasonable distribution. The spreading of the monthly precipitation by the spline over all the days in a month is useful for accumulating amounts over specified time intervals. A climatologically reasonable normal precipitation, based on daily data, for any one date would be much different from the published normals.

For some dates, at most locations, the published degree days are shown by an asterisk. The symbol represents a value of less than one degree day, but more than zero degree days. It is used to smooth through aperiodic oscillations of zeroes and ones that are climatologically unreasonable. For example, if a station has 17, 15, and 18 normal heating degree days in June, July, and August, respectively, it is not possible to distribute the 15 July degree days evenly throughout the month using integer values (zeroes and ones) without creating unrealistic oscillations through the 3-mo period. The use of fractional degree days (asterisks) does allow for a smooth transition from June through July to August.





## 15. COMMENTS

It is important here to make a few comments. In addition to the more common aspects of climate, discussion of trace gases is included. Intergovernmental panels produce studies of climate and climate change. The following references, among many, mirror the development of interest in the warming of the atmosphere and oceans. These are in addition to those previously cited. They are Boldirev (1992), Obasi (1995), Houghton et al. (1994), and Houghton et al. (1996).

Rind (1999) suggests that our present climate is the result both of an ordered forcing and an admixture of chaotic behavior. A multimodal, multidisciplinary approach would appear to be required for research. The reader may wish to revisit the first portion of this study. With time, other disciplines will be drawn under the climate umbrella. The generalist approach, or in lieu thereof the team approach of specialists, will be needed. The door is wide open to the interested, serious research individual.



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## **APPENDIX A—SUPPORTING TABLES**

Table A-1 shows Sun, Earth, Earth's atmosphere, and the Moon physical constants.





Table A-1. Some physical constants for the Sun, Earth, and Moon. These tables are derived from, modified from, or rearranged from List (1958), Huschke (1959), Mechtly (1969), Huheey (1978), Ryan and Pesek (1978), Hartman (1983), Chang (1986), and Wayne (1988).

<b>Sun</b>	
Age	= $4.6 \times 10^9$ y; 4.6 Gy
Equatorial radius	= $6.599 \times 10^8$ m
Mass	= $1.99 \times 10^{30}$ kg
Density	= $1.41 \times 10^3$ kg m <sup>-3</sup>
Effective emission temperature	= 5.783 kK
Mean angle subtended by photosphere at Earth rotation	= 31.988 arc min
Polar photosphere	= 37 Earth days
High latitude	= 29 Earth days
Equatorial	= 26 Earth days
<b>Earth</b>	
Age	= $4.6 \times 10^9$ y; 4.6 Gy
Equatorial radius	= $6.378 \times 10^6$ m; 6.378 Mm
Mean Earth-Sun distance, AU	= $1.4960 \times 10^{11}$ m
Mass	= $5.974 \times 10^{24}$ kg
Mean density (water = 1)	= 5.52
Volume	= $1.084 \times 10^{12}$ km <sup>3</sup>
Standard surface gravity	= $9.806$ m s <sup>-2</sup>
Rotation period	= 1 Earth day
Escape velocity	= $1.120 \times 10^4$ m s <sup>-1</sup>
Albedo	= 0.30 to 0.40
Present axis inclination of rotation	= 23.45
<b>Earth's Atmosphere</b>	
Standard surface pressure, $p_s$	= 1.01325 bar = 1.01325 kPa
Loschmidt number, $n_s$	= $2.686754 \times 10^{25}$ m <sup>-2</sup> (at STP)
Density (at STP), $\rho_s$	= $1.2925$ kg m <sup>-3</sup>
Specific gas constant, $r$	= $2.8700 \times 10^2$ J K <sup>-1</sup> kg <sup>-1</sup>
Mean molecular mass, $M$	= 28.964 amu
Specific heats (at STP): $c_p$ (at constant pressure)	= $1.006 \times 10^3$ J kg <sup>-1</sup> K <sup>-1</sup>
$c_v$ (at constant volume)	= $7.18 \times 10^2$ J kg <sup>-1</sup> K <sup>-1</sup>
$c_p/c_v$	= 1.401
<b>Moon</b>	
Age	= $4.6 \times 10^9$ y; 4.6 Gy
Mass	= $7.3483 \times 10^{22}$ kg
Mean density (water = 1)	= 3.34
Volume (Earth = 1)	= 0.02
Equatorial radius	= $1.738 \times 10^6$ m
Mean Earth-Moon distance	= $3.844 \times 10^2$ Mm
Inclination to ecliptic	= 18–29 degrees
Rotation period	= $2.732 \times 10^1$ Earth days
Escape velocity	= 2.380 km s <sup>-1</sup>
Albedo	= 0.07
Present inclination of axis	= 1.53

Tables A-2-1 through A-4-3 are taken from NBS Special Publication 330, 1986 Edition, p. 9, Rules for writing and using the International System of Units (SI) unit symbols. See Goldman and Bell (1980). The units shown may not be precisely those shown. Differences and errors must be attributed to the writer. Goldman and Bell provide attributions.

Table A-2-1. Prefixes used with SI units.

Prefix	Symbol	Multiply By
Atto	a	$10^{-18}$
Femto	f	$10^{-15}$
Pico	p	$10^{-12}$
Nano	n	$10^{-9}$
Micro	$\mu$	$10^{-6}$
Milli	m	$10^{-3}$
Centi	c	$10^{-2}$
Deci	d	$10^{-1}$
Deka	da	$10^1$
Hecto	h	$10^2$
Kilo	k	$10^3$
Mega	M	$10^6$
Giga	G	$10^9$
Tera	T	$10^{12}$
Peta	P	$10^{15}$
Exa	E	$10^{18}$

Table A-2-2. SI base units.

Quantity	Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Thermodynamic temperature	kelvin	K
Amount of substance	mole	mol
Luminous intensity	candela	cd

Table A-2-3. Examples of SI derived units expressed in terms of base units.

Quantity	Unit	Symbol
Area	square meter	m <sup>2</sup>
Volume	cubic meter	m <sup>3</sup>
Speed, velocity	meter per second	m/s
Acceleration	meter per second squared	m/s <sup>2</sup>
Wave number	reciprocal meter	m <sup>-1</sup>
Entropy	joule per kelvin	JK <sup>-1</sup>
Specific heat capacity	joule per kilogram kelvin	J/(kg·K)
Density, mass density	kilogram per cubic meter	kg/m <sup>3</sup>
Specific volume	cubic meter per kilogram	m <sup>3</sup> /kg
Current density	ampere per square meter	A/m <sup>2</sup>
Magnetic field strength	ampere per meter	A/m
Concentration (of amount of substance)	mole per cubic meter	mol/m <sup>3</sup>
Luminance	candela per square meter	cd/m <sup>2</sup>

Table A.2.4. SI derived units with special names.

Physical Quantity	Name	Expression Symbol	Expression (in SI Units)	(Other Units)
Frequency	hertz	Hz	s <sup>-1</sup>	
Force	newton	N	m · kg · s <sup>-2</sup>	J m <sup>-1</sup>
Pressure, stress	pascal	Pa	m <sup>-1</sup> · kg · s <sup>-2</sup>	N m <sup>-2</sup>
Energy, work, quantity of heat	joule	J	m <sup>2</sup> · kg · s <sup>-2</sup>	N m
Power, radiant flux	watt	W	m <sup>2</sup> · kg · s <sup>-3</sup>	J s <sup>-1</sup>
Radiant intensity	watt per steradian	Wsr <sup>-1</sup>		
Electric charge, quantity of electricity	coulomb	C	s · A	A s
Electric potential, potential difference, electromotive force	volt	V	m <sup>2</sup> · kg · s <sup>-3</sup> · A <sup>-1</sup>	J A <sup>-1</sup> s <sup>-1</sup>
Electric capacitance	farad	F	m <sup>-2</sup> · kg <sup>-1</sup> · s <sup>4</sup> · A <sup>2</sup>	A s V <sup>-1</sup>
Electric resistance	ohm	m <sup>2</sup>	kg · s <sup>-3</sup> · A <sup>-2</sup>	V A <sup>-1</sup>
Electric conductance	siemens	S	m <sup>-2</sup> · kg <sup>-1</sup> · s <sup>3</sup> · A <sup>2</sup>	A V <sup>-1</sup>
Magnetic flux	weber	Wb	m <sup>2</sup> · kg · s <sup>-2</sup> · A <sup>-1</sup>	V s
Magnetic flux density	tesla	T	kg · s <sup>-2</sup> · A <sup>-1</sup>	Wb m <sup>-2</sup>
Inductance	henry	H	m <sup>2</sup> · kg · s <sup>-2</sup> · A <sup>-2</sup>	Wb A <sup>-1</sup>
Celsius temperature	degree Celsius	°C	°C	
Luminous flux	lumen	lm	cd · sr	
Illuminance	lux	lx	m <sup>-2</sup> · cd · sr	lm/m <sup>2</sup>

\*Dimension: M=mass, L=length, and T=time, such as kilogram, meter, and second.

\*\*Multiplication is indicated by a space or a dot between the units.

Table A-2-5. SI derived units with special names admitted for reasons of safe-guarding human health.

Quantity	Name	Expression Symbol	Expression (in SI Units)	(Other Units)
Activity (of a radionuclide)	becquerel	Bq	s <sup>-1</sup> absorbed dose	
Specific energy imparted, kerma, absorbed dose index	gray	Gy	m <sup>2</sup> · s <sup>-2</sup>	J/kg
Dose equivalent, dose equivalent index	sievert	Sv	m <sup>2</sup> · s <sup>-2</sup>	J/kg

Table A-2-6. Examples of SI derived units expressed by means of special names.

Quantity	Name	Symbol	Expression (in SI units)
Dynamic viscosity	pascal second	Pa · s	m <sup>-1</sup> · kg · s <sup>-1</sup>
Moment of force	newton meter	N · m	m <sup>2</sup> · kg · s <sup>-2</sup>
Surface tension	newton per meter	N/m	kg · s <sup>-2</sup>
Heat flux density, irradiance	watts per square meter	W/m <sup>2</sup>	kg · s <sup>-3</sup>
Heat capacity, entropy	joule per kelvin	J/K	m <sup>2</sup> · kg · s <sup>-2</sup> · K <sup>-1</sup>
Specific heat capacity, specific entropy	joule per kilogram kelvin	J/(kg · K)	m <sup>2</sup> · s <sup>-2</sup> · K <sup>-1</sup>
Specific energy	joule per kilogram	J/kg	m <sup>2</sup> · s <sup>-2</sup>
Thermal conductivity	watt per meter kelvin	W/(m · K)	m · kg · s <sup>-3</sup> · K <sup>-1</sup>
Energy density	joule per cubic meter	J/m <sup>3</sup>	m <sup>-1</sup> · kg · s <sup>-2</sup>
Electric field strength	volt per meter	V/m	m · kg · s <sup>-3</sup> · A <sup>-1</sup>
Electric charge density	coulomb per cubic meter	C/m <sup>3</sup>	m <sup>-3</sup> · s · A
Electric flux density	coulomb per square meter	C/m <sup>2</sup>	m <sup>2</sup> · s · A
Permittivity	farad per meter	F/m	m <sup>-3</sup> · kg <sup>-1</sup> · s <sup>4</sup> · A <sup>2</sup>
Permeability	henry per meter	H/m	m · kg · s <sup>-2</sup> · A <sup>-2</sup>
Molar energy	joule per mole	J/mol	m <sup>2</sup> · kg · s <sup>-2</sup> · mol <sup>-1</sup>
Molar entropy, molar heat capacity	joule per mole kelvin	J/(mol · K)	m <sup>2</sup> · kg · s <sup>-2</sup> · K <sup>-1</sup> · mol <sup>-1</sup>
Exposure (x and rays)	coulomb per kilogram	C/kg	kg <sup>-1</sup> · s · A
Absorbed dose rate	gray per second	Gy/s	m <sup>2</sup> · s <sup>-3</sup>

A single SI unit name may correspond to several different quantities. In the above tables, where the list of quantities is not exhaustive, one finds several examples. Thus the joule per kelvin (J/K) is the SI unit for the quantity heat capacity as well as for the quantity entropy. Also, the ampere (A) is the SI unit for the base quantity electric current as well as for the derived quantity magnetomotive force. The name of the unit is thus not sufficient to define the quantity measured; in particular, measuring instruments should indicate not only the unit but also the measured quantity concerned.

Table A-2-7. SI supplementary units.

Quantity	Name	Symbol	Expression (in SI units)
Plane angle	radian	rad	m · m <sup>-1</sup> = 1
Solid angle	steradian	sr	m <sup>2</sup> · m <sup>-2</sup> = 1

Table A-2-8. Examples of SI derived units formed by using supplementary units.

Quantity	Name	Symbol
Angular velocity	radian per second	rad/s
Angular acceleration	radian per second squared	rad/s <sup>2</sup>
Radiant intensity	watt per steradian	W/sr
Radiance	watt per square meter steradian	W · m <sup>-2</sup> · sr <sup>-1</sup>

Table A-2-9. Units in use with SI.

Name	Symbol	Value in SI units
Minute	min	1 min = 60 s
Hour	h	1 h = 60 min = 3600 s
Day	d	1 d = 24 h = 86,400 s
Degree	°	1 ° = (π /180) rad
Minute	'	1 ' = (1/60) ° = (π /10,800) rad
Second	''	1 '' = (1/60)' = (π /648,000) rad
Liter	l, L	1 L = 1 dm <sup>3</sup> = 10 <sup>-3</sup> m <sup>3</sup>
Metric ton	t	1 t = 10 <sup>3</sup> kg = 1 Mg

Table A-2-10. Units used with the International System whose values in SI units are obtained experimentally.

Name	Symbol	Definition
Electronvolt	eV	The electronvolt is the kinetic energy acquired by an electron in passing through a potential difference of 1 volt in vacuum; 1 eV = 1.602 19 × 10 <sup>-19</sup> J approximately.
Unified atomic mass unit	u	The unified atomic mass unit is equal to (1/12) of the mass of an atom of the nuclide <sup>12</sup> C; 1 u = 1.660 57 × 10 <sup>-27</sup> kg approximately.

Please note the spacing of the numbers to the right of the decimal point in terms of three.

Table A-2-11. Units in use temporarily with the International System.

Name	Symbol	Value in SI Units
Nautical mile	nm	1 nautical mile = 1,852 m
Knot	kt	1 nautical mile per hour = (1,852/3,600) m/s
Angstrom	Å	1 Å = 0.1 nm = $10^{-10}$ m
Are	a	1 a = 1 dam <sup>2</sup> = $10^2$ m <sup>2</sup>
Hectare	ha	1 ha = 1 hm <sup>2</sup> = $10^4$ m <sup>2</sup>
Barn	b	1 b = 100 fm <sup>2</sup> = $10^{-28}$ m <sup>2</sup>
Bar	bar	1 bar = 0.1 MPa = 100 kPa = 1,000 hPa = $10^{-5}$ Pa
Gal	Gal	1 Gal = 1 cm/s <sup>2</sup> = $10^{-2}$ m/s <sup>2</sup>
Curie	Ci	1 Ci = $3.7 \times 10^{10}$ Bq; $3.7 \times 10^{10}$ s <sup>-1</sup>
Roentgen	R*	1 R = $2.58 \times 10^{-4}$ C/kg
Rad	rad	1 rad = 1 cGy = $10^{-2}$ Gy
Rem	rem	1 rem = 1 cSv = $10^{-2}$ Sv

\*The symbol R (subscripted or not) also refers to the gas constant(s).

Table A-2-12. CGS units with special names.

Name	Symbol	Value in SI Units
Erg*	erg	1 erg = $10^{-7}$ J
Dyne*	dyn	1 dyn = $10^{-5}$ N
Poise*	P	1 P = 1 dyn · s/cm <sup>2</sup> = 0.1 pa · s
Stokes	ST	1 St = 1 cm <sup>2</sup> /s = $10^{-4}$ m <sup>2</sup> /s
Gauss**	Gs, G	1 Gs corresponds to $10^{-4}$ T
Oersted**	Oe	1 Oe corresponds to (1,000/4) A/m
Maxwell**	Mx	1 Mx corresponds to $10^{-8}$ Wb
Stilb**	sb	1 sb = 1 cd/cm <sup>2</sup> = $10^4$ cd/m <sup>2</sup>
Phot	ph	1 ph = $10^4$ lx

\* This unit and its symbol were included in Resolution 7 of the 9th CGPM (1948).

\*\*This unit is part of the so-called "electromagnetic" three-dimensional CGS system and cannot, strictly speaking, be compared to the corresponding unit of the International System, which has four dimensions when only mechanical and electric quantities are considered.

Table A-2-13. Other units generally deprecated.

Name	Value in SI unit
Fermi	1 fermi = 1 fm = $10^{-15}$ m
Metric carat*	1 metric carat = 200 mg = $2 \times 10^{-4}$ kg
Torr	1 torr = (101,325/760) Pa
Standard atmosphere (atm)**	1 atm = 101,325 Pa
Kilogram-force (kgf)	1 kgf = 9.806 65 N
Calorie (cal)†	
Micron ( $\mu$ )‡	1 $\mu$ m = $10^{-6}$ m
X unit§	
Stere (st)	1 st = 1 m <sup>3</sup>

\* This term was used in dealing with diamonds, pearls, and precious stones.

\*\*Resolution 4 of the 10 CGPM (1954). The designation "standard atmosphere" for a reference pressure of 101 325 Pa is still acceptable.

† Several "calories" have been in use:

Calorie labeled "at 15 C": 1 cal<sub>15</sub> = 4.185 5 J (value adopted by the CIPM in 1950 (Proces-Verbaux CIPM, 22, 1950, pp. 79–80));

A calorie labeled "IT" (International Table): 1 cal = 4.186 8 J (5th International Conference on the Properties of Steam, London, 1956);

A calorie labeled "thermochemical": 1 cal<sub>th</sub> = 4.184 J.

‡ The name of this unit and its symbol, adopted by the CIPM in 1879 (Proces-Verbaux CIPM, 1879, p. 41) and repeated in Resolution 7 of the 9th CGPM (1948) were abolished by the 13th CGPM (1967, Resolution 7). This special unit name is no longer accepted.

§ This special unit was employed to express wavelengths of x rays:  
1 x unit =  $1.002 \times 10^{-4}$  nm approximately.

As regards units outside the International System which do not come under sections IV.1, 2, and 3, the CIPM considers that it is in general preferable to avoid them, and to use instead units of the International System. Some of those units are listed in table A-2-13. For further comments, see Goldman and Bell (1986, p. 15).

Table A-4-1. Selected conversion factors.

Multiply	By	To Obtain
Length		
cm	$10^8$	Å
cm	$10^7$	nm
cm	$10^{10}$	pm
Å	100	pm
Energy		
kcal mol <sup>-1</sup>	4.184	kJ mol <sup>-1</sup>
eV	23.06	kcal mol <sup>-1</sup>
eV	96.49	kJ mol <sup>-1</sup>
erg	$1 \times 10^{-7}$	J
wave numbers (cm <sup>-1</sup> )	$1.19627 \times 10^{-2}$	kJ mol <sup>-1</sup>
kJ mol <sup>-1</sup>	83.59	cm <sup>-1</sup>
Pressure		
atmosphere	$1.01325 \times 10^5$	Pa
atmosphere	$1.01325 \times 10^3$	mb
mm Hg (torr)	$1.32 \times 10^5$	Pa
pascal	$9.869 \times 10^{-6}$	atm
pascal	$7.501 \times 10^{-3}$	mm Hg (torr)
pascal	$1 \times 10^{-2}$	mb

Table A-4-2. Numerical conversion factors for energy units.

Unit	cm <sup>-1</sup>	J	eV	K
1 cm <sup>-1</sup>	1	$1.986 \times 10^{-23}$	$1.240 \times 10^{-4}$	1.439
1 J	$5.034 \times 10^{22}$	$1 \times 10^{18}$	$6.241 \times 10^{22}$	7.243
1 eV	$8.066 \times 10^3$	$1.602 \times 10^{-19}$	$1 \times 10^4$	1.160
1 K	$6.950 \times 10^{-1}$	$1.381 \times 10^{-23}$	$8.617 \times 10^{-5}$	1

Table A-4-3. Numerical conversion factors for energy units in terms of moles.

	cm <sup>-1</sup>	J mol <sup>-1</sup>	eV	cal mol <sup>-1</sup>
1 cm <sup>-1</sup>	1	$1.196 \times 10^1$	$1.240 \times 10^{-4}$	2.859
1 J mol <sup>-1</sup>	$8.359 \times 10^{-2}$	1	$1.036 \times 10^{-5}$	$2.390 \times 10^{-1}$
1 eV	$8.066 \times 10^3$	$9.649 \times 10^4$	1	$2.306 \times 10^4$
1 cal mol <sup>-1</sup>	$3.498 \times 10^{-1}$	4.184	$4.336 \times 10^{-5}$	1

All numbers have been rounded to four significant numbers. Table A-4-3 may be used as follows: Multiply values given in units under "A" by figure in same row of "B" to obtain the value in the units of the relevant column of "B". For example, to convert 100,000 J mol<sup>-1</sup> to cal mol<sup>-1</sup>, multiply by  $2.390 \times 10^{-1}$  to obtain  $2.390 \times 10^4$  cal mol<sup>-1</sup>. The reader may refer to Chantry (1984), Wayne (1988), and Goody and Yung (1989).



Tables A-5-1 through A-5-3 are adapted from *Climates of the World*.

Table A-5-1. Selected world temperature data (adapted from *Climates of the World*, U.S. Dept of Commerce (1969); reprinted 1977).

Country and Station	Latitude		Longitude		Elevation	Length of Record	Temperature									
							Average								Extreme	
	January		April		July		October		Max.	Min.						
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.				
North America																
United States (Conterminous):																
Albuquerque, N. Mex.	35	03N	106	37W	1,619	30	8	-4	21	6	33	19	22	7	40	-27
Asheville, N.C.	35	26N	82	32W	652	30	9	-2	19	6	29	16	20	7	37	-22
Atlanta, Ga.	33	39N	84	26W	308	30	11	3	21	10	31	22	22	11	39	-23
Austin, Tex.	30	18N	97	42W	182	30	16	5	26	14	35	23	28	16	43	-19
Birmingham, Ala.	33	34N	86	45W	189	30	14	2	24	10	34	22	26	11	42	-23
Bismarck, N. Dak.	46	46N	100	45W	502	30	-7	-18	13	0	30	14	15	1	46	-43
Boise, Idaho	43	34N	116	13W	865	30	2	-6	17	3	33	15	18	3	44	-33
Brownsville, Tex.	25	54N	97	26W	5	30	22	11	28	19	34	24	29	19	40	-11
Buffalo, N.Y.	42	56N	78	44W	215	30	-1	-8	12	1	27	15	16	5	37	-29
Cheyenne, Wyo.	41	09N	104	49W	1,867	30	3	-10	13	-1	29	13	17	0	38	-39
Chicago, Ill.	41	47N	87	45W	185	30	1	-7	14	5	29	19	17	8	41	-31
Des Moines, Iowa	41	32N	903	39W	286	30	-2	-12	15	3	31	18	19	6	43	-34
Dodge City, Kans.	37	46N	99	58W	787	30	6	-7	19	5	34	20	22	8	43	-32
El Paso, Tex.	31	48N	106	24W	1,194	30	13	-1	26	9	35	21	26	10	43	-22
Indianapolis, Ind.	39	44N	86	17W	241	30	3	-6	16	4	30	18	19	7	42	-32
Jacksonville, Fla.	30	25N	81	39W	6	30	19	7	27	14	33	23	27	17	41	-12
Kansas City, Mo.	39	07N	94	36W	226	30	4	-5	19	8	33	22	22	9	45	-30
Las Vegas, Nev.	36	05N	115	10W	659	30	12	0	26	11	40	24	27	12	47	-13
Los Angeles, Calif.	33	56N	118	23W	30	30	18	7	19	11	24	17	23	14	43	-5
Louisville, Ky.	38	11N	85	44W	145	30	7	-3	19	6	32	19	21	8	42	-29
Miami, Fla.	25	48N	80	16W	2	30	24	14	28	19	32	24	29	22	38	-2
Minneapolis, Minn.	44	53N	93	13W	254	30	-6	-17	13	1	29	16	16	3	42	-37
Missoula, Mont.	46	55N	114	05W	972	30	-2	-12	14	-1	29	9	14	-1	41	-36
Nashville, Tenn.	36	07N	86	41W	180	30	9	-1	22	9	33	21	23	9	42	-26
New Orleans, La.	29	59N	90	15W	1	30	18	7	26	14	33	23	27	16	39	-14
New York, N.Y.	40	47N	73	58W	40	30	4	-3	16	6	29	20	19	10	41	-26
Oklahoma City, Okla.	35	24N	97	36W	392	30	8	-2	22	9	34	22	23	11	45	-27
Phoenix, Ariz.	33	26N	112	01W	340	30	18	2	29	10	41	24	31	13	48	-9
Pittsburgh, Pa.	40	27N	80	00W	228	30	4	-4	17	6	29	18	18	7	39	-29
Portland, Maine	43	39N	70	19W	14	30	0	-11	12	0	27	14	16	3	39	-39
Portland, Oreg.	45	36N	122	36W	6	30	7	1	17	6	26	13	17	7	42	-19
Reno, Nev.	39	30N	119	47W	1,342	30	7	-9	18	-1	32	8	21	-2	41	-28
Salt Lake City, Utah	40	46N	111	58W	1,286	30	3	-8	17	2	34	16	18	3	42	-34
San Francisco, Calif.	37	37N	122	23W	2	30	13	6	18	8	22	12	22	11	41	-7
Sault Ste. Marie, Mich.	46	28N	84	22W	220	30	-5	-13	8	-1	24	12	13	3	37	-38
Seattle, Wash.	47	27N	122	18W	122	30	7	1	14	4	24	12	16	7	38	-18

Country and Station	Latitude		Longitude		Elevation	Length of Record	Temperature									
							Average								Extreme	
	January		April		July		October		Max.	Min.	Max.	Min.				
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.				
°C		°C		°C		°C		°C		°C		°C				
Sheridan, Wyo.	44	46N	106	58W	1,208	30	1	-13	13	-1	31	13	17	1	41	-41
Spokane, Wash.	47	38N	117	32W	718	30	-1	-7	15	2	30	13	16	3	42	-34
Washington, D.C.	38	51N	77	03W	4	30	7	-1	19	8	31	21	20	10	41	-26
Wilmington, N.C.	34	16N	77	55W	9	30	14	3	23	11	32	22	24	13	40	-15
United States, Alaska:																
Anchorage	61	13N	149	52W	26	30	-6	-16	7	-2	18	10	6	-2	30	-39
Annette	55	02N	131	34W	34	30	3	-1	10	3	17	11	11	6	32	-20
Barrow	71	18N	156	47W	9	30	-23	-31	-14	-22	7	1	-6	-11	26	-49
Bethel	60	47N	161	48W	38	30	-12	-20	1	-8	17	9	3	-4	32	-47
Cold Bay	55	12N	162	43W	29	30	1	-5	3	-2	12	7	7	2	26	-23
Fairbanks	64	49N	147	52W	133	30	-18	-29	6	-8	22	9	2	-8	37	-54
Juneau	58	22N	134	35W	4	30	-1	-7	7	-1	17	9	8	3	32	-29
King Salmon	58	41N	156	39W	15	30	-6	-14	5	-4	17	8	6	-2	31	-40
Nome	64	30N	165	26W	4	30	-11	-19	-2	-10	13	7	2	-4	29	-44
St. Paul Island	57	09N	170	13W	7	30	-1	-6	1	-4	9	6	5	1	18	-32
Shemya	52	43N	174	06E	37	30	1	-2	3	1	9	7	6	3	17	-9
Yakutat	59	31N	139	40W	9	30	1	-7	7	-2	16	9	9	2	30	-31
Canada:																
Aklavik, N.W.T.	68	14N	135	00W	9	22	-23	-32	-7	-19	19	8	-4	-9	34	-52
Alert, N.W.T.	82	31N	62	20W	29	9	-28	-34	-22	-28	7	2	17	-22	19	-47
Calgary, Alta.	51	06N	114	01W	1,079	55	-4	-17	12	-3	24	8	12	-2	36	-45
Charlottetown, P.E.I.	46	17N	63	08W	55	65	-3	-12	6	-1	23	14	12	5	37	-33
Chatham, N.B.	47	00N	65	27W	33	50	-5	-17	8	-2	25	13	13	3	39	-42
Churchill, Man.	58	45N	94	04W	29	30	-24	-33	-4	-16	18	6	1	-7	36	-49
Edmonton, Alta.	53	34N	113	31W	676	71	-9	-19	11	-2	23	10	11	-1	37	-49
Fort Nelson, B.C.	58	50N	122	35W	382	12	-17	-26	8	-4	23	11	6	-4	37	-52
Fort Simpson, N.W.T.	61	45N	121	14W	169	42	-23	-33	3	-10	23	10	2	-6	36	-57
Frobisher Bay, N.W.T.	63	45N	68	33W	34	18	-23	-31	-9	-19	12	4	-2	-8	24	-45
Gander, Nfld.	48	57N	54	34W	151	14	-3	-11	4	-3	22	11	11	3	36	-27
Halifax, N.S.	44	39N	63	34W	25	75	0	-9	8	-1	23	13	14	5	37	-29
Kapuskasing, Ont.	49	25N	82	28W	226	19	-12	-26	6	-7	24	10	8	-1	38	-47
Knob Lake, Que.	54	48N	66	49W	522	30	-19	-29	-1	-11	18	8	3	-4	31	-51
Montreal, Que.	45	30N	73	34W	57	67	-6	-14	10	1	26	16	12	4	36	-37
North Bay, Ont.	46	21N	79	25W	371	17	-6	-17	9	-2	26	13	9	2	37	-43
Ottawa, Ont.	45	19N	75	40W	114	65	-6	-16	11	-1	27	14	12	3	39	-39
Penticton, B.C.	49	28N	119	36W	344	32	0	-6	16	2	29	12	15	3	41	-27
Port Arthur, Ont.	48	22N	89	19W	196	62	-8	-20	7	-3	23	11	10	1	40	-41
Prince George, B.C.	53	53N	122	41W	676	27	-5	-16	12	-3	24	7	11	-1	39	-50
Prince Rupert, B.C.	54	17N	130	23W	52	26	4	-1	10	3	17	9	12	6	32	-19
Quebec, Que.	46	48N	71	23W	73	72	-8	-17	7	-2	24	14	11	3	36	-37
Regina, Sask.	50	26N	104	40W	574	55	-12	-24	10	-3	26	11	11	-3	43	-49
Resolute, N.W.T.	74	43N	94	59W	67	13	-29	-36	-18	-27	7	2	12	-18	16	-52
St. John, N.B.	45	17N	66	04W	36	61	-2	-12	6	0	21	12	12	5	34	-31
St. Johns, Nfld.	47	32N	52	44W	64	68	-1	-8	5	-2	21	11	12	4	34	-29

Country and Station	Latitude		Longitude		Elevation	Length of Record	Temperature									
							Average								Extreme	
	January		April		July		October		Max.	Min.	Max.	Min.				
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.				
°C		°C		°C		°C		°C		°C		°C				
Saskatoon, Sask.	52	08N	106	38W	515	38	-13	-24	9	-3	25	11	11	-3	40	-48
The Pas, Man.	53	49N	101	15W	271	27	-17	-28	7	-6	24	12	7	-3	38	-48
Toronto, Ont.	43	40N	79	24W	116	105	-1	-9	10	1	26	15	13	4	41	-32
Vancouver, B.C.	49	17N	123	05W	39	43	5	0	14	4	23	12	14	7	33	-17
Whitehorse, Y.T.	60	43N	135	04W	702	10	-11	-19	5	-6	19	7	5	-2	33	-52
Winnipeg, Man.	49	54N	97	14W	239	66	-14	-25	9	-3	26	13	11	-1	42	-48
Yellow Knife, N.W.T.	62	28N	114	27W	205	13	-22	-31	-2	-13	21	11	2	-3	32	-51
Greenland:																
Angmagssalik	65	36N	37	33W	29	30	-5	-12	2	-9	12	3	2	-4	25	-32
Danmarkshaven	76	46N	19	00W	2	2	-18	-26	-14	-25	8	1	11	-17	17	-41
Eismitte	70	53N	40	42W	3,000	1	-36	-47	-26	-38	-7	-17	31	-41	-3	-65
Godthaab	64	10N	51	43W	20	40	-7	-12	-1	-7	11	3	2	-3	24	-29
Iviglut	61	12N	48	10W	30	48	-4	-11	3	-4	14	6	4	-2	30	-29
Jacobshavn	69	13N	51	02W	32	32	-13	-22	-4	-14	11	4	-1	-7	22	-43
Nord	81	36N	16	40W	36	8	-26	-33	-21	-28	7	2	16	-21	16	-51
Scoresbysund	70	29N	21	58W	17	12	-11	-19	-6	-14	9	2	-4	-9	17	-41
Thule	76	31N	68	44W	77	12	-20	-27	-12	-22	8	3	-7	-13	17	-42
Upernivik	72	47N	56	07W	18	40	-18	-25	-9	-18	9	2	-2	-6	21	-42
Mexico:																
Acapulco	16	50N	99	56W	3	8	29	21	31	22	32	24	31	23	36	16
Chihuahua	28	42N	105	57W	1,350	9	18	2	27	11	32	19	26	11	39	-11
Guadalajara	20	41N	103	20W	1,583	26	23	7	29	12	26	16	26	13	38	-3
Guaymas	27	57N	110	55W	18	9	23	14	29	18	36	28	33	24	47	5
La Paz	24	07N	110	17W	26	9	23	12	30	14	36	23	32	20	42	-1
Lerdo	25	30N	103	32W	1,140	10	22	7	30	14	32	20	28	14	41	-5
Manzanillo	19	04N	104	20W	8	17	30	20	31	19	34	24	33	24	39	12
Mazatlan	23	11N	106	25W	78	10	22	16	24	18	30	25	29	24	34	11
Merida	20	58N	89	38W	22	22	28	17	33	21	33	23	31	22	41	11
Mexico City	19	26N	99	04W	2,237	42	19	6	26	11	23	12	21	10	33	-4
Monterrey	25	40N	100	18W	528	11	20	9	29	17	32	22	27	18	42	-4
Salina Cruz	16	12N	95	12W	56	10	29	22	31	24	32	24	31	24	37	17
Tampico	22	16N	97	51W	24	12	24	15	28	21	32	24	29	22	40	1
Vera Cruz	19	12N	96	08W	16	10	25	19	28	22	31	23	29	23	37	12
Central America																
Belize:																
Belize	17	31N	88	11W	5	27	27	19	30	23	31	24	30	22	36	9
Canal Zone:																
Balboa Heights	8	57N	79	33W	36	34	31	22	32	23	31	23	29	23	36	17
Cristobal	9	21N	79	54W	11	36	29	24	30	25	29	24	30	24	36	19
Costa Rica:																
San Jose	9	56N	84	08W	1,146	8	24	14	26	17	25	17	25	16	33	9
El Salvador:																
San Salvador	13	42N	89	13W	682	39	32	16	34	18	32	18	31	18	41	7

Country and Station	Latitude		Longitude		Elevation	Length of Record	Temperature									
							Average								Extreme	
	January		April		July		October		Max.	Min.	Max.	Min.				
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.				
°C		°C		°C		°C		°C		°C		°C				
Guatemala:																
Guatemala City	14	37N	90	31W	1,480	6	23	12	28	14	26	16	24	16	32	5
Honduras:																
Tela	15	46N	87	27W	12	4	28	19	31	22	31	23	30	22	36	14
West Indies																
Bridgetown, Barbados	13	08N	59	36W	55	35	28	21	30	22	30	23	30	23	35	16
Camp Jacob, Guadeloupe	16	01N	61	42W	533	19	25	18	26	18	27	20	27	20	33	12
Fort-de-France, Martinique	14	37N	61	05W	4	22	28	21	30	22	30	23	31	23	36	13
Hamilton, Bermuda	32	17N	64	46W	46	59	20	14	22	15	29	23	26	21	37	4
Havana, Cuba	23	08N	82	21W	24	25	26	18	29	21	32	24	29	23	40	6
Kingston, Jamaica	17	58N	76	48W	34	33	30	19	31	21	32	23	31	23	36	13
La Guerite, St. Christopher (St. Kitts)	17	20N	62	45W	48	19	27	22	28	23	30	24	29	24	33	16
Nassau, Bahamas	25	05N	77	21W	4	35	25	18	27	21	31	24	29	23	34	5
Fort-au-Prince, Haiti	18	33N	72	20W	37	42	31	20	32	22	34	23	32	22	38	14
Saint Clair, Trinidad	10	40N	61	31W	20	49	31	21	32	21	31	22	32	22	38	11
Saint Thomas, Virgin Is.	18	20N	64	58W	3	9	28	22	29	23	31	25	31	24	33	17
San Juan, Puerto Rico	18	26N	66	00W	4	30	27	19	29	21	31	23	31	23	34	16
Santo Domingo, Dominican Rep.	18	29N	69	54W	17	26	29	19	29	21	31	22	31	22	37	15
South America																
Argentina:																
Bahia Blanca	38	43S	62	16W	29	33	31	17	22	11	14	4	22	9	43	-8
Buenos Aires	34	35S	58	29W	27	23	29	17	22	12	14	6	21	10	40	-6
Cipolletti	38	57S	64	59W	271	9	32	13	22	4	13	-2	22	6	42	-13
Corrientes	27	28S	58	50W	54	39	34	22	27	17	22	12	28	16	44	-1
La Quiaca	22	06S	65	36W	3,458	23	21	5	21	0	16	-9	22	0	35	-18
Mendoza	32	53S	68	49W	800	23	32	16	23	8	15	2	24	10	43	-9
Parana	31	44S	60	31W	64	12	33	19	25	14	17	7	24	12	45	-6
Puerto Madryn	42	47S	65	01W	8	50	27	14	21	8	13	2	20	7	40	-12
Santa Cruz	50	01S	68	32W	12	12	21	9	14	4	5	-2	14	4	34	-17
Santiago del Estero	27	46S	64	18W	199	28	36	21	28	15	21	7	31	15	47	-7
Ushuaia	54	50S	68	20W	8	16	14	5	9	1	4	-3	11	2	29	-21
Bolivia:																
Concepcion	16	15S	62	03W	490	5	29	19	30	17	27	12	31	17	38	0
La Paz	16	30S	68	08W	3,658	31	17	6	18	4	17	1	19	4	27	-3
Sucre	19	03S	65	17W	2,848	5	17	9	17	7	16	3	18	8	31	-4
Brazil:																
Barra do Corda	5	35S	45	28W	81	9	32	22	32	22	33	18	34	22	39	7
Bela Vista	22	06S	56	22W	160	13	33	19	29	16	25	9	31	16	42	-7
Belem	1	27S	48	29W	13	16	31	22	31	23	31	22	32	22	37	16
Brasilia	15	51S	47	56W	1,061	3	27	18	28	17	26	11	28	18	34	8
Conceicao do Araguaia	8	15S	49	12W	16	5	31	21	33	20	35	17	34	20	39	13
Corumba	19	00S	57	39W	116	8	34	23	33	23	29	18	34	21	41	1

Country and Station	Latitude		Longitude		Elevation Meters	Length of Record Years	Temperature									
							Average								Extreme	
							January		April		July		October			
							Max. °C	Min. °C	Max. °C	Min. °C	Max. °C	Min. °C	Max. °C	Min. °C	Max. °C	Min. °C
Florianopolis	27	35S	48	33W	29	17	28	22	23	18	20	14	23	17	39	0
Goias	15	58S	50	04W	520	11	30	17	33	17	32	13	34	17	40	5
Guarapuava	25	16S	51	30W	1,095	10	26	16	23	13	19	8	23	12	34	-5
Manaus	3	08S	60	01W	44	11	31	24	31	24	32	24	33	24	38	17
Natal	5	46S	35	12W	16	18	31	24	30	23	28	21	29	24	38	16
Parana	12	26S	48	06W	260	19	32	14	32	14	33	9	34	14	41	3
Porto Alegre	30	02S	51	13W	10	22	31	19	26	16	19	9	23	14	41	-4
Quixeramobim	5	12S	39	18W	199	9	33	26	30	24	31	23	34	25	38	17
Recife	8	04S	34	53W	30	27	30	25	29	24	27	22	29	24	34	10
Rio de Janeiro	22	55S	43	12W	61	38	29	23	27	21	24	17	25	19	39	8
Salvador (Bahia)	13	00S	38	30W	47	25	30	23	29	23	26	21	28	22	38	10
Santarem	2	30S	54	42W	20	22	30	23	29	23	31	22	33	23	37	18
Sao Paulo	23	37S	46	39W	801	44	25	17	23	15	19	12	20	14	38	0
Sena Madureira	9	04S	68	39W	135	12	33	21	33	20	33	17	34	21	38	5
Uaupes	0	08S	67	05W	83	15	31	22	31	22	29	21	32	22	38	11
Uruguiana	29	46S	57	07W	75	15	33	21	26	15	19	9	25	13	42	-3
Chile:																
Ancud	41	47S	73	52W	56	30	17	11	14	8	10	6	13	7	28	-1
Antofagasta	23	42S	70	24W	94	22	24	17	21	14	17	11	19	13	30	3
Arica	18	28S	70	20W	29	15	26	18	23	16	19	12	21	14	34	4
Cabo Raper	46	50S	75	38W	40	8	14	8	12	7	8	3	11	4	22	-2
Los Evangelistas	52	23S	75	07W	58	16	10	7	9	5	6	2	7	4	19	-7
Portrerillos	26	30S	69	27W	2,850	7	18	9	17	8	14	4	16	7	24	-7
Puerto Aisen	42	24S	72	42W	10	8	17	10	13	6	7	3	13	6	34	-8
Punta Arenas	53	10S	70	54W	8	15	14	7	10	4	4	-1	11	3	30	-12
Santiago	33	27S	70	42W	520	14	29	12	23	7	15	3	22	7	37	-4
Valdivia	39	48S	73	14W	5	29	23	11	17	8	11	5	17	7	36	-7
Valparaiso	33	01S	71	38W	41	30	22	13	19	11	16	8	18	10	34	0
Colombia:																
Andagoya	5	06N	76	40W	60	8	32	24	32	24	32	23	32	23	36	17
Bogota	4	42N	74	08W	2,547	10	19	9	19	11	18	10	19	10	24	-1
Cartagena	10	28N	75	30W	12	6	29	23	31	24	31	26	31	25	37	16
Ipiales	0	50N	77	42W	2,950	9	16	10	16	9	14	6	17	9	25	0
Tumaco	1	49N	78	45W	2	10	28	24	29	24	28	24	28	24	32	18
Ecuador:																
Cuenca	2	53S	78	39W	2,530	7	21	10	21	10	18	8	21	9	27	-2
Guayaquil	2	10S	79	53W	6	5	31	22	31	22	29	19	30	20	37	11
Quito	0	08S	78	29W	2,811	54	19	8	21	8	22	7	22	8	30	-4
French Guiana:																
Cayenne	4	56N	52	27W	6	38	29	23	30	24	31	23	33	23	36	18
Guyana:																
Georgetown	6	50N	58	12W	2	54	29	23	29	24	29	24	31	24	34	20
Lethem	3	24N	59	38W	82	3	33	23	33	23	31	23	33	24	36	17
Paraguay:																

Country and Station	Latitude		Longitude		Elevation	Length of Record	Temperature									
							Average								Extreme	
	January		April		July		October		Max.	Min.	Max.	Min.				
	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C				
Asuncion	25	17S	57	30W	139	15	35	22	29	18	23	12	30	17	43	-2
Bahia Negra	20	14S	58	10W	97	20	33	23	31	20	26	16	32	21	41	2
Peru:																
Arequipa	16	21S	71	34W	2,579	13	19	9	19	9	19	8	20	8	28	-4
Cajamarca	7	09S	78	30W	2,640	9	22	9	21	8	21	5	22	8	26	-4
Cusco	13	33S	71	59W	3,312	13	20	7	22	4	21	-1	22	6	30	-9
Iquitos	3	45S	73	13W	117	5	32	22	31	22	31	20	32	21	38	12
Lima	12	05S	77	03W	120	15	28	19	27	17	19	14	22	14	34	9
Mollendo	17	00S	72	07W	24	10	26	19	24	17	19	14	21	15	32	10
Suriname:																
Paramaribo	5	49N	55	09W	4	35	29	22	30	23	31	23	33	23	37	17
Uruguay:																
Artigas	30	24S	56	23W	117	13	33	18	25	13	18	7	24	12	42	-4
Montevideo	34	52S	56	12W	22	56	28	17	22	12	14	6	20	9	43	-4
Venezuela:																
Caracas	10	30N	66	56W	1,042	30	24	13	27	16	26	16	26	16	33	7
Ciudad Bolivar	8	07N	63	32W	60	10	32	22	34	24	32	24	34	24	38	18
Maracaibo	10	39N	71	36W	6	12	32	23	33	24	34	24	33	24	39	19
Merida	8	36N	71	10W	1,613	14	23	13	24	16	24	15	24	16	32	9
Santa Elena	4	36N	61	07W	907	10	28	16	28	17	27	16	29	16	35	9
Pacific Islands																
Easter Is. (Isla de Pascua)	27	10S	109	26W	30	4	25	18	26	17	21	14	23	14	31	8
Mas a Tierra (Juan Fernandez)	33	37S	78	52W	6	25	22	16	20	14	16	10	16	11	30	4
Seymour Is. (Galapagos Is.)	00	28S	90	18W	11	3	30	22	31	24	27	21	27	19	34	14
Atlantic Islands																
Fernando de Noronha	3	50S	32	25W	45	32	29	24	28	24	27	23	28	24	34	17
Cumberland Bay, South Georgia	54	16S	36	30W	2	23	9	2	6	-2	1	-5	5	-2	29	-19
Laurie Is., South Orkneys	60	44S	44	44W	4	48	2	-2	-1	-6	-7	-16	-1	-7	12	-40
Stanley, Falkland Isles	51	42S	57	51W	2	25	13	6	9	3	4	-1	9	2	24	-11
Europe																
Albania:																
Durres	41	19N	19	28E	7	10	11	6	17	13	28	23	20	14	35	-6
Andorra:																
Les Escaldes	42	30N	1	31E	1,080	5	6	-2	15	4	26	13	16	6	33	-18
Austria:																
Innsbruck	47	16N	11	24E	582	34	1	-7	16	4	26	13	14	4	36	-27
Vienna (Wien)	48	15N	16	22E	202	50	1	-3	14	5	24	15	13	7	37	-26
Bulgaria:																
Sofiya (Sofia)	42	42N	23	20E	550	30	1	-6	17	5	28	14	17	6	37	-27
Varna	43	12N	27	55E	35	30	4	-1	15	6	29	17	19	10	42	-24
Cyprus:																
Nicosia	35	09N	33	17E	218	40	14	6	23	10	36	21	27	14	47	-5

Country and Station	Latitude		Longitude		Elevation	Length of Record	Temperature									
							Average								Extreme	
	January		April		July		October		Max.	Min.						
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.								
°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C			
Czechoslovakia:																
Praha (Prague)	50	05N	14	25E	202	40	1	-4	13	4	23	14	12	7	37	-27
Prerov	49	27N	17	27E	214	20	1	-4	14	3	25	13	13	4	38	-31
Denmark:																
Copenhagen (Kobenhavn)	55	41N	12	33E	13	30	2	-2	10	3	22	13	12	6	33	-19
Aarhus	56	08N	10	12E	49	21	2	-3	11	3	21	12	12	6	31	-24
Finland:																
Helsinki	60	10N	24	57E	9	20	-3	-8	6	-1	22	14	7	3	32	-31
Kuusamo	65	57N	29	12E	257	20	-8	-17	2	-8	20	10	2	-3	32	-40
Vaasa	63	05N	21	36E	4	18	-3	-9	5	-2	21	13	7	2	32	-34
France:																
Ajaccio (Corsica)	41	52N	8	35E	74	46	13	4	19	9	29	18	22	13	39	-5
Bordeaux	44	50N	0	43W	48	51	9	2	17	7	27	14	19	8	39	-13
Brest	48	19N	4	47W	17	56	9	4	14	7	21	13	16	9	35	-14
Cherbourg	49	39N	1	38W	9	47	8	4	12	6	19	14	15	10	33	-10
Lille	50	35N	3	05W	43	40	6	1	14	4	24	13	15	7	36	-18
Lyon	45	42N	4	47E	286	70	5	-1	16	6	27	14	16	7	41	-25
Marseille	43	18N	5	23E	75	72	12	3	15	5	26	14	24	14	38	-13
Paris	48	49N	2	29E	50	66	6	0	16	5	24	13	15	7	41	-17
Strasbourg	48	35N	7	46E	142	20	4	-1	15	5	26	14	14	6	38	-22
Toulouse	43	33N	1	23E	164	47	8	2	17	6	28	15	19	9	44	-17
Germany:																
Berlin	52	27N	13	18E	57	50	2	-3	13	3	23	13	13	5	36	-26
Bremen	53	05N	8	47E	16	50	3	-1	12	3	22	13	12	6	34	-22
Frankfurt A/M	50	07N	8	40E	103	50	3	-2	14	5	24	13	13	6	38	-22
Hamburg	53	33N	9	58E	20	50	2	-2	11	4	21	13	12	7	33	-20
Munchen (Munich)	48	09N	11	34E	530	50	1	-5	12	3	22	12	12	4	33	-26
Munster	51	58N	7	38E	63	50	4	-2	13	3	23	12	13	6	36	-27
Nurnberg	49	27N	11	03E	320	50	2	-3	13	3	23	13	13	5	37	-28
Gibraltar:																
Windmill Hill	36	06N	5	21W	122	12	14	10	18	13	25	19	21	16	36	2
Greece:																
Athinai (Athens)	37	58N	23	43E	107	72	12	6	19	11	32	22	23	16	43	-7
Iraklion (Crete)	35	20N	25	08E	30	21	16	9	21	12	29	22	25	17	46	0
Rodhos (Rhodes)	36	26N	28	15E	88	10	15	11	19	15	28	23	24	20	40	-1
Thessaloniki (Salonika)	40	37N	22	57E	24	9	9	3	19	9	32	21	23	13	42	-9
Hungary:																
Budapest	47	31N	19	02E	120	50	2	-3	17	7	28	16	16	7	39	-23
Debrecen	47	36N	21	39E	131	50	1	-6	16	4	27	14	16	5	39	-30
Iceland:																
Akureyri	65	41N	18	05W	5	23	1	-3	4	-1	14	8	6	1	28	-22
Reykjavik	64	09N	21	56W	28	25	2	-2	6	1	14	9	7	2	23	-16
Ireland:																
Cork	51	54N	8	29W	17	27	9	3	13	5	20	12	14	7	29	-9

Country and Station	Latitude		Longitude		Elevation Meters	Length of Record Years	Temperature									
							Average								Extreme	
							January		April		July		October			
							Max. °C	Min. °C	Max. °C	Min. °C	Max. °C	Min. °C	Max. °C	Min. °C	Max. °C	Min. °C
Dublin	53	22N	6	21W	47	30	8	2	12	3	19	11	14	6	30	-13
Shannon Airport	52	41N	8	55W	2	9	8	2	13	5	19	12	14	7	31	-11
Italy:																
Ancona	43	37N	13	32E	16	30	8	2	17	10	28	20	19	13	39	-8
Cagliari (Sardinia)	39	15N	9	03E	1	30	13	6	19	10	30	19	22	14	39	-4
Genova (Genoa)	44	24N	8	55E	97	10	10	5	18	12	28	21	23	14	38	-8
Napoli (Naples)	40	51N	14	15E	25	30	12	4	18	11	29	21	22	16	38	-4
Palermo (Sicily)	38	07N	13	19E	108	10	14	8	19	12	30	22	24	17	45	-1
Rome	41	48N	12	36E	115	10	12	4	20	8	31	18	23	12	40	-7
Taranto	40	28N	17	17E	17	10	13	6	15	10	32	21	23	14	42	-3
Venezia (Venice)	45	26N	12	23E	25	10	6	1	17	9	28	19	18	11	36	-10
Luxembourg:																
Luxembourg	49	37N	6	03E	334	7	2	-2	14	4	23	13	13	6	37	-23
Malta:																
Valletta	35	54N	14	31E	71	90	15	11	19	13	29	22	24	19	41	1
Monaco:																
Monaco	43	44N	7	25E	55	60	12	8	16	12	25	21	19	16	34	-3
Netherlands:																
Amsterdam	52	23N	4	55E	2	29	4	1	11	6	21	15	13	9	35	-16
Norway:																
Bergen	60	24N	5	19E	43	49	6	-3	13	1	22	11	14	3	32	-16
Kristiansand	58	10N	7	59E	53	11	0	-4	10	2	22	12	12	4	32	-26
Oslo	59	56N	10	44E	94	44	-1	-7	10	1	23	13	9	3	34	-29
Tromso	69	39N	18	57E	102	47	-1	-6	3	-3	15	9	4	1	28	-18
Trondheim	63	25N	10	27E	127	44	-1	-6	7	0	19	11	8	2	35	-30
Vardo	70	22N	31	06E	13	40	-3	-7	1	-3	12	7	3	0	27	-24
Poland:																
Gdansk (Danzig)	54	24N	18	40E	11	36	1	-4	9	3	21	13	12	6	34	-27
Krakow	50	04N	19	57E	220	35	0	-6	13	3	24	14	13	5	36	-33
Warsaw	52	13N	21	02E	90	25	-1	-6	12	3	24	13	12	5	37	-30
Wroclaw (Breslau)	51	07N	17	05E	147	50	2	-4	13	4	23	14	13	6	37	-32
Portugal:																
Braganca	41	49N	6	47W	730	11	8	-1	15	4	27	12	17	6	39	-12
Lagos	37	06N	8	38W	14	21	16	8	19	11	28	18	23	14	42	-2
Lisbon	38	43N	9	08W	95	75	13	8	18	11	26	17	21	14	39	-2
Romania:																
Bucuresti (Bucharest)	44	25N	26	06E	82	41	1	-7	17	5	30	16	18	7	41	-28
Cluj	46	47N	23	40E	392	15	-1	-8	14	3	26	13	16	5	38	-32
Constanta	44	11N	28	39E	4	20	3	-4	13	6	26	17	17	9	38	-25
Spain:																
Almeria	36	51N	2	28W	65	20	16	8	21	12	29	21	24	17	42	1
Barcelona	41	24N	2	09E	95	20	13	6	18	11	27	21	22	14	37	-4
Burgos	42	20N	3	42W	861	29	6	-1	14	3	25	12	16	6	37	-18
Madrid	40	25N	3	41W	667	30	8	1	18	7	31	17	19	9	39	-10



Country and Station	Latitude		Longitude		Elevation	Length of Record	Temperature									
							Average								Extreme	
	January		April		July		October		Max.	Min.						
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.			Max.	Min.				
°	'	°	'	Meters	Years	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	
Sevilla	37	29N	5	59W	30	26	15	5	23	11	36	19	26	14	47	-3
Valencia	39	28N	0	23W	24	26	14	5	19	11	28	20	23	14	42	-7
Sweden:																
Abisko	68	21N	18	49E	388	11	-7	-14	1	-7	16	7	2	-4	28	-34
Goteberg	57	42N	11	58E	17	39	2	-3	9	2	21	13	11	6	31	-25
Haparanda	65	50N	24	09E	9	20	-6	-12	3	-5	22	12	4	-1	32	-37
Karlstad	59	23N	13	30E	50	30	-1	-7	9	0	23	13	9	3	34	-29
Sarna	61	41N	13	07E	458	20	-7	-16	6	-5	21	8	6	-2	33	-46
Stockholm	59	21N	18	04E	45	30	-1	-5	7	0	21	13	9	4	36	-32
Visby (Gotland)	57	39N	18	18E	11	30	2	-2	7	1	19	13	10	5	31	-17
Switzerland:																
Berne	46	57N	7	26E	572	30	2	-3	13	4	23	13	13	6	36	-13
Geneve (Geneva)	46	12N	6	09E	405	30	4	-2	14	5	25	14	14	7	38	-17
Zurich	47	23N	8	33E	493	23	3	-2	14	4	24	13	14	6	37	-24
Turkey:																
Edirne (Adrianople)	41	39N	26	34E	47	18	5	-2	19	7	31	17	21	9	42	-22
Istanbul (Constantinople)	40	58N	28	50E	18	18	7	2	16	7	27	18	19	12	38	-8
United Kingdom:																
Belfast	54	35N	5	56W	17	7	6	1	12	3	18	11	13	7	28	-10
Birmingham	52	29N	1	56W	163	30	6	2	12	4	21	12	13	7	33	-12
Cardiff	51	28N	3	10W	62	30	7	2	13	5	21	12	14	7	33	-17
Dublin	53	22N	6	21W	47	30	8	2	12	3	19	11	14	6	30	-13
Edinburgh	55	55N	3	11W	134	30	6	2	10	4	18	11	12	7	28	-9
London	51	29N	0	0	45	30	7	2	13	4	23	13	14	7	37	-13
Liverpool	53	24N	3	04W	60	30	7	2	11	5	19	13	13	8	31	-9
Perth	56	24N	3	27W	23	30	6	0	12	3	20	11	13	5	32	-18
Plymouth	50	21N	4	07W	27	30	8	4	12	6	19	13	14	9	31	-9
Wick	58	26N	3	05W	36	30	6	2	9	3	15	10	11	6	27	-13
U.S.S.R.:																
Arkhangelsk	64	33N	40	32E	7	23	-13	-17	2	-5	18	11	2	-1	33	-45
Astrakhan	46	21N	48	02E	14	10	-5	-10	14	4	29	21	13	4	37	-30
Dnepropetrovsk	48	27N	35	04E	79	18	-4	-9	12	4	27	17	13	4	38	-32
Kaunas	54	54N	23	53E	36	19	-3	-8	9	1	22	12	10	3	36	-31
Kirov	58	36N	49	41E	181	20	-14	-19	5	-3	22	13	3	-2	33	-42
Kursk	51	45N	36	12E	236	15	-7	-12	8	2	23	14	9	2	33	-31
Leningrad	59	56N	30	16E	5	26	-5	-11	7	-1	22	14	7	3	33	-38
Lvov	49	50N	24	01E	298	9	-1	-6	12	3	25	15	13	6	36	-34
Minsk	53	54N	27	33E	225	12	-6	-11	8	1	21	12	8	2	33	-33
Moskva (Moscow)	55	46N	37	40E	154	15	-6	-13	8	-1	24	13	8	1	36	-33
Odessa	46	29N	30	44E	65	20	-2	-6	11	5	26	18	14	8	37	-25
Riga	56	57N	24	06E	20	30	-2	-7	9	2	22	13	9	4	34	-29
Saratov	51	32N	46	03E	60	14	-9	-14	10	2	28	18	9	2	39	-33
Sevastopol	44	37N	33	31E	23	20	4	-1	13	6	26	18	17	10	36	-16

Country and Station	Latitude		Longitude		Elevation	Length of Record	Temperature									
							Average								Extreme	
					January		April		July		October					
	°	'	°	'	Meters	Years	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.
						°C		°C		°C		°C		°C		
Stalingrad	48	42N	44	31E	41	8	-9	-16	11	2	29	18	12	3	41	-34
Stavropol	45	02N	41	58E	575	18	-3	-8	10	3	24	16	13	6	35	-30
Tallin	59	26N	24	48E	45	15	-3	-8	6	-1	21	13	8	3	32	-28
Tbilisi	41	43N	44	48E	404	10	4	-3	16	7	28	18	18	9	35	-14
Ust'Shchugor	64	16N	57	34E	85	15	-16	-26	2	-8	18	9	1	-5	32	-55
Ufy	54	43N	55	56E	174	20	-14	-16	7	-1	24	14	5	-1	37	-41
Yugoslavia:																
Beograd (Belgrade)	44	48N	20	28E	138	16	3	-3	18	7	29	16	18	8	42	-26
Skoje	41	59N	21	28E	240	10	4	-3	19	6	31	16	18	6	41	-24
Split	43	31N	16	26E	128	14	11	-2	18	10	31	20	21	13	38	-8
Ocean Islands																
Bjornoya, Bear Island	74	31N	19	01E	15	10	-3	-8	-3	-9	7	2	2	-2	22	-32
Gronfjorden, Spitzbergen	78	02N	14	15E	7	19	-12	-20	-9	-16	8	3	-4	-8	16	-49
Horta, Azores	38	32N	28	38W	61	30	17	12	18	13	24	18	22	17	31	3
Jan Mayen	71	01N	8	28W	40	5	-1	-6	-1	-6	8	3	4	-2	16	-28
Lerwick, Shetland Island	60	08N	1	11W	82	30	6	2	8	3	14	9	10	6	22	-8
Matochkin Shar, Novaya Zemlya	73	16N	56	24E	19	9	-13	-21	-11	-18	8	2	-1	-6	20	-41
Ponta Delgada, Azores	37	45N	25	40W	36	30	17	12	18	13	24	18	22	16	29	3
Stornoway, Hebrides	58	11N	6	21W	10	30	7	3	9	4	16	11	12	7	26	-12
Thorshavn, Faeroes	62	02N	6	45W	25	50	6	1	7	2	13	8	14	4	21	-13
Africa																
Algeria:																
Adrar	27	52N	0	17W	286	15	21	4	33	16	46	28	33	17	51	-4
Alger (Algiers)	36	46N	3	03E	59	25	15	9	20	13	28	21	23	17	42	0
Bone	36	54N	7	46E	20	26	15	8	19	11	29	21	24	16	46	0
El Golea	30	35N	2	53E	380	15	17	3	29	13	42	26	31	16	49	-5
Fort Flatters	28	06N	6	42E	373	15	19	3	32	15	43	26	33	17	51	-7
Tamanrasset	22	42N	5	31E	1,400	15	19	4	30	13	35	22	29	15	39	-7
Touggourt	33	07N	6	04E	69	26	17	3	28	13	42	25	29	15	50	-3
Angola:																
Cangamba	13	41S	19	52E	1,320	6	29	17	32	14	17	8	31	15	43	-7
Luanda	8	49S	13	13E	59	27	28	23	29	24	23	18	26	22	37	14
Mocamedes	15	12S	12	09E	3	15	26	18	28	19	20	13	23	16	39	7
Nova Lisboa	12	48S	15	45E	1,700	14	26	14	26	14	25	8	27	14	32	2
Benim:																
Cotonou	6	21N	2	26E	7	5	27	23	28	26	26	23	27	24	35	18
Botswana:																
Francistown	21	13S	27	30E	1,004	20	31	18	28	13	24	5	32	16	42	-4
Maun	19	59S	23	25E	942	20	32	19	31	14	25	6	35	18	43	-4
Tsabong	26	03S	22	27E	962	10	34	18	28	11	22	1	31	12	42	-9
Cameroon:																
Ngaoundere	7	17N	13	19E	1,098	9	31	13	31	18	28	17	28	16	39	8
Yaounde	3	53N	11	32E	770	11	29	19	29	19	27	19	27	18	36	14

Country and Station	Latitude		Longitude		Elevation	Length of Record	Temperature									
							Average								Extreme	
	January		April		July		October		Max.	Min.						
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.			Max.	Min.				
°	'	°	'	Meters	Years	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	
Central African Republic:																
Bangui	4	22N	18	34E	387	5	32	20	33	22	29	21	31	21	38	14
Ndele	8	24N	20	39E	591	3	37	19	37	23	30	21	32	20	43	14
Chad:																
Am Timan	11	02N	20	17E	436	3	37	13	41	20	32	21	36	19	45	6
Fort Lamy	12	07N	15	02E	295	5	34	14	42	23	33	22	36	21	46	8
Largeau (Faya)	18	00N	19	10E	255	5	29	12	40	21	43	24	39	22	49	3
Congo, Republic of:																
Brazzaville	4	15S	15	15E	318	15	31	21	33	22	28	17	32	21	37	12
Quesso	1	37N	16	04E	345	4	31	21	33	22	29	21	31	21	41	16
Pointe Noire (Loango)	4	39S	11	48E	50	7	29	23	31	23	26	19	28	22	34	15
Egypt:																
Alexandria	31	12N	29	53E	32	45	18	11	23	15	29	23	28	20	44	3
Aswan	24	02N	32	53E	112	46	23	10	36	19	41	26	37	22	51	2
Cairo	29	52N	31	20E	116	42	18	8	28	14	36	21	30	18	47	1
Ethiopia:																
Addis Ababa	9	20N	38	45E	2,450	15	24	6	25	10	21	10	24	7	34	0
Asmara	15	17N	38	55E	2,325	9	23	7	26	11	22	12	22	12	31	-1
Diredawa	9	02N	41	45E	1,200	8	27	14	33	21	32	20	32	19	38	9
Gambela	8	15N	34	35E	410	26	37	18	37	22	31	21	33	19	44	9
French Territory of Afars and Issas (F.T.A.E.):																
Djibouti	11	36N	43	09E	7	16	29	23	32	26	41	31	33	27	47	17
Gabon:																
Libreville	0	23N	9	26E	35	11	31	23	32	23	28	20	30	22	37	17
Mayoumba	3	25S	10	38E	61	8	29	23	30	23	26	20	28	22	33	16
Gambia:																
Bathurst	13	21N	16	40W	27	9	31	15	33	18	30	23	32	22	41	7
Ghana:																
Accra	5	33N	0	12W	27	17	31	23	31	24	27	23	29	23	38	15
Kumasi	6	40N	1	37W	287	10	31	19	32	22	28	21	30	21	38	11
Guinea:																
Conakry	9	31N	13	43W	7	7	31	22	32	23	28	22	31	23	36	17
Kouroussa	10	39N	9	53W	371	9	34	16	37	23	31	21	32	21	43	4
Ifni (now in Morocco):																
Sidi Ifni	29	27N	10	11W	45	14	19	11	22	15	24	18	24	17	51	4
Ivory Coast:																
Abidjan	5	19N	4	01W	20	13	31	23	32	24	28	23	29	23	36	15
Bouake	7	42N	5	00W	364	12	33	20	33	21	29	20	32	20	40	14
Kenya:																
Mombasa	4	03S	39	39E	16	45	31	24	30	24	27	22	29	23	36	16
Nairobi	1	16S	36	48E	1,820	15	25	12	24	14	21	11	24	13	31	5
Liberia:																
Monrovia	6	18N	10	48W	23	6	32	22	32	22	27	22	30	22	36	17

Country and Station	Latitude		Longitude		Elevation	Length of Record	Temperature									
							Average								Extreme	
	January		April		July		October		Max.	Min.						
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.								
°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C			
Libya:																
Banghazi (Benghazi)	32	06N	20	04E	25	46	17	10	23	14	29	22	27	19	43	3
Cufra	24	12N	23	21E	389	7	21	6	32	17	38	24	32	18	50	-3
Sabhah	27	01N	14	26E	444	3	18	5	32	16	39	23	33	18	49	-4
Tarabulus (Tripoli)	32	54N	13	11E	22	47	16	8	22	14	29	22	27	18	46	1
Madagascar:																
Diego Suarez	12	17S	49	17E	30	11	31	24	31	24	29	21	30	22	37	17
Tananarive	18	55S	47	33E	1,372	44	26	16	24	14	20	9	27	12	35	1
Tulear	23	20S	43	41E	6	27	33	22	32	18	27	14	30	18	42	6
Malawi:																
Karonga	9	57S	33	56E	486	8	30	22	29	21	27	15	33	19	37	11
Zomba	15	23S	35	19E	957	27	27	18	26	17	22	12	29	18	35	5
Mali:																
Araouane	18	54N	3	33W	285	8	27	9	43	19	44	26	39	21	54	3
Bamako	12	39N	7	58W	340	11	33	16	39	24	32	22	34	22	47	8
Gao	16	16N	0	03W	275	15	28	14	41	25	36	27	38	26	47	7
Mauritania:																
Atar	20	31N	13	04W	232	7	29	12	36	19	41	27	37	22	47	4
Nema	16	36N	7	16W	269	9	30	17	41	26	37	26	38	26	49	8
Nouakchott	18	07N	15	36W	21	5	29	14	32	18	32	23	33	22	46	7
Morocco:																
Casablanca	33	35N	7	39W	50	48	17	7	21	11	26	18	24	14	43	-1
Marrakech	31	36N	8	01W	460	35	18	4	26	11	38	19	28	14	49	-3
Rabat	34	00N	6	50W	65	35	17	8	22	11	28	17	25	14	48	0
Tangier	35	48N	5	49W	73	35	16	8	18	11	27	18	22	15	41	-2
Mozambique:																
Beira	19	50S	34	51E	9	37	32	24	30	22	25	16	31	22	43	9
Chicoa	15	36S	32	21E	274	8	36	18	34	17	30	13	38	20	47	0
Lourenco Marques	25	58S	32	36E	59	42	30	22	28	19	24	13	28	18	46	7
Niger:																
Agades	16	59N	7	59E	520	8	30	10	41	21	40	24	38	20	46	4
Bilma	18	41N	12	55E	357	9	27	7	38	17	42	24	38	17	47	-2
Niamey	13	31N	2	06E	216	10	34	14	42	25	34	23	38	23	46	8
Nigeria:																
Enugu	6	27N	7	29E	233	11	32	22	33	23	28	22	31	22	37	13
Kaduna	10	35N	6	26E	644	18	32	15	35	22	28	20	32	19	41	8
Lagos	6	27N	3	24E	3	32	31	23	32	25	28	23	29	23	40	16
Maiduguri	11	51N	13	05E	354	15	32	12	40	22	32	23	36	20	44	6
Portuguese Guinea:																
Bolama	11	34N	15	26W	19	31	31	19	33	23	29	23	31	23	41	15
Senegal:																
Dakar	14	42N	17	29W	40	25	26	18	27	18	31	24	32	24	43	12
Kaolack	14	08N	16	04W	6	9	34	16	39	20	33	24	34	23	46	9

Country and Station	Latitude		Longitude		Elevation Meters	Length of Record Years	Temperature									
							Average								Extreme	
							January		April		July		October			
							Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.
°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C			
Sierra Leone:																
Freetown/Lungi	8	37N	13	12W	28	8	31	23	31	24	28	23	29	22	37	17
Somalia:																
Berbera	10	26N	45	02E	14	30	29	20	32	25	42	31	33	24	47	14
Mogadishu (Mogadiscio)	2	02N	45	21E	12	13	30	23	32	26	28	23	30	24	36	15
South Africa, Republic of:																
Capetown	33	54S	18	32E	17	19	26	16	22	12	17	7	21	11	39	-2
Durban	29	50S	31	02E	5	15	27	21	26	18	22	11	24	17	42	4
Kimberley	28	48S	24	46E	1,197	19	33	18	25	11	18	2	28	12	39	-7
Port Elizabeth	33	59S	25	36E	58	14	26	16	23	13	19	7	21	12	40	-1
Port Nolloth	29	14S	16	52E	7	20	19	12	19	10	17	7	18	9	42	-1
Pretoria	25	45S	28	14E	1,369	13	27	16	24	10	19	3	27	13	36	-4
Walvis Bay	22	56S	14	30E	7	20	23	15	24	13	21	8	19	11	40	-4
Southwest Africa:																
Keetmanshoop	26	35S	18	08E	1,004	17	35	18	29	14	21	6	31	13	42	-3
Windhoek	22	34S	17	06E	1,728	30	29	17	25	13	20	6	29	15	36	-4
Sudan:																
El Fasher	13	38N	25	21E	730	17	31	10	39	18	36	21	37	18	45	1
Khartoum	15	37N	32	33E	390	46	32	15	41	22	38	25	40	24	48	5
Port Sudan	19	37N	37	13E	5	30	27	20	32	22	41	28	34	24	47	10
Wadi Halfa	21	55N	31	20E	125	39	24	8	37	17	41	23	37	19	53	-2
Wau	7	42N	28	03E	440	38	36	18	37	22	32	21	34	21	46	10
Tanzania, United Republic of:																
Dar es Salaam	6	50S	39	18E	14	44	28	25	30	23	28	19	29	21	36	15
Iringa	7	47S	35	42E	1,625	14	24	15	24	15	22	11	27	14	32	6
Kigoma	4	53S	29	38E	885	26	27	19	27	19	28	17	29	21	38	12
Togo:																
Lome	6	10N	1	15E	22	5	29	22	30	23	27	22	28	22	34	14
Tunisia:																
Gabes	33	53N	10	07E	2	50	16	6	23	12	32	22	27	17	50	-3
Tunis	36	47N	10	12E	66	50	14	6	21	11	32	20	25	15	48	-1
Uganda:																
Kampala	0	20N	32	36E	1,312	15	28	18	26	18	25	17	27	17	36	12
Lira	2	15N	32	54E	1,085	14	33	16	30	18	27	16	30	16	38	10
Upper Volta:																
Bobo Dioulasso	11	10N	4	15W	430	11	33	14	37	22	31	21	32	21	46	8
Quagadougou	12	22N	1	31W	302	10	33	16	39	26	33	23	35	23	48	9
Western Sahara:																
Semara	26	46N	11	31W	460	6	23	8	31	14	37	19	31	16	49	3
Villa Cisneros	23	42N	15	52W	11	12	22	13	23	16	26	18	27	18	42	9
Zaire:																
Kalemie	5	54S	29	12E	760	5	29	19	28	19	28	14	31	19	33	10
Kananga	5	54S	22	25E	670	3	29	20	30	20	29	17	29	20	34	14
Kinshasa	4	20S	15	18E	325	8	31	21	32	22	27	18	31	21	36	14

Country and Station	Latitude		Longitude		Elevation Meters	Length of Record Years	Temperature									
							Average								Extreme	
	January		April		July		October		Max.	Min.	Max.	Min.				
	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C				
Kisangani	0	26N	25	14E	418	8	31	21	31	21	29	19	30	20	36	16
Zambia:																
Balovale	13	34S	23	06E	1,090	8	28	18	29	16	27	8	33	18	42	3
Kasama	10	12S	31	11E	1,385	10	26	16	26	16	24	10	31	17	35	4
Lusaka	15	25S	28	19E	1,277	10	26	17	26	15	23	9	31	18	38	4
Zimbabwe:																
Bulawayo	20	09S	28	37E	1,343	15	27	16	26	13	21	7	29	15	37	-2
Salisbury	17	50S	31	08E	1,472	15	26	16	26	13	21	7	28	14	35	0
Atlantic Islands																
Funchal, Madeira Island	32	38N	16	55W	25	30	19	13	19	14	24	19	23	18	39	4
Georgetown, Ascension Island	7	56S	14	25W	17	29	29	23	31	24	29	22	28	22	35	18
Hutts Gate, St. Helena	15	57S	5	40W	628	30	20	16	21	16	17	13	16	12	28	10
Las Palmas, Canary Islands	28	11N	15	28W	6	45	21	14	22	16	25	19	26	19	37	8
Porto de Praia, Cape Verde Islands	14	54N	23	31W	34	25	25	20	26	21	28	24	29	24	34	13
Santa Isabel, Fernando Po	3	46N	8	46E	0	2	31	19	32	21	29	21	30	21	39	16
Sao Tome, Sao Tome	0	20N	6	43E	5	10	30	23	30	23	28	21	29	22	33	13
Tristan da Cunha	37	03S	12	19W	23	5	19	15	18	14	14	10	15	11	24	3
Indian Ocean Islands																
Agalega Island	10	26S	56	40E	3	3	30	25	31	25	28	24	29	24	33	21
Cocos (Keeling) Island	12	05S	96	53E	5	36	30	25	29	26	28	24	29	24	34	20
Heard Island	53	01S	73	23E	5	5	5	2	4	1	1	-3	2	-2	14	-11
Hellburg, Reunion Island	21	04S	55	22E	936	5	23	15	23	13	18	9	21	11	29	4
Fort Victoria, Seychelles	4	37S	55	27E	5	60	28	24	30	25	27	24	28	24	33	19
Royal Alfred Observatory, Mauritius	20	06S	57	32E	55	40	30	23	28	21	24	17	27	18	35	10
Asia Far East																
China:																
Canton	23	10N	113	20E	18	26	18	9	25	18	33	25	29	19	38	-1
Chanasha	28	15N	112	58E	49	14	7	2	21	13	34	26	24	15	43	-9
Chungking	29	30N	106	33E	261	27	11	6	23	15	34	24	22	16	44	-2
Hankow	30	35N	114	17E	23	29	8	1	21	13	34	26	23	16	42	-13
Harbin (Ha-erh-pin)	45	45N	126	38E	145	35	-14	-26	12	-1	29	18	12	-1	39	-42
Kashgar	39	24N	76	07E	1,309	27	1	-11	22	9	33	20	22	6	41	-26
Kunming	25	02N	102	43E	1,893	32	16	3	24	11	25	17	21	12	33	-6
Lanchow	36	06N	103	55E	1,556	8	1	-14	18	4	29	16	17	4	38	-16
Mukden (Shen-yang)	41	47N	123	24E	42	40	-7	-17	16	2	31	21	17	4	39	-33
Shanghai	31	12N	121	26E	5	56	8	0	19	9	33	24	24	13	40	-12
Tientsin	39	10N	117	10E	4	24	1	-9	20	7	32	23	20	9	43	-16
Urumchi	43	45N	87	40E	906	6	-11	-14	16	2	28	14	10	-1	44	-34
Hong Kong:	22	18N	114	10E	33	50	18	13	24	19	31	26	27	23	36	0
Japan:																
Kushiro	43	02N	144	12E	96	41	-1	-13	7	-1	19	13	14	4	31	-28

Country and Station	Latitude		Longitude		Elevation	Length of Record	Temperature									
							Average								Extreme	
	January		April		July		October		Max.	Min.	Max.	Min.				
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.				
°C		°C		°C		°C		°C		°C		°C				
Miyako	39	38N	141	59E	30	30	6	-5	14	3	25	17	19	8	37	-17
Nagasaki	32	44N	129	53E	133	59	9	2	19	10	29	23	22	14	37	-6
Osaka	34	47N	135	26E	15	60	8	0	18	8	31	23	22	13	39	-7
Tokyo	35	41N	139	46E	6	60	8	-2	17	8	28	21	21	13	38	-8
Korea:																
Pusan	35	10N	129	07E	2	36	6	-2	17	8	27	22	21	12	36	-14
P'yongyang	39	01N	125	49E	29	43	-3	-13	16	3	29	21	18	6	38	-28
Seoul	37	31N	126	55E	10	22	0	-9	17	5	29	21	19	7	37	-24
Mongolia:																
Ulan Bator	47	54N	106	56E	1,307	13	-	-952	7	-8	22	10	7	-8	36	-44
Taiwan:																
Tainan	22	57N	120	12E	16	13	22	13	28	19	32	25	30	21	35	4
Taipei	25	04N	121	32E	6	12	19	12	25	18	33	24	27	20	38	0
Union of Soviet Socialist Republics:																
Alma-Ata	43	16N	76	53E	775	19	-5	-14	13	3	27	16	13	2	38	-34
Chita (Tchita)	52	02N	113	30E	676	10	-23	-33	6	-7	24	11	3	-8	37	-47
Dubinka	69	07N	87	00E	43	5	-31	-35	-14	-23	15	8	-7	-12	29	-52
Irkutsk	52	16N	104	19E	467	10	-16	-26	6	-7	21	10	5	-6	37	-50
Kazalinsk	45	46N	62	06E	63	10	-9	-15	14	-3	32	18	14	2	42	-33
Khabarovsk	48	28N	135	03E	50	7	-19	-25	5	-2	24	17	9	1	33	-43
Kirensk	57	47N	108	07E	286	18	-26	-33	3	-9	23	11	12	-20	35	-57
Krasnoyarsk	56	01N	92	52E	152	10	-16	-23	1	-5	19	13	1	-3	39	-44
Markovo	64	45N	170	50E	26	15	-28	-34	-15	-22	15	8	-9	-13	29	-58
Naryn	58	50N	81	39E	60	13	-22	-28	2	-7	22	13	2	-4	34	-52
Okhotsk	59	21N	143	17E	5	19	-21	-27	-2	-12	14	9	1	-6	26	-46
Omsk	54	58N	73	20E	85	19	-18	-26	4	-6	23	13	4	-3	39	-49
Petropavlovsk	52	53N	158	42E	87	7	-5	-12	2	-4	13	8	8	1	29	-34
Salehkard	66	31N	66	35E	18	18	-25	-29	-8	-16	16	9	-3	-7	29	-54
Semipalatinsk	50	24N	80	13E	216	10	-13	-22	7	-3	27	14	8	-1	38	-44
Sverdlovsk	56	49N	60	38E	272	21	-14	-21	6	-3	21	12	3	-2	34	-43
Tashkent	41	20N	69	18E	478	19	3	-6	18	8	33	18	18	5	41	-28
Verkhoyansk	67	34N	133	51E	100	24	-48	-53	-7	-23	19	8	11	-16	37	-68
Vladivostok	43	07N	131	55E	29	14	-11	-18	8	1	22	16	13	5	33	-30
Yakutsk	62	01N	129	43E	163	19	-43	-47	-3	-14	23	12	-5	-12	36	-64
Asia Southeast																
Brunei:																
Brunei	4	55N	114	55E	3	5	29	24	31	25	31	24	30	25	37	21
Burma:																
Mandalay	21	59N	96	06E	77	20	28	13	38	25	34	26	32	23	44	7
Moulmein	16	26N	97	39E	46	43	32	18	35	25	28	23	31	24	39	11
Democratic Kampuchea:																
Phnom Penh	11	33N	104	51E	12	37	31	22	35	24	32	24	31	24	41	13

Country and Station	Latitude		Longitude		Elevation	Length of Record	Temperature									
							Average								Extreme	
	January		April		July		October		Max.	Min.	Max.	Min.				
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	°C	°C	°C	°C	°C	°C		
Indonesia:																
Batavia (Jakarta)	6	11S	106	50E	8	80	29	23	31	24	31	23	31	23	37	19
Manokwari	0	53S	134	03E	3	5	30	23	30	23	30	23	31	23	34	20
Mapanget	1	32N	124	55E	80	21	29	23	30	23	31	23	32	22	36	18
Penfui	10	10S	123	39E	102	21	31	24	32	22	31	21	33	22	38	14
Pontianak	0	00N	109	20E	4	20	31	23	32	24	32	23	32	24	36	20
Tabing	0	52S	100	21E	6	21	31	23	31	24	31	23	30	23	34	20
Tarakan	3	19N	117	33E	6	19	29	23	30	24	31	23	31	23	34	19
Lao, Peoples Democratic Republic:																
Vientiane	17	58N	102	34E	170	13	28	14	35	23	32	24	31	22	42	0
Malaya, Fed.:																
Kuala Lumpur	3	06N	101	42E	34	19	32	22	33	23	32	22	32	23	37	18
Singapore	1	18N	103	50E	10	39	30	23	31	24	31	24	31	23	36	19
North Borneo:																
Sanda Kan	5	54N	118	03E	12	45	29	23	32	24	32	24	31	24	37	21
Philippine Islands:																
Davao	7	07N	125	38E	27	15	31	22	33	23	31	23	32	23	36	18
Manila	14	31N	121	00E	15	61	30	21	34	23	31	24	31	23	38	14
Sarawak:																
Kuching	1	29N	110	20E	26	5	29	22	32	23	32	22	32	23	37	18
Thailand:																
Bangkok	13	44N	100	30E	16	10	32	19	35	26	32	24	31	24	40	10
Vietnam																
Hanoi	21	03N	105	52E	6	12	20	14	27	21	33	26	29	22	42	5
Saigon	10	49N	106	39E	10	31	32	21	35	24	31	24	31	23	40	14
Asia Middle East																
Afghanistan:																
Kabul	34	30N	69	13E	1,815	9	2	-8	19	6	33	16	23	6	40	-21
Kandhar	31	36N	65	40E	1,055	7	13	-1	28	10	39	19	29	7	44	-10
Bangladesh:																
Dacca	23	46N	90	23E	7	60	25	13	33	23	31	26	31	24	42	6
India:																
Ahmadabad	23	03N	72	37E	55	45	29	14	40	24	34	26	36	23	48	2
Bangalore	12	57N	77	40E	895	60	27	14	34	21	27	19	28	18	39	8
Bombay	19	06N	72	51E	8	60	31	17	34	23	31	24	34	23	43	8
Calcutta	22	32N	88	20E	6	60	27	13	36	24	32	26	32	23	44	7
Cherrapunji	25	15N	91	44E	1,313	35	16	8	22	15	22	18	22	16	31	1
Hyderabad	17	27N	78	28E	531	50	29	15	38	24	31	23	31	20	44	6
Jalpaiguri	26	32N	88	43E	83	50	23	10	32	20	32	25	31	21	40	2
Lucknow	26	45N	80	52E	122	60	23	8	38	22	33	27	33	19	48	1
Madras	13	04N	80	15E	16	60	29	19	35	26	36	26	32	24	45	14
Mormugao	15	22N	73	49E	48	10	30	21	31	26	28	24	30	24	37	15
New Delhi	28	35N	77	12E	212	10	22	6	36	20	35	27	34	18	46	-1



Country and Station	Latitude		Longitude		Elevation	Length of Record	Temperature									
							Average								Extreme	
	January		April		July		October		Max.	Min.						
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.			Max.	Min.				
°	'	°	'	Meters	Years	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	
Silchar	24	49N	92	48E	29	60	26	11	31	21	32	25	31	22	39	5
Srinagar	33	58N	74	46E	1,664	50	5	-4	19	7	31	18	23	5	41	-16
Indian Ocean Islands:																
Port Blair, Andaman Is.	11	40N	92	43E	80	60	29	22	32	24	29	24	29	23	36	17
Amini Divi, Laccadive Is.	11	07N	72	44E	4	29	30	23	33	27	30	25	30	25	37	18
Minicoy, Maldives Is.	8	18N	73	00E	3	20	29	23	31	27	29	24	29	24	37	17
Car Nicobar, Nicobar Is.	9	09N	92	49E	14	13	30	25	32	25	30	25	29	24	35	19
Iran:																
Abadan	30	21N	48	13E	3	12	18	7	32	17	44	27	37	17	53	-4
Esfahan (Isfahan)	32	37N	51	41E	1,597	45	8	-4	22	8	37	19	26	8	42	-16
Kermanshah	34	19N	47	07E	1,320	15	7	-5	20	3	37	13	26	3	42	-25
Rezaieyeh	37	32N	45	05E	1,330	3	0	-8	19	7	33	18	19	8	37	-24
Tehran	35	41N	51	19E	1,200	24	7	-3	22	9	37	22	24	12	43	-15
Iraq:																
Baghdad	33	20N	44	24E	34	15	16	4	29	14	43	24	33	16	49	-8
Basra	30	34N	47	47E	2	10	18	7	29	17	40	27	34	18	51	-4
Mosul	36	19N	43	09E	223	26	12	2	25	9	43	22	31	11	51	-11
Israel:																
Haifa	32	48N	35	02E	7	16	18	9	25	14	31	24	29	20	44	-3
Jerusalem	31	47N	35	13E	809	19	13	5	23	10	31	17	27	15	42	-3
Tel Aviv	32	06N	34	46E	10	10	18	10	21	14	28	22	26	18	39	1
Jordan:																
Amman	31	58N	35	59E	776	25	12	4	23	9	32	18	27	14	43	-6
Kuwait:																
Kuwait	29	21N	48	00E	5	14	16	9	28	20	39	30	33	23	48	1
Lebanon:																
Beirut	33	54N	35	28E	34	62	17	11	22	14	31	23	27	21	42	-1
Nepal:																
Katmandu	27	42N	85	22E	1,348	27	18	2	29	12	29	21	27	13	37	-3
Oman and Muscat:																
Muscat	23	37N	58	35E	5	23	25	19	32	26	36	31	34	27	47	11
Pakistan (West):																
Karachi	24	48N	66	59E	4	43	25	13	32	23	33	27	33	22	48	4
Multan	30	11N	71	25E	122	60	20	6	35	20	39	30	34	18	50	-2
Rawalpindi (Dhamial)	33	35N	73	03E	511	60	17	3	30	15	37	25	32	14	48	-4
Saudi Arabia:																
Dhahran	26	16N	50	10E	24	10	21	12	32	21	42	30	35	23	49	4
Jedda	21	28N	39	10E	6	5	29	19	33	21	37	26	35	23	47	9
Riyadh	24	39N	46	42E	591	3	21	8	32	18	42	26	34	16	45	-7
Sri Lanka:																
Colombo	6	54N	79	52E	7	25	30	22	31	24	29	25	29	24	37	15
Syria:																
Deir Ez Zor	35	21N	40	09E	213	5	12	2	27	11	41	26	30	13	46	-9

Country and Station	Latitude		Longitude		Elevation	Length of Record	Temperature									
							Average								Extreme	
	January		April		July		October		Max.	Min.						
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.								
°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C					
Dimashq (Damascus)	33	30N	36	20E	720	13	12	2	24	9	36	18	27	12	45	-6
Halab (Aleppo)	36	14N	37	08E	390	8	10	1	24	9	36	21	27	12	47	-13
Turkey:																
Adana	36	59N	35	18E	25	21	14	4	23	11	34	22	29	14	43	-7
Ankara	39	57N	32	53E	861	26	4	-4	17	4	30	15	21	7	40	-25
Erzurum	39	54N	41	16E	1,951	16	-4	-13	10	0	26	12	15	3	34	-30
Izmir (Smyrna)	38	27N	27	15E	28	39	13	4	21	9	33	21	24	13	42	-11
Samsun	41	17N	36	19E	40	24	10	3	15	7	26	18	21	13	39	-7
United Arab Emirates																
Sharjah	25	20N	55	24E	5	11	23	12	30	18	38	28	33	22	48	3
Yeman, Democratic:																
Kamaran I.	15	20N	42	37E	6	26	28	23	32	26	37	29	34	28	41	19
Riyan	14	39N	49	19E	25	13	28	19	31	23	33	25	31	22	44	14
See Footnotes at end of Table																
Australia & Pacific Islands																
Australia:																
Adelaide	34	57S	138	32E	6	86	30	16	23	13	15	7	23	11	48	0
Alice Springs	23	48S	133	53E	546	62	36	21	27	12	19	4	31	14	44	-7
Bourke	30	05S	145	58E	110	63	37	21	28	13	18	4	29	13	52	-4
Brisbane	27	25S	153	05E	5	53	29	21	26	16	20	9	27	16	43	2
Broome	17	57S	122	13E	17	41	33	26	34	22	28	14	33	22	45	4
Burketown	17	45S	139	33E	9	31	34	25	33	21	28	13	34	21	43	4
Canberra	35	18S	149	11E	575	23	28	13	19	7	11	1	20	6	43	-10
Carnarvon	24	53S	113	40E	4	43	31	22	29	19	22	11	26	16	48	3
Cloncurry	20	40S	140	30E	190	32	37	25	32	19	25	11	35	20	53	2
Esperance	33	50S	121	55E	4	44	25	16	22	12	17	7	20	10	47	-1
Laverton	28	40S	122	23E	460	30	36	21	27	14	18	5	28	13	46	-4
Melbourne	37	49S	144	58E	35	88	26	14	20	11	13	6	19	9	46	-3
Mundiwindi	23	52S	120	10E	561	15	38	18	31	16	21	5	32	14	44	-6
Perth	31	56S	115	58E	20	44	29	17	24	14	17	9	21	12	44	-1
Port Darwin	12	25S	130	52E	32	58	32	25	33	24	31	19	34	25	41	13
Sydney	33	52S	151	02E	19	87	26	18	22	14	16	8	22	13	46	2
Thursday Island	10	35S	142	13E	61	31	31	25	30	25	28	23	30	24	37	18
Townsville	19	15S	146	46E	5	31	31	24	29	21	24	15	28	22	43	4
William Creek	28	55S	136	21E	75	39	36	21	27	13	18	5	29	13	48	-4
Windorah	25	26S	142	36E	119	29	38	23	30	15	21	6	33	16	47	-3
Tasmania:																
Hobart	42	53S	147	20E	54	70	22	12	17	9	11	4	17	8	41	-2
New Zealand:																
Auckland	37	00S	174	47E	7	36	23	16	19	13	13	8	17	11	32	1
Christchurch	43	29S	172	32E	36	52	21	12	17	7	10	2	17	7	36	-6
Dunedin	45	55S	170	12E	1	77	19	10	15	7	9	3	15	6	34	-5

Country and Station	Latitude		Longitude		Elevation	Length of Record	Temperature									
							Average								Extreme	
							January		April		July		October			
							Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.
°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C			
Wellington	41	17S	174	46E	126	66	21	13	17	11	12	6	16	9	31	-2
Pacific Islands																
Canton, Phoenix Is.	2	46S	171	43W	3	12	31	26	32	26	32	26	32	26	37	21
Guam, Marianas Is.	13	33N	144	50E	110	30	29	22	30	23	31	22	30	23	35	12
Honolulu, Hawaii	21	20N	157	55W	2	30	26	19	27	20	29	23	29	22	34	13
Iwo Jima, Bonin Is.	24	47N	141	19E	108	15	22	18	25	21	30	26	29	24	35	8
Madang, New Guinea	5	12S	145	47E	6	12	31	24	31	23	31	23	31	24	37	17
Midway Is.	28	13N	177	23W	9	21	21	17	22	18	27	23	26	22	33	8
Naha, Okinawa	26	12N	127	39E	29	30	19	13	24	18	32	25	27	21	36	5
Noumes, New Caledonia	22	16S	166	27E	75	24	30	22	28	21	24	17	27	18	37	11
Pago Pago, Samoa	14	19S	170	43W	9	2	31	24	31	24	28	23	29	24	37	19
Ponape, Caroline Is.	6	58N	158	13E	37	30	30	24	30	24	31	23	31	22	36	19
Port Moresby, New Guinea	9	29S	147	09E	38	20	32	24	31	24	28	23	30	24	37	18
Rabaul, New Guinea	4	13S	152	11E	9	19	32	23	32	23	32	23	33	23	38	18
Suva, Fiji Is.	18	08S	178	26E	6	43	30	23	29	23	26	20	27	21	37	13
Tahiti, Society Is.	17	33S	149	36W	2	23	32	22	32	22	30	20	31	21	34	16
Tulagi, Solomon Is.	9	05S	160	10E	2	20	31	24	31	24	30	24	31	24	36	20
Wake Is.	19	17N	166	39E	3	30	28	23	28	23	31	25	30	25	33	18
Yap, Caroline Is.	9	31N	138	08E	19	30	29	24	31	25	31	24	31	24	36	21
Antarctica																
Byrd Station	80	01S	119	32W	1,553	6	-12	-19	-24	-34	-32	-43	-26	-36	-1	-63
Ellsworth	77	44S	41	07W	42	6	-6	-11	-23	-32	-29	-37	-19	-26	2	-57
McMurdo Station	77	53S	166	48W	2	10	-1	-6	-18	-25	-23	-31	-17	-24	6	-51
South Pole Station	89	59S	0	00W	2,800	5	-27	-31	-54	-62	-55	-63	-48	-53	-14	-77
Wilkes	66	16S	110	31E	9	7	1	-2	-8	-13	-13	-19	-9	-14	8	-37

NOTE: "Length of Record" refers to average daily maximum and minimum temperatures. A standard period of the 30 years from 1931-1960 had been used for locations in the United States and some other countries. The length and minimum temperatures includes all available years of data for a given location and is usually for a longer period of time. All temperature data have been changed from Fahrenheit to Celsius.

Table A-5-2. Selected world precipitation data (adapted from *Climates of the World*, U.S. Dept of Commerce (1969); reprinted 1977).

Country and Station	Latitude		Longitude		Elevation Meters	Length of Record Years	Precipitation												
	°	'	°	'			Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
							mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
United States (Conterminous):																			
Albuquerque, N. Mex.	35	03N	106	37W	1,619	30	10	10	13	13	20	15	30	33	25	20	10	13	213
Asheville, N.C.	35	26N	82	32W	652	30	107	102	122	102	94	89	150	124	91	79	71	91	1,222
Atlanta, Ga.	33	39N	84	26W	308	30	112	114	137	114	81	97	119	91	84	61	76	112	1,199
Austin, Tex.	30	18N	97	42W	182	30	61	66	53	91	94	81	56	48	86	71	53	64	826
Birmingham, Ala.	33	34N	86	45W	189	30	127	135	152	114	86	102	132	124	84	76	89	127	1,349
Bismarck, N. Dak.	46	46N	100	45W	502	30	10	10	20	30	51	86	56	43	30	23	15	10	386
Boise, Idaho	43	34N	116	13W	865	30	33	33	33	30	33	23	5	5	10	20	30	33	290
Brownsville, Tex.	25	54N	97	26W	5	30	36	38	25	41	61	76	43	71	127	89	33	43	683
Buffalo, N.Y.	42	56N	78	44W	215	30	71	69	81	76	76	64	66	79	79	76	91	76	904
Cheyenne, Wyo.	41	09N	104	49W	1,867	30	13	15	30	48	64	53	46	36	28	20	15	13	381
Chicago, Ill.	41	47N	87	45W	185	30	48	41	69	76	94	104	86	81	69	71	56	48	843
Des Moines, Iowa	41	32N	903	39W	286	30	33	28	53	64	104	119	79	94	74	53	46	28	775
Dodge City, Kans.	37	46N	99	58W	787	30	15	18	30	46	81	76	58	61	38	36	15	13	488
El Paso, Tex.	31	48N	106	24W	1,194	30	13	10	10	8	10	18	33	30	28	23	8	13	203
Indianapolis, Ind.	39	44N	86	17W	241	30	79	58	86	94	102	117	89	76	81	66	79	69	996
Jacksonville, Fla.	30	25N	81	39W	6	30	64	74	89	91	89	160	196	175	193	132	43	56	1,361
Kansas City, Mo.	39	07N	94	36W	226	30	36	30	64	91	112	117	81	97	84	74	46	38	869
Las Vegas, Nev.	36	05N	115	10W	659	30	13	10	10	5	3	0	13	13	8	5	8	10	97
Los Angeles, Calif.	33	56N	118	23W	30	30	69	74	46	28	3	3	0	0	5	10	28	61	325
Louisville, Ky.	38	11N	85	44W	145	30	104	84	117	97	99	102	86	76	66	58	81	81	1,052
Miami, Fla.	25	48N	80	16W	2	30	51	48	58	99	163	188	173	178	241	208	71	43	1,521
Minneapolis, Minn.	44	53N	93	13W	254	30	18	20	38	48	81	102	84	81	61	41	36	23	632
Missoula, Mont.	46	55N	114	05W	972	30	23	23	18	25	48	48	23	18	25	25	23	28	328
Nashville, Tenn.	36	07N	86	41W	180	30	140	114	132	94	94	84	94	74	74	58	84	107	1,148
New Orleans, La.	29	59N	90	15W	1	30	97	102	135	117	112	112	170	135	127	71	84	104	1,364
New York, N.Y.	40	47N	73	58W	40	30	84	71	102	86	94	84	94	112	99	79	86	84	1,074
Oklahoma City, Okla.	35	24N	97	36W	392	30	33	36	51	79	132	114	61	64	76	64	41	36	785
Phoenix, Ariz.	33	26N	112	01W	340	30	18	23	18	8	3	3	20	28	18	13	13	23	185

North America

Country and Station	Latitude		Longitude		Elevation Meters	Length of Record Years	Precipitation												
	°	'	°	'			Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
							mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Pittsburgh, Pa.	40	27N	80	00W	228	30	71	58	89	86	97	102	91	89	69	64	58	64	937
Portland, Maine	43	39N	70	19W	14	30	112	97	109	94	86	81	74	61	89	81	107	99	1,090
Portland, Oreg.	45	36N	122	36W	6	30	137	107	97	53	51	43	10	18	41	91	135	163	945
Reno, Nev.	39	30N	119	47W	1,342	30	30	25	18	13	13	10	8	5	5	13	15	28	183
Salt Lake City, Utah	40	46N	111	58W	1,286	30	36	30	41	46	36	25	15	23	13	30	33	30	358
San Francisco, Calif.	37	37N	122	23W	2	30	102	89	69	33	13	3	0	0	5	18	41	104	475
Sault Ste. Marie, Mich.	46	28N	84	22W	220	30	53	38	46	56	71	84	64	74	97	71	84	58	795
Seattle, Wash.	47	27N	122	18W	122	30	145	107	97	61	43	41	20	25	53	102	137	160	991
Sheridan, Wyo.	44	46N	106	58W	1,208	30	15	18	36	56	66	66	30	23	30	28	20	15	404
Spokane, Wash.	47	38N	117	32W	718	30	61	48	38	23	30	38	10	10	20	41	56	61	437
Washington, D.C.	38	51N	77	03W	4	30	76	64	81	81	104	81	107	124	97	79	71	71	1,036
Wilmington, N.C.	34	16N	77	55W	9	30	74	86	102	74	89	109	196	175	160	76	79	86	1,306
United States, Alaska:																			
Anchorage	61	13N	149	52W	26	30	20	18	13	10	13	25	48	66	64	48	25	23	373
Annette	55	02N	131	34W	34	30	290	216	244	231	180	145	152	191	251	429	373	307	3,010
Barrow	71	18N	156	47W	9	30	5	5	3	3	3	10	20	23	15	13	5	5	109
Belhel	60	47N	161	48W	38	30	28	28	25	15	25	30	51	107	66	38	28	25	467
Cold Bay	55	12N	162	43W	29	30	58	81	46	38	58	51	46	109	109	117	97	66	876
Fairbanks	64	49N	147	52W	133	30	23	13	10	8	18	36	46	56	28	23	15	13	287
Juneau	58	22N	134	35W	4	30	102	79	84	74	81	86	114	127	170	211	155	107	1,389
King Salmon	58	41N	156	39W	15	30	28	25	25	15	25	36	53	86	79	56	38	25	493
Nome	64	30N	165	26W	4	30	25	23	23	20	18	23	58	97	69	43	30	25	455
St. Paul Island	57	09N	170	13W	7	30	46	30	28	533	33	30	58	84	79	81	64	46	605
Shemya	52	43N	174	06E	37	30	64	58	66	53	61	33	56	53	58	71	69	53	696
Yakutat	59	31N	139	40W	9	30	277	208	221	183	203	130	213	277	422	498	409	312	3,353
Canada:																			
Aklavik, N.W.T.	68	14N	135	00W	9	22	13	13	10	13	13	20	36	36	23	23	20	10	229
Alert, N.W.T.	82	31N	62	20W	29	10	5	8	8	8	13	15	13	28	25	23	5	10	160
Calgary, Alta.	51	06N	114	01W	1,079	55	13	13	20	25	58	79	64	58	38	18	18	15	424
Charlottetown, P.E.I.	46	17N	63	08W	55	65	97	76	81	71	69	66	76	86	86	104	97	102	1,011
Chatham, N.B.	47	00N	65	27W	33	50	86	69	84	76	81	91	99	102	79	102	86	81	1,036
Churchhill, Man.	58	45N	94	04W	29	30	13	15	23	23	23	48	56	69	58	36	25	18	406
Edmonton, Alta.	53	34N	113	31W	676	71	23	18	18	25	48	81	84	61	33	20	23	23	457

Country and Station	Latitude		Longitude		Elevation Meters	Length of Record Years	Precipitation												
	°	'	°	'			Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
							mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Fort Nelson, B.C.	58	50N	122	35W	382	13	23	30	18	20	36	64	61	38	33	25	36	30	414
Fort Simpson, N.W.T.	61	45N	121	14W	169	42	18	18	13	18	36	38	51	38	33	28	23	20	333
Frobisher Bay, N.W.T.	63	45N	68	33W	34	10	18	23	20	18	23	38	38	51	46	28	28	25	338
Gander, Nfld.	48	57N	54	34W	151	14	66	84	71	66	66	71	91	91	94	104	107	94	1,006
Halifax, N.S.	44	39N	63	34W	25	71	137	112	124	114	104	102	97	112	104	137	135	137	1,415
Kapuskasing, Ont.	49	25N	82	28W	226	19	51	28	41	46	53	58	86	74	89	64	61	48	699
Knob Lake, Que.	54	48N	66	49W	522	10	48	48	36	41	43	84	84	112	86	74	61	38	754
Montreal, Que.	45	30N	73	34W	57	77	97	76	89	66	79	86	94	89	94	86	89	91	1,036
North Bay, Ont.	46	21N	79	25W	371	23	51	38	46	56	64	81	81	69	94	81	69	53	782
Ottawa, Ont.	45	19N	75	40W	114	65	74	56	71	69	64	89	86	66	81	74	76	66	871
Penticton, B.C.	49	28N	119	36W	344	32	25	18	18	18	28	30	20	20	25	20	23	28	274
Port Arthur, Ont.	48	22N	89	19W	196	59	23	20	25	38	53	71	91	71	86	64	38	23	605
Prince George, B.C.	53	53N	122	41W	676	27	46	30	36	20	33	53	41	48	51	51	48	48	505
Prince Rupert, B.C.	54	17N	130	23W	52	26	249	193	213	170	135	104	122	130	196	310	312	287	2,421
Quebec, Que.	46	48N	71	23W	73	72	89	69	76	61	79	94	102	102	91	86	81	81	1,011
Regina, Sask.	50	26N	104	40W	574	49	13	8	18	18	46	84	61	46	33	23	15	10	373
Resolute, N.W.T.	74	43N	94	59W	67	7	3	3	5	5	13	20	23	28	20	13	5	3	140
St. John, N.B.	45	17N	66	04W	36	61	104	79	94	81	79	81	79	91	94	104	99	97	1,082
St. Johns, Nfld.	47	32N	52	44W	64	58	135	130	117	97	99	79	79	102	94	122	145	152	1,349
Saskatoon, Sask.	52	08N	106	38W	515	38	23	13	18	18	36	66	61	48	38	23	13	15	371
The Pas, Man.	53	49N	101	15W	271	27	15	13	18	20	36	56	56	53	51	30	25	20	394
Toronto, Ont.	43	40N	79	24W	116	105	69	61	66	64	74	69	76	69	74	61	71	66	818
Vancouver, B.C.	49	17N	123	05W	39	41	218	147	127	84	71	64	30	43	91	147	211	224	1,458
Whitehorse, Y.T.	60	43N	135	04W	702	10	15	13	15	10	15	25	41	38	33	18	25	20	269
Winnipeg, Man.	49	54N	97	14W	239	66	23	23	30	36	58	79	79	64	58	38	28	23	538
Yellow Knife, N.W.T.	62	28N	114	27W	205	13	20	15	18	10	18	15	38	36	25	33	25	20	274
Greenland:																			
Angmagssalik	65	36N	37	33W	29	38	74	61	66	53	51	46	38	53	84	119	76	69	790
Danmarkshaven	76	46N	19	00W	2	2	30	18	18	3	5	5	13	15	8	8	25	18	152
Eismitte	70	53N	40	42W	3,000	1	15	5	8	5	3	3	3	10	8	13	13	25	109
Godthaab	64	10N	51	43W	20	45	36	43	41	30	43	36	56	79	84	64	48	38	597
Ivigut	61	12N	48	10W	30	50	84	66	86	64	89	81	79	94	150	145	117	79	1,133
Jacobshavn	69	13N	51	02W	32	52	10	10	13	13	15	20	30	36	33	23	18	13	234

Country and Station	Latitude		Longitude		Elevation Meters	Length of Record Years	Precipitation														
							Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year		
	°	'	°	'			mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Nord	81	36N	16	40W	36	8	20	20	13	8	3	8	25	36	30	15	36	13	226		
Scoresbysund	70	29N	21	58W	17	12	46	36	23	36	10	20	38	18	43	36	28	48	381		
Thule	76	31N	68	44W	77	12	10	8	5	5	8	5	18	15	15	18	13	5	124		
Upernivik	72	47N	56	07W	18	50	10	13	18	15	15	13	23	28	28	28	28	15	234		
Mexico:																					
Acapulco	16	50N	99	56W	3	40	8	0	0	36	325	231	236	353	170	30	10	1,400			
Chihuahua	28	42N	105	57W	1,350	22	5	10	8	5	43	91	94	84	23	13	10	391			
Guadalajara	20	41N	103	20W	1,583	33	10	5	5	28	224	239	216	183	56	20	18	1,008			
Guaymas	27	57N	110	55W	18	41	13	5	5	3	0	3	43	69	53	18	8	20	239		
La Paz	24	07N	110	17W	26	12	5	3	0	0	5	10	30	36	15	13	28	145			
Lerdo	25	30N	103	32W	1,140	14	10	3	5	8	20	38	38	51	20	20	13	259			
Manzanillo	19	04N	104	20W	8	17	3	5	0	3	119	145	163	368	130	23	46	1,003			
Mazatlan	23	11N	106	25W	78	46	20	13	5	3	38	150	211	203	66	23	33	767			
Merida	20	58N	89	38W	22	40	30	23	18	20	81	142	132	142	173	97	33	927			
Mexico City	19	26N	99	04W	2,237	48	5	8	13	18	48	104	114	109	104	41	13	8	584		
Monterrey	25	40N	100	18W	528	33	15	18	20	33	33	76	58	61	132	76	38	20	582		
Salina Cruz	16	12N	95	12W	56	22	0	10	15	13	84	295	114	140	180	102	23	3	978		
Tampico	22	16N	97	51W	24	12	38	30	25	38	48	221	124	122	274	127	51	41	1,140		
Vera Cruz	19	12N	96	08W	16	40	23	15	15	20	66	264	104	282	353	175	76	25	1,669		
Central America																					
Belize:																					
Belize	17	31N	88	11W	5	33	137	61	38	56	109	196	163	170	244	305	226	185	1,890		
Canal Zone:																					
Balboa Heights	8	57N	79	33W	36	46	25	10	18	74	203	213	180	201	208	257	259	122	1,770		
Cristobal	9	21N	79	54W	11	73	86	38	38	104	318	353	396	389	323	401	566	297	3,310		
Costa Rica:																					
San Jose	9	56N	84	08W	1,146	34	15	5	20	46	229	241	211	241	305	300	145	41	1,798		
El Salvador:																					
San Salvador	13	42N	89	13W	682	39	8	5	10	43	196	328	292	297	307	241	41	10	1,778		
Guatemala:																					
Guatemala City	14	37N	90	31W	1,480	29	8	3	13	30	152	274	203	198	231	173	23	8	1,316		
Honduras:																					
Tela	15	46N	87	27W	12	20	226	130	66	84	109	127	163	239	196	343	404	356	2,441		

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							mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
West Indies																			
Bridgetown, Barbados	13	08N	59	36W	55	22	66	28	33	36	58	112	147	147	170	178	206	97	1,278
Camp Jacob, Guadeloupe	16	01N	61	42W	533	21	234	155	206	185	292	358	447	389	417	315	312	257	3,566
Fort-de-France, Martinique	14	37N	61	05W	4	31	119	109	74	99	119	188	239	262	236	246	201	150	2,042
Hamilton, Bermuda	32	17N	64	46W	46	62	112	119	122	104	117	112	114	137	132	147	127	119	1,463
Havana, Cuba	23	08N	82	21W	24	72	71	46	46	58	119	165	124	135	150	173	79	58	1,224
Kingston, Jamaica	17	58N	76	48W	34	59	23	15	23	30	102	89	38	91	99	180	74	36	800
La Guerite, St. Christopher (St. Kitts)	17	20N	62	45W	48	21	104	51	58	58	97	91	112	132	152	137	185	114	1,293
Nassau, Bahamas	25	05N	77	21W	4	57	36	38	36	64	117	163	147	135	175	165	71	33	1,179
Fort-au-Prince, Haiti	18	33N	72	20W	37	70	33	58	86	160	231	102	74	145	152	170	86	33	1,354
Saint Clair, Trinidad	10	40N	61	31W	20	97	69	41	46	53	94	193	218	246	193	170	183	124	1,173
Saint Thomas, Virgin Is.	18	20N	64	58W	3	9	64	48	43	56	117	81	81	104	175	142	99	99	1,110
San Juan, Puerto Rico	18	26N	66	00W	4	30	119	74	56	94	180	145	160	180	173	147	165	137	1,631
Santo Domingo, Dominican Rep.	18	29N	69	54W	17	25	61	36	48	99	173	157	163	160	185	152	122	61	1,417
South America																			
Argentina:																			
Bahia Blanca	38	43S	62	16W	29	46	43	56	64	58	30	23	25	25	41	56	53	48	523
Buenos Aires	34	35S	58	29W	27	70	79	71	109	89	76	61	56	61	79	86	84	99	950
Cipolletti	38	57S	64	59W	271	24	10	10	18	10	15	15	13	8	15	23	13	13	163
Corrientes	27	28S	58	50W	54	40	119	114	135	142	84	48	43	38	71	119	132	132	1,179
La Quiaca	22	06S	65	36W	3,458	25	89	66	46	8	0	0	0	0	3	8	25	69	312
Mendoza	32	53S	68	49W	800	46	23	30	28	13	10	8	5	8	13	18	18	18	191
Parana	31	44S	60	31W	64	23	79	79	99	124	66	30	30	41	61	71	94	114	889
Puerto Madryn	42	47S	65	01W	8	50	10	15	18	13	23	15	15	10	15	18	10	15	178
Santa Cruz	50	01S	68	32W	12	20	15	8	8	15	10	13	10	13	8	8	10	18	135
Santiago del Estero	27	46S	64	18W	199	20	86	76	76	33	15	8	5	5	13	36	64	104	518
Ushuaia	54	50S	68	20W	8	21	51	66	48	53	38	30	30	28	33	41	38	48	505
Bolivia:																			
Concepcion	16	15S	62	03W	490	16	183	119	112	46	51	38	28	229	30	74	127	150	980
La Paz	16	30S	68	08W	3,658	50	114	107	66	33	13	8	10	13	28	41	48	94	574
Sucre	19	03S	65	17W	2,848	52	185	124	94	41	5	3	5	8	25	41	66	109	706



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							mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Brazil:																			
Barra do Corda	5	35S	45	28W	81	9	170	221	203	155	58	25	18	18	25	64	99	145	1,199
Bela Vista	22	06S	56	22W	160	20	168	124	112	109	127	71	33	46	74	137	147	178	1,326
Belem	1	27S	48	29W	13	20	318	358	358	320	259	170	150	112	89	84	66	155	2,438
Brasilia	15	51S	47	56W	1,061	3	229	198	122	86	36	0	0	0	33	124	246	297	1,372
Conceicao do Araguaia	8	15S	49	12W	16	5	378	307	274	104	48	10	0	13	38	168	124	218	1,681
Corumba	19	00S	57	39W	116	11	185	150	130	117	74	48	8	30	66	102	142	180	1,232
Florianopolis	27	35S	48	33W	29	25	193	142	160	104	91	89	56	94	109	130	89	109	1,349
Goiias	15	58S	50	04W	520	11	318	251	259	117	10	8	0	8	58	135	239	241	1,646
Guarapuava	25	16S	51	30W	1,095	5	221	147	137	114	117	165	69	91	117	175	168	155	1,671
Manaus	3	08S	60	01W	44	25	249	231	262	221	170	84	58	38	46	107	142	203	1,811
Natal	5	46S	35	12W	16	18	48	122	178	234	180	221	196	97	36	20	18	28	1,377
Parana	12	26S	48	06W	260	19	287	236	239	102	13	0	3	5	28	127	231	310	1,582
Porto Alegre	30	02S	51	13W	10	22	89	81	99	104	114	130	114	127	132	86	79	89	1,247
Quixeramobim	5	12S	39	18W	199	13	18	127	168	127	178	43	18	15	10	15	18	15	752
Recife	8	04S	34	53W	30	56	53	84	160	221	267	277	254	152	64	25	25	28	1,610
Rio de Janeiro	22	55S	43	12W	61	84	124	122	130	107	79	53	41	43	66	79	104	137	1,082
Salvador (Bahia)	13	00S	38	30W	47	20	66	135	155	284	274	239	183	122	84	102	114	142	1,900
Santarem	2	30S	54	42W	20	22	173	277	335	328	287	175	104	43	38	48	58	104	1,979
Sao Paulo	23	37S	46	39W	801	24	224	198	152	56	76	61	38	53	89	117	152	239	1,455
Sena Madureira	9	04S	68	39W	135	17	284	287	259	239	104	56	28	38	102	178	191	297	2,062
Uaupes	0	08S	67	05W	83	10	262	196	254	269	305	234	224	183	130	175	183	264	2,677
Uruguaiana	29	46S	57	07W	75	12	91	91	142	130	94	107	81	71	91	104	74	104	1,184
Chile:																			
Ancud	41	47S	73	52W	56	46	79	94	135	188	251	279	262	239	165	107	119	117	2,035
Antofagasta	23	42S	70	24W	94	32	0	0	0	0	0	3	5	3	0	3	13	3	13
Arica	18	28S	70	20W	29	25	0	0	0	0	0	0	0	0	0	0	0	0	*0
Cabo Raper	46	50S	75	38W	40	10	198	147	180	196	191	201	241	191	142	178	170	178	2,212
Los Evangelistas	52	23S	75	07W	58	27	297	254	287	290	244	239	239	218	234	224	251	257	3,033
Poirretillos	26	30S	69	27W	2,850	7	0	0	8	0	18	0	13	8	5	5	0	0	56

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							mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Puerto Aisen	42	24S	72	42W	10	11	198	198	211	191	373	264	282	282	165	198	178	201	2,741
Punta Arenas	53	10S	70	54W	8	15	38	23	33	36	33	41	28	30	23	28	18	36	366
Santiago	33	27S	70	42W	520	58	3	3	5	13	64	84	76	56	30	15	8	5	361
Valdivia	39	48S	73	14W	5	60	66	74	132	234	361	450	394	328	208	127	124	104	2,601
Valparaiso	33	01S	71	38W	41	41	3	0	8	15	104	150	99	74	33	10	5	5	505
Colombia:																			
Andagoya	5	06N	76	40W	60	15	635	544	495	663	648	655	592	643	625	577	569	495	7,140
Bogota	4	42N	74	08W	2,547	49	58	66	102	147	114	61	51	56	61	160	119	66	1,062
Cartagena	10	28N	75	30W	12	10	10	0	10	23	86	86	76	15	13	274	226	114	935
IpiALES	0	50N	77	42W	2,950	13	79	58	89	89	71	48	33	28	36	79	84	66	759
Tumaco	1	49N	78	45W	2	10	429	297	244	371	442	305	196	185	185	150	124	178	3,106
Ecuador:																			
Cuenca	2	53S	78	39W	2,530	10	51	46	81	109	109	43	23	28	41	79	46	64	719
Guayaquil	2	10S	79	53W	6	10	211	290	292	206	53	10	5	0	0	0	3	28	1,097
Quito	0	08S	78	29W	2,811	33	99	112	142	175	137	43	20	30	69	112	97	79	1,115
French Guiana:																			
Cayenne	4	56N	52	27W	6	51	366	312	401	480	551	394	175	71	30	33	117	272	3,203
Guyana:																			
Georgetown	6	50N	58	12W	2	35	203	114	175	140	290	302	254	175	81	76	155	287	2,253
Leithern	3	24N	59	38W	82	9	30	36	33	145	292	302	376	239	86	58	109	33	1,740
Paraguay:																			
Asuncion	25	17S	57	30W	139	30	140	130	109	132	117	69	56	38	79	140	150	157	1,316
Bahia Negra	20	14S	58	10W	97	20	137	135	124	74	58	41	38	15	58	107	135	107	1,021
Peru:																			
Arequipa	16	21S	71	34W	2,579	37	33	46	18	5	0	0	0	0	0	0	0	10	112
Cajamarca	7	09S	78	30W	2,640	9	91	107	117	86	43	241	234	236	58	58	48	81	716
Cusco	13	33S	71	59W	3,312	12	163	150	109	51	15	5	5	10	25	66	76	137	813
Iquitos	3	45S	73	13W	117	5	231	264	239	345	272	145	163	132	267	185	231	262	2,736
Lima	12	05S	77	03W	120	15	3	0	0	0	5	5	8	8	8	3	3	0	41
Mollendo	17	00S	72	07W	24	10	0	3	0	0	3	3	0	5	5	3	3	0	23
Suriname:																			
Paramaribo	5	49N	55	09W	4	75	213	165	201	229	310	302	231	157	79	76	124	224	2,311

Country and Station	Latitude		Longitude		Elevation Meters	Length of Record Years	Precipitation													
	°	'	°	'			Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year	
							mm													
Uruguay:																				
Artigas	30	24S	56	23W	117	50	109	99	119	130	104	104	104	71	76	102	119	97	104	1,234
Montevideo	34	52S	56	12W	22	56	74	66	99	99	84	81	74	79	76	66	66	74	79	950
Venezuela:																				
Caracas	10	30N	66	56W	1,042	46	23	10	15	33	79	102	109	109	107	109	109	94	46	836
Ciudad Bolívar	8	07N	63	32W	60	10	36	20	18	25	97	140	160	180	91	102	102	71	33	973
Maracaibo	10	39N	71	36W	6	36	3	0	8	20	69	56	46	56	71	150	84	15	577	
Merida	8	36N	71	10W	1,613	14	64	38	91	170	249	185	119	145	170	241	208	86	1,770	
Santa Elena	4	36N	61	07W	907	10	81	81	81	145	244	241	231	193	135	124	124	114	1,796	
Pacific Islands																				
Easter Is. (Isla de Pascua)	27	10S	109	26W	30	10	122	94	117	107	117	109	89	76	69	94	117	124	1,234	
Mas a Tierra (Juan Fernandez)	33	37S	78	52W	6	29	20	30	41	86	150	163	147	112	74	48	41	25	914	
Seymour Is. (Galapagos Is.)	00	28S	90	18W	11	3	20	36	28	18	0	0	0	0	0	0	0	0	102	
Atlantic Islands																				
Fernando de Noronha	3	50S	32	25W	45	32	43	119	188	267	267	185	137	48	18	8	10	13	1,303	
Cumberland Bay, South Georgia	54	16S	36	30W	2	24	84	109	135	137	132	124	140	135	89	66	86	76	1,313	
Laurie Is., South Orkneys	60	44S	44	44W	4	46	36	38	48	41	30	25	33	33	28	28	33	25	399	
Stanley, Falkland Isles	51	42S	57	51W	2	41	71	58	64	66	66	53	51	51	38	41	51	71	681	
Europe																				
Albania:																				
Durrës	41	19N	19	28E	7	10	76	84	99	56	41	48	13	48	43	180	216	185	1,090	
Andorra:																				
Les Escaldes	42	30N	1	31E	1,080	9	38	43	74	61	119	79	56	86	79	89	84	64	871	
Austria:																				
Innsbruck	47	16N	11	24E	582	35	53	46	38	56	74	104	130	114	79	61	56	48	859	
Vienna (Wien)	48	15N	16	22E	202	100	38	36	46	51	71	69	76	69	51	51	48	46	650	
Bulgaria:																				
Sofiya (Sofia)	42	42N	23	20E	550	27	33	28	43	58	84	81	61	51	58	53	48	36	635	

Country and Station	Latitude		Longitude		Elevation Meters	Length of Record Years	Precipitation											
	°	'	°	'			Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Varna	43	12N	27	55E	35	20	38	23	30	30	46	66	48	30	38	48	51	498
Cyprus:																		
Nicosia	35	09N	33	17E	218	64	74	51	33	20	28	10	0	0	5	23	43	371
Czechoslovakia:																		
Praha (Prague)	50	05N	14	25E	202	70	23	20	28	38	61	71	66	56	43	30	30	490
Prerov	49	27N	17	27E	214	21	33	28	28	51	61	74	89	81	51	61	38	630
Denmark:																		
Copenhagen (Kobenhavn)	55	41N	12	33E	13	30	41	33	30	43	43	53	56	81	48	53	56	592
Aarhus	56	08N	10	12E	49	21	58	38	36	46	30	56	64	84	81	66	64	676
Finland:																		
Helsinki	60	10N	24	57E	9	50	56	43	43	43	48	51	58	84	71	74	69	701
Kuusamo	65	57N	29	12E	257	20	28	28	28	28	36	58	71	76	53	53	41	528
Vaasa	63	05N	21	36E	4	19	28	20	20	25	36	46	61	64	69	58	43	498
France:																		
Ajaccio (Corsica)	41	52N	8	35E	74	86	76	58	66	56	41	23	71	18	43	97	112	739
Bordeaux	44	50N	0	43W	48	47	69	71	74	66	64	58	51	48	56	76	99	831
Brest	48	19N	4	47W	17	56	89	76	64	64	48	51	51	56	58	91	107	866
Cherbourg	49	39N	1	38W	9	47	84	74	69	51	48	46	48	76	74	117	130	947
Lille	50	35N	3	05W	43	40	64	48	64	51	61	56	71	58	66	76	76	770
Lyon	45	42N	4	47E	286	70	36	36	46	53	71	74	71	74	79	79	66	732
Marseille	43	18N	5	23E	75	102	48	38	46	51	48	25	15	23	66	94	79	589
Paris	48	49N	2	29E	50	118	38	33	38	43	51	53	53	51	51	56	51	566
Strasbourg	48	35N	7	46E	142	20	41	36	43	66	66	79	86	86	79	69	51	749
Toulouse	43	33N	1	23E	164	47	48	43	58	69	74	61	38	53	58	56	61	678
Germany:																		
Berlin	52	27N	13	18E	57	40	48	33	38	43	48	58	79	56	48	43	43	587
Bremen	53	05N	8	47E	16	80	48	41	46	38	53	66	81	71	53	56	51	660
Frankfurt A/M	50	07N	8	40E	103	80	43	33	41	38	51	64	71	66	48	56	51	612
Hamburg	53	33N	9	58E	20	80	53	48	51	46	53	69	86	81	64	66	53	734
Munich (Munich)	48	09N	11	34E	530	80	43	36	48	69	94	117	119	107	81	56	48	866
Munster	51	58N	7	38E	63	40	66	48	56	51	56	69	84	79	64	69	61	775

Country and Station	Latitude	Longitude		Elevation Meters	Length of Record Years	Precipitation													
		°	'			Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year	
						mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Nurnberg	49° 27'N	11	03E	320	80	38	30	33	43	56	64	79	79	53	53	48	43	620	
Gibraltar:																			
Windmill Hill	36° 06'N	5	21'W	122	12	117	86	94	64	36	5	0	3	20	89	104	137	754	
Greece:																			
Athina (Athens)	37° 58'N	23	43E	107	80	56	41	36	20	20	15	5	10	15	43	71	71	401	
Iraklion (Crete)	35° 20'N	25	08E	30	22	94	76	41	23	18	3	0	3	18	43	69	102	488	
Rodhos (Rhodes)	36° 26'N	28	15E	88	6	145	99	66	43	13	8	0	0	10	43	132	170	724	
Thessaloniki (Salonika)	40° 37'N	22	57E	24	26	38	38	41	48	51	30	25	18	30	61	53	48	483	
Hungary:																			
Budapest	47° 31'N	19	02E	120	50	38	38	43	51	69	66	51	48	46	53	61	51	615	
Debrecen	47° 36'N	21	39E	131	80	30	28	36	46	61	71	64	58	46	56	51	41	587	
Iceland:																			
Akureyri	65° 41'N	18	05W	5	26	43	38	43	33	15	23	33	41	48	58	48	48	472	
Reykjavik	64° 09'N	21	56W	28	30	102	79	76	53	41	43	51	66	79	86	91	94	861	
Ireland:																			
Cork	51° 54'N	8	29W	17	35	124	91	84	66	74	51	74	79	74	99	114	119	1,049	
Dublin	53° 22'N	6	21W	47	35	69	56	51	48	58	51	71	76	71	69	69	66	754	
Shannon Airport	52° 41'N	8	55W	2	12	97	76	51	56	61	53	79	76	76	86	107	109	927	
Italy:																			
Ancona	43° 37'N	13	32E	16	30	66	43	41	58	53	48	38	38	89	94	64	76	711	
Cagliari (Sardinia)	39° 15'N	9	03E	1	25	56	38	38	30	38	13	3	10	25	76	46	58	432	
Genova (Genoa)	44° 24'N	8	55E	97	10	99	102	84	86	117	36	41	58	119	155	183	104	1,184	
Napoli (Naples)	40° 51'N	14	15E	25	30	94	81	76	66	46	46	15	18	71	130	114	137	894	
Palermo (Sicily)	38° 07'N	13	19E	108	30	97	86	61	48	28	15	5	15	51	94	104	114	719	
Rome	41° 48'N	12	36E	115	30	84	74	51	51	48	18	10	18	71	109	112	104	749	
Taranto	40° 28'N	17	17E	17	10	41	23	33	20	25	15	10	18	25	56	46	48	361	
Venezia (Venice)	45° 26'N	12	23E	25	30	51	53	61	71	81	84	66	66	66	94	89	66	848	
Luxembourg:																			
Luxembourg	49° 37'N	6	03E	334	100	58	51	48	53	61	64	71	66	61	69	69	71	742	
Malta:																			
Valetta	35° 54'N	14	31E	71	90	84	58	38	20	10	3	0	5	33	69	91	99	516	
Monaco:																			
Monaco	43° 44'N	7	25E	55	60	61	58	79	56	53	36	18	28	58	119	109	89	765	

Country and Station	Latitude		Longitude		Elevation	Length of Record	Precipitation													
							Years	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
							Meters	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Netherlands:																				
Amsterdam	52	23N	4	55E	2	29	51	36	33	41	46	46	66	69	71	71	66	56	650	
Norway:																				
Bergen	60	24N	5	19E	43	75	201	152	137	112	99	107	132	185	234	234	203	206	2,002	
Kristiansand	58	10N	7	59E	53	56	127	91	91	69	64	71	89	135	119	157	145	163	1,321	
Oslo	59	56N	10	44E	94	56	43	33	36	41	46	61	74	97	64	74	58	58	683	
Tromso	69	39N	18	57E	102	75	104	97	84	61	53	53	58	74	119	114	102	99	1,019	
Trondheim	63	25N	10	27E	127	65	79	69	66	51	43	48	61	76	86	94	71	71	815	
Vardo	70	22N	31	06E	13	56	64	64	58	38	33	33	38	43	48	64	53	36	597	
Poland:																				
Gdansk (Danzig)	54	24N	18	40E	11	35	30	25	33	38	46	58	71	66	53	46	46	38	551	
Krakow	50	04N	19	57E	220	35	28	33	36	46	71	102	114	97	69	56	43	33	726	
Warsaw	52	13N	21	02E	90	113	30	28	33	38	48	66	76	76	48	43	36	36	559	
Wroclaw (Breslau)	51	07N	17	05E	147	40	38	28	38	43	61	61	86	69	46	43	38	38	589	
Portugal:																				
Braganca	41	49N	6	47W	730	11	302	175	196	94	76	41	13	15	38	76	160	180	1,367	
Lagos	37	06N	8	38W	14	17	81	66	71	36	20	5	0	0	10	38	66	71	465	
Lisbon	38	43N	9	08W	95	75	84	81	79	61	43	18	5	5	36	79	107	91	686	
Romania:																				
Bucuresti (Bucharest)	44	25N	26	06E	82	41	38	28	43	41	64	97	58	46	38	41	48	38	579	
Cluj	46	47N	23	40E	392	16	33	30	25	53	84	84	66	84	51	43	25	30	610	
Constanta	44	11N	28	39E	4	39	30	30	28	28	33	43	33	28	28	36	30	36	384	
Spain:																				
Almeria	36	51N	2	28W	65	20	23	25	18	23	18	5	0	3	15	23	38	28	218	
Barcelona	41	24N	2	09E	95	30	30	53	48	46	46	33	30	43	66	86	69	46	597	
Burgos	42	20N	3	42W	861	29	38	38	53	48	61	43	20	18	36	51	56	51	513	
Madrid	40	25N	3	41W	667	30	28	43	43	43	38	30	10	8	30	48	56	41	419	
Sevilla	37	29N	5	59W	30	26	56	74	84	58	33	23	3	3	28	66	94	71	592	
Valencia	39	28N	0	23W	24	29	23	38	23	30	28	33	10	13	56	41	64	33	391	
Sweden:																				
Abisko	68	21N	18	49E	388	11	18	15	13	13	18	46	41	46	30	25	15	15	297	
Goteberg	57	42N	11	58E	17	61	64	51	51	43	48	56	71	94	79	79	69	71	775	

Country and Station	Latitude		Longitude		Elevation Meters	Length of Record Years	Precipitation												
	°	'	°	'			Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
							mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Haparanda	65	50N	24	09E	9	20	56	41	30	38	36	43	71	66	71	64	51	620	
Karlstad	59	23N	13	30E	50	30	48	30	30	36	48	48	66	79	74	61	48	630	
Sarna	61	41N	13	07E	458	20	41	20	23	30	41	71	91	84	66	58	46	617	
Stockholm	59	21N	18	04E	45	30	38	28	28	38	41	48	71	79	53	48	48	569	
Vfsby (Gotland)	57	39N	18	18E	11	30	43	28	30	36	28	36	51	69	43	48	53	516	
Switzerland:																			
Berne	46	57N	7	26E	572	7	48	51	66	76	94	112	112	109	89	89	69	64	978
Geneve (Geneva)	46	12N	6	09E	405	125	48	46	56	64	76	79	74	91	91	97	79	61	861
Zurich	47	23N	8	33E	493	23	58	48	74	86	102	124	127	117	84	81	64	74	1,039
Turkey:																			
Edirne (Adrianople)	41	39N	26	34E	47	18	56	48	43	48	43	53	38	28	28	53	74	76	589
Istanbul (Constantinople)	40	58N	28	50E	18	18	94	58	66	48	36	33	43	38	58	97	104	124	800
United Kingdom:																			
Belfast	54	35N	5	56W	17	30	107	71	58	61	58	64	89	89	86	97	91	99	970
Birmingham	52	29N	1	56W	163	30	74	53	43	56	64	46	71	69	58	74	81	66	754
Cardiff	51	28N	3	10W	62	30	117	76	58	64	76	56	86	99	91	114	117	109	1,064
Dublin	53	22N	6	21W	47	35	69	56	51	48	58	51	71	76	71	69	69	66	754
Edinburgh	55	55N	3	11W	134	30	64	41	41	41	56	48	79	79	66	74	61	53	701
London	51	29N	0	0	45	30	51	38	36	46	46	41	51	56	46	58	64	51	582
Liverpool	53	24N	3	04W	60	30	69	48	38	41	56	51	71	79	66	76	76	64	734
Perth	56	24N	3	27W	23	30	79	56	48	43	58	51	79	74	71	84	69	69	780
Plymouth	50	21N	4	07W	27	30	109	76	66	58	64	51	66	74	71	97	117	112	960
Wick	58	26N	3	05W	36	30	74	53	46	53	46	51	66	66	74	81	79	74	762
U.S.S.R.:																			
Arkhangelsk	64	33N	40	32E	7	25	30	28	28	18	33	48	66	69	56	48	41	33	503
Astrakhan	46	21N	48	02E	14	25	13	13	10	15	15	18	13	10	15	10	15	15	163
Dnepropetrovsk	48	27N	35	04E	79	17	36	28	30	36	46	76	48	41	25	46	41	41	493
Kaunas	54	54N	23	53E	36	19	41	33	33	46	51	81	84	64	48	48	41	41	635
Kirov	58	36N	49	41E	181	29	30	25	23	23	48	64	53	74	58	51	41	33	523
Kursk	51	45N	36	12E	236	20	38	33	30	38	56	64	81	58	41	46	38	43	566
Leningrad	59	56N	30	16E	5	95	25	23	23	25	41	51	64	71	53	46	36	30	488
Lvov	49	50N	24	01E	298	35	33	38	46	51	71	94	104	79	61	53	20	41	716

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	°	'	°	'			Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
							mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Minsk	53	54N	27	33E	225	20	36	38	33	38	51	71	76	79	41	38	38	43	582
Moskva (Moscow)	55	46N	37	40E	154	11	38	36	28	48	56	74	76	74	48	69	43	41	630
Odessa	46	29N	30	44E	65	15	25	18	18	28	28	48	41	36	28	36	28	28	363
Riga	56	57N	24	06E	20	57	33	25	28	30	43	61	76	76	53	51	48	38	564
Saratov	51	32N	46	03E	60	15	25	25	20	25	33	46	30	33	28	36	36	30	368
Sevastopol	44	37N	33	31E	23	30	28	28	28	23	15	28	20	15	28	38	30	28	310
Stalingrad	48	42N	44	31E	41	12	23	25	15	15	25	48	23	20	18	25	38	33	310
Stavropol	45	02N	41	58E	575	41	36	28	38	61	76	104	76	51	64	58	46	46	683
Tallin	59	26N	24	48E	45	63	28	25	23	28	43	48	53	69	58	53	48	38	513
Tbilisi	41	43N	44	48E	404	10	18	20	33	41	91	79	56	43	48	33	51	30	544
Ust'Shchugor	64	16N	57	34E	85	15	28	20	20	18	36	56	76	81	61	56	38	33	523
Uly	54	43N	55	56E	174	23	41	33	30	23	41	61	66	56	46	58	56	58	572
Yugoslavia:																			
Beograd (Belgrade)	44	48N	20	28E	138	16	41	33	41	56	66	71	48	64	43	69	46	48	625
Skioje	41	59N	21	28E	240	10	38	30	33	38	48	48	33	28	28	66	58	46	495
Split	43	31N	16	26E	128	51	79	64	81	76	64	53	30	41	74	112	107	112	892
Ocean Islands																			
Bjornoya, Bear Island	74	31N	19	01E	15	25	41	33	33	23	20	18	20	30	46	43	36	41	384
Gronfjorden, Spitzbergen	78	02N	14	15E	7	15	36	33	28	23	13	10	15	23	25	30	23	38	297
Horta, Azores	38	32N	28	38W	61	30	114	104	107	76	74	51	38	48	81	112	104	114	1,024
Jan Mayen	71	01N	8	28W	40	29	53	43	41	36	23	23	36	46	64	64	56	56	538
Lerwick																			
Shetland Island	60	08N	1	11W	82	30	114	86	74	69	56	56	69	74	94	109	114	114	1,029
Matochkin Shar, Novaya Zemlya	73	16N	56	24E	19	9	15	15	15	10	8	10	36	38	38	15	15	10	226
Ponta Delgada, Azores	37	45N	25	40W	36	30	102	89	89	64	58	36	25	30	74	91	94	76	828
Stornoway, Hebrides	58	11N	6	21W	10	15	163	81	81	79	64	61	76	109	119	157	117	140	1,247
Thorshavn, Faeroes	62	02N	6	45W	25	50	168	132	122	91	86	64	79	89	119	150	160	168	1,427
Africa																			
Algeria:																			
Adrar	27	52N	0	17W	286	15	0	0	3	0	0	0	0	0	0	5	5	0	15
Alger (Algiers)	36	46N	3	03E	59	25	112	84	74	41	46	15	0	5	41	79	130	137	762



Country and Station	Latitude		Longitude		Elevation Meters	Length of Record Years	Precipitation												
	°	'	°	'			Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
							mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Bone	36	54N	7	46E	20	26	142	104	74	56	38	15	3	8	30	76	109	132	787
El Golea	30	35N	2	53E	380	15	3	8	13	0	0	0	0	0	0	8	10	8	48
Fort Flatters	28	06N	6	42E	373	15	8	3	3	5	0	0	0	0	0	0	5	5	28
Tamanrasset	22	42N	5	31E	1,400	15	5	0	0	5	10	3	3	10	3	0	0	0	38
Touggourt	33	07N	6	04E	69	26	5	10	13	5	5	5	0	0	3	8	13	8	74
Angola:																			
Cangamba	13	41S	19	52E	1,320	7	226	188	173	46	3	0	0	5	5	41	130	216	1,031
Luanda	8	49S	13	13E	59	59	25	36	76	117	13	0	0	0	3	5	28	20	323
Mocamedes	15	12S	12	09E	3	21	8	10	18	13	0	0	0	0	0	0	3	3	53
Nova Lisboa	12	48S	15	45E	1,700	14	221	198	249	145	10	0	0	0	15	140	244	226	1,448
Benim:																			
Colonou	6	21N	2	26E	7	10	33	33	117	124	254	366	89	38	66	135	58	13	1,331
Botswana:																			
Francistown	21	13S	27	30E	1,004	28	107	79	71	18	5	3	0	0	0	23	58	86	450
Maun	19	59S	23	25E	942	20	109	97	89	28	5	0	0	0	0	13	48	71	462
Tsabong	26	03S	22	27E	962	14	51	48	48	33	10	10	3	0	5	18	28	38	292
Cameroon:																			
Ngaoundere	7	17N	13	19E	1,098	10	0	0	28	140	178	213	269	244	234	135	13	0	1,453
Yaounde	3	53N	11	32E	770	11	23	66	147	170	196	152	74	79	213	295	117	23	1,554
Central African Republic:																			
Bangui	4	22N	18	34E	387	5	25	43	127	135	188	114	226	206	150	201	124	5	1,544
Ndele	8	24N	20	39E	591	3	5	33	15	43	213	155	211	257	272	198	15	0	1,417
Chad:																			
Am Timan	11	02N	20	17E	436	3	0	0	3	30	109	127	185	312	147	30	0	0	945
Fort Lamy	12	07N	15	02E	295	5	0	0	0	3	30	66	170	320	119	36	0	0	744
Largeau (Faya)	18	00N	19	10E	255	5	0	0	0	0	0	0	0	18	0	0	0	0	18
Congo, Republic of:																			
Brazzaville	4	15S	15	15E	318	18	160	124	188	178	109	15	0	0	56	137	292	213	1,473
Quesso	1	37N	16	04E	345	4	61	91	163	81	147	117	74	94	201	254	145	61	1,488
Pointe Noire (Loango)	4	39S	11	48E	50	7	137	170	163	203	99	0	0	0	10	104	168	168	1,222
Egypt:																			
Alexandria	31	12N	29	53E	32	61	48	23	10	3	0	0	0	0	0	5	33	56	178
Aswan	24	02N	32	53E	112	11	0	0	0	0	0	0	0	0	0	0	0	0	0*

Country and Station	Latitude		Longitude		Elevation	Length of Record	Precipitation														
							Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year		
							mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Cairo	29° 52'N	31° 20'E	116	42	5	5	5	3	3	0	0	0	0	0	0	0	0	3	5	28	
Ethiopia:																					
Addis Ababa	9° 20'N	38° 45'E	2,450	37	13	38	66	86	86	137	279	300	191	20	15	5	1,237				
Asmara	15° 17'N	38° 55'E	2,325	17	0	0	10	38	38	33	170	127	33	8	10	0	467				
Diredawa	9° 02'N	41° 45'E	1,200	8	20	20	84	76	71	38	109	97	56	13	8	20	612				
Gambela	8° 15'N	34° 35'E	410	30	5	10	36	81	150	170	216	241	185	89	46	10	1,240				
French Territory of Afars and Issas (F.T.A.E.):																					
Djibouti	11° 36'N	43° 09'E	7	46	10	13	25	13	5	0	3	8	8	10	23	13	130				
Gabon:																					
Libreville	0° 23'N	9° 26'E	35	21	249	236	335	340	244	13	3	18	104	345	373	249	2,510				
Mayoumba	3° 25'S	10° 38'E	61	8	165	236	157	259	58	3	0	5	66	236	272	117	1,575				
Gambia:																					
Bathurst	13° 21'N	16° 40'W	27	9	3	3	0	0	10	58	282	500	310	109	18	3	1,295				
Ghana:																					
Accra	5° 33'N	0° 12'W	27	65	15	33	56	81	142	178	46	15	36	64	36	23	724				
Kumasi	6° 40'N	1° 37'W	287	10	20	58	145	130	191	201	109	79	173	180	94	20	1,402				
Guinea:																					
Conakry	9° 31'N	13° 43'W	7	10	3	3	10	23	157	559	1,298	1,054	683	371	122	10	4,293				
Kouroussa	10° 39'N	9° 53'W	371	10	10	8	23	71	135	246	297	345	340	168	33	10	1,687				
Ifni (now in Morocco):																					
Sidi Ifni	29° 27'N	10° 11'W	45	14	25	15	13	15	3	3	0	0	10	3	23	46	155				
Ivory Coast:																					
Abidjan	5° 19'N	4° 01'W	20	10	41	53	99	124	361	495	213	53	71	168	201	79	1,958				
Bouake	7° 42'N	5° 00'W	364	10	10	38	104	147	135	152	79	117	208	132	38	25	1,186				
Kenya:																					
Mombasa	4° 03'S	39° 39'E	16	54	25	18	64	196	320	119	89	64	64	86	97	61	1,201				
Nairobi	1° 16'S	36° 48'E	1,820	17	38	64	124	211	157	46	15	23	30	53	109	86	958				
Liberia:																					
Monrovia	6° 18'N	10° 48'W	23	4	5	3	112	297	340	917	615	472	759	640	208	74	4,442				
Libya:																					
Banghazi (Benghazi)	32° 06'N	20° 04'E	25	46	66	41	20	5	3	0	0	0	3	18	46	66	267				
Cufra	24° 12'N	23° 21'E	389	7	0	0	0	0	0	0	0	0	0	0	0	0	*0				

Country and Station	Latitude		Longitude		Elevation	Length of Record	Precipitation														
							Years	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year	
	°	'	°	'	Meters		mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm		
Sabah	27	01N	14	26E	444	10	0	0	0	0	3	3	0	0	0	0	0	0	0	8	
Tarabulus (Triopoli)	32	54N	13	11E	22	56	81	46	28	10	5	3	0	0	0	10	41	66	94	384	
Madagascar:																					
Diego Suarez	12	17S	49	17E	30	31	269	241	193	56	8	5	5	8	8	8	18	28	147	983	
Tananarive	18	55S	47	33E	1,372	62	300	279	178	53	18	8	8	10	18	61	135	287	1,356		
Tulear	23	20S	43	41E	6	15	79	81	36	8	18	10	3	5	8	18	36	43	343		
Malawi:																					
Karonga	9	57S	33	56E	486	8	180	178	274	157	43	3	0	0	0	0	8	8	119	973	
Zomba	15	23S	35	19E	957	29	307	251	257	69	18	10	8	8	5	25	109	277	1,344		
Mali:																					
Araouane	18	54N	3	33W	285	10	0	0	0	0	0	5	5	13	15	3	3	0	43		
Bamako	12	39N	7	58W	340	10	0	0	3	15	74	137	279	348	206	43	15	0	1,120		
Gao	16	16N	0	03W	275	19	0	0	0	3	10	25	74	137	38	5	0	0	292		
Mauritania:																					
Atar	20	31N	13	04W	232	10	0	0	0	0	0	3	8	30	28	3	0	0	71		
Nema	16	36N	7	16W	269	10	3	0	0	0	18	28	58	119	53	18	0	3	295		
Nouakchott	18	07N	15	36W	21	10	0	3	0	0	0	3	13	104	229	10	3	0	157		
Morocco:																					
Casablanca	33	35N	7	39W	50	40	53	48	56	36	23	5	0	0	8	38	66	71	404		
Marrakech	31	36N	8	07W	460	31	25	28	33	30	15	8	3	3	10	23	30	30	239		
Rabat	34	00N	6	50W	65	29	66	64	66	43	28	8	0	0	10	48	84	86	503		
Tangier	35	48N	5	49W	73	35	114	107	122	89	43	15	0	0	23	99	147	137	897		
Mozambique:																					
Beira	19	50S	34	51E	9	39	277	213	257	107	56	33	30	28	20	132	135	234	1,521		
Chicoa	15	36S	32	21E	274	8	198	145	112	15	0	0	0	0	0	28	66	132	696		
Lourenco Marques	25	58S	32	36E	59	42	130	124	124	53	28	20	13	13	28	48	81	97	759		
Niger:																					
Agades	16	59N	7	59E	520	10	0	0	0	0	5	8	48	94	18	0	0	0	173		
Blima	18	41N	12	55E	357	10	0	0	0	0	0	0	3	13	8	0	0	0	23		
Niamey	13	31N	2	06E	216	10	0	0	5	8	33	81	132	188	94	13	0	0	549		
Nigeria:																					
Enugu	6	27N	7	29E	233	33	18	28	66	150	264	290	193	170	325	249	53	13	1,816		
Kaduna	10	35N	6	26E	644	34	0	3	13	64	150	180	216	302	269	74	3	0	1,273		

Country and Station	Latitude		Longitude		Elevation Meters	Length of Record Years	Precipitation															
							Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year			
	°	'	°	'			mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Lagos	6	27N	3	24E	3	47	28	46	102	150	269	460	279	64	140	213	69	25	1,836			
Maiduguri	11	51N	13	05E	354	40	0	0	0	8	41	69	180	221	107	18	0	0	643			
Portuguese Guinea:																						
Bolama	11	34N	15	26W	19	37	0	0	0	0	20	198	587	701	429	203	41	3	2,182			
Senegal:																						
Dakar	14	42N	17	29W	40	26	0	0	0	0	0	18	89	254	132	38	3	8	541			
Kaolack	14	08N	16	04W	6	10	0	0	0	0	8	66	175	272	178	69	3	0	770			
Sierra Leone:																						
Freetown/Lungi	8	37N	13	12W	28	8	10	5	30	79	241	363	742	927	566	361	140	30	3,495			
Somalia:																						
Berbera	10	26N	45	02E	14	30	8	3	5	13	8	0	0	3	0	3	5	5	51			
Mogadishu (Mogadiscio)	2	02N	45	21E	12	21	0	0	0	58	58	97	64	48	25	23	41	13	429			
South Africa, Republic of:																						
Capetown	33	54S	18	32E	17	18	15	8	18	48	79	84	89	66	43	30	18	10	508			
Durban	29	50S	31	02E	5	78	109	122	130	76	51	33	28	38	71	109	122	119	1,008			
Kimberley	28	48S	24	46E	1,197	57	61	64	79	38	18	5	5	8	15	25	41	51	409			
Port Elizabeth	33	59S	25	36E	58	84	30	33	48	46	61	46	48	51	58	56	56	43	577			
Port Nolloth	29	14S	16	52E	7	64	3	3	5	5	8	8	8	8	5	3	3	3	58			
Pretoria	25	45S	28	14E	1,369	12	127	109	114	43	23	15	8	5	20	56	132	132	785			
Walvis Bay	22	56S	14	30E	7	20	0	5	8	3	3	0	0	3	0	0	0	0	251			
Southwest Africa:																						
Keetmanshoop	26	35S	18	08E	1,004	45	20	28	36	15	5	0	0	0	3	5	8	10	132			
Windhoek	22	34S	17	06E	1,728	60	76	74	79	41	8	0	0	0	3	10	23	48	363			
Sudan:																						
El Fasher	13	38N	25	21E	730	17	0	0	0	0	8	18	114	135	30	5	0	0	310			
Khartoum	15	37N	32	33E	390	46	0	0	0	0	3	8	53	71	18	5	0	0	157			
Port Sudan	19	37N	37	13E	5	40	5	3	0	0	0	0	8	3	0	10	43	23	94			
Wadi Halfa	21	55N	31	20E	125	39	0	0	0	0	0	0	0	0	0	0	0	0	0			
Wau	7	42N	28	03E	440	38	0	5	23	66	135	165	191	208	168	124	15	0	1,100			
Tanzania, United Republic of:																						
Dar es Salaam	6	50S	39	18E	14	49	66	66	130	290	188	33	30	25	30	41	74	91	1,064			

Country and Station	Latitude		Longitude		Elevation	Length of Record	Precipitation												
	°	'	°	'			Years	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
					Meters		mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Iringa	7	47S	35	42E	1,625	24	173	130	180	89	13	0	0	0	3	5	38	114	744
Kigoma	4	53S	29	38E	885	18	122	127	150	130	43	5	3	5	18	48	142	135	927
Togo:																			
Lome	6	10N	1	15E	22	15	15	23	48	117	145	224	71	10	36	61	28	10	787
Tunisia:																			
Gabes	33	53N	10	07E	2	50	23	18	20	10	8	0	0	3	13	30	30	15	170
Tunis	36	47N	10	12E	66	50	64	51	41	36	18	8	3	8	33	51	48	61	419
Uganda:																			
Kampala	0	20N	32	36E	1,312	15	46	61	130	175	147	74	33	86	91	97	122	99	1,173
Lira	2	15N	32	54E	1,085	14	18	25	89	175	201	124	163	254	211	155	81	46	1,542
Upper Volta:																			
Bobo Dioulasso	11	10N	4	15W	430	10	3	5	28	53	117	122	249	305	216	64	18	0	1,179
Ouagadougou	12	22N	1	31W	302	15	*0	3	13	15	84	122	203	277	145	33	0	0	894
Western Sahara:																			
Semara	26	46N	11	31W	460	6	3	0	0	0	0	0	0	0	25	0	10	0	38
Villa Cisneros	23	42N	15	52W	11	14	0	0	0	0	3	0	0	5	36	3	5	25	76
Zaire:																			
Kalemie	5	54S	29	12E	760	20	107	119	160	213	84	8	3	8	20	71	201	160	1,153
Kananga	5	54S	22	25E	670	14	137	142	196	193	84	20	13	58	117	165	231	226	1,582
Kinshasa	4	20S	15	18E	325	12	135	145	196	196	157	8	3	3	30	119	221	142	1,354
Kisangani	0	26N	25	14E	418	14	53	84	178	157	137	114	132	165	183	218	198	84	1,704
Zambia:																			
Balovale	13	34S	23	06E	1,090	9	216	175	147	30	0	0	0	0	8	58	112	226	973
Kasama	10	12S	31	11E	1,385	10	272	251	277	71	13	0	0	0	0	20	163	241	1,308
Lusaka	15	25S	28	19E	1,277	10	231	191	142	18	3	0	0	0	0	10	91	150	836
Zimbabwe:																			
Bulawayo	20	09S	28	37E	1,343	50	142	109	84	18	10	3	0	0	5	20	81	122	594
Salisbury	17	50S	31	08E	1,472	50	196	178	117	28	13	3	0	3	5	28	97	163	828
Atlantic Islands																			
Funchal, Madeira Island	32	38N	16	55W	25	30	64	74	79	33	18	5	0	0	25	76	89	84	546
Georgetown, Ascension Island	7	56S	14	25W	17	45	5	10	18	28	13	13	13	10	8	8	5	3	132

Country and Station	Latitude		Longitude		Elevation	Length of Record	Precipitation												
	°	'	°	'			Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
					Meters	Years	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Huils Gale, St. Helena	15	57S	5	40W	628	30	53	79	107	79	71	81	109	66	56	43	30	41	815
Las Palmas, Canary Islands	28	11N	15	28W	6	48	36	23	23	13	5	0	0	0	5	28	53	41	218
Porto de Praia, Cape Verde Is.,	14	54N	23	31W	34	25	3	0	0	0	0	0	5	97	114	30	8	3	259
Santa Isabel, Fernando Po	3	46N	8	46E	0	16	33	64	107	183	239	282	188	168	244	264	89	43	1,902
Sao Tome, Sao Tome	0	20N	6	43E	5	10	81	107	150	127	135	28	0	0	23	109	117	89	965
Tristan da Cunha	37	03S	12	19W	23	5	89	89	163	119	180	150	155	175	201	147	109	102	1,679
Indian Ocean Islands:																			
Agalega Island	10	26S	56	40E	3	2	150	257	124	175	335	226	221	81	46	107	178	254	2,151
Cocos (Keeling) Island	12	05S	96	53E	5	38	137	196	216	264	201	229	221	122	94	84	107	117	1,986
Heard Island	53	01S	73	23E	5	5	147	147	145	155	147	99	91	56	64	94	102	130	1,379
Heilburg, Reunion Island	21	04S	55	22E	936	11	569	203	417	183	135	112	79	76	51	58	89	328	2,299
Fort Victoria, Seychelles	4	37S	55	27E	5	64	386	267	234	183	170	102	84	69	130	155	231	340	2,350
Royal Alfred Observatory, Mauritius	20	06S	57	32E	55	43	216	198	221	127	97	66	58	64	36	41	46	117	1,285
Asia Far East																			
China:																			
Canton	23	10N	113	20E	18	36	23	48	107	173	269	269	206	216	165	86	30	23	1,615
Chanasha	28	15N	112	58E	49	26	48	94	135	145	208	221	112	109	69	76	69	38	1,323
Chungking	29	30N	106	33E	261	60	18	20	38	97	145	180	142	119	147	109	48	20	1,090
Hankow	30	35N	114	17E	23	55	46	48	91	147	178	229	178	104	76	79	48	30	1,255
Harbin (Ha-erh-pin)	45	45N	126	38E	145	38	5	5	10	23	43	94	168	119	58	30	13	5	574
Kashgar	39	24N	76	07E	1,309	18	15	3	13	5	8	5	10	8	3	3	5	8	81
Kunming	25	02N	102	43E	1,893	31	10	13	18	20	109	160	224	218	127	76	43	10	1,029
Lanchow	36	06N	103	55E	1,556	4	5	5	5	13	20	18	84	130	56	15	0	8	358
Mukden (Shen-yang)	41	47N	123	24E	42	42	5	5	18	30	66	97	178	160	74	43	23	10	716
Shanghai	31	12N	121	26E	5	81	48	61	84	91	97	178	147	140	132	74	53	38	1,143
Tientsin	39	10N	117	10E	4	25	5	3	10	13	28	61	193	152	43	15	10	5	533
Urumchi	43	45N	87	40E	906	6	15	8	13	38	28	38	18	25	15	43	41	10	292
Hong Kong:	22	18N	114	10E	33	50	33	46	74	137	292	394	381	361	257	114	43	30	2,162

Country and Station	Latitude		Longitude		Elevation Meters	Length of Record Years	Precipitation												
	°	'	°	'			Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
							mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Japan:																			
Kushiro	43	02N	144	12E	96	41	46	36	71	91	97	104	112	124	168	102	79	51	1,090
Miyako	39	38N	141	59E	30	30	74	76	81	89	114	127	127	183	241	173	76	66	1,427
Nagasaki	32	44N	129	53E	133	59	71	84	124	185	170	312	257	175	249	114	94	81	1,918
Osaka	34	47N	135	26E	15	60	43	58	97	132	124	188	150	112	178	130	76	48	1,336
Tokyo	35	41N	139	46E	6	60	48	74	107	135	147	165	142	152	234	208	97	56	1,565
Korea:																			
Pusan	35	10N	129	07E	2	36	43	36	69	140	132	201	295	130	173	74	41	30	1,361
P'yongyang	39	01N	125	49E	29	43	15	10	25	46	66	76	236	229	112	46	41	20	925
Seoul	37	31N	126	55E	10	22	30	20	38	76	81	130	376	267	119	41	46	25	1,250
Mongolia:																			
Ulan Bator	47	54N	106	56E	1,307	15	0	0	3	5	8	25	74	48	20	5	5	3	196
Taiwan:																			
Tainan	22	57N	120	12E	16	13	18	18	28	81	160	396	406	401	213	30	23	15	1,791
Taipei	25	04N	121	32E	6	12	97	135	109	135	175	224	224	221	208	140	107	74	1,847
Union of Soviet Socialist Republics:																			
Alma-Ata	43	16N	76	53E	775	27	33	23	56	102	94	66	36	30	25	51	48	33	597
Chita (Tchita)	52	02N	113	30E	676	24	3	3	3	10	28	46	84	84	30	13	5	5	312
Dubinka	69	07N	87	00E	43	5	8	10	5	8	15	48	38	53	46	23	10	8	272
Irkutsk	52	16N	104	19E	467	38	13	10	8	15	33	56	79	71	43	18	15	15	378
Kazalinsk	45	46N	62	06E	63	19	10	10	13	13	15	5	5	8	8	10	13	15	124
Khabarovsk	48	28N	135	03E	50	8	8	5	8	18	51	89	104	84	76	18	15	13	488
Kirensk	57	47N	108	07E	286	19	20	13	13	13	25	46	53	53	43	25	25	25	356
Krasnoyarsk	56	01N	92	52E	152	8	3	5	3	5	25	36	30	53	43	23	13	10	249
Markovo	64	45N	170	50E	26	16	5	5	8	3	8	20	25	48	28	10	10	8	178
Naryn	58	50N	81	39E	60	14	20	13	20	13	33	66	61	69	43	36	28	23	427
Okhotsk	59	21N	143	17E	5	25	3	3	5	10	23	41	56	66	61	25	5	3	300
Omsk	54	58N	73	20E	85	22	15	8	8	13	30	51	51	51	28	25	18	20	318
Petropavlovsk	52	53N	158	42E	87	35	76	56	86	64	56	51	79	81	97	99	91	76	912
Salekhard	66	31N	66	35E	18	27	8	8	8	8	18	33	48	51	38	18	13	10	259
Semipalatinsk	50	24N	80	13E	216	10	23	13	13	15	30	38	28	33	18	30	28	25	295
Sverdlovsk	56	49N	60	38E	272	29	13	10	13	18	48	69	66	69	41	30	28	20	424

Country and Station	Latitude		Longitude		Elevation	Length of Record	Precipitation												
							Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
	°	'	°	'	Meters	Years	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Tashkent	41	20N	69	18E	478	19	53	28	66	58	36	13	5	3	3	30	38	41	373
Verkhoyansk	67	34N	133	51E	100	44	5	5	3	5	8	23	28	25	13	8	8	5	135
Vladivostok	43	07N	131	55E	29	53	8	10	18	30	53	74	84	119	109	48	30	15	599
Yakutsk	62	01N	129	43E	163	22	8	5	3	8	10	28	41	33	28	13	10	8	188
Asia South East																			
Brunei:																			
Brunei	4	55N	114	55E	3	12	371	193	198	249	277	241	229	185	300	368	386	330	3,327
Burma:																			
Mandalay	21	59N	96	06E	77	20	3	3	5	30	147	160	69	104	137	109	51	10	828
Moulmein	16	26N	97	39E	46	60	5	5	13	76	505	942	1,207	1,123	688	216	43	8	4,831
Democratic Kampuchea:																			
Phnom Penh	11	33N	104	51E	12	49	8	10	36	79	145	147	152	155	226	251	140	43	1,392
Indonesia:																			
Batavia (Jakarta)	6	11S	106	50E	8	78	300	300	211	147	114	97	64	43	66	112	142	203	1,798
Manokwari	0	53S	134	03E	3	40	305	239	335	282	198	183	137	142	124	119	165	262	2,492
Mapangt	1	32N	124	55E	80	63	472	351	310	203	163	165	122	102	84	124	226	373	2,695
Pentui	10	10S	123	39E	102	63	386	348	234	66	30	10	5	0	0	18	84	231	1,415
Pontianak	0	00N	109	20E	4	63	274	208	241	277	282	221	165	203	229	366	389	323	3,178
Tabing	0	52S	100	21E	6	63	353	257	310	368	325	297	267	348	411	511	521	488	4,455
Tarakan	3	19N	117	33E	6	31	277	259	356	353	343	320	262	315	295	363	386	340	3,868
Lao, Peoples Democratic Republic:																			
Vientiane	17	58N	102	34E	170	27	5	15	38	99	267	302	267	292	302	109	15	3	1,715
Malaya, Fed.:																			
Kuala Lumpur	3	06N	101	42E	34	19	157	201	259	292	224	130	99	163	218	249	259	191	2,441
Singapore	1	18N	103	50E	10	64	251	173	193	188	173	173	170	196	178	208	254	257	2,413
North Borneo:																			
Sanda Kan	5	54N	118	03E	12	46	483	277	218	114	157	188	170	201	236	259	368	470	3,142
Philippine Islands:																			
Davao	7	07N	125	38E	27	34	122	114	132	147	234	231	165	165	170	201	135	155	1,971
Manila	14	31N	121	00E	15	75	23	13	18	33	130	254	432	422	356	193	145	66	2,083
Sarawak:																			
Kuching	1	29N	110	20E	26	19	610	511	328	279	262	180	196	234	218	267	358	462	3,904



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	°	'	°	'			Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
							mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Thailand:																			
Bangkok	13	44N	100	30E	16	10	5	28	28	58	132	152	175	234	356	251	46	3	1,468
Viet Nam																			
Hanoi	21	03N	105	52E	6	12	20	30	64	91	104	284	302	386	254	89	66	71	1,763
Saigon	10	49N	106	39E	10	33	15	3	13	43	221	330	315	269	335	269	114	56	1,984
Asia Middle East																			
Afghanistan:																			
Kabul	34	30N	69	13E	1,815	45	33	38	91	84	23	5	3	3	0	10	15	15	320
Kandhar	31	36N	65	40E	1,055	7	79	43	20	8	5	0	0	0	3	0	0	20	178
Bangladesh:																			
Dacca	23	46N	90	23E	7	61	8	30	61	137	244	315	330	338	249	135	25	5	1,877
India:																			
Ahmedabad	23	03N	72	37E	55	45	0	3	3	0	10	94	310	206	107	10	3	0	744
Bangalore	12	57N	77	40E	895	60	5	8	10	41	107	74	99	127	170	150	69	10	869
Bombay	19	06N	72	51E	8	60	3	3	3	0	18	485	617	340	264	64	13	3	1,808
Calcutta	22	32N	88	20E	6	60	10	30	36	43	140	297	325	328	251	114	20	5	1,600
Cherrapunji	25	15N	91	44E	1,313	35	18	53	185	665	1,280	2,692	2,446	1,781	1,100	493	69	13	10,798
Hyderabad	17	27N	78	28E	531	45	8	10	13	30	28	112	152	135	165	64	28	8	752
Jaipalguri	26	32N	88	43E	83	55	8	18	33	94	300	658	818	643	538	142	13	5	3,269
Lucknow	26	45N	80	52E	122	60	20	18	8	8	20	114	305	292	188	33	5	8	1,019
Madras	13	04N	80	15E	16	60	36	10	8	15	25	48	91	117	119	305	356	140	1,270
Mormugao	15	22N	73	49E	48	30	0	0	0	18	66	752	792	404	241	97	33	5	2,408
New Delhi	28	35N	77	12E	212	75	23	18	13	8	13	74	180	173	117	10	3	10	640
Silchar	24	49N	92	48E	29	53	20	53	201	363	396	551	500	500	366	165	38	10	3,162
Srinagar	33	58N	74	46E	1,664	50	74	71	91	94	61	36	58	61	38	30	10	33	658
Indian Ocean Islands:																			
Port Blair, Andaman Is.	11	40N	92	43E	80	60	46	28	28	61	384	551	391	414	442	318	267	201	3,129
Amni Divi, Laccadive Is.	11	07N	72	44E	4	30	18	0	0	38	94	363	305	196	160	147	66	33	1,422
Miticoy, Maldive Is.	8	18N	73	00E	3	50	46	18	23	58	178	295	226	198	160	185	140	86	1,613
Car Nicobar, Nicobar Is.	9	09N	92	49E	14	30	99	30	53	89	318	315	236	259	328	295	290	198	2,510

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	°	'	°	'			Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year		
							mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm		
Iran:																					
Abadan	30	21N	48	13E	3	10	38	43	15	20	3	0	0	0	0	0	0	3	25	46	193
Esfahan (Isfahan)	32	37N	51	41E	1,597	45	18	15	20	15	8	0	3	0	0	0	0	3	10	18	112
Kermanshah	34	19N	47	07E	1,320	15	66	58	71	56	41	0	0	0	0	0	0	10	51	61	417
Rezajeh	37	32N	45	05E	1,330	3	48	58	51	43	30	13	0	3	5	38	20	41	20	41	351
Tehran	35	41N	51	19E	1,200	33	46	38	46	36	13	3	3	3	3	8	20	30	20	30	246
Iraq:																					
Baghdad	33	20N	44	24E	34	15	23	25	28	13	3	0	0	0	0	0	0	3	20	25	140
Basra	30	34N	47	47E	2	10	36	28	30	30	5	0	0	0	0	0	0	0	36	20	185
Mosul	36	19N	43	09E	223	29	71	79	53	48	18	0	0	0	0	0	5	48	61	61	386
Israel:																					
Haifa	32	48N	35	02E	7	30	175	109	41	25	5	0	0	0	0	3	25	94	185	185	665
Jerusalem	31	47N	35	13E	809	50	130	119	74	23	3	0	0	0	0	0	8	56	89	89	500
Tel Aviv	32	06N	34	46E	10	10	124	69	51	18	3	0	0	0	0	3	10	104	155	155	536
Jordan:																					
Amman	31	58N	35	59E	776	25	69	74	30	15	5	0	0	0	0	0	5	33	46	46	277
Kuwait:																					
Kuwait	29	21N	48	00E	5	10	23	23	28	5	0	0	0	0	0	0	3	15	28	28	130
Lebanon:																					
Beirut	33	54N	35	28E	34	71	191	157	94	56	18	3	0	0	5	51	132	185	185	185	892
Nepal:																					
Katmandu	27	42N	85	22E	1,348	9	15	41	23	58	122	246	373	345	155	38	8	3	8	3	1,427
Oman and Muscat:																					
Muscat	23	37N	58	35E	5	38	28	18	10	10	0	3	0	0	0	3	10	18	18	18	99
Pakistan (West):																					
Karachi	24	48N	66	59E	4	59	13	10	8	3	3	18	81	41	13	3	3	3	3	5	198
Multan	30	11N	71	25E	122	60	10	10	10	8	8	15	51	46	13	3	3	3	3	5	180
Rawalpindi (Dharmial)	33	35N	73	03E	511	60	64	64	69	48	33	58	206	234	99	15	8	30	8	30	927
Saudi Arabia:																					
Dhahran	26	16N	50	10E	24	10	28	15	10	5	3	0	0	0	0	0	0	5	23	23	89
Jedda	21	28N	39	10E	6	5	5	0	0	0	0	0	0	0	0	0	0	25	30	30	64
Riyadh	24	39N	46	42E	591	3	3	20	23	25	10	0	0	0	0	0	0	0	0	0	81

Country and Station	Latitude		Longitude		Elevation Meters	Length of Record Years	Precipitation												
	°	'	°	'			Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
							mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Sri Lanka:																			
Colombo	6	54N	79	52E	7	40	89	69	147	231	371	224	135	109	160	348	315	147	2,344
Syria:																			
Deir Ez Zor	35	21N	40	09E	213	8	41	20	8	20	3	0	0	0	0	5	38	23	157
Dimashq (Damascus)	33	30N	36	20E	720	7	43	43	8	13	3	0	0	0	18	10	41	41	218
Halab (Aleppo)	36	14N	37	08E	390	10	89	64	38	28	8	3	0	0	0	25	56	84	394
Turkey:																			
Adana	36	59N	35	18E	25	31	109	102	64	41	51	18	5	5	18	48	61	97	617
Ankara	39	57N	32	53E	861	24	33	30	33	33	48	25	13	10	18	23	30	48	345
Erzurum	39	54N	41	16E	1,951	16	36	41	51	64	79	53	33	23	28	58	46	28	538
Izmir (Smyrna)	38	27N	27	15E	28	58	112	84	76	43	33	15	5	5	20	53	84	122	648
Samsun	41	17N	36	19E	40	27	74	66	69	58	46	38	38	33	61	81	89	61	739
United Arab Emirates																			
Sharjah	25	20N	55	24E	5	12	23	23	10	5	0	0	0	0	0	0	10	36	107
Yemen, Democratic:																			
Kamaran I.	15	20N	42	37E	6	21	5	5	3	3	3	0	13	18	3	3	10	23	86
Riyan	14	39N	49	19E	25	13	8	3	15	5	0	3	3	3	0	0	18	8	64
Australia & Pacific Islands																			
Australia:																			
Adelaide	34	57S	138	32E	6	104	20	18	25	46	69	76	66	66	53	43	28	25	536
Alice Springs	23	48S	133	53E	546	30	43	33	28	10	15	13	8	8	8	18	30	38	251
Bourke	30	05S	145	58E	110	72	36	38	28	28	25	28	23	20	20	23	30	36	335
Brisbane	27	25S	153	05E	5	91	163	160	145	94	71	66	56	48	48	64	94	127	1,135
Broome	17	57S	122	13E	17	50	160	147	99	30	15	23	5	3	0	0	15	84	582
Burketown	17	45S	139	33E	9	53	208	160	132	25	5	8	0	0	0	10	38	112	699
Canberra	35	18S	149	11E	575	25	48	43	56	41	46	53	46	56	41	56	48	51	584
Carmanvon	24	53S	113	40E	4	57	10	18	18	15	38	61	41	18	5	3	0	5	231
Cloncurry	20	40S	140	30E	190	59	112	107	61	18	13	15	8	3	8	13	33	69	457
Esperance	33	50S	121	55E	4	60	18	18	30	46	84	104	102	97	69	56	25	23	671
Laverton	28	40S	122	23E	460	30	20	20	41	20	23	18	15	13	5	8	20	20	224
Melbourne	37	49S	144	58E	35	88	48	46	56	58	53	53	48	48	58	66	58	58	653
Mundiwindi	23	52S	120	10E	561	15	25	48	51	20	15	23	3	8	8	13	13	30	257

Country and Station	Latitude		Longitude		Elevation Meters	Length of Record Years	Precipitation												
	°	'	°	'			Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
							mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm	mm
Perth	31	56S	115	58E	20	63	8	10	20	43	130	180	170	145	86	56	20	13	881
Port Darwin	12	25S	130	52E	32	70	386	312	254	97	15	3	0	3	13	51	119	239	1,491
Sydney	33	52S	151	02E	19	87	89	102	127	135	127	117	117	76	74	71	74	74	1,181
Thursday Island	10	35S	142	13E	61	49	462	401	353	203	41	13	10	5	3	8	38	178	1,715
Townsville	19	15S	146	46E	5	67	277	284	183	84	33	36	15	13	18	33	48	137	1,161
William Creek	28	55S	136	21E	75	30	13	15	8	8	8	13	5	8	8	13	13	18	127
Windsorah	25	26S	142	36E	119	50	36	41	41	23	20	20	13	10	13	15	23	36	290
Tasmania:																			
Hobart	42	53S	147	20E	54	100	48	38	46	48	46	56	53	48	53	58	61	53	610
New Zealand:																			
Auckland	37	00S	174	47E	7	92	79	94	81	97	127	137	145	117	102	102	89	79	1,247
Christchurch	43	29S	172	32E	36	64	56	43	48	48	66	66	69	48	46	43	48	56	638
Dunedin	45	55S	170	12E	1	77	86	71	76	71	81	81	79	76	69	76	81	89	937
Wellington	41	17S	174	46E	126	79	81	81	81	97	117	117	137	117	97	102	89	89	1,204
Pacific Islands																			
Canton, Phoenix Is.	2	46S	171	43W	3	30	66	56	64	91	109	66	66	64	30	28	41	66	747
Guam, Marianas Is.	13	33N	144	50E	110	30	117	89	66	76	107	150	229	325	340	333	262	155	2,248
Honolulu, Hawaii	21	20N	157	55W	2	30	97	84	74	33	25	8	10	23	25	46	56	76	556
Iwo Jima, Bonin Is.	24	47N	141	19E	108	17	81	64	53	94	124	102	163	165	117	150	122	109	1,341
Madang, New Guinea	5	12S	145	47E	6	20	307	302	378	429	384	274	193	122	135	257	338	368	3,485
Midway Is.	28	13N	177	23W	9	20	117	94	79	64	48	33	74	99	94	94	91	107	1,034
Naha, Okinawa	26	12N	127	39E	29	30	135	137	155	155	203	254	180	254	180	168	150	109	2,103
Noumes, New Caledonia	22	16S	166	27E	75	52	94	130	145	132	112	94	91	66	64	51	61	66	1,105
Pago Pago, Samoa	14	19S	170	43W	9	41	622	521	488	419	391	312	254	208	333	378	488	503	4,917
Ponape, Caroline Is.	6	58N	158	13E	37	30	282	246	371	508	516	424	411	414	401	406	429	465	4,874
Port Moresby, New Guinea	9	29S	147	09E	38	38	178	193	170	107	64	33	28	18	25	36	48	112	1,011
Rabaul, New Guinea	4	13S	152	11E	9	24	376	264	259	254	132	84	137	94	89	130	180	257	2,256
Suva, Fiji Is.	18	08S	178	26E	6	43	290	272	368	310	257	170	124	211	196	211	249	318	2,974
Tahiti, Society Is.	17	33S	149	36W	2	27	335	292	165	173	124	81	66	48	58	86	165	302	1,897
Tulagi, Solomon Is.	9	05S	160	10E	2	37	363	401	381	254	206	173	193	221	203	221	254	264	3,134
Wake Is.	19	17N	166	39E	3	30	28	36	38	48	51	48	117	180	132	135	79	46	937

Country and Station	Latitude		Longitude		Elevation Meters	Length of Record Years	Precipitation												
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Yap, Caroline Is.	9	31N	138	08E	19	30	201	117	137	163	241	272	351	373	356	335	284	259	3,089
Byrd Station	80	01S	119	32W	1,553	6	10	10	5	8	10	13	18	18	8	18	0	8	124
Ellsworth	77	44S	41	07W	42	6	8	5	8	15	5	5	5	5	8	10	13	5	91
McMurdo Station	77	53S	166	48W	2	10	13	18	10	10	10	8	5	8	10	5	5	8	109
South Pole Station	89	59S	0	00W	2,800	5	0	3	0	0	0	0	0	0	0	0	0	0	3
Wilkes	66	16S	110	31E	9	7	13	10	43	28	36	30	33	20	38	30	20	8	310

NOTE:

1. "Length of Record" refers to precipitation. A standard period of the 30 years from 1931–1960 had been used for locations in the United States and some other countries.
2. \*Less than 1.27 mm. All precipitation data have been changed from inches to millimeters. The annual totals, therefore, may not be equal exactly to the summed monthly values due to rounding errors.
3. Except for Antarctica, amounts of solid precipitation such as snow or hail have been converted to their water equivalent. Because of the frequent occurrence of blowing snow, it has not been possible to determine the precise amount of precipitation actually falling in Antarctica. Values shown are average amounts of solid snow accumulating in a given period as determined by snow markers. The liquid content of the accumulation is undetermined.

Table A-5-3. Normals, means, and extremes for Asheville, NC.

# NORMALS, MEANS, AND EXTREMES

ASHEVILLE, NORTH CAROLINA

LATITUDE: 35°26'N	LONGITUDE: 82°33'W	ELEVATION: FT. GRND	2140	BARO	2161	TIME ZONE: EASTERN	WBAN: 03812							
(a)	JAN	FEB	MAR	APR	MAY	JUNE	JULY	AUG	SEP	OCT	NOV	DEC	YEAR	
<b>TEMPERATURE °F:</b>														
Normals														
-Daily Maximum	47.5	50.6	58.4	68.6	75.6	81.4	84.0	83.5	77.9	68.7	58.6	50.3	67.1	
-Daily Minimum	26.0	27.6	34.4	42.7	51.0	58.2	62.4	61.6	55.8	43.3	34.2	28.2	43.8	
-Monthly	36.8	39.1	46.4	55.7	63.3	69.8	73.2	72.6	66.9	56.0	46.4	39.3	55.5	
Extremes														
-Record Highest	23	78	77	83	89	91	96	96	100	92	86	81	100	
-Year		1975	1986	1985	1972	1969	1969	1983	1983	1975	1986	1974	1971	
-Record Lowest	23	-16	-2	9	22	29	35	46	42	30	21	8	-7	
-Year		1985	1967	1980	1987	1986	1966	1967	1986	1967	1976	1970	1983	
<b>NORMAL DEGREE DAYS:</b>														
Heating (base 65°F)		874	725	577	283	114	23	0	0	57	286	558	797	4294
Cooling (base 65°F)		0	0	0	0	61	167	254	239	114	7	0	0	842
<b>% OF POSSIBLE SUNSHINE</b>														
	23	56	60	62	66	60	64	59	54	55	60	58	57	59
<b>MEAN SKY COVER (tenths)</b>														
Sunrise - Sunset	23	6.0	5.9	5.9	5.5	6.2	6.1	6.4	6.3	6.2	5.2	5.5	5.8	5.9
<b>MEAN NUMBER OF DAYS:</b>														
Sunrise to Sunset														
-Clear	23	9.9	9.1	9.3	10.2	7.6	6.5	5.2	5.0	7.0	12.2	10.5	10.2	102.5
-Partly Cloudy	23	7.2	6.2	8.4	8.6	9.7	12.2	13.5	13.9	10.5	7.7	7.2	7.1	112.2
-Cloudy	23	14.0	13.0	13.3	11.2	13.7	11.3	12.3	12.2	12.6	11.0	12.3	13.7	150.5
<b>Precipitation</b>														
.01 inches or more	23	10.1	9.3	11.2	9.1	11.9	11.2	11.9	12.1	9.4	8.2	9.4	9.7	123.7
Snow, ice pellets														
1.0 inches or more	23	1.6	1.4	0.8	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.5	4.6
<b>Thunderstorms</b>														
Heavy Fog Visibility	23	0.4	0.8	2.2	3.0	7.3	7.9	9.1	9.0	3.4	1.0	0.7	0.4	45.2
1/4 mile or less	23	3.7	3.0	2.3	2.4	5.8	8.1	9.9	14.3	12.1	8.4	4.6	4.8	79.4
<b>Temperature °F</b>														
-Maximum														
30° and above	23	0.0	0.0	0.0	0.0	0.*	1.7	4.4	2.5	0.3	0.0	0.0	0.0	9.0
32° and below	23	3.6	1.5	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.8	6.3
-Minimum														
32° and below	23	24.3	20.9	13.8	4.2	0.3	0.0	0.0	0.0	0.*	4.0	13.1	20.7	101.3
0° and below	23	0.6	0.*	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.8
<b>AVG. STATION PRESS. (mb)</b>														
	15	940.9	940.8	940.1	940.2	940.7	942.3	943.4	944.1	943.8	944.2	943.3	942.4	942.2
<b>RELATIVE HUMIDITY (%)</b>														
Hour 01	23	81	78	79	78	90	94	95	96	96	91	86	83	87
Hour 07 (Local Time)	23	85	84	85	85	92	95	96	98	97	94	89	86	91
Hour 13	23	59	56	53	50	58	60	64	64	64	58	57	59	59
Hour 19	23	68	63	60	56	67	70	74	79	81	75	70	70	69
<b>PRECIPITATION (inches):</b>														
<b>Water Equivalent</b>														
-Normal		3.48	3.60	5.13	3.84	4.19	4.20	4.43	4.79	3.96	3.29	3.29	3.51	47.71
-Maximum Monthly	23	7.47	7.02	9.86	7.26	8.83	8.94	9.92	11.28	9.12	7.05	7.76	8.48	11.28
-Year		1978	1982	1975	1979	1973	1987	1982	1967	1977	1971	1979	1973	AUG 1967
-Minimum Monthly	23	0.45	0.44	0.77	0.25	1.59	1.28	0.46	0.52	0.16	0.30	1.19	0.16	0.16
-Year		1981	1978	1985	1976	1985	1986	1986	1981	1984	1978	1981	1965	SEP 1984
-Maximum in 24 hrs	23	2.95	3.47	5.13	3.06	4.95	3.93	4.02	4.12	3.41	2.95	4.03	2.66	5.13
-Year		1978	1982	1968	1973	1973	1987	1969	1967	1975	1977	1977	1973	MAR 1968
<b>Snow, Ice pellets</b>														
-Maximum Monthly	23	17.6	25.5	13.0	11.5	T	T	T	T	T	9.6	16.3	25.5	25.5
-Year		1966	1969	1969	1987	1979	1979	1979	1979	1977	1977	1968	1971	FEB 1969
-Maximum in 24 hrs	23	9.6	11.7	10.9	11.5	T	T	T	T	T	5.7	16.3	16.3	16.3
-Year		1987	1969	1969	1987	1979	1979	1979	1979	1977	1968	1971	1971	DEC 1971
<b>WIND:</b>														
Mean Speed (mph)	23	9.8	9.5	9.4	8.9	7.0	6.1	5.8	5.4	5.6	6.7	8.2	8.9	7.6
Prevailing Direction														
<b>Fastest Obs. 1 Min.</b>														
-Direction (!!!)	23	34	34	35	22	34	36	35	34	32	33	32	34	34
-Speed (MPH)	23	40	60	46	44	40	40	43	40	35	35	40	44	60
-Year		1975	1972	1969	1970	1971	1977	1966	1973	1980	1972	1974	1965	FEB 1972
<b>Peak Gust</b>														
-Direction (!!!)	4	NW	NW	SW	NW	N	N	SW	NW	SW	N	N	N	NW
-Speed (mph)	4	49	54	45	48	37	52	36	36	37	38	41	46	54
-Date		1984	1987	1984	1987	1984	1987	1985	1985	1985	1987	1987	1987	FEB 1987

(!!!) See Reference Notes on Page 6B.  
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Tables A-6-1 through A-6-3 show U.S. Standard Atmosphere for 0–30, 30–100, and 100–1,000 km, respectively.

Table A-6-1. U.S. Standard Atmosphere, 0–30 km.

Geometric Altitude (km)	Temperature (K)	Pressure (mb)	Density (g cm <sup>-3</sup> )	Pressure Scale Height (km)	Number Density (cm <sup>-3</sup> )	Molecular Weight (amu)
0	288.150	$1.01325 \times 10^3$	$1.2250 \times 10^{-3}$	8.4345	$2.5470 \times 10^{19}$	28.964
2	275.154	$7.9501 \times 10^2$	$1.0066 \times 10^{-3}$	8.0592	$2.0928 \times 10^{19}$	28.964
4	262.166	$6.1660 \times 10^2$	$8.1935 \times 10^{-4}$	7.6836	$1.7036 \times 10^{19}$	28.964
6	249.187	$4.7217 \times 10^2$	$6.6011 \times 10^{-4}$	7.3078	$1.3725 \times 10^{19}$	28.964
8	236.215	$3.5651 \times 10^2$	$5.2579 \times 10^{-4}$	6.9317	$1.0932 \times 10^{19}$	28.964
10	223.252	$2.6499 \times 10^2$	$4.1351 \times 10^{-4}$	6.5554	$8.5976 \times 10^{18}$	28.964
12	216.650	$1.9399 \times 10^2$	$3.1194 \times 10^{-4}$	6.3656	$6.4857 \times 10^{18}$	28.964
14	216.650	$1.4170 \times 10^2$	$2.2786 \times 10^{-4}$	6.3696	$4.7375 \times 10^{18}$	28.964
16	216.650	$1.0352 \times 10^2$	$1.6647 \times 10^{-4}$	6.3736	$3.4612 \times 10^{18}$	28.964
18	216.650	$7.5652 \times 10^1$	$1.2165 \times 10^{-4}$	6.3776	$2.5292 \times 10^{18}$	28.964
20	216.650	$5.5293 \times 10^1$	$8.8910 \times 10^{-5}$	6.3816	$1.8486 \times 10^{18}$	28.964
22	218.574	$4.0475 \times 10^1$	$6.4510 \times 10^{-5}$	6.4423	$1.3413 \times 10^{18}$	28.964
24	220.560	$2.9717 \times 10^1$	$4.6938 \times 10^{-5}$	6.5049	$9.7591 \times 10^{17}$	28.964
26	222.544	$2.1883 \times 10^1$	$3.4257 \times 10^{-5}$	6.5675	$7.1225 \times 10^{17}$	28.964
28	224.527	$1.6161 \times 10^1$	$2.5076 \times 10^{-5}$	6.6302	$5.2138 \times 10^{17}$	28.964
30	226.509	$1.1970 \times 10^1$	$0.8410 \times 10^{-5}$	6.6929	$3.8278 \times 10^{17}$	28.964

Table A-6-2. U.S. Standard Atmosphere, 30–100 km.

Geometric Altitude (km)	Temperature (K)	Pressure (mb)	Density (g cm <sup>-3</sup> )	Pressure Scale Height (km)	Number Density (cm <sup>-3</sup> )	Molecular Weight (amu)
30	226.509	$1.1970 \times 10^1$	$1.8410 \times 10^{-5}$	6.6929	$3.8278 \times 10^{17}$	28.964
35	236.513	5.7459	$8.4634 \times 10^{-6}$	6.9995	$1.7597 \times 10^{17}$	28.964
40	250.350	2.8714	$3.9957 \times 10^{-6}$	7.4206	$8.3077 \times 10^{16}$	28.964
45	264.164	1.4910	$1.9663 \times 10^{-6}$	7.8423	$4.0882 \times 10^{16}$	28.964
50	270.650	$7.9779 \times 10^{-1}$	$1.0269 \times 10^{-6}$	8.0474	$2.1351 \times 10^{16}$	28.964
55	260.771	$4.2525 \times 10^{-1}$	$5.6810 \times 10^{-7}$	7.7658	$1.1812 \times 10^{16}$	28.964
60	247.021	$2.1958 \times 10^{-1}$	$3.0968 \times 10^{-7}$	7.3678	$6.4387 \times 10^{15}$	28.964
65	233.292	$1.0929 \times 10^{-1}$	$1.6321 \times 10^{-7}$	6.9691	$3.3934 \times 10^{15}$	28.964
70	219.585	$5.2209 \times 10^{-2}$	$8.2829 \times 10^{-8}$	6.5699	$1.7222 \times 10^{15}$	28.964
75	208.399	$2.3881 \times 10^{-2}$	$3.9921 \times 10^{-8}$	6.2449	$8.3003 \times 10^{14}$	28.964
80	198.639	$1.0524 \times 10^{-2}$	$1.8458 \times 10^{-8}$	5.9617	$3.8378 \times 10^{14}$	28.964
85	188.893	$4.4568 \times 10^{-3}$	$8.2196 \times 10^{-9}$	5.6780	$1.7090 \times 10^{14}$	28.964
90	186.870	$1.8359 \times 10^{-3}$	$3.4160 \times 10^{-9}$	5.6360	$7.1160 \times 10^{13}$	28.910
95	188.420	$7.5966 \times 10^{-4}$	$1.3930 \times 10^{-9}$	5.7270	$2.9200 \times 10^{13}$	28.730
100	195.080	$3.2011 \times 10^{-4}$	$5.6040 \times 10^{-10}$	6.0090	$1.1890 \times 10^{13}$	28.400

Table A-6-3. U.S. Standard Atmosphere, 100–1,000 km.

Geometric Altitude (km)	Temperature (K)	Pressure (mb)	Density (g cm <sup>-3</sup> )	Pressure Scale Height (km)	Number Density (cm <sup>-3</sup> )	Molecular Weight (amu)
100	195.080	$3.2011 \times 10^{-4}$	$5.6040 \times 10^{-10}$	6.0090	$1.1890 \times 10^{13}$	28.400
120	360.000	$2.5382 \times 10^{-5}$	$2.2220 \times 10^{-11}$	12.0910	$5.1070 \times 10^{11}$	26.200
140	559.630	$7.2028 \times 10^{-6}$	$3.8310 \times 10^{-12}$	20.0250	$9.3220 \times 10^{10}$	24.750
160	696.290	$3.0395 \times 10^{-6}$	$1.2330 \times 10^{-12}$	26.4140	$3.1620 \times 10^{10}$	23.490
180	790.070	$1.5271 \times 10^{-6}$	$5.1940 \times 10^{-13}$	31.7030	$1.4000 \times 10^{10}$	22.340
200	854.560	$8.4736 \times 10^{-7}$	$2.5410 \times 10^{-13}$	36.1830	$7.1820 \times 10^9$	21.300
300	976.010	$8.7704 \times 10^{-8}$	$1.9160 \times 10^{-14}$	51.1930	$6.5090 \times 10^8$	17.730
400	995.830	$1.4518 \times 10^{-8}$	$2.8030 \times 10^{-15}$	59.6780	$1.0560 \times 10^8$	15.980
500	999.240	$3.0236 \times 10^{-9}$	$5.2150 \times 10^{-16}$	68.7850	$2.1920 \times 10^7$	14.330
600	999.850	$8.2130 \times 10^{-10}$	$1.1370 \times 10^{-16}$	88.2440	$5.9500 \times 10^6$	11.510
800	999.990	$1.7036 \times 10^{-10}$	$1.1360 \times 10^{-17}$	193.8620	$1.2340 \times 10^6$	5.540
1,000	1,000.000	$7.5138 \times 10^{-11}$	$3.5610 \times 10^{-18}$	288.2030	$5.4420 \times 10^5$	3.940

Reference: U.S. Standard Atmosphere, 1976, Publication NOAA-S/T76-1562. Washington DC: U.S. Government Printing Office. This reference also contains altitudes in geopotential terms with corresponding changes in the other data.

Atomic weights are shown in table A-11-1.

Table A-11-1. Atomic weights to four significant figures\* (scaled to the relative atomic mass of <sup>12</sup>C = 12 exactly).

Atomic weight values quoted in table A-11-1 are reliable to ±1 or better in the fourth significant figure except for the five elements for which the larger indicated uncertainties apply. Each element that has neither a stable isotope nor a characteristic natural isotopic composition is represented in this table by one of that element's commonly known radioisotopes identified by its mass number (in superscript preceding the chemical symbol) and its relative atomic mass, in the Atomic Weight column.

Atomic Number	Name	Symbol	Atomic Weight	Atomic Number	Name	Symbol	Atomic Weight
1	Hydrogen	H	1.008	38	Strontium	Sr	87.62
2	Helium	He	4.003	39	Yttrium	Y	88.91
3	Lithium	Li	6.941±2	40	Zirconium	Zr	91.22
4	Beryllium	Be	9.012	41	Niobium	Nb	92.91
5	Boron	B	10.81	42	Molybdenum	Mo	95.94
6	Carbon	C	12.01	43	Technetium	<sup>99</sup> Tc	98.91
7	Nitrogen	N	14.01	44	Ruthenium	Ru	101.1
8	Oxygen	O	16.00	45	Rhodium	Rh	102.9
9	Fluorine	F	19.00	46	Palladium	Pd	106.4
10	Neon	Ne	20.18	47	Silver	Ag	107.9
11	Sodium	Na	22.99	48	Cadmium	Cd	112.4
12	Magnesium	Mg	24.30	49	Indium	In	114.8
13	Aluminium	Al	26.98	50	Tin	Sn	118.7
14	Silicon	Si	28.09	51	Antimony	Sb	121.8
15	Phosphorus	P	30.97	52	Tellurium	Te	127.6



Table A-11-1. Atomic weights to four significant figures\* (scaled to the relative atomic mass of  $^{12}\text{C} = 12$  exactly) (Continued).

Atomic Number	Name	Symbol	Atomic Weight	Atomic Number	Name	Symbol	Atomic Weight
16	Sulfur	S	32.07	53	Iodine	I	126.9
17	Chlorine	Cl	35.45	54	Xenon	Xe	131.3
18	Argon	Ar	39.95	55	Caesium	Cs	132.9
19	Potassium	K	39.10	56	Barium	Ba	137.3
20	Calcium	Ca	40.08	57	Lanthanum	La	138.9
21	Scandium	Sc	44.96	58	Cerium	Ce	140.1
22	Titanium	Ti	47.88±3	59	Praseodymium	Pr	140.9
23	Vanadium	V	50.94	60	Neodymium	Nd	144.2
24	Chromium	Cr	52.00	61	Promethium	$^{145}\text{Pm}$	144.9
25	Manganese	Mn	54.94	62	Samarium	Sm	150.4
26	Iron	Fe	55.85	63	Europium	Eu	152.0
27	Cobalt	Co	58.93	64	Gadolinium	Gd	157.2
28	Nickel	Ni	58.69	65	Terbium	Tb	158.9
29	Copper	Cu	63.55	66	Dysprosium	Dy	162.5
30	Zinc	Zn	65.39±2	67	Holmium	Ho	164.9
31	Gallium	Ga	69.72	68	Erbium	Er	167.3
32	Germanium	Ge	72.61±2	69	Thulium	Tm	168.9
33	Arsenic	As	74.92	70	Ytterbium	Yb	173.0
34	Selenium	Se	78.96±3	71	Lutetium	Lu	175.0
35	Bromine	Br	79.90	72	Hafnium	Hf	178.5
36	Krypton	Kr	83.80	73	Tantalum	Ta	180.9
37	Rubidium	Rb	85.47	74	Wolfram (Tungsten)	W	183.8
75	Rhenium	Re	186.2	90	Thorium	Th	232.0
76	Osmium	Os	190.2	91	Protactinium	Pa	231.0
77	Iridium	Ir	192.2	92	Uranium	U	238.0
78	Platinum	Pt	195.1	93	Neptunium	$^{237}\text{Np}$	237.0
79	Gold	Au	197.0	94	Plutonium	$^{239}\text{Pu}$	239.1
80	Mercury	Hg	200.6	95	Americium	$^{243}\text{Am}$	243.1
81	Thallium	Tl	204.4	96	Curium	$^{247}\text{Cm}$	247.1
82	Lead	Pb	207.2	97	Berkelium	$^{247}\text{Bk}$	247.1
83	Bismuth	Bi	209.0	98	Californium	$^{252}\text{Cf}$	252.1
84	Polonium	$^{270}\text{Po}$	210.0	99	Einsteinium	$^{252}\text{Es}$	252.1
85	Astatine	$^{210}\text{At}$	210.0	100	Fermium	$^{257}\text{Fm}$	257.1
86	Radon	$^{222}\text{Rn}$	222.0	101	Mendelevium	$^{256}\text{Md}$	256.1
87	Francium	$^{223}\text{Fr}$	223.0	102	Nobelium	$^{259}\text{No}$	259.1
88	Radium	$^{226}\text{Ra}$	226.0	103	Lawrencium	$^{260}\text{Lr}$	260.1
89	Actinium	$^{227}\text{Ac}$	227.0				

\*The table may be reprinted provided:

(i) The source is acknowledged thus:

Prepared by N.N. Greenwood and H.S. Peiser, on behalf of the Committee on Teaching of Chemistry of the International Union of Pure and Applied Chemistry (IUPAC) in consultation with the IUPAC Commission on Atomic Weights and Isotopic Abundances;

(ii) It is used in its entirety, including the paragraph at the head of the table.

Tables A-11-2 through A-11-5 show various atmospheric gases—main constituent, minor, trace, and synthetic.

Table A-11-2. Main constituent gases of the atmosphere.

Gas	Symbol Molecular (major)	Volume (percent)	Mass (percent)	Molecular Weight	Density (g/l, 0)	Melting Point (°C)	Boiling Point (°C)	Point Temp. (°C)	Triple Point Pressure (mm)	Triple Critical Temp. (°C)	Critical Pressure (atm)
Nitrogen	N <sub>2</sub>	78.09 <sup>a,b,c,h</sup>	75.52	28.016 <sup>f,h,i</sup>	1.2506 <sup>h</sup>	-209.8 <sup>f,h,i,j</sup>	-195.8 <sup>f,h,i,j</sup>	-209.8 <sup>e</sup>	96.4 <sup>e</sup>	-147.1 <sup>h,i</sup>	33.5 <sup>h,i</sup>
Oxygen	O <sub>2</sub>	20.95 <sup>a,b,c,h</sup>	23.14	32.000 <sup>f,h,i</sup>	1.429 <sup>h</sup>	-218.4 <sup>f,h,i</sup>	-183.0 <sup>f,h,i,j</sup>	-218.4 <sup>e,j</sup>	<sup>d,j</sup>	-118.8 <sup>h,j</sup>	49.7 <sup>h,j</sup>
Argon	Ar	0.93 <sup>a,b,c,h</sup>	1.28	39.944 <sup>f,h,i</sup>	1.784 <sup>h</sup>	-189.2 <sup>f,h,i,j</sup>	-185.9 <sup>f,h,i,j</sup>	-189.4 <sup>e</sup>	516 <sup>e</sup>	-122.0 <sup>d,h,i</sup>	48 <sup>h,i</sup>
Carbon dioxide	*CO <sub>2</sub>	0.03 <sup>a,b,c,h</sup>	0.046	44.000 <sup>h</sup>	1.977 <sup>h</sup>	(5.2 atm)	-78.5(s) <sup>f</sup>	-56.6 <sup>e,i</sup>	3,880 <sup>e,i</sup>	31 <sup>h,i</sup>	73 <sup>h,i</sup>

\*May be described as variable over extremely long time periods.

The above data have been adapted from (a) Paneth (1939), (b) Haurwitz (1941), (c) Glueckauf (1951), (d) Guggenheim (1950), (e) Zemansky (1951), (f) Sanderson (1960), (g) Huheey (1978), (h) AFCRL (1985), (i) Chang (1986), and (j) Weast (1988). There may be some small variance amongst the attributions.

Table A-11-3. Minor and some trace gases of the atmosphere.

Gas	Symbol Molecular (Major)	Volume (Percent)	Mass (Percent)	Molecular Weight	Density (g/l, 0)	Melting Point (°C)	Boiling Point (°C)	Point Temp. (°C)	Triple Point Pressure (mm)	Triple Critical Temp. (°C)	Critical Pressure (atm)
Neon	Ne	18.0 × 10 <sup>-4c,h</sup>	1.25 × 10 <sup>-3</sup>	20.183 <sup>f,h,i</sup>	0.9002 <sup>h,j</sup>	-248.67 <sup>f,h,i</sup>	-245.9 <sup>f,h,i,j</sup>	-248.6 <sup>d</sup>	323.7 <sup>d</sup>	-228.7 <sup>f,h</sup>	26.9 <sup>d,f</sup>
Helium	He	5.24 × 10 <sup>-4c,h</sup>	7.24 × 10 <sup>-5</sup> 4.003 <sup>f,h,i</sup> (26 atm)	0.1785 <sup>h</sup>	-272.2 <sup>f,i</sup>	-268.9 <sup>f,i,j</sup>	-271.0	38.65	-268 <sup>f,h</sup>	2.3 <sup>f,h</sup>	
Methane	*CH <sub>4</sub>	1.4 × 10 <sup>-4c,h</sup>	7.75 × 10 <sup>-5</sup>	16.031	0.7168 <sup>h</sup>	-184.0 <sup>h</sup>	-161.5 <sup>h</sup>			-82.5 <sup>h,i</sup>	45.8 <sup>h,i</sup>
Krypton	Kr	1.14 × 10 <sup>-4c,h</sup>	3.30 × 10 <sup>-4</sup>	83.80 <sup>f,h,i</sup>	3.708 <sup>h</sup>	-156.6 <sup>f,h,i</sup>	-152.9 <sup>f,h,i,j</sup>	-57.2 <sup>d</sup>	548.0 <sup>d</sup>	-63.0 <sup>f,h</sup>	54 <sup>f,h</sup>
Nitrous oxide	N <sub>2</sub> O	5 × 10 <sup>-5h</sup>	7.6 × 10 <sup>-5</sup>	44.016	1.977 <sup>h</sup>	-102.4 <sup>h</sup>	-89.49 <sup>h</sup>			36.5 <sup>h</sup>	71.7 <sup>h</sup>
Xenon	Xe	8.6 × 10 <sup>-6c,h</sup>	3.90 × 10 <sup>-5</sup>	131.3 <sup>f,h,i</sup>	5.851 <sup>h</sup>	-112.0 <sup>f,i,j</sup>	-107.1 <sup>f,i,j</sup>	-111.9 <sup>d</sup> 615.6 <sup>d</sup>	16.6 <sup>d,f,h</sup>	58.2 <sup>d,f,h</sup>	
Hydrogen	H <sub>2</sub>	5 × 10 <sup>-5h</sup>	3.48 × 10 <sup>-6</sup>	2.016	0.0899 <sup>h,j</sup>	-259.4 <sup>i,j</sup>	-252.8 <sup>i,j</sup>	-259.2 <sup>d,h</sup> 54.1 <sup>d</sup>	-239.9 <sup>h,i</sup>	12.8 <sup>h,i</sup>	
Ammonia	NH <sub>3</sub>	0 to trace	17.034 <sup>h</sup>							-132.4 <sup>i</sup>	111.5 <sup>j</sup>
Ozone	O <sub>3</sub>	variable-0 to 0.05 ppm	48.000	2.144 <sup>h</sup>	-192.5 <sup>h,j</sup>	-111.9 <sup>h,j</sup>				-12.1 <sup>h</sup>	54.6 <sup>h</sup>
Water	H <sub>2</sub> O(g)*	variable (0-4%)		18.016	1.000 (l)	0 (l)	100 (l)	0.0098 <sup>d</sup>	4.579 <sup>d</sup>	374.4	219.5
Radon	Rn	0 to trace		222 <sup>f</sup>	4.4 <sup>f-</sup>	71 <sup>f,j</sup>	-65 <sup>f</sup> -61.8 <sup>j</sup>		104.5 <sup>f</sup>	62.4 <sup>f</sup>	

\* Can be described as variable over a long period of time.

\*\*The basis for the Celsius scale is the triple point for water.

The above data have been adapted from (a) Paneth (1939), (b) Haurwitz (1941), (c) Glueckauf (1951), (d) Guggenheim (1950), (e) Zemansky (1951), (f) Sanderson (1960), (g) Huheey (1978), (h) AFCRL (1985), (i) Chang (1986), and (j) Weast (1988). There may be some small variance amongst the attributions.

Table A-11-4. Additional trace gases of the atmosphere. (With increasing molecular weights, many of these will cease to exist as gases and will change to liquids or solids, particularly at low temperatures and higher pressures.)

1. Other oxides of hydrogen such as hydrogen peroxide,  $H_2O_2$ , OH,  $HO_2$ , and  $HO_x$ .
2. Other oxides of carbon such as CO.
3. Other oxides of nitrogen such as NO,  $NO_2$ ,  $NO_3$ , ...  $N_yO_x$ .
4. The oxides of sulfur such as SO,  $SO_2$ ,  $SO_3$ , ...  $S_yO_x$ .
5. The sulfides such as hydrogen sulfide,  $H_2S$ .
6. The halogens, fluorine, chlorine, bromine, and iodine,  $F_2$ ,  $Cl_2$ ,  $Br_2$ , and  $I_2$  and their combining forms such as FCl, FBr, FI, ClBr, ClI, and BrI. Due to the heavy molecular weights of Bromine and Iodine and their higher boiling points, complex molecules involving these may cause them to settle out of the atmosphere or not even be carried into the atmosphere in the first place.
7. The hydrocarbons  $C_nH_{2(n+1)}$ , the alkanes, such as ethane, propane, butane, etc., and their derivatives; the alkenes and the alkyls. The halides of the hydrocarbons such as the so-called fluorochlorocarbons or the CFMs, for example  $CH_3Cl$ ,  $CCl_4$ ,  $CH_2FC_1$ , etc. Most of these are derived from the basic methane molecule,  $CH_4$ , where the halogens replace the hydrogens.
8. Halides of other elements such as  $SF_6$ , HCl, OCl, etc.
9. The radioactive gases Radon (Rn), Thoron (Tn), and Actinon (An); half lives of 3.825 days, 54.5 sec. and 3.92 sec., respectively. (See Israel (1951).) One of the disintegration products of these is the alpha particle with a charge of (+2), being neutralized to a helium isotope. Because of their ground source and small half-lives, most of these in the convective and mechanical turbulence do not get beyond the tropopause.  $^5He$  and  $^6He$  are unstable and their half-lives are so small that they are almost undetectable. However, their disintegration emissions will produce ions and therefore contribute some small effect in the production of aerosols.
10. The isotopes of all of these and those of the gases of the foregoing tables exist but their amounts are still yet smaller.

Table A-11-5. Synthetic gases—halocarbons.

The halocarbons include all permutations and combinations of the halogens with the alkanes and other hydrocarbons, straight chain, linear, and cyclic. With increasing molecular weights and generally higher boiling points, these will tend to be liquid or solid and not particularly volatile.

The halocarbons also were mentioned above in table A-11-4. Because all of these were not detected prior to say 100 years ago, and because some, say carbon tetrachloride,  $CCl_4$ , have been detected only recently in bottom ocean currents, a preliminary assumption is that these exist only as man-made or so-called synthetic products. Some fluorochlorohydrocarbons are extremely stable, long lived, rather unreactive (in a sense of changing and generally not interacting with other gases under tropospheric conditions). However, after diffusing through the tropopause and on reaching upper reaches of the stratosphere they are subject to intense, harsh, short-wave radiation. This radiation serves to dissociate the halocarbons and to dislodge reactive halogen radicals. They then can enter into catalytic cyclic reactions, wreaking havoc with ozone molecules as well as other gases.

Table A-11-6 shows aerosols and table A-11-7 shows comparative weights, and melting and boiling points for air, alkanes, and alkane halides.

Table A-11-6. Aerosols including particulates (SMIC (1971), AFCRL (1985, p. 18-9)).

1. Estimates of particles smaller than 20 $\mu\text{m}$ radius emitted into or formed in the atmosphere (106 metric tons/year) (SMIC (1971)).	
Natural	
Soil and rock debris*	100-500
Forest fires and slash-burning debris*	3-150
Sea salt	300
Volcanic debris	25-150
Particles formed from gaseous emissions:	
Sulfate from $\text{H}_2\text{S}$	130-200
Ammonium salts from $\text{NH}_3$	80-270
Nitrate from $\text{NO}_x$	60-430
Hydrocarbons from plant exudations	75-200
Subtotal	773-2,200
Man-made Particles (direct emissions)	10-90
Particles formed from gaseous emissions:	
Sulfate from $\text{SO}_2$	130-200
Nitrate from $\text{NO}_x$	30-35
Hydrocarbons	15-90
Subtotal	185-415
<b>Total</b>	<b>958-2615</b>
2. Additions	
A. Peroxyacetylnitrate (PAN) formed from gaseous emitted pollutants with ultraviolet photolytic reactions	
B. Haze droplets formed	
1. By adsorption of water on particulate matter.	
2. By hydration of gaseous molecules.	
3. By interaction of the hydroxyl radical ( $\text{OH}^-$ ) with other constituents.	
4. By interaction of water vapor or the hydroxyl radical with emissions from radioactive materials.	

\*Includes unknown amounts of indirect man-made contributions.

Table A-11-7. A few comparative weights, melting points (m.p.), and boiling points (b.p.) of air, alkanes, and alkane halides.\* See Weast (1985).

	Name	Molecular Weight	m.p. (°C)	b.p. (°C)
<b>Linear</b>				
Air (dry)		28.87	*	*
CH <sub>4</sub>	Methane	16.012	-184.0	-161.5
CH <sub>3</sub> CH <sub>3</sub> ; (C <sub>2</sub> H <sub>6</sub> )	Ethane	30.605	-183.3	-88.6
CH <sub>3</sub> F	Methyl fluoride	34.023	-141.8	-78.6
CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> ; (C <sub>3</sub> H <sub>8</sub> )	Propane	44.064	-189.7	-42.1
CH <sub>3</sub> Cl	Methyl chloride	50.49	-97.7	-24.2
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	Butane	58.08	-138.3	-0.5
CF <sub>4</sub>	Carbon tetrafluoride	68.00	-183.7	-128.0
CH <sub>3</sub> Br	Methyl bromide	94.94	-93.7	3.6
CH <sub>3</sub> I	Methyl iodide	141.95	-64.1	42.5
CCl <sub>4</sub>	Carbon tetrachloride	153.80	-22.9	76.7
CBr <sub>4</sub>	Carbon tetrabromide	331.60	93.7	
Cl <sub>4</sub>	Carbon tetraiodide	519.60	171.0	
C <sub>6</sub> H <sub>14</sub>	Hexane	86.18	-95.0	68.0
C <sub>6</sub> H <sub>12</sub>	Hexene	84.16	-146.0	68.0
C <sub>6</sub> H <sub>10</sub>	Hexyne	82.15	-132.0	71.0
<b>Cyclic</b>				
C <sub>6</sub> H <sub>6</sub>	Benzene	78.11	5.5	80.1

\*The melting point and boiling point cannot be given for the mixture. The m.p. and b.p. of the major gases are given in table A-11-2.

Molecular bond energies and some atmospheric gases and their absorption regions are shown in table A-11-8 and A-11-9, respectively.

Table A-11-8. Molecular bond energies for selected atmospheric gases. These are enthalpies of dissociation (association). Bonds may exist which are not indicated here.

Element (molecule)	Symbol	Gas	+	Energy (kJ mol <sup>-1</sup> ) To Obtain (kcal mol <sup>-1</sup> )			Wavelength		Wave Number		Source*
				Energy	Gases		Divide by 4.184	(nm)	×10 <sup>4</sup> (cm <sup>-1</sup> )		
Hydrogen	(H <sub>2</sub> )	(H - H) <sub>g</sub>	+	$h\nu \rightarrow$	(H) <sub>g</sub>	+	(H) <sub>g</sub>	435	275	3.64;	a,b,c,d
Hydroxyl ion	(OH)	(H - O) <sub>g</sub>	+	$h\nu \rightarrow$	(H) <sub>g</sub>	+	(O) <sub>g</sub>	459	261	3.83;	a,b,d
Water	(HOH)	(H - OH) <sub>g</sub>	+	$h\nu \rightarrow$	(H) <sub>g</sub>	+	(OH) <sub>g</sub>	502	238	4.20;	a,b,d
Nitrogen	(N <sub>2</sub> )	(N - N) <sub>g</sub>	+	$h\nu \rightarrow$	(N) <sub>g</sub>	+	(N) <sub>g</sub>	942	127	7.87;	a,b,c,d
Oxygen	(O <sub>2</sub> )	(O = O) <sub>g</sub>	+	$h\nu \rightarrow$	(O) <sub>g</sub>	+	(O) <sub>g</sub>	499	240	4.17;	a,b,d
Nitric oxide	(NO)	(N = O) <sub>g</sub>	+	$h\nu \rightarrow$	(N) <sub>g</sub>	+	(O) <sub>g</sub>	678	191	5.24;	a
Nitrous oxide	(N <sub>2</sub> O)	(NN - O) <sub>g</sub>	+	$h\nu \rightarrow$	(N <sub>2</sub> ) <sub>g</sub>	+	(O) <sub>g</sub>	167	710	1.41;	b
Nitrogen dioxide	(NO <sub>2</sub> )	(O - NO) <sub>g</sub>	+	$h\nu \rightarrow$	(O) <sub>g</sub>	+	(NO) <sub>g</sub>	305	389	2.57;	b
Nitrogen trioxide	(N <sub>2</sub> O <sub>3</sub> )	(ON - NO <sub>2</sub> ) <sub>g</sub>	+	$h\nu \rightarrow$	(ON) <sub>g</sub>	+	(NO <sub>2</sub> ) <sub>g</sub>	57	2098	0.40;	a,b
Nitrogen tetraoxide	(N <sub>2</sub> O <sub>4</sub> )	(O <sub>2</sub> N - NO <sub>2</sub> ) <sub>g</sub>	+	$h\nu \rightarrow$	(O <sub>2</sub> N) <sub>g</sub>	+	(NO <sub>2</sub> ) <sub>g</sub>	40	2990	0.33;	b
Ozone	(O <sub>3</sub> )	(O - O <sub>2</sub> ) <sub>g</sub>	+	$h\nu \rightarrow$	(O) <sub>g</sub>	+	(O <sub>2</sub> ) <sub>g</sub>	540-373	220-320	4.54-313;	a
Carbon	(C <sub>2</sub> )	(C - C) <sub>g</sub>	+	$h\nu \rightarrow$	(C) <sub>g</sub>	+	(C) <sub>g</sub>	812	147	6.80;	a,b,d
Carbon monoxide	(CO)	(C - O) <sub>g</sub>	+	$h\nu \rightarrow$	(C) <sub>g</sub>	+	(O) <sub>g</sub>	1072	112	8.93;	a,b
Carbon dioxide	(CO <sub>2</sub> )	(O = CO) <sub>g</sub>	+	$h\nu \rightarrow$	(O) <sub>g</sub>	+	(CO) <sub>g</sub>	536	223	4.48;	b
Methane	(CH <sub>4</sub> )	(H <sub>3</sub> C - H) <sub>g</sub>	+	$h\nu \rightarrow$	(H) <sub>g</sub>	+	(CH <sub>3</sub> ) <sub>g</sub>	435	275	3.64;	a,b,c
Methyl group	(CH <sub>3</sub> )	(H <sub>2</sub> C - H) <sub>g</sub>	+	$h\nu \rightarrow$	(H) <sub>g</sub>	+	(CH <sub>2</sub> ) <sub>g</sub>	469	255	3.92;	a,b
Methylene group	(CH <sub>2</sub> )	(HC - H) <sub>g</sub>	+	$h\nu \rightarrow$	(H) <sub>g</sub>	+	(CH) <sub>g</sub>	415	288	3.47;	a,b
	(CH)	(H - C) <sub>g</sub>	+	$h\nu \rightarrow$	(H) <sub>g</sub>	+	(C) <sub>g</sub>	335	357	2.80;	a,b
Average (C-H) bond	(CH)	(H - C) <sub>g</sub>	+	$h\nu \rightarrow$	(H) <sub>g</sub>	+	(C) <sub>g</sub>	410	292	3.42;	a,b,d
Ethane	(C <sub>2</sub> H <sub>6</sub> )	(H - C <sub>2</sub> H <sub>5</sub> ) <sub>g</sub>	+	$h\nu \rightarrow$	(H) <sub>g</sub>	+	(C <sub>2</sub> H <sub>5</sub> ) <sub>g</sub>	410	292	3.42;	b
Ethene group	(C <sub>2</sub> H <sub>4</sub> )	(CH <sub>2</sub> = CH <sub>2</sub> ) <sub>g</sub>	+	$h\nu \rightarrow$	(CH <sub>2</sub> ) <sub>g</sub>	+	(CH <sub>2</sub> ) <sub>g</sub>	698	171	5.85;	b
		(CH <sub>2</sub> = CH - H) <sub>g</sub>	+	$h\nu \rightarrow$	(CH <sub>2</sub> =CH) <sub>g</sub>	+	(H) <sub>g</sub>	452	264	3.79;	c
Ethyne (acetylene)	(C <sub>2</sub> H <sub>2</sub> )	(CH ≡ CH) <sub>g</sub>	+	$h\nu \rightarrow$	(CH) <sub>g</sub>	+	(CH) <sub>g</sub>	962	124	8.06;	b
Fluorine	(F <sub>2</sub> )	(F - F) <sub>g</sub>	+	$h\nu \rightarrow$	(F) <sub>g</sub>	+	(F) <sub>g</sub>	149	803	1.25;	a,b,c,d
Chlorine	(Cl <sub>2</sub> )	(Cl - Cl) <sub>g</sub>	+	$h\nu \rightarrow$	(Cl) <sub>g</sub>	+	(Cl) <sub>g</sub>	243	492	7.03;	a,b,c,d
Bromine	(Br <sub>2</sub> )	(Br - Br) <sub>g</sub>	+	$h\nu \rightarrow$	(Br) <sub>g</sub>	+	(Br) <sub>g</sub>	193	619	1.62;	a,b,c,d
Iodine	(I <sub>2</sub> )	(I - I) <sub>g</sub>	+	$h\nu \rightarrow$	(I) <sub>g</sub>	+	(I) <sub>g</sub>	151	792	1.26;	a,b,c,d
Hydrogen fluoride	(HF)	(H - F) <sub>g</sub>	+	$h\nu \rightarrow$	(H) <sub>g</sub>	+	(F) <sub>g</sub>	568	210	4.76;	a,c,d
Hydrogen chloride	(HCl)	(H - Cl) <sub>g</sub>	+	$h\nu \rightarrow$	(H) <sub>g</sub>	+	(Cl) <sub>g</sub>	430	278	3.60;	a,b,c,d
Hydrogen bromide	(HBr)	(H - Br) <sub>g</sub>	+	$h\nu \rightarrow$	(H) <sub>g</sub>	+	(Br) <sub>g</sub>	365	327	3.06;	a,b,c,d
Hydrogen iodide	(HI)	(H - I) <sub>g</sub>	+	$h\nu \rightarrow$	(H) <sub>g</sub>	+	(I) <sub>g</sub>	299	400	2.50;	a,b,c,d

Table A-11-8. Molecular bond energies for selected atmospheric gases. These are enthalpies of dissociation (association). Bonds may exist which are not indicated here (Continued).

Element (molecule)	Symbol	Gas	+	Energy (kJ mol <sup>-1</sup> ) To Obtain (kcal mol <sup>-1</sup> )			Wavelength Divide by 4.184		Wave Number		Source*
				Energy	Gases				(nm)	×10 <sup>4</sup> (cm <sup>-1</sup> )	
Methyl fluoride	(CH <sub>3</sub> F)	(CH <sub>3</sub> - F) <sub>g</sub>	+	$h\nu \rightarrow$	(CH <sub>3</sub> ) <sub>g</sub>	+	(F) <sub>g</sub>	452	264	3.78	b,c
Methyl chloride	(CH <sub>3</sub> Cl)	(CH <sub>3</sub> - Cl) <sub>g</sub>	+	$h\nu \rightarrow$	(CH <sub>3</sub> ) <sub>g</sub>	+	(Cl) <sub>g</sub>	350	341	2.93	c
Methyl bromide	(CH <sub>3</sub> Br)	(CH <sub>3</sub> - Br) <sub>g</sub>	+	$h\nu \rightarrow$	(CH <sub>3</sub> ) <sub>g</sub>	+	(Br) <sub>g</sub>	292	409	2.45	c
Methyl iodide	(CH <sub>3</sub> I)	(CH <sub>3</sub> - I) <sub>g</sub>	+	$h\nu \rightarrow$	(CH <sub>3</sub> ) <sub>g</sub>	+	(I) <sub>g</sub>	236	506	1.98	b,c

\*Sources are: (a) Wayne (1985, 1988), (b) Weast (1969), (c) Fessenden and Fessenden (1986), and (d) Chang (1986).

Notes:

- The easier bond energies to assess are those of the diatomic molecules. Values vary from source to source.
- Though precise in each source, biases may exist. Therefore, use these numbers with care.
- The subscript "g" indicates that this is considered a gas.
- The products are all radicals. Though not done here, a prior or post ( ) could have been used to signify.
- Ionizing energies are not indicated here.

Table A-11-9. Some atmospheric gases and their absorption (emission) regions (adapted from Smith (1985), Mitchell (1989), and Goody and Yung (1989)).

Absorber	Symbol	Spectral Region
Nitrous oxide	N <sub>2</sub> O	4.5, 7.8, and 17 μ, plus 251, 75, 50, and 25 GHz
Molecular oxygen	O <sub>2</sub>	1.07 and 1.27 μ, a series of lines between 50–70 GHz, one line at 118.75 GHz; also weak bands in the visible, with centers between 538.4 and 762.1 nm.
Methane	CH <sub>4</sub>	3.3 and 7.7 μ
Carbon dioxide	CO <sub>2</sub>	13.5–16.5 μ (center at 15 μ), 4.2–4.4 μ (center at 4.3 μ), 10.4, 9.4, 5.2, 2.7, 2, 1.6, and 1.4 μ; also a series of weak bands in the 0.78–1.24 μ range.
Carbon monoxide	CO	4.67, 2.35, 1.57, 1.19 μ, 2.38–25 μ (several centers), plus 230.77 and 115.27 GHz
Ozone	O <sub>3</sub>	14.1, 9.6, 9, 5.75, 4.75, 3.59, 3.27, 2.7 μ, 18 lines between 9.2 and 43.65 GHz, lines at 96.23, 101.74, and 118.36 GHz, plus 20 lines between 160 and 380 GHz; also 180–340 nm (center at 260 nm), 320–360 nm, 440–740 nm
Halocarbons	CFC11–12	9–12 μ, 9.1, 9.2, 8.7, 10.9, and 11.8 μ
Water vapor	H <sub>2</sub> O	5.5–7.5 μ (center at 6.3 μ), 2.6–3.3 μ (several centers), 1.9, 1.4, 1.1, 0.94, 0.81, and 0.72 μ, 22.24 and 183.31 GHz, plus lines at frequencies higher than 300 GHz that extend all the way to 8 μ; a few weak bands in the visible.
Windows		8–13 μ, 18, 4.7, 4, 3.8, 2.3, 1.65, 1.25, 1.05 μ, regions of the interval 1.4–10 GHz, 33–36 GHz, 80–100 GHz, 125–140 GHz, 210–235 GHz, plus the visible region 400–700 nm. Note that the CFCs are beginning to obstruct the 8–13 μ window.





**APPENDIX B—INDIVIDUALS REFERENCED, QUOTED, OR WHO PROVIDED  
PERMISSION, MATERIAL, AND/OR HELP**

Arkin, M.L.	Gringorten, Irving I.	Ohring, George
Austin, G.L.	Guttman, Nathaniel B.	Palmer, Wayne
Bess, T. Dale	Hadeen, K.D.	Paulhus Joseph L.H.
Blake, Donald R.	Hasler, A. Frederick	Pauling, Linus
Bluestein, Howard	Haurwitz, Bernhard	Pierson, Willard J.
Boden, Thomas A.	Hickman, John	Puskin, Jerome S.
Broecker, Wallace S.	Howard, J.N.	Quayle, Robert G.
Brown, Otis B.	Jenne, Roy L.	Quinlan, Frank T.
Carle, M.	Johnson, Dale L.	Rasmussen, R.A.
Carson, James E.	Joiner, Raymond L.	Rasmusson, Eugene
Cayan, Daniel R.	Karl, Thomas R.	Ratcliffe, C.I.
Chang, Raymond	Keeling, C.D.	Rhodes, Raymond C.
Changery, Michael J.	Khalil, M.A.K.	Riordan, Pauline
Chantry, George W.	Komhyr, Walter	Ripmeester, J.A.
Christy, John	Koss, Walter James	Ropelewski, Chester J.
Collett, Timothy S.	Kvenvolden, Keith A.	Rowland, F.S.
Court Arnold	Kyle, Thomas G.	Schmidli, Robert J.
Cox, R.A.	Landsberg, Helmut E.	Schmidlin, Francis J.
Currie, Robert	Lorenz, Edward N.	Sherr, Paul E.
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