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CHEMICAL KINETICS AND MODELING OF PLANETARY ATMOSPHERES

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ABSTRACT

A unified overview is presented for chemical kinetics and chemical modeling in planetary atmospheres. The recent major advances in our understanding of the chemistry of the terrestrial atmosphere make the study of planets more interesting and relevant. A deeper understanding suggests that the important chemical cycles have a universal character that connects the different planets and ultimately link us together to the origin and evolution of the solar system.

The completeness (or incompleteness) of the data base for chemical kinetics in planetary atmospheres will always be judged by comparison with that for the terrestrial atmosphere. In the latter case, the chemistry of H, O, N, and Cl species is well understood. S chemistry is poorly understood. In the atmospheres of Jovian planets and Titan, the C–H chemistry of simple species (containing 2 or less C atoms) is fairly well understood. The chemistry of higher hydrocarbons and the C–N, P–N chemistry is much less understood. In the atmosphere of Venus, the dominant chemistry is that of chlorine and sulfur, and very little is known about Cl–S coupled chemistry.

A new frontier for chemical kinetics both in the Earth and planetary atmospheres is the study of heterogeneous reactions. The formation of the ozone hole on Earth, the ubiquitous photochemical haze on Venus and in the Jovian planets and Titan all testify to the importance of heterogeneous reactions. It remains a challenge to connect the gas phase chemistry to the production of aerosols.

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INTRODUCTION

In this review I will give a highly personal overview of chemical modeling in planetary atmospheres. I will show why it is interesting, important, and exciting. I will also suggest how laboratory kinetics studies can make this enterprise more interesting, important, and exciting. No attempt is made to survey the field. The interested reader may pursue a particular subject more deeply by reading the references.

In the beginning, Nature in her infinite kindness gave us matter. This is designated by the box "origin" in Figure 1. The distribution of various elements is not arbitrary, but is determined by a cosmic yardstick called the cosmic abundance, as shown in Table 1. This table is the result of synthesizing recent observations of the sun and Cl chondrites, but the results are believed to be representative of the cosmos at large.

Nature manifested her kindness again in giving us chemical kinetics, the time rate of chemical reactions. Once determined in the laboratory (or computed accurately enough), a kinetic rate coefficient sets the absolute yardstick governing the rate of transformation of one species into another. Why is this so important? I will illustrate my view by a quote from Robert Emden:

> As a student, I read with advantage a small book by F. Wald entitled 'The Mistress of the World and her Shadow'. These meant energy and entropy. In the course of advancing knowledge the two seem to me to have exchanged places. In the huge manufactory of natural processes, the principle of entropy occupies the position of manager, for it dictates the manner and methods of the whole business, whilst the principle of energy merely does the bookkeeping, balancing credits and debits.

Now read the sentences again after substituting the words "energy" and "entropy" by "chemical species" and "chemical kinetics", respectively.

As an illustration of the above ideas, consider the relative abundance of C and O in Table 1. As given in this table the ratio C/O is 0.42 making C slightly less abundant than O in the solar nebula. This implies that CO would be the dominant form of carbon in the solar nebula. Its subsequent reduction to CH_4 would depend on the kinetic rate of the reduction reactions, the rate of mixing in the nebula, and the lifetime of the nebula. Now there is sufficient uncertainty in the C/O ratio that the possibility C/O > 1 cannot be ruled out. In this case CO might not be the dominant form of carbon. Additional reservoirs of carbon (such as graphite) could exist. In this case the reduction of carbon to CH_4 could happen more readily. We can start to appreciate the importance of just a little difference in the relative abundance of chemical species at the time of the origin of the solar system, and the rate of interconversion of these species.
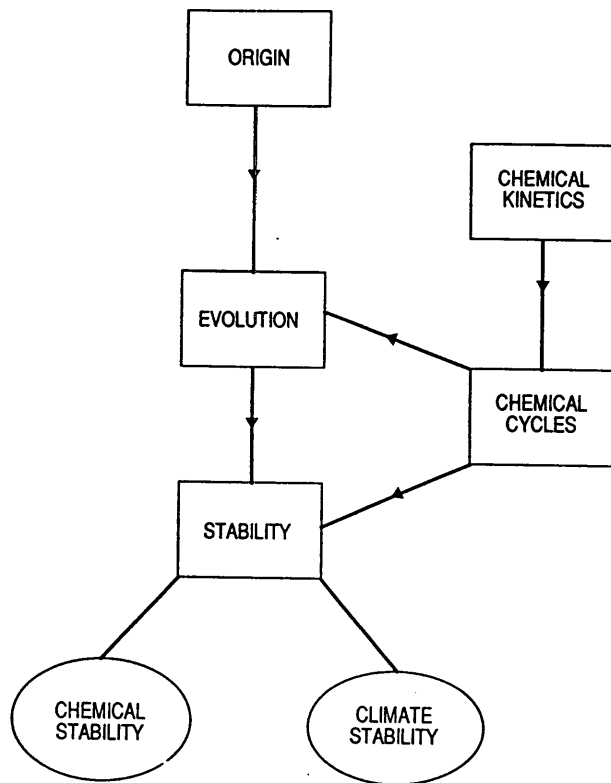
Fig 1

Schematic diagram showing the relation of chemical kinetics and chemical modeling

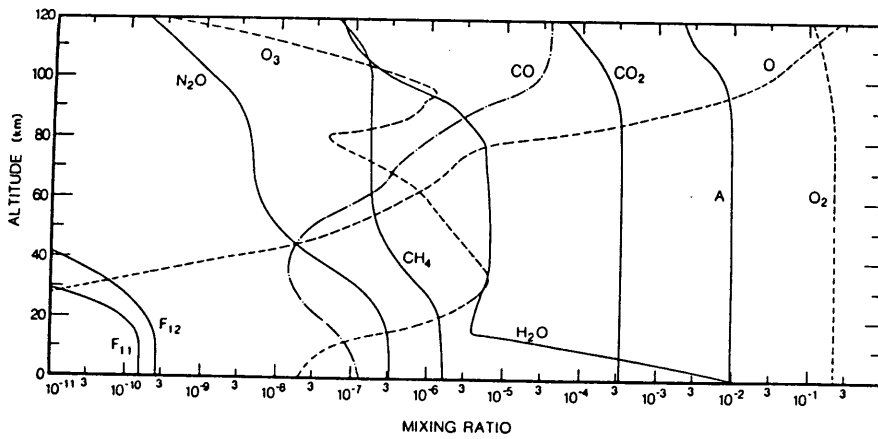to origin, evolution, and stability of planetary atmospheres.

Fig 2

Vertical profiles of mixing ratios of selected species in the terrestrial atmosphere at mid-latitude at equinox.

TABLE 1

Solar-System Abundances of the First 35 Elements, Based on Meteorites (Atoms/10^6 Si)

Element	Abundance
1 H	2.79×10^{10}
2 He	2.72×10^9
3 Li	57.1
4 Be	0.73
5 B	21.2
6 C	1.01×10^7
7 N	3.13×10^6
8 O	2.38×10^7
9 F	843
10 Ne	3.44×10^6
11 Na	5.74×10^4
12 Mg	1.074×10^6
13 Al	8.49×10^4
14 Si	1.00×10^6
15 P	1.04×10^4
16 S	5.15×10^5
17 Cl	5240
18 Ar	1.01×10^5
19 K	3770
20 Ca	6.1×10^4
21 Sc	34.2
22 Ti	2400
23 V	293
24 Cr	1.35×10^4
25 Mn	9550
26 Fe	9.00×10^5
27 Co	2250
28 Ni	4.93×10^4
29 Cu	522
30 Zn	1260
31 Ga	37.8
32 Ge	119
33 As	6.56
34 Se	62.1
35 Br	11.8

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Figure 1 gives the intellectual framework in which our field of study is imbedded. The unifying theme that ties the planets in the solar system is "origin" — we all share a common origin, about 5 billion years ago. The subsequent divergence in the solar system is attributed to evolution. Now the time rate of change becomes crucial and this is where the chemical cycles and their kinetic rates play a pivotal role. The fact that a certain reaction proceeds in a microsecond rather than in a billion years has the most profound consequences for the speciation observed in planetary atmospheres. However, the purpose of science is not just to reconstruct the past or to explain the present. It has a more aggressive motive. That is, to predict the future. Thus, we are deeply interested in studying the response of atmospheres to perturbations, i.e., the stability (chemical and climatic) of atmospheres. The exercise is more than academic, because we now live on a planet whose composition we seriously perturbing in an irreversible fashion. The answer to the questions we ask will have immediate impact on our welfare and style of living.

In the following sections, I will highlight the current chemical modeling efforts in planetary atmospheres from the perspective described in Figure 1, with emphasis on problems that present new challenges and opportunities to chemical kinetics.

EARTH

Earth is a planet and comparative studies between the terrestrial atmosphere and planetary atmospheres are interesting for at least two reasons. First, although the chemical species and their interactions in planetary atmospheres exhibit bewildering richness and variety, we note with satisfaction that underneath this apparent diversity is a pattern of simplicity, order, and unity. The chemical cycles that are important in one planetary atmosphere may also be important in other planetary atmospheres (as will be seen in subsequent sections). Second, current modeling of the terrestrial atmosphere is strongly motivated by the need to answer two very important questions: How stable is the ozone layer to anthropogenic perturbations (chemical stability, see Fig. 1)? How stable is the global climate in response to a doubling of CO_2 concentration in the atmosphere (climatic stability, see Fig. 1)? These questions have analogs in planetary atmospheres, where the physical and chemical parameters are extended over a much wider range.

The principal constituents of the Earths atmosphere are listed in Table 2. The vertical profiles of these species are presented in Figure 2. A primary focus of photochemical modeling in the terrestrial atmosphere is stratospheric O_3, formed by the photolysis of O_2,

$$O_2 + h\nu \rightarrow O + O \qquad (R1)$$

TABLE 2

The composition of dry air

Molecule	Fraction by volume in the troposphere	Comments
N_2	7.8084×10^{-1}	Photochemical dissociation high in the ionosphere; mixed at lower levels
O_2	2.0946×10^{-1}	Photochemical dissociation above 95 km; mixed at lower levels
A	9.34×10^{-3}	Mixed up to 110 km; diffusive separation above
CO_2	3.45×10^{-4}	Slightly variable; mixed up to 100 km; dissociated above
CH_4	1.6×10^{-6}	Mixed in troposphere; dissociated in mesosphere
N_2O	3.5×10^{-7}	Slightly variable at surface; dissociated in stratosphere and mesosphere
CO	7×10^{-8}	Variable photochemical and combustion product
O_3	$\sim 10^{-8}$	Highly variable; photochemical origin
$CFCl_3$ and CF_2Cl_2	$1-2 \times 10^{-10}$	Industrial origin; mixed in troposphere, dissociated in stratosphere

$$O + O_2 + M \rightarrow O_3 + M \tag{R2}$$
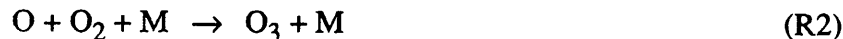
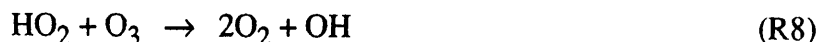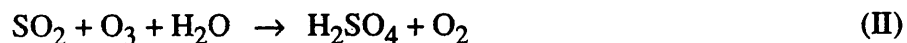In a pure oxygen atmosphere, O_3 is removed by reacting with O,

$$O_3 + O \rightarrow 2O_2 , \tag{R3}$$

with kinetic rate coefficient $k_3 = 8.0 \times 10^{-12} e^{-2060/T}$ cm^3 s^{-1}. At stratospheric temperatures (~250 K) $k_3 = 2.1 \times 10^{-15}$ cm^3 s^{-1}. This is a very slow reaction indeed. It should be noted that if k_3 were as high as 1×10^{-11} cm^3 s^{-1}, we would have an ozone layer about 1% of the current layer, and all the anthropogenic perturbations would be utterly trivial. However, because the pure oxygen reactions are so inefficient for destroying O_3, this gives rise to a number of catalytic mechanisms for removing O_3,

$$O_3 + X \rightarrow XO + O_2 \tag{R4}$$

$$XO + O \rightarrow O_2 + X \tag{R5}$$

$$\text{net} \quad O_3 + O \rightarrow 2O_2 , \tag{I}$$
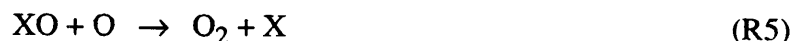
where X = OH, NO, ClO, or BrO. The reactive species "X" are supplied by source molecules in the troposphere such as H_2O, CH_4, N_2O, $CFCl_3$, CF_2Cl_2, CH_3Cl, CH_3Br. Since the tropospheric concentrations of CH_4, N_2O, $CFCl_3$, CF_2Cl_2, and CH_3Br are increasing due to industrial and agricultural activities, this would result in a depletion of the O_3 layer. The consequences can be quantitatively predicted using measured rate coefficients for the appropriate reactions. This predictive capability of current models lead M.B. McElroy to announce "Give us the perfect rate constants, and we will compute the perfect answer." It is a triumph of chemical kinetics and photochemical models that there is satisfactory agreement between the observations and models.

I will not say more about CO_2 and climatic change mainly because CO_2 is regulated by ocean chemistry and biochemistry. This is still chemical kinetics in a generalized sense, but it is remote from this community. I will, however, say something about photochemical aerosols and their impact on climate. Volcanoes inject large quantities of SO_2 into the stratosphere, where it is oxidized by

$$SO_2 + OH \rightarrow SO_3 + H \tag{R6}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{R7}$$

$$HO_2 + O_3 \rightarrow 2O_2 + OH \tag{R8}$$

$$SO_3 + H_2O + M \rightarrow H_2SO_4 + M \tag{R9}$$

$$SO_2 + O_3 + H_2O \rightarrow H_2SO_4 + O_2 \qquad \text{(II)}$$

(Note that HO_x is used as catalyst and not consumed. The amount of H_2O consumed is negligible.) The presence of this photochemical aerosol can affect the UV radiation field in the stratosphere and troposphere, and the thermal radiation budget of the atmosphere. The current kinetics suggests that the oxidation of SO_2 to sulfate is fairly rapid, and aerosol formation is completed in less than three months. There are indications that these aerosols may provide sites for heterogeneous reactions in the stratosphere, such as denitrification, and decomposition of $ClONO_2$ into more reactive species such as

$$ClONO_2 + H_2O \xrightarrow{\text{aerosol}} HOCl + HNO_3 \text{ (sequestered)} \qquad \text{(R10)}$$
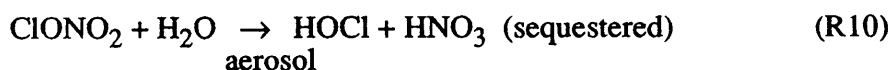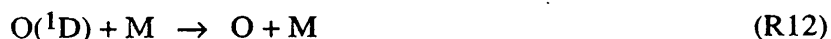
analogous to what is believed to be taking place in the Antarctic O_3 hole in springtime. I would like to point out that the study of heterogeneous reactions is the frontier of chemical kinetics, and these reactions now appear to be important in planetary atmospheres and the solar nebula.

MARS

The composition of the atmosphere of Mars is given in Table 3. CO_2 is the principal constituent, followed by N_2, Ar, H_2O, O_2, CO, and O_3. In the upper atmosphere (~100 km), H, O, as well as ionic species have been detected. The atmosphere is thin, with surface pressure equal to 5.5 mb (4.2 Torr). The mean surface temperature is 220 K, close to the equilibrium temperature of 216 K. (This means that there is no "greenhouse effect" to make the surface warmer.)

The central theme of the photochemistry of the Martian atmosphere is CO_2 stability. The problem can be stated very simply as follows. CO_2 photolyzes readily with absorption of UV radiation $\lambda < 2300$ Å,

$$CO_2 + hv \rightarrow CO + O(^1D) \qquad \text{(R11a)}$$

$$\rightarrow CO + O \qquad \text{(R11b)}$$

$$O(^1D) + M \rightarrow O + M \qquad \text{(R12)}$$

Regardless of the initial state of O in R11, the ultimate product is always CO and O in the ground state (^3P). The recombination of CO and O is spin forbidden

$$CO + O + M \rightarrow CO_2 + M \qquad \text{(R13)}$$

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TABLE 3

Principal Constituents in the Martian Atmosphere

Species	Volume mixing ratio
CO_2	0.9532
N_2	2.7×10^{-2}
A	1.6×10^{-2}
H_2O	3.3×10^{-3}
O_2	1.3×10^{-3}
CO	7×10^{-4}
O_3	5×10^{-8}

Table 4

Comparison of some important features of the stratospheres of Earth and Venus.

Feature	Earth	Venus
Altitude (km)	20–40	60–80
Pressure (mbar)	100–5	300–5
Temperature (K)	200–250	270–200
Mixing ratios of major constituents		
N_2	78.1 percent	3–4 percent
O_2	21.0 percent	$< 1 \times 10^{-6}$
Ar	0.93 percent	0.01 percent
CO_2	0.03 percent	96 percent
Mixing ratios of minor constituents		
Total chlorine	2.3×10^{-9}	4×10^{-7}
Total sulfur	$\sim 1 \times 10^{-9}$	$\sim 2 \times 10^{-6}$
Total NO_x	2×10^{-8}	$\leq 3 \times 10^{-8}$
Water	$\sim 5 \times 10^{-6}$	$1\text{–}30 \times 10^{-6}$
Methane	$\sim 1 \times 10^{-6}$	~ 0
Hydrogen	0.5×10^{-6}	Unknown*
N_2O	0.25×10^{-6}	~ 0

with rate coefficient $k_{13} = 6.5 \times 10^{-33}\, e^{-2184/T}\, cm^6\, s^{-1}$. At 220 K, $k_{13} = 3.2 \times 10^{-37}\, cm^6\, s^{-1}$, a very slow rate constant indeed. The challenge then is to explain the low abundances of CO and O_2 in Table 3, since they could all be generated in less than 10^3 years. The resolution of the problem lies in the trace amount of H_2O in the atmosphere as listed in Table 3. Photolysis of H_2O produces OH and H radicals (HO_x), which catalyze the recombination of CO and O,

$$CO + OH \rightarrow CO_2 + H \tag{R14}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{R15}$$

$$O + HO_2 \rightarrow OH + O_2 \tag{R16}$$

$$net \quad CO + O \rightarrow CO_2 \tag{III}$$

The results of a photochemical modeling incorporating the chemical cycle (III) are shown in Figure 3. Three things are noteworthy: (a) The stability problem was solely "created" by the fact that k_{13} is so small. If k_{13} were as large as $1 \times 10^{-31}\, cm^6\, s^{-1}$, the direct recombination of CO and O could account for the low concentrations of CO and O_2 on Mars, and there is no need to invent cycle III. (b) This cycle, first identified for the Martian atmosphere, is important in the terrestrial mesosphere and thermosphere. The crucial reaction CO + OH is known to be important also in the terrestrial troposphere and the atmosphere of Titan. (c) The abundance of the reactive radical OH in the atmosphere is of the order of 10^5 molecules cm^{-3}, and yet it exerts a major control over the composition of this atmosphere via catalytic cycle (III). This is an illustration of the beauty, subtlety, and extraordinary power of photochemistry.

The field of Martian photochemistry reaches its apex through the early work of Hunten and the later classic studies of McElroy and Donahue, with kinetics data on HO_x chemistry being supplied by DeMore and Kaufman. Since HO_x chemistry is a very well defined subject nowadays, it is hard to envision any breakthrough, except perhaps for one loose end. The reaction

$$H + HO_2 \rightarrow 2OH \tag{R17a}$$

$$\rightarrow H_2O + O \tag{R17b}$$

$$\rightarrow H_2 + O_2 \tag{R17c}$$

has been well studied. The rate constant $k_{17} = k_{17a} + k_{17b} + k_{17c} = 8.1 \times 10^{-11}$ is known to within 30% with no temperature dependence. However, the branch R17c is poorly known:
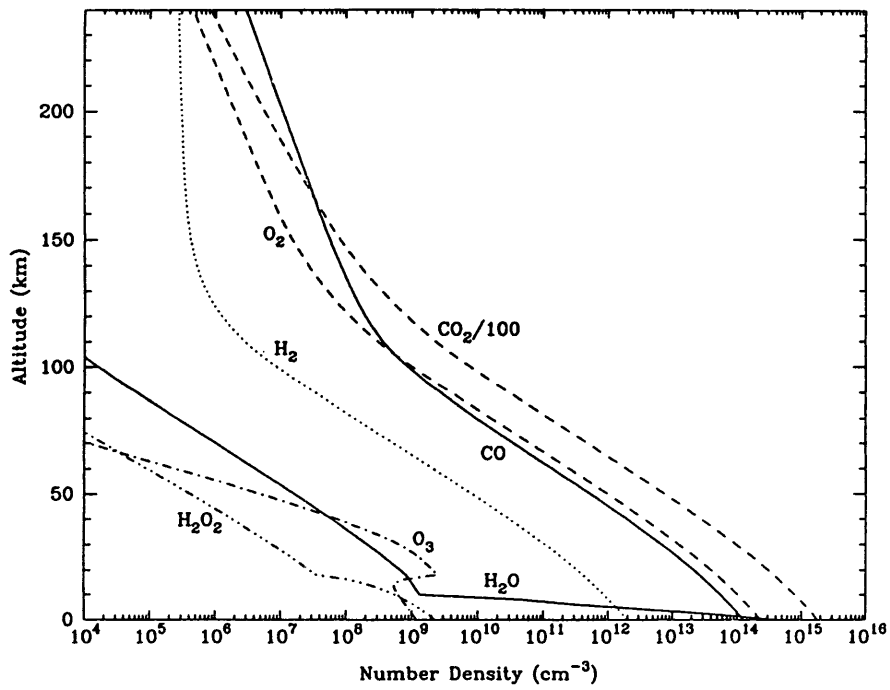
Fig 3
Vertical profiles of concentrations of selected major species in the Martian atmosphere.
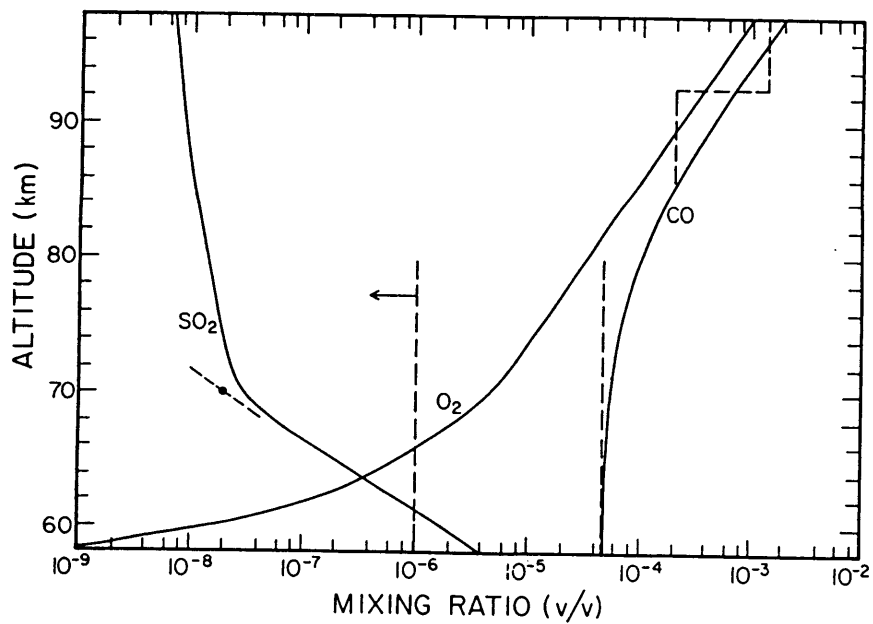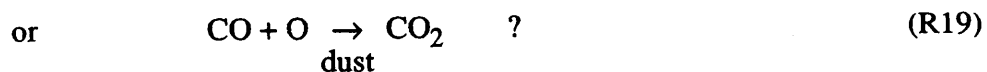

Fig 4
Same as Figure 3 for Venus.

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$k_{17c}/k_{17} = 0.08 \pm 0.04$. This branch is important for the evolution of the Martian atmosphere because it is the primary source of H_2, and H_2 is the major carrier of hydrogen from the surface to the exosphere to fuel the escape of hydrogen from Mars (H_2O does not reach the top of the atmosphere due to condensation at high altitudes). A better determination of this branch of R17 would constrain the escape rate of hydrogen from Mars. Incidentally, this branch also has an impact on the HO_x chemistry in the terrestrial mesosphere and the escape of hydrogen.

Recent revival in our interest for Martian photochemistry (after the field was perfected and closed by the brilliant pioneers) was motivated by progress in heterogeneous chemistry associated with the Antarctic ozone hole. It was recognized that ice particles (H_2O) could denitrify the Martian atmosphere, and that on average, the molecules in the Martian atmosphere collide with a dust grain (mainly silicate) every 10^3 sec. Therefore, heterogeneous chemistry may play a hitherto unsuspected role in the Martian atmosphere. Is it possible that

$$N_2O_5, NO_3 + ice \rightarrow HNO_3 \qquad \text{(R18)}$$

$$\text{or} \qquad CO + O \underset{dust}{\rightarrow} CO_2 \quad ? \qquad \text{(R19)}$$

Is it possible to sequester large amounts of NO_x on the surface of Mars via R18? This is a unique atmosphere in the sense that the "surface" extends into the atmosphere (up to 60 km) via the ubiquitous Martian dust. These questions can only be answered by a series of well designed laboratory experiments on the kinetics of the above reactions on ice and dust grains.
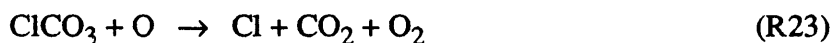

VENUS

Although the surface of Venus is 95 bars and at 750 K, it is of little interest to photochemistry due to the lack of UV photons. The part of the atmosphere of Venus that is most interesting to us is the stratosphere region, where the physical conditions are comparable to the terrestrial stratosphere. As shown in Table 4, the chemical composition also has striking similarity to the Earth's due to the presence of chlorine and sulfur on both planets.
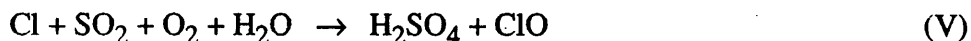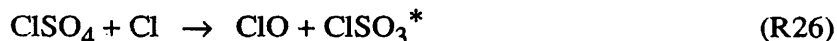
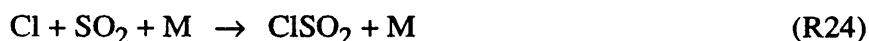Since the atmosphere is primarily composed of CO_2, the stability problem first discussed on Mars is more serious here. The mixing ratios of CO and O_2 are even lower than those on Mars. Catalysis by chlorine was finally recognized as the key to the resolution of the stability problem. The atmosphere contains 4×10^{-7} HCl, which readily photolyzes in the UV,

$$HCl + h\nu \rightarrow H + Cl \qquad \text{(R20)}$$

releasing the reactive Cl radical. Subsequent reactions may be summarized by the cycle

$$Cl + CO + M \;\rightarrow\; ClCO + M \tag{R21}$$

$$ClCO + O_2 + M \;\rightarrow\; ClCO_3 + M \tag{R22}$$

$$ClCO_3 + O \;\rightarrow\; Cl + CO_2 + O_2 \tag{R23}$$

$$\text{net} \quad CO + O \;\rightarrow\; CO_2 \tag{IV}$$

The stratosphere of Venus also contains huge amounts (by terrestrial standards, see Table 4) of SO_2. Oxidation of SO_2 to sulfate is again readily catalyzed by Cl

$$Cl + SO_2 + M \;\rightarrow\; ClSO_2 + M \tag{R24}$$

$$ClSO_2 + O_2 + M \;\rightarrow\; ClSO_4 + M \tag{R25}$$

$$ClSO_4 + Cl \;\rightarrow\; ClO + ClSO_3^* \tag{R26}$$

$$ClSO_3^* \;\rightarrow\; Cl + SO_3 \tag{R27}$$

$$SO_3 + H_2O + M \;\rightarrow\; H_2SO_4 + M \tag{R9}$$

$$Cl + SO_2 + O_2 + H_2O \;\rightarrow\; H_2SO_4 + ClO \tag{V}$$

Note that the oxidation of SO_2 provides an effective sink for O_2 on Venus. The photochemical aerosols generated by (V) have profound consequences for the planet. First, they completely envelope the planet with a white scattering cloud, increasing the planetary albedo and filtering out most UV radiation. Second, they dry the upper atmosphere (since H_2SO_4 is hydroscopic).

Figure 4 shows the vertical profiles of the most important minor species in the stratosphere. The photochemical model is based on the chemistry summarized by Scheme IV. Needless to say, much of the kinetics associated with cycles IV and V remains to be studied in detail. In general, the photochemistry of sulfur species is poorly known, due in part to the difficulty of handling sulfur compounds in the laboratory. Major uncertainty exists, for example, on the quantum yield of predissociation for SO

$$SO + hv \;\rightarrow\; SO^* \;\rightarrow\; S + O \tag{R28}$$

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This molecule has recently been detected on Venus. It is produced from SO_2 photolysis. The analogous reaction (R1) predissociates 100% in the Schumann-Runge bands. However, the lifetime of SO^* is nanoseconds, whereas that for O_2^* is picoseconds. Therefore, it appears that the quantum yield for photolysis may be considerably less than unity. A careful laboratory experiment monitoring the fluorescence of SO^* would be able to determine the quantum yield. Why is this reaction important? It can drive a cycle for breaking the O–O bond,

$$SO + h\nu \rightarrow S + O \qquad\qquad (R28)$$

$$S + O_2 \rightarrow SO + O \qquad\qquad (R29)$$

$$net \quad O_2 \rightarrow 2O \qquad\qquad (VI)$$

In addition, R28 is a source of S atoms, and ultimately of polysulfur (S_x), which is a leading candidate for the unidentified UV absorber on Venus. (A similar mechanism using S_x has been suggested for shielding the primitive Earth from UV radiation — sort of a primordial UV shield without O_3.) I will leave it as a challenge to the laboratory chemical kineticist to settle this issue.

JOVIAN PLANETS

The chemistry of the giant planets, Jupiter, Saturn, Uranus, and Neptune, has a distinct character of their own. Tables 5a,b summarize the composition of the atmospheres of Jupiter and Saturn, respectively. Very little is known about the atmospheres of Uranus and Neptune and this knowledge is summarized in a comparative study with the other planets in Table 5c. The chemistry is completely dominated by the huge amount of H_2 present in these atmospheres. The abundance of other elements roughly follows that of cosmic abundance (see Table 1).

The questions of chemical stability and evolution, which are the compelling themes in the atmospheres of the inner planets, do not concern us here. The giant planets have undergone little or no evolution since formation, and whatever disequilibrium in speciation produced in the upper atmosphere is ultimately restored to thermodynamic equilibrium in the planetary interiors, where the pressures and temperatures exceed 1 kilobar and 10^3 K, respectively. Therefore, the observed chemical composition of these atmospheres represents a "tug-of-war" between photochemistry (driven by the sun) and thermodynamics (drive by interior heat left over from the time of formation of the planets). A schematic diagram showing the recycling of hydrocarbons between the upper atmosphere and the planetary interior is shown in Figure 5a for Saturn, but this figure applies to all the other giant planets.

TABLE 5a

Composition of Jupiter's Atmosphere

Constituent	Volume mixing ratio
H_2	0.89
He	0.11
CH_4	1.75×10^{-3}
C_2H_2	2×10^{-8}
C_2H_4	7×10^{-9}
C_2H_6	5×10^{-6}
CH_3C_2H	2.5×10^{-9}
C_6H_6	2×10^{-9}
CH_3D	3.5×10^{-7}
NH_3	1.8×10^{-4}
PH_3	6×10^{-7}
H_2O	$1-30 \times 10^{-6}$
GeH_4	7×10^{-10}
CO	$1-10 \times 10^{-9}$

TABLE 5b

Composition of Saturn's Atmosphere

Constituent	Volume mixing ratio
H_2	0.94
He	0.06
CH_4	1.75×10^{-3}
C_2H_2	1.1×10^{-7}
C_2H_6	4.8×10^{-6}
CH_3D	2.3×10^{-7}
PH_3	2×10^{-7}
CO	2×10^{-9}
H_2O	1×10^{-7}

Table 5c

OBSERVED ABUNDANCES OF SIMPLE HYDROCARBONS

	CH_4	C_2H_6	C_2H_2
Jupiter	1.75×10^{-3}	5×10^{-6}	2×10^{-8}
Saturn	1.76×10^{-3}	4.8×10^{-6}	1.1×10^{-7}
Titan	$1-3 \times 10^{-2}$	2×10^{-5}	2×10^{-6}
Uranus	$< 3 \times 10^{-6}$	$< 1 \times 10^{-8}$	8×10^{-9}
Neptune	$1-10 \times 10^{-3}$	2×10^{-6}	1×10^{-6}

Table 5d

GEOMETRIC ALBEDO AT 3075 Å

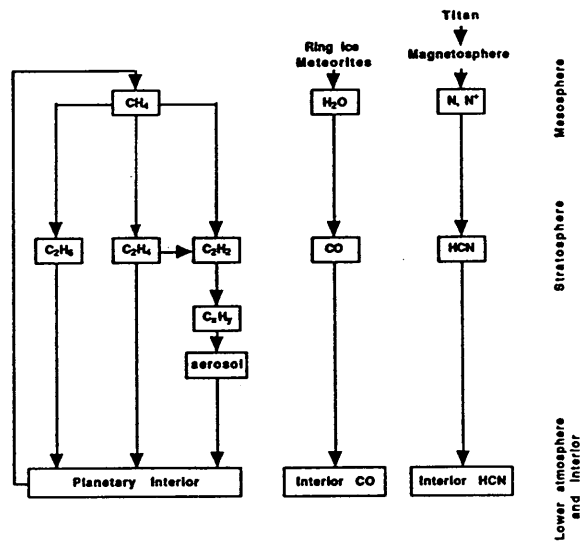|	
Jupiter	0.25
Saturn	0.3
Titan	0.054
Uranus	0.5
Neptune	0.5
Mars	0.15
Venus	0.3
Conservative Isotropic	0.69
Conservative Rayleigh Scattering	0.80

195

Fig 5a.

Schematic diagram showing the major chemical cycles in the atmosphere of Saturn.
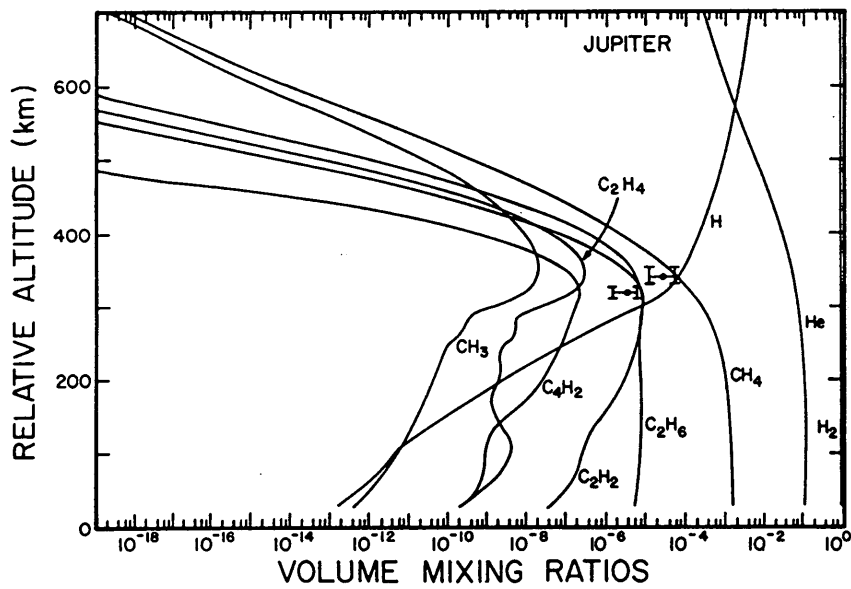

Fig 5b.

Same as Figure 3 for Jupiter.

The dominant theme of the chemistry of the outer solar system is organic synthesis. Since CH_4 is an abundant source molecule, its breakdown leads to a large number of simple organic compounds, such as C_2H_6, C_2H_4, and C_2H_2. Since the pioneering work of Strobel, the chemistry of CH_4 conversion to C_2 (containing two carbon atoms) compounds is fairly well understood. Figure 5b shows the results of a photochemical model for the simple hydrocarbons on Jupiter. But there remains the challenge to quantitatively account for the difference in C_2H_6 to C_2H_2 ratio in the outer solar system (see Table 5c). This ratio is predicted by current models is about unity, and should be compared with the observed values ~100 for Jupiter and Saturn.

The most important chemical input in the photochemical model is the rate coefficient for chemical reactions, $k(T, P)$. In general, this quantity is a function of temperature (T) and pressure (P). To be useful for application to planetary atmospheres, we must know $k(T, P)$ for the ambient atmospheric environments. Typical values for P varies from 1 to 10^{-9} bars, and T ranges from 300 K in the inner solar system to less than 100 K in the outer solar system. Since the bulk of chemical kinetics data is related to work on combustion (at higher temperature and pressure), it remains a challenge to extract useful information from the combustion literature and apply them to the planetary atmospheres. In addition to T and P dependence is the important evaluation of $k(T, P)$ for the different product channels. We have reasons to believe that the hydrocarbon chemistry may still be incomplete or improperly extrapolated to low temperatures. As most reactions involve transfer of an H atom, extrapolation of a rate constant based on activation energies measured at high temperatures may be disastrous due to the possibility of H atom tunnelling (because it is so small) at low temperatures.

But looking at Table 5d, we may perceive that Nature is hinting at a more imaginative solution to the C_2H_6/C_2H_2 ratio problem. We note that at 3075 Å, Jupiter and Saturn are quite dark whereas Uranus and Neptune are much brighter, and Titan is extremely dark (I also show Mars, Venus, and theoretical models for comparison). Something other than Rayleigh scattering is going on in these atmospheres. The UV absorption is believed to be caused by photochemical aerosols made from hydrocarbons (the Axel-Danielson dust). It is most likely that the hydrocarbon haze is made from C_2H_2 and not from C_2H_6 since we know that C_2H_2 but not C_2H_6 can polymerize in the laboratory experiments. Suppose there is a photopolymerization reaction that turn C_2H_2 into more complex hydrocarbons,

$$C_2H_2 + h\nu \rightarrow C_2H_2^* \qquad \text{(R30a)}$$

$$C_2H_2^* + C_2H_2 \rightarrow C_4H_4 \qquad \text{(R30b)}$$

$$C_2H_2^* + C_2H_4 \rightarrow C_6H_6 \qquad \text{(R30c)}$$

As the carbon number increases, the saturated vapor decreases, and the excess gas molecules would form aerosols. This would kill two birds with one stone. It provides a sink for C_2H_2, thus raising the value of the ratio C_2H_6/C_2H_2 in the model to agree with the observations, and at the same time create more UV opacity to explain the lower albedo of Jupiter and Saturn relative to Uranus and Neptune. The detailed chemical kinetics of C_2H_2 polymerization remains a challenge to the laboratory chemist. I would not be surprised if it turns out to be related to soot formation in combustion of hydrocarbons.

The presence of the ubiquitous Axel-Danielson dust in the outer solar system has a profound consequence on the climatology of these planets. A large amount of solar energy is absorbed by these aerosols, creating a thermal inversion. (A similar process takes place in the terrestrial stratosphere where UV radiation is absorbed by O_3.) The thermal inversion inhibits transport between the stratosphere and the troposphere. This means that the aerosols have an even longer lifetime in the stratosphere, absorbing more solar energy. Hence, the feedback is positive. One can imagine a clear and turbulent stratosphere with little aerosol content, and that would be allowed by the laws of chemistry and physics. Why Nature does not choose this particular solution for any planet in the outer solar system remains a mystery to me. I hope some brilliant kineticist or climatologist can take this challenge one day.

A planet like Saturn is surrounded by objects with large volatile content (such as H_2O in the rings and N_2 from Titan). The planet serves as the ultimate "garbage can" for the entire Saturnian system. The fate of these extraplanetary material in the upper atmosphere of Saturn is to be converted to the most stable molecules. As shown in Figure 5a, I believe that all oxygen and nitrogen species would wind up as CO and HCN, respectively. The chemistry is fairly well understood, thanks to the extensive research in combustion.

Now according to thermodynamics, the planetary interior is also a source of CO and HCN (produced as products of CH_4 and H_2O equilibrium, and NH_3 and CH_4 equilibrium, respectively). A sensitive issue arises as to the lifetimes of CO and HCN as they emerge from the region of thermodynamic equilibrium. It was conjectured that the lifetime of CO is determined by the following reactions,

$$4(H + CO + M \rightarrow HCO + M) \tag{R31}$$

$$HCO + HCO \rightarrow H_2CO + CO \tag{R32}$$

$$H + H_2CO + M \rightarrow CH_3O + M \tag{R33b}$$

$$CH_3O + HCO \rightarrow CH_3OH + CO \tag{R34}$$

$$CH_3OH + H \rightarrow CH_3 + H_2O \tag{R35}$$

$$CH_3 + HCO \rightarrow CH_4 + CO \qquad \text{(R36)}$$

$$CO + 6H \rightarrow H_2O + CH_4 \qquad \text{(VII)}$$

The crucial part of Scheme VII is the reaction R33b forming the methoxy radical. Actually the dominant path of R33 is

$$H + H_2CO \rightarrow H_2 + HCO \qquad \text{(R33a)}$$

which does not lead to the conversion of the carbonyl bond to a single bond (as in CH_3O). However, if k_{33b}/k_{33a} were as high as 1%, it would be significant. Note that it is always exceedingly hard to convert CO to CH_4 (because C–O is one of the strongest bonds in chemical kinetics). If this scheme works on the giant planets, it may also be important in the solar nebula, where a similar problem exists for converting CO to CH_4. Again, the challenge is to the laboratory kineticist.

In the lower atmosphere of Jupiter and Saturn there is interesting photochemistry involving NH_3, PH_3, GeH_4, and AsH_3. Very little is known about the chemistry of these compounds. We do not know, for example, whether P_2H_4 (produced from PH_3 photolysis) and N_2H_4 (produced from NH_3 photolysis) are stable to UV irradiation in the form of ices. There may be "mixed" compounds involving C–P and P–N bonds that we currently know little about. I will only conclude that whoever leads a laboratory investigation in studying these species will be pioneering the field for planetary atmospheres.

TITAN

Titan occupies a unique position in the photochemistry of the solar system. It is a moon of Saturn with a massive atmosphere. The important physical parameters and compositional data are summarized in Table 6 (see also Figs. 6b-d). Note that the surface pressure is 1.5 bar. (This is a lot more N_2 than at the Earth's surface because T is so low.) In many ways Titan resembles a small planet in the inner solar system rather than a kin of the giant planets family. In terms of chemical composition, Titan's atmosphere is intermediate between the highly oxidized atmospheres in the inner solar system and the Jovian planets with massive amounts of H_2. Both reducing species H_2, CH_4, and oxidized species CO_2 are present. Why is Titan so interesting?

Simplicity underlying complexity. The large number of chemical species listed in Table 6 can all be derived from three parent molecules, N_2, H_2O, and CH_4 using known chemical kinetics. The chemical network connecting these species is presented in Figure 6a. Due to the

Table 6

Titan

Physical or Chemical Data

At the Surface (altitude $z = 0$):
 r_0 = distance to center = 2575 km
 g_0 = gravity = 135 cm s^{-2}
 P_0 = total pressure = 1.50 bar
 T_0 = temperature = 94 K
 n_0 = number density = 1.2×10^{20} cm^{-3}

Composition of the Troposphere (volume mixing ratio):
 $N_2 > 0.97$
 $CH_4 < 0.03$
 $H_2 = 0.002$

At the Tropopause ($z = 45$ km):
 $P = 130$ mbar
 $T = 71.4$ K
 $n = 1.1 \times 10^{19}$ cm^{-3}

Composition of the Stratosphere (volume mixing ratio):
 $CH_4 = 1-3 \times 10^{-2}$
 $H_2 = 2.0 \times 10^{-3}$
 $C_2H_6 = 2 \times 10^{-5}$
 $C_2H_2 = 2 \times 10^{-6}$
 $C_2H_4 = 4 \times 10^{-7}$
 $C_3H_8 = 2-4 \times 10^{-6}$
 $CH_3C_2H = 3 \times 10^{-8}$
 $C_4H_2 = 10^{-8}-10^{-7}$
 $HCN = 2 \times 10^{-7}$
 $HC_3N = 10^{-8}-10^{-7}$
 $C_2N_2 = 10^{-8}-10^{-7}$
 $CO = 6 \times 10^{-5}$

 $CO_2 = 1.5 \times 10^{-9}$
 $H_2O < 1 \times 10^{-9}$
 CH_3D detected, abundance not available

Composition of Mesosphere and Thermosphere:
 $N_2 = 2.7 \times 10^{8}$ cm^{-3} at $z = 1280$ km
 $CH_4 = 1.2 \times 10^{8}$ cm^{-3} at $z = 1140$ km
   (mixing ratio = 0.08)
 C_2H_2 mixing ratio 1%-2% at $z = 840$ km
 H atoms: disk-averaged Lyα airglow ~ 500 R[a]

Haze Layers:
 optical haze $z = 300$ km
 UV haze $z = 400$ km

Observed isotopic ratio of deuterium to hydrogen, normalized with respect to the Jovian standard (1.6×10^{-5}).

Planetary body (species used)	D/H
Jupiter (CH3D)	1
Saturn (CH3D)	1
Uranus (CH3D)	6
Titan (CH3D)	30
	10
Comet Halley (HDO)	4-30
Earth (HDO)	10
Venus (HD, HDO)	1000
Mars (HDO)	60
Meteorite (organic)	5-100

Table 7b

Fractional abundances by volume of the major carbon species in planetary atmospheres.

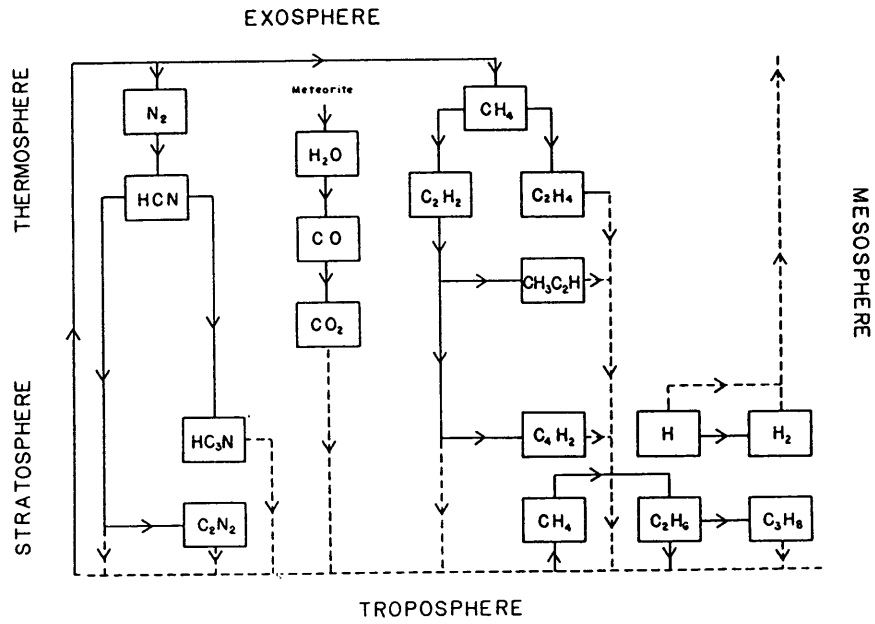| Planet	CO2	CO	CH4
Earth	3.2×10^{-4}	1.7×10^{-7}	1.5×10^{-6}
Mars	0.95	7×10^{-4}	—
Venus	0.96	5×10^{-5}	—
Jupiter	—	2×10^{-9}	1.8×10^{-3}
Saturn	—	2×10^{-9}	4.5×10^{-3}
Titan	1.5×10^{-9}	6×10^{-5}	2×10^{-2}
Comet	4×10^{-2}	0.2	2×10^{-2}

EXOSPHERE

Fig 6a
Schematic diagram showing the relation between the parent molecules, N_2, CH_4, and

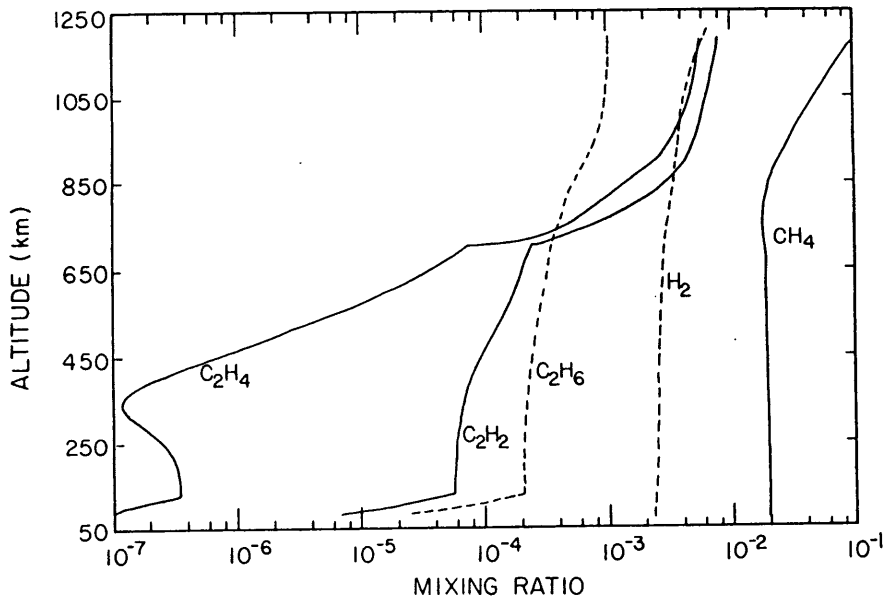H_2O and the photochemical products derived in a photochemical model.

Fig 6b
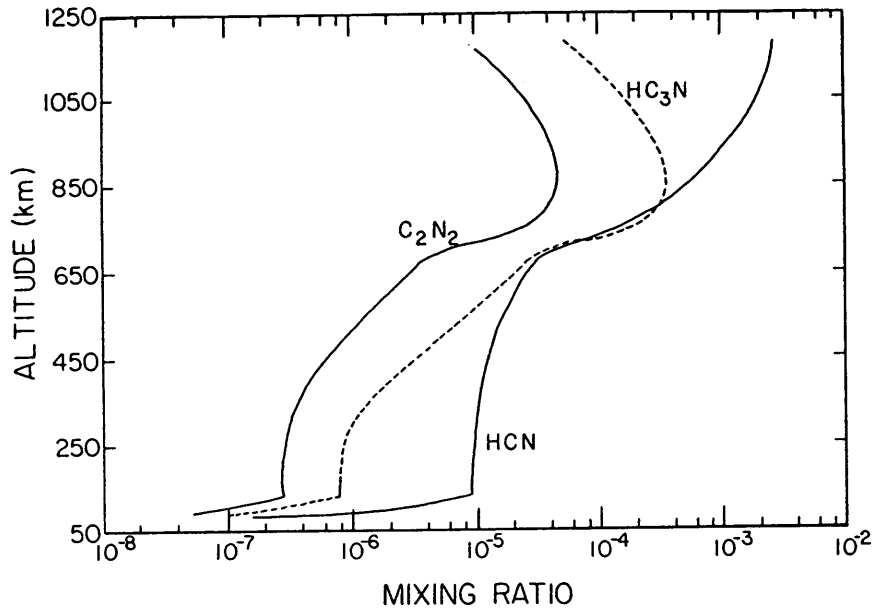Vertical profiles of the mixing ratios of the principal hydrocarbon species in the atmosphere of Titan.

Fig 6c

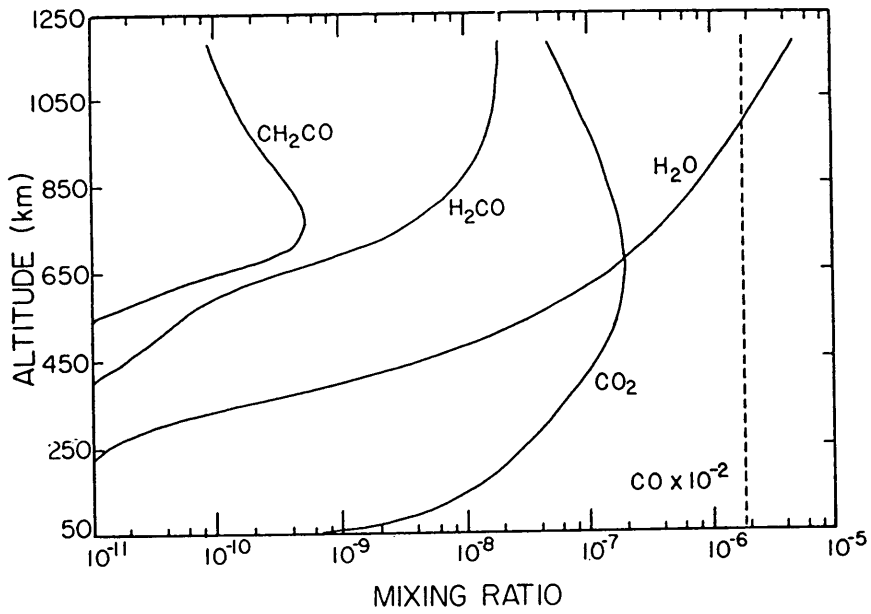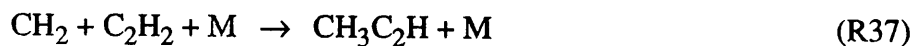Same as Figure 6b, for nitrogen bearing species.

Fig 6d

Same as Figure 6b, for oxygen bearing species.

unique ability of carbon to form complex compounds, we can generate more complex compounds from the simpler ones. For example:

$$CH_2 + C_2H_2 + M \rightarrow CH_3C_2H + M \qquad (R37)$$

Early work on this reaction suggests that R37 is a fast reaction. Recent work indicates that R37 is much slower (it is spin forbidden). Why is it so easy to synthesize higher hydrocarbons on Titan? There is a beautifully simple kinetic reason. UV sunlight provide a source of radicals. The recombination of organic radicals to form complex organic compounds is extremely rapid in a place like Titan. For example, the reaction
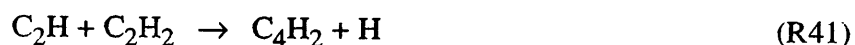
$$C_2H_5 + CH_3 + M \rightarrow C_3H_8 + M \qquad (R38)$$
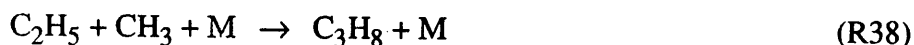
is believed to have a three body rate constant $k_{38} = 5.6 \times 10^{-22}$ cm^6 s^{-1} in Titan's atmosphere (the two-body limit is "normal", $k = 4.2 \times 10^{-11}$ e$^{-200/T}$ cm^3 s^{-1}). Now this is a fantastically large rate constant compared with that for

$$O + O_2 + M \rightarrow O_3 + M \qquad (R2)$$

$k_2 = 6 \times 10^{-34}$ cm^6 s^{-1} at 300 K. The reason for the enormous discrepancy between k_{41} and k_2 is contained in the framework of RRKM theory. A molecule like C_3H_8 has so many degrees of freedom that the energy of formation can be distributed over the tens of vibrational modes. Thus the intermediate complex can be stabilized, leading to the formation of C_3H_8. However, I should point out that the kinetic rates of very low pressures (10^{-3}–1 Torr) for associative reactions have not been well studied experimentally.

A great deal remains to be investigated in the chemical kinetics of Titan's atmosphere. The important reactions,

$$C_2H + H_2 \rightarrow C_2H_2 + H \qquad (R39)$$

$$C_2H + CH_4 \rightarrow C_2H_2 + CH_3 \qquad (R40)$$

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H \qquad (R41)$$

respectively, lead to photosensitized dissociation of H_2, CH_4, and polyacetylene chain propagation. There are major discrepancies (factors of 10) for the rate constants of the above reactions at room temperatures reported in the literature. At lower temperatures, appropriate for

the outer solar system, there is practically no information. This is an extremely unsatisfactory situation.

The quantum yield and fragmentation patterns of the hydrocarbons and the nitrile compounds are poorly known. For example, we do not accurately know the following yields as a function of wavelengths

$$C_2H_2 + h\nu \rightarrow C_2H + H \qquad \text{(R42a)}$$

$$\rightarrow C_2 + H_2 \qquad \text{(R42b)}$$

$$C_4H_2 + h\nu \rightarrow C_4H + H \qquad \text{(R43a)}$$

$$\rightarrow 2C_2H \qquad \text{(R43b)}$$

$$C_2N_2 + h\nu \rightarrow 2CN \qquad \text{(R44)}$$

Other compounds whose photofragmentation patterns remain to be determined include C_3H_8, C_4H_{10}, HC_3N, and C_4N_2.

Since Titan is a tiny planetary body carrying a massive atmosphere, the atmosphere is not stable both physically and chemically. Physically, hydrogen species and N atoms produced in exothermic reactions can escape from the satellite. Chemically there is an inexorable drive towards the synthesis of complex organic compounds, which are removed from the atmosphere by condensation at the tropopause, and ultimately on the surface. With the irreversible loss of hydrogen due to escape from the top of the atmosphere, recycling back to CH_4 is impossible. Therefore, the chemistry represents a one-way evolution towards species with heavier molecular weight and their permanent sequestering on the surface. For comparison, we note that H escapes from all the inner planets. Since H_2O is the obvious reservoir of hydrogen, this irreversible loss of hydrogen results in the accumulation of oxygen on these planets. This may be one reason why their atmospheres are so oxidizing. On Titan the physical and chemical environment is such that a molecule like CH_4 with H/C ratio of 4 is intrinsically unstable. Evolution would inevitably lead to the production of more sooty or tarry materials (of low H/C ratio).

The continuing chemical evolution of the atmosphere produces large amounts of dark photochemical aerosols. As can be seen in Table 5d, Titan is one of the darkest objects in the solar system in the UV, with geometric albedo less than 5% (geometric albedo (p) = brightness of planet at zero solar phase relative to a white disk of the same diameter. p = 2/3 for a white ping pong ball). A thick photochemical haze completely envelopes the satellite. The impact on the climatology of the stratosphere is similar to that of the O_3 layer on Earth, the dust on Mars, and the unidentified UV absorber (most probably polysulfur) on Venus. However, on Titan,

there is an even deeper chemical implication. The sequence of events leading to the current state of the atmosphere is as follows:

1. Photolysis of CH_4 in the mesosphere leads to a production of C_2H_2 and C_2H_4.

2. C_2H_2 abundance builds up in the stratosphere.

3. Photosensitized dissociation of CH_4 becomes important, producing C_2H_6, polymers, and aerosols.

4. Sunlight absorption by aerosols leads to thermal inversion, dynamic stability.

5. Stratosphere becomes more stable, resulting in a further increase of the abundances of higher hydrocarbons and leading back to step 3.

Therefore, in addition to a dynamical positive feedback discussed in the section "Jovian Planets", there is a strong chemical positive feedback in the generation of the hydrocarbon aerosols. And that is how we end up with such a dark body. Magic without magic results when chemical kinetics is coupled to all other processes in the atmosphere: radiation and dynamics. However, it is still mysterious to me why this particular planetary state is chosen, given Nature has many alternatives.

An intriguing observation reported by the Voyager UVS instrument is the detection of a high altitude (400 km) UV haze. It is probably created by the condensation of a complex hydrocarbon (such as a polyacetylene), but no one has sufficient kinetic information to predict such a haze layer in a photochemical model.

DEUTERONOMY

Again Nature has been kind in giving us deuterium as well as hydrogen. This is like Moses giving us the laws of God once in Exodus and once again in Deuteronomy (from Greek Deuteronomion, a second law, literally meaning "a copy of the law." Although I am not a scholar in ancient classics, I have no doubt that all these words: deuterium, deuteron, duo, deuce, duel, and duologue are derived from the same source with meaning associated with two, number two, second, and a copy of). Deuterium is, of course, "a copy of" hydrogen with nearly the same chemical properties. There is a difference due to mass, which allows us to trace and check the origin and evolution of planetary systems. Table 7a gives a compilation of D/H ratio in the solar system. An inspection of this Table enables us to assess how closely the various parts of the solar system are related to a common origin. It is convenient to divide the deuterium inventory in the solar system into three types: the primordial nebula gas (HD), the organics, and the ices (HDO and CH_3D). It is known that the water in hydrated silicates have D/H ratios close

to the terrestrial value. Suppose we consider a uniformitarian hypothesis that all ices in the solar nebula were enriched by the same factor (about 10) relative to the molecular hydrogen reservoir. (The kinetics of this fractionation has not been worked out.) This will have little effect on the observed D/H ratio on Jupiter and Saturn because of dilution by the massive H_2 atmospheres in these planets. However, on planetary bodies with large rocky cores, the isotopic signature will be preserved, and in some cases, may be further enhanced by subsequent planetary evolution. Such an enhancement has obviously occurred on Mars and Venus due to the preferential escape of H over D.

On Titan, preferential escape of H will apparently not work, because the gravity is so low that H and D will both escape. Therefore, in order to explain the large observed enrichment of D/H (relative to Saturn), we have to explore the possibility of a chemical enrichment such as a difference in the following reactions,

$$C_2H + CH_4 \rightarrow C_2H_2 + CH_3 \tag{R45}$$

$$C_2H + CH_3D \rightarrow C_2H_2 + CH_2D \tag{R46}$$

Since these are the primary sinks for CH_4 and CH_3D (more important than direct photolysis) a faster rate for R45 will result in an enrichment of CH_3D over CH_4 over geological time. However, reaction R46 has never been studied in the laboratory and this whole idea of chemical enrichment remains speculative. I would like to point out a similar idea is being pursued in the terrestrial atmosphere in trying to track down the sources of CH_4 (which is increasing) using $^{13}CH_4$. The analogous reactions in this case are

$$OH + CH_4 \rightarrow H_2O + CH_3 \tag{R47}$$

$$OH + {}^{13}CH_4 \rightarrow H_2O + {}^{13}CH_3 \tag{R48}$$
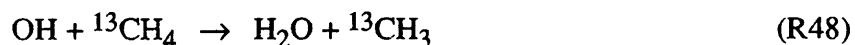
(These experiments are much harder to do because the difference between k_{47} and k_{48} is only 0.5–1.0%! Please try to study R45 and R46 first. The difference here is about 25%.)

I will conclude by pointing out what is behind this unity of chemical kinetics for the solar system. The reason, I think, lies in the fact that there is a common set of molecules that occur throughout the solar system. God gave us multiple copies of the same laws (multironomy). As an illustration of this idea, consider all the observed carbon species in planetary atmospheres summarized in Table 7b. Given one species, the laws demand that it be connected to the other species via chemical reactions. Indeed, as discussed in previous sections, some of the most interesting chemistry in the solar system involves changes in the oxidation state of the simple carbon species. The chemical pathways for the conversion of CH_4 to CO and CO_2 in an

oxidizing atmosphere are for the most part known. The reverse process, the reduction of CO to CH_4 in an H_2 atmosphere is, however, poorly understood. This is, of course, the key to organic synthesis in a mildly reducing atmosphere. One such scheme (VII) has been proposed and it is up to the kineticist to face the challenge of proving or disproving it. The reward is a deep satisfaction that this scheme works in all the Jovian planets, solar nebula, and even the primitive Earth's atmosphere.

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