CALCULATION OF THE VAPOR PRESSURE AND HEATS OF VAPORIZATION

AND SUBLIMATION OF LIQUIDS AND SOLIDS

ESPECIALLY BELOW ONE ATMOSPHERE PRESSURE


by


WALDEMAR T. ZIEGLER

⸢and others⸥


Project No. A-460

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⌐Letter Report⌐.

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   No. 1-3 by Ziegler, W. T.; Mullins, J. C.; and Kirk, B. S.
     No. 1.    I.  Ethylene. June 2, 1962.
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           III.  Methane. August 31, 1962.

# GEORGIA INSTITUTE OF TECHNOLOGY
## ENGINEERING EXPERIMENT STATION
### ATLANTA. GEORGIA

January 7, 1960

Contracting Officer
National Bureau of Standards
Boulder, Colorado

Attention:  Mr. Russell B. Scott
            Cryogenic Engineering Laboratory

Subject:  Surface area and nitrogen gas adsorption isotherm measurements
          on two adsorbents and four ortho-para hydrogen conversion
          catalysts submitted by Mr. T. M. Flynn, Cryogenic Engineering
          Laboratory, for study under Contract CST-7238 between the
          National Bureau of Standards, Boulder, Colorado and the
          Engineering Experiment Station, Georgia Institute of Technology,
          Atlanta, Georgia.  (Engineering Experiment Station Project No. A-460.)

Gentlemen:

Measurements have been made of the nitrogen gas adsorption isotherms and
surface areas of two adsorbents (an activated carbon and a high-capacity
silica gel) and four ortho-para hydrogen conversion catalysts received from
Mr. T. M. Flynn of the Cryogenic Engineering Laboratory on October 9, 1959.
These measurements and calculations were carried out by Mrs. Miriam Gandy under
the supervision of Dr. Clyde Orr, Jr., Director of the Micrometrics Laboratory
of the Engineering Experiment Station.

The nitrogen gas adsorption isotherms were measured in a conventional
apparatus at approximately $77^{\circ}$K. Before beginning each run the samples were
activated by simultaneous heating and evacuation according to the schedule
given in Table I, the final system pressure being about $10^{-4}$ mm Hg. Also shown
in Table I are the weights of the samples used in the measurements and the re-
sults of the surface area determinations.

The results of the nitrogen adsorption isotherm measurements are shown in
Table II. Table II shows for each sample the actual adsorption temperature,
the equilibrium adsorption pressure, P, the relative pressure, $P/P_s$, where $P_s$
is the vapor pressure of liquid nitrogen at the adsorption temperature, and
the volume, V, of nitrogen gas adsorbed, expressed in $cm^3$ at $0^{\circ}$C and 760 mm Hg
per gram of adsorbent. The adsorption temperatures are believed to be correct
to about $0.1^{\circ}$C. The volume adsorbed has been corrected for the dead-space in
the apparatus and the pores of the adsorbent and for the fact that nitrogen is
not a perfect gas. The dead space volume was determined by admission of a
measured volume of helium gas to the activated adsorbent at $77^{\circ}$K. The helium

Table I

Surface Area Measurements

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| Sample Identification | Sample wgt. | Activation | | Surface area[*] |
| | | Hours heated | Average temp. $^{\circ}F$ | (Meters)$^2$ per gm. |
|---|---|---|---|---|
| Activated Carbon Barnebey-Cheney Adsorbite, Type IGI 8/10 mesh | 1.8560 | 19 | 272 | 903.7 |
| Silica Gel "Davison High Capacity" (NBS-PUR) Drum 2 | 3.409 | 18 | 272 | 711.9 |
| Tla[**] | 4.585 | 17 | 337 | 185.4 |
| Tla | 2.208 | 18 | 270 | 186.2 |
| Tlb | 2.388 | 19 | 305 | 186.3 |
| Tlc | 2.707 | 16 4 | 169 337 | 183.5 |
| Tld | 2.928 | 17 | 337 | 174.3 |

_____

[*] Using $15.8A^2$ as the area of the nitrogen molecule

[**] Tla was activated at a lower temperature to examine the effect of activation temperature on the surface area measurement.

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was assumed to be a perfect gas. The helium gas was removed by heating and evacuation for about 20 minutes before admission of the nitrogen gas.

The surface area was computed from the adsorption measurements using the Brunauer-Emmett-Teller method. A discussion of the theory and technique of the BET method is given by Orr and Dalla Valle, Fine Particle Measurement MacMillan, New York, 1959, Chap. 7.) This computation entails the use of the equation

$$\frac{x}{V(1-x)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} x \qquad (1)$$

where $x = P/P_s$, the relative pressure of $N_2$ gas

$V_m$ = volume of $N_2$ gas, measured at standard conditions, required to give one monolayer on the surface per gm. of adsorbent.

$V$ = $cm^3$ $N_2$ gas ($0^\circ C$, 1 atm.) adsorbed per gm. of adsorbent

$C$ = a constant

The surface area, in square meters per gram, is given by the relation

$$S(m^2/g) = \frac{A \, N \, V_m}{V_o} \times 10^{-20} \tag{2}$$

where $V_o$ = molal volume of $N_2$ gas at $0^\circ C$ and 1 atm

$N$ = Avogadro's number

$A$ = Area of an adsorbed $N_2$ molecule in square Angstrom units.

The factor $10^{-20}$ is a factor conversion from $A^2$ units to $(meter)^2$.

Inspection of Equation (1) shows that a plot of $x/V$ (1-x) vs. $x$ should give a straight line, from the slope and intercept of which the quantities $V_m$ and $C$ and be determined. The adsorption data given in Table II have been plotted in this manner and the values of $V_m$ so found used to compute the surface areas. In each instance the region $0.05 \leq x \leq 0.15$ has been given the greatest weight in obtaining $V_m$. A value of 15.8 $A^2$ has been used for the area of the nitrogen molecule, this value being reported by Joy (Vacuum, 3, 254-78 (1953)) to be uncertain to only $\pm$ 3%.

Three of the four catalyst samples (Tla, Tlb and Tlc) gave very nearly the same surface area; the fourth (Tld) gave an area about 7% smaller. The effect of the activation temperature was studied only for sample Tla. As may be seen from Table I no significant change was observed in the surface area by activation at $337^\circ F$ instead of $270^\circ F$.

## Table II

## Nitrogen Gas Adsorption Isotherms

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| Sample | Adsorption Temp. $^{o}K$ | Saturation Press., $P_s$ mm. Hg | Pressure P mm. Hg | Relative Press., $P/P_s$ | Volume adsorbed $cm^3 N_2$ S.T.P. Per gm. solid |
|---|---|---|---|---|---|
| Activated Carbon Barnebey-Cheney Adsorbite Type IGI, 8/10 mesh | 77.6 | 790 | 3.2 | 0.0041 | 190.7 |
| | | | 13.7 | 0.0173 | 209.9 |
| | | | 29.8 | 0.0377 | 221.1 |
| | | | 37.9 | 0.0480 | 224.3 |
| | | | 45.2 | 0.0572 | 226.3 |
| | | | 53.5 | 0.0677 | 228.1 |
| | | | 63.9 | 0.0809 | 230.1 |
| | | | 75.8 | 0.0959 | 231.7 |
| | | | 86.9 | 0.1100 | 233.0 |
| | | | 102.4 | 0.1296 | 234.3 |
| | | | 112.1 | 0.1419 | 234.9 |
| | | | 124.1 | 0.1571 | 235.6 |
| Silica gel "Davison High Capacity" (NBS-PUR) Drum 2 | 77.7 | 790 | 0.3 | 0.00038 | 87.3 |
| | | | 0.6 | 0.0076 | 98.5 |
| | | | 2.8 | 0.00354 | 113.0 |
| | | | 7.3 | 0.00924 | 127.4 |
| | | | 22.0 | 0.0278 | 147.7 |
| | | | 41.6 | 0.0527 | 161.9 |
| | | | 68.1 | 0.0862 | 174.2 |
| | | | 93.9 | 0.1189 | 183.3 |
| | | | 117.3 | 0.1485 | 190.3 |
| | | | 147.4 | 0.1866 | 197.4 |
| | | | 178.2 | 0.2256 | 203.4 |
| Tla (Activated 17 hrs. at 337$^{o}$F) | 77.85 | 810 | 4.1 | 0.0051 | 31.8 |
| | | | 37.8 | 0.0467 | 40.6 |
| | | | 61.4 | 0.0758 | 43.8 |
| | | | 76.3 | 0.0942 | 45.6 |
| | | | 91.1 | 0.1125 | 47.2 |
| | | | 109.2 | 0.1348 | 49.2 |
| | | | 126.6 | 0.1563 | 50.9 |
| Tla (Activated 18 hrs. at 270$^{o}$F) | 77.6 | 780 | 42.8 | 0.0549 | 40.5 |
| | | | 72.0 | 0.0923 | 44.4 |
| | | | 100.4 | 0.1287 | 47.2 |
| | | | 118.1 | 0.1514 | 49.3 |

Table II (Continued)

| | | | | | |
|---|---|---|---|---|---|
| Tlb | 77.7 | 790 | 38.3 | 0.0485 | 39.0 |
| | | | 60.3 | 0.0763 | 41.9 |
| | | | 77.3 | 0.0979 | 43.9 |
| | | | 96.7 | 0.1224 | 45.9 |
| | | | 119.5 | 0.1513 | 48.0 |
| | | | 139.4 | 0.1765 | 49.9 |
| Tlc | 77.7 | 790 | 16.5 | 0.0209 | 36.4 |
| | | | 32.7 | 0.0414 | 39.5 |
| | | | 45.0 | 0.0570 | 41.3 |
| | | | 58.9 | 0.0746 | 43.1 |
| | | | 80.4 | 0.1018 | 45.5 |
| | | | 100.5 | 0.1272 | 47.5 |
| Tld | 77.85 | 810 | 15.5 | 0.0191 | 34.7 |
| | | | 35.8 | 0.0442 | 38.9 |
| | | | 57.8 | 0.0714 | 41.8 |
| | | | 76.7 | 0.0947 | 44.2 |
| | | | 99.3 | 0.1226 | 46.7 |

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In accordance with the contractual arrangements we are submitting three copies of this letter report to you as the Contracting Officer. Two additional copies are being submitted to you for transmittal to Mr. R. B. Scott for the use of his staff.

Respectfully submitted,


W. T. Ziegler
Project Director

Approved:


Wyatt C. Whitley, Chief
Chemical Sciences Division

TECHNICAL REPORT NO. 1

PROJECT NO. A-460

CALCULATION OF THE VAPOR PRESSURE AND HEATS OF VAPORIZATION
AND SUBLIMATION OF LIQUIDS AND SOLIDS, ESPECIALLY BELOW
ONE ATMOSPHERE PRESSURE.  I.  ETHYLENE

By

W. T. ZIEGLER, J. C. MULLINS and B. S. KIRK

CONTRACT NO. CST-7238
NATIONAL BUREAU OF STANDARDS
BOULDER, COLORADO

JUNE 2, 1962

REVIEW

PATENT .....7-10..... 19..6Y. BY...........

FORMAT .........✓......... 19......... BY...........

Engineering Experiment Station

Georgia Institute of Technology

Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia


TECHNICAL REPORT NO. 1

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W. T. ZIEGLER, J. C. MULLINS and B. S. KIRK

JUNE 2, 1962

ABSTRACT

A number of thermodynamic relations are presented for computing, or assessing the probable accuracy of, the vapor pressure and heat of vaporization and sublimation of liquids and solids as a function of temperature. The relations are exact and take into account gas imperfection in the vapor phase. The solution of the equations, in general, requires iterative procedures which can be readily handled on an automatic digital computer. Applications of certain of the relations to the computation of the vapor pressure and heat of vaporization and sublimation of ethylene from its normal boiling point (169.40° K) to 20° K are presented. The computed results are given at 2 degree intervals from 168° to 100° K and 5 degree intervals from 100° to 20° K. The computed results are compared with the available experimental data. The calculated results are thermodynamically consistent with the available experimental data and represent a thermodynamically acceptable extrapolation of these data to 20° K.

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## I.  THERMODYNAMIC RELATIONS

### A.  Introduction

The need often arises for computing, or assessing the probable reliability of, vapor pressures and heats of vaporization and sublimation of liquids and solids.  The present paper is concerned with the development and use of several equations based on exact thermodynamic relations which can be applied to this problem.  The relations presented are not new, being explicitly given or implied in the published literature.[1,2,3,4,5*]  However, they appear not to have been collected together in one place nor discussed from a systematic point of view.

The relations presented for vapor pressure and heat of vaporization or sublimation take into account gas imperfection.  They can be applied over any desired temperature range from the critical point to 0° K provided the necessary experimental data are available.  In general, the experimental data needed are:  (1) the thermal properties of the saturated condensed phase, including the heat capacity, heat of fusion, heats of solid phase transition (if any) and volume of the saturated condensed phase as a function of temperature over the range of interest; one heat of vaporization or sublimation at a known temperature and pressure (e.g. the normal boiling point); the temperatures of all condensed phase transitions (including the triple point); (2) the heat capacity of the gas phase or thermodynamic functions of the ideal gas calculated from spectroscopic and molecular structure data; and (3) an equation of state for the gas phase.

The several exact thermodynamic relations can be written in different forms depending upon the property being computed, the method of computation, and the nature of the available experimental data and equation of state.  Thus, Gottschal

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*Superscript numbers refer to references given in the Bibliography.

and Korvezee[1,2] have chosen to express their relations in terms of the heat capacity of the vapor and condensed phases at constant pressure, $C_p$, whereas we, like van Dijk and Durieux,[3] have expressed our equations in terms of the heat capacity of the saturated condensed phase and the thermodynamic properties of the ideal gas.

In the present paper our particular concern has been the formulation of appropriate thermodynamic relations to compute vapor pressures and heats of vaporization and sublimation as a function of temperature from approximately the normal boiling point to temperatures of 20° K or less for substances of cryogenic interest. We have emphasized the use of relations which do not require extrapolation of experimental data to 0° K. We have compared the computed and experimentally measured vapor pressures and heats of vaporization where possible. Application of the exact equations to this low pressure region permits some simplification. Thus, an equation of state involving only the second virial coefficient is usually adequate to represent the gas imperfection.

We have chosen to use statistical thermodynamic relations to compute the thermodynamic properties of the ideal gas, since for the low temperatures considered the vapor pressures are so small that no experimental measurements of the heat capacity of the gas exist or seem possible. However, if thermal data for the vapor are available, the ideal gas properties can be calculated using the equation of state and the appropriate thermodynamic relations.

The use of the thermodynamic relations presented in this paper requires that all thermal data used be expressed in terms of a consistent <u>thermodynamic temperature scale</u> <u>and</u> <u>consistent energy units</u>. In practice, thermal data come from various sources, based on different temperature scales and employing different energy units. In the present paper all temperatures have been

reduced, where possible, to the thermodynamic temperature scale with an assigned ice point of 273.150° K by appropriate adjustments of the reported temperatures. Energy units have been expressed in terms of the defined calorie (1 cal. = 4.1840 ab. joules = 4.1833 int. joules). Unfortunately, many published papers do not contain sufficient information to permit these temperature and energy corrections to be made.

## B. Variation of Heat of Vaporization and Sublimation with Temperature

Consider two points, $(P,T)$ and $(P_1,T_1)$ with, say, $T < T_1$, on the vapor pressure curve of a pure substance and perform an enthalpy cycle, beginning at the point $(P,T)$, which involves the following steps: (1) heating the condensed phase along the saturation line from $(P,T)$ to $(P_1,T_1)$; (2) vaporization of the condensed phase at $(P_1,T_1)$; (3) isothermal conversion of the vapor to the ideal gas state at $T_1$; (4) cooling the ideal gas from $T_1$ to $T$; (5) isothermal conversion of gas from the ideal gas state at $T$ to the real gas state at $(P,T)$; and (6) condensation of the vapor at $(P,T)$ to condensed state at $(P,T)$. The sum of the enthalpy changes around this closed path is zero. The heat of vaporization (or sublimation) at $(P,T)$ can therefore be computed as shown in Equation (1).

$$(\Delta H_v)_T = (\Delta H_v)_{T_1} + \int_T^{T_1} c_s' \, dT + \sum_T^{T_1} (\Delta H_{tr})' - \left[ (H^o - H_o^o)''_{T_1} - (H^o - H_o^o)''_T \right]$$

$$- RT_1 \, \delta_1 + RT\delta + \int_P^{P_1} v_s' \, dP \qquad (1)$$

In this equation the quantity $\delta$ is given by the relation

$$RT\delta = \left[ H(P,T) - H^o(T) \right]'' \qquad (2)$$

and $\delta_1$ is the value of $\delta$ at the point $(P_1,T_1)$. The prime (') and double prime

(") symbols refer to the condensed and vapor phases, respectively. All other symbols are explicitly defined in Appendix A. The evaluation of the right-hand side of Equation (2) requires an equation of state for the vapor. If a virial form of the equation of state is used, namely,

$$PV = RT\left(1 + \frac{B}{V} + \frac{C}{V^2} + \dots\right) \tag{3}$$

where the virial coefficients are assumed to be functions of temperature only, then one obtains

$$\delta = (B - T\frac{dB}{dT})/V + (C - \frac{1}{2}T\frac{dC}{dT})/V^2 \tag{4}$$

For $T < T$ (triple point), $(\Delta H_v)_T$ in Equation (1) is the heat of sublimation rather than the heat of vaporization. The evaluation of the last two terms of Equation (1) requires a value of the vapor pressure at T. If vapor pressure calculations are made by an iterative procedure, then this iterative procedure also provides the pressure necessary to compute the last two terms of Equation (1).

As $T \to 0°K$, $V \to \infty$, $P \to 0$, $PV \to RT$, $\delta \to 0$ and Equation (1) reduces to

$$\Delta H_o^o = (\Delta H_v)_{T_1} + \int_0^{T_1} c_s' \, dT + \sum_{T=0}^{T_1} (\Delta H_{tr})' - (H^o - H_o^o)_{T_1}''$$

$$- RT_1 \delta_1 + \int_0^{P_1} v_s' \, dP \tag{5}$$

Equation (5) permits the evaluation of $\Delta H_o^o$, the heat of sublimation of 0° K, from a known value of $(\Delta H_v)_{T_1}$ at a known temperature and pressure, $(T_1, P_1)$, e.g., the normal boiling point or triple point, together with thermal data for the saturated condensed phase between 0° K and $T_1°$ K. The virial coefficients

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and their temperature derivatives need be known only at $T_1$. The value of $\Delta H_o^c$ obtained from Equation (5) depends upon the assumptions used in computing the enthalpy function $(H^o - H_o^o)''$ for the ideal gas from statistical mechanics.

## C. Vapor Pressure Relations

### 1. Relations Requiring Thermal Data to 0° K

The thermodynamic condition for equilibrium between a saturated condensed phase and a saturated vapor phase is that the Gibbs free energy per mole of the phases be equal

$$G''(P,T) = G'(P,T) \tag{6}$$

By computing the free energy of each phase separately and equating them, one can obtain the following relation for the vapor pressure of the condensed phase at T

$$\ln P = -[(G^o - H_o^o)'' - (G^o - H_o^o)']/RT - \Delta H_o^o/RT - (S_o)'/R + \varepsilon \tag{7}$$

where

$$\varepsilon = [G^o(P,T) - G(P,T)]''/RT$$
$$= [H^o(T) - H(P,T)]''/RT - [S^*(P,T) - S(P,T)]''/R \tag{8}$$

In this expression $(G^o - H_o^o)''$ is the free energy function of the ideal gas calculated from statistical thermodynamic relations for the standard state pressure, $P = 1$ atmosphere; $(G^o - H_o^o)'$ is the free energy function of the saturated condensed phase at P,T relative to 0° K. The standard state chosen for the condensed phase is the condensed phase at its saturation pressure and temperature. The quantities $\Delta H_o^o$ and $(S_o)'$ are the heat of sublimation and entropy of the condensed phase of 0° K, respectively.

The terms in brackets in Equation (8) represent the effect of gas imperfection and can be computed from an equation of state for the gas. If the virial form of the equation of state is assumed, i.e., Equation (3), then $\varepsilon$ becomes

$$\varepsilon = \ln(PV/RT) - 2B/V - 3C/2V^2 - \cdots \cdots \quad (9)$$

Substitution of the appropriate relations for $(G^\circ - H_o^\circ)''$ and $(G^\circ - H_o^\circ)'$ into Equation (7) yields the expression

$$\ln P = [(H^\circ - H_o^\circ)_T' - (H^\circ - H_o^\circ)_T'']/RT + [(S^\circ)_T'' - (S^\circ - S_o)_T' - (S_o)']/R$$
$$- \Delta H_o^\circ/RT + \varepsilon \quad (10)$$

where

$$(H^\circ - H_o^\circ)_T' = \int_0^T c_s' \, dT + \sum_0^T (\Delta H_{tr})' + \int_0^P v_s' \, dP \quad (11)$$

$$(S^\circ - S_o)_T' = \int_0^T \frac{c_s'}{T} \, dT + \sum_0^T (\Delta H_{tr})'/T_{tr} \quad (12)$$

The use of Equation (10) to compute the vapor pressure implies: (1) availability of at least one heat of vaporization (or sublimation) at a known temperature and pressure or at least two points on the vapor pressure curve to compute $\Delta H_o^\circ$; (2) thermal data to 0° K; and (3) knowledge of the entropy $(S_o)'$ of the condensed phase at 0° K.

If one assumes that thermal data for the condensed phase are available down to a lowest temperature $T_L$, then the integrals involving $c_s'$ in Equations (11) and (12) can be written as

$$\int_0^T c_s' \, dT = \int_0^{T_L} c_s' \, dT + \int_{T_L}^T c_s' \, dT \quad (13)$$

$$\int_0^T \frac{c_s'}{T}\,dT = \int_0^{T_L} \frac{c_s'}{T}\,dT + \int_{T_L}^T \frac{c_s'}{T}\,dT \tag{14}$$

Estimation of the contribution of the integrals below $T_L$ is usually made by assuming a Debye model for the solid.

If one also assumes that (1) no phase transitions occur below $T_L$ and (2) the vapor pressure is already very small at $T_L$ then no contribution to the remaining terms of Equations (11) and (12) arises for $0 \leq T \leq T_L$.

Insertion of Equations (11), (12), (13) and (14) into Equation (10) and rearrangement of the relation results in an expression of the form

$$D = a - bT \tag{15}$$

where

$$D = RT \ln P + (H^0 - H_0^0)_T'' - \int_{T_L}^T c_s'\,dT - \sum_0^T (\Delta H_{tr})'$$

$$- \int_0^P v_s'\,dP + T\int_{T_L}^T \frac{c_s'}{T}\,dT + T\sum_0^T (\Delta H_{tr})'/T_{tr} - T(S^0)_T'' - RT\varepsilon \tag{16}$$

$$a = -\Delta H_0^0 + \int_0^{T_L} c_s'\,dT \tag{17}$$

$$b = \int_0^{T_L} \frac{c_s'}{T}\,dT + (S_0)' \tag{18}$$

Equation (15) can be used to test the thermodynamic consistency of vapor pressure and thermal data. Since the quantity $D$ can be determined from the indicated experimental data, a plot of $D$ vs $T$ should result in a straight line if the data are thermodynamically consistent. The intercept and slope of the straight

line provide information about $\Delta H_o^o$ and $(S_o)'$, respectively. It may be noted that the temperature $T_L$ may be chosen to be any value $T_L < T$, thus making it possible to examine the effect of the low temperature heat capacity data on this consistency test.

Modifications of Equations (7) and (10) with $(S_o)' = 0$ have been rather widely used. Thus, van Dijk and Durieux[3] have used a form of these equations to describe the vapor pressure-temperature relation for liquid helium. The integral involving $v_s' dP$ is usually small and is often neglected as, for instance, in the vapor pressure equation used by Fisher and McMillan[4] for krypton. In still other instances, where $(S_o)' = 0$ and the vapor can be considered to be an ideal gas, only the first two terms of Equation (7) need be retained, as in the vapor pressure equation of Shirley and Giauque[5] for solid iodine.

### 2. Relations Not Requiring Thermal Data to 0° K

Another approach to computing vapor pressure as function of temperature is to consider Equation (7) or (10) to apply to two different points, say $(P_1, T_1)$ and $(P, T)$ on the vapor pressure curve. Subtraction of two such equations leads to an expression which may be considered to be an integration of the Clapeyron equation. It is to be noted that the zero point entropy $(S_o)'$ is thus eliminated from the resulting equation. This equation does not require the use of thermodynamic data below the lowest temperature $T$ at which the vapor pressure is to be computed, if substitution for $\Delta H_o^o$ is made from Equation (5).

If we assume that $(\Delta H_v)_{T_1}$, $T_1$ and $P_1$ are known, as well as thermal data for the condensed phase between $T_1$ and $T$, and the requisite spectroscopic, molecular structure, and virial coefficient data for the gas, then Equations (5) and (10) may be combined in the form

$$\ln P = \ln P_1 - (\Delta H_v)_{T_1}(T_1 - T)/RTT_1 + [(H^o - H_o^o)_{T_1}'' - (H^o - H_o^o)_T'']/RT$$

$$- [(S^o)_{T_1}'' - (S^o)_T'']/R - \left(\int_T^{T_1} c_s' \, dT\right)/RT$$

$$- \left(\sum_T^{T_1} (\Delta H_{tr})'\right)/RT + \left(\int_T^{T_1} c_s' \, dT/T\right)/R$$

$$+ \left(\sum_T^{T_1} (\Delta H_{tr})'/T_{tr}\right)/R + \delta_1(T_1 - T)/T$$

$$- \varepsilon_1 + \varepsilon - \left(\int_P^{P_1} v_s' \, dP\right)/RT \tag{19}$$

Solution of Equation (19) requires iteration since the last two terms of this equation are pressure dependent.

Equation (19) can be solved for $(\Delta H_v)_{T_1}$ as follows:

$$(\Delta H_v)_{T_1} = \left\{ RT \ln P_1/P + \left[(H^o - H_o^o)_{T_1}'' - (H^o - H_o^o)_T''\right] \right.$$

$$- \int_T^{T_1} c_s' \, dT - \sum_T^{T_1} (\Delta H_{tr})' - T\left[(S^o)_{T_1}'' - (S^o)_T''\right]$$

$$+ T\int_T^{T_1} c_s' \, dT/T + T \sum_T^{T_1} (\Delta H_{tr})'/T_{tr}$$

$$\left. + R(T_1-T)\delta_1 - RT\varepsilon_1 + RT\varepsilon - \int_P^{P_1} v_s' \, dP \right\} T_1/(T_1-T) \tag{20}$$

Equation (20) may be used to compute the heat of vaporization at a fixed point $P_1, T_1$ (say the normal boiling point or triple point) from two points $(P_1, T_1)$ and $(P, T)$ on the vapor pressure curve. It may also be used to check the consistency of vapor pressure data by computing $(\Delta H_v)_{T_1}$ for various experimental $(P,T)$ points.

Neither of these uses of Equation (20) requires any iterative procedures in the calculation. It may be shown that as $T$ approaches $T_1$ Equation (20) reduces to the Clapeyron equation.

Gottschal and Korvezee[1,2] have used thermodynamic relations similar in principle to Equations (1), (19) and (20) to compute the vapor pressure and heat of vaporization of liquid benzene from $280°$ K to the normal boiling point by assuming two points on the vapor pressure curve to be known from experimental data.

### 3. Relation Between Equation (10) and Equation (19)

A simple relation exists between the vapor pressure calculated from Equation (10), which involves thermal properties of the substance to $0°$ K, and Equation (19) which does not require such information. Combination of Equations (10) and (19) and elimination of $\Delta H_0^o$ by means of Equation (5) gives

$$\ln P_j - \ln P_i = [(S^o)_{cal}'' - (S^o)_{spect}'']/R + (S_o)'/R \qquad (21)$$

where

$P_i$ = vapor pressure at $T$ calculated using Equation (10) and Equation (5)

$P_j$ = vapor pressure at $T$ calculated using Equation (19)

$(S^o)_{cal}''$ = calorimetric entropy of gas in ideal gas state at $T = T_1$, $P = 1$ atm, relative to condensed phase at $0°$ K

$(S^o)_{spect}''$ = statistically calculated entropy of gas in ideal gas state at $T = T_1$, $P = 1$ atm, using spectroscopic data

$(S_o)'$ = entropy of condensed phase at $0°$ K.

It is to be noted that Equation (21) implies that $\Delta H_o^o$ from Equation (5) has been obtained by using the same thermal data as are used in Equation (19).

Equation (21) implies that the ratio $P_j/P_i$ is a constant for all temperatures $0 \leqq T \leqq T_c$ and thus permits evaluation of $P_i$ from $P_j$ provided $(S^o)_{cal}''$ at $(T_1, P_1)$ and $(S_o)'$ are known. It may readily be shown that

$$\left[(S^o)_{cal}''\right]_{T_1, P=1 \text{ atm}} = \int_0^{T_1} \frac{c_s'}{T} \, dT + \sum_0^T (\Delta H_{tr})'/T_{tr} + R \ln P_1$$

$$+ (\Delta H_v)_{T_1}/T_1 - R(\varepsilon_1 + \delta_1) \qquad (22)$$

## II.  APPLICATION OF THERMODYNAMIC RELATIONS TO ETHYLENE

### A.  Introduction

Applications of the various equations presented in Chapter I have been made to a number of substances of cryogenic interest.  The results for ethylene are reported in the present paper.  Application to parahydrogen[6] from 1° to 22° K and oxygen[7] from 20° to 100° K have been reported elsewhere.  Similar calculations also have been completed for argon, methane and nitrogen.  Primary emphasis has been given to the solution of Equations (19) and (1) which permit the calculation of vapor pressure and heat of vaporization (or sublimation) as a function of temperature.  The experimental data required were $(\Delta H_v)_{T_1}$, $P_1$, $T_1$, $c_s'$ and $v_s'$ as a function of temperature, the heat of fusion and triple point temperature.  In these calculations the point $(P_1, T_1)$ on the saturation curve corresponded to the normal boiling point.  Also needed was a representation of the second virial coefficient as a function of temperature.  In addition, sufficient molecular structure and spectroscopic data were needed to permit calculation of $(H^o - H_o^o)''$ and $(S^o)''$ for the ideal gas at one atmosphere pressure by statistical mechanical methods.

Sufficient experimental data were available for ethylene to compute the vapor pressure and heat of vaporization and sublimation as a function of temperature from the normal boiling point (169.40° K) to 20° K.  The computed results have been compared with the available experimental vapor pressure data.

All experimental data for vapor pressures and fixed points used, such as the normal boiling point and triple point temperatures, have been adjusted, where possible, to a thermodynamic temperature scale having a defined ice point of 273.15° K.  The "best" value of the normal boiling point of oxygen on this scale

has been taken to be 90.168° K, the value selected by van Dijk.[9] The various methods used for making these conversions are described in detail in Appendix B. No adjustments were made to temperatures reported for virial coefficient, density and heat capacity data since the effect of such changes on the calculations is negligible. All thermal quantities have been expressed, where possible, in defined calories, using the relation: 1 defined cal. = 4.1840 ab. joules = 4.1833 int. joules. All calculations involving gas imperfection have been made using an equation of state of the form of Equation (3) which included the second virial coefficient only.

The physical constants used in this work were taken from Rossini et al[8] and were corrected to an ice point of 273.15° K. The values used are given in Appendix A.

All computations were made on an automatic digital computer. A number of different basic programs were written to solve the several equations. In addition a number of other programs of special nature were written to provide input data for the basic programs. Among these were programs designed to provide least squares fits to experimental heat capacity and second virial coefficient data.

## B.  Experimental Data

### 1.  Phase Transition Temperatures

a.  Normal Boiling Point. The most reliable values of the normal boiling point appear to be those of Egan and Kemp[10] and Michels and Wassenaar.[11] The selected value is an average of these values. These values together with other reported values are given in Table I. The value of Lamb and Roper[12] was

TABLE I

TRANSITION TEMPERATURES OF ETHYLENE

| Temperature Reported | Ice Point ($^\circ$K) | Method of Temperature Correction[a] | Temperature, $T_o=273.15^\circ$K ($^\circ$K) | Pressure (Mm Hg) | Investigator |
|---|---|---|---|---|---|
| A. Normal Boiling Point | | | | | |
| 169.40$^\circ$ K | 273.10 | A | 169.431 | 760 | Egan and Kemp[10] |
| -103.78$^\circ$ C | 273.15 | C | 169.370 | 760 | Michels and Wassenaar[11] |
| -103.81$^\circ$ C | 273.16 | C | 169.333 | 760 | Lamb and Roper[12] |
| -103.72$^\circ$ C | 273.10 | C | 169.411 | 760 | Henning and Stock[14] |
| | Selected Value | | 169.40 | | |
| B. Triple Point | | | | | |
| 103.95$^\circ$ K | 273.10 | A | 103.969 | – | Egan and Kemp[10] |
| | | B | 103.965[b] | – | Clusius and Wiegand[15] |
| -169.50$^\circ$ C | (c) | | | – | Kistiakowsky et al[13] |
| -169.10$^\circ$ C | (c) | | | – | Tickner and Lossing[17] |
| | Selected Value | | 103.97 | | |

[a]See Appendix B.

[b]Clusius and Wiegand used a methane vapor pressure thermometer. Their measured methane vapor pressure 384.3 mm Hg was first converted to $^\circ$C (Int.) using the vapor pressure equation of Armstrong et al,[16] then converted to $^\circ$K using Method B (Appendix B).

[c]Temperature scale uncertain.

not used because they reportedly used the same sample of ethylene as Kistiakowsky et al,[13] which appears to have been somewhat impure as indicated by its low melting point (see Table II). The value of Henning and Stock[14] was not considered because the value reported by them was obtained by extrapolation of vapor pressure data ending at 162.80° K, approximately 7 degrees below the normal boiling point.

b. Triple Point. The triple point temperature has been measured by Egan and Kemp[10] and the melting curve by Clusius and Wiegand.[15] The temperature scale of Clusius and Wiegand was based on a methane vapor pressure thermometer. The selected triple point temperature was taken as an average of the values of Egan and Kemp, and Clusius and Wiegand after re-evaluating the temperatures of the latter investigators using the methane vapor pressure data of Armstrong et al.[16] Other reported values of the triple point of ethylene are those of Kistiakowsky et al[13] and Tickner and Lossing.[17] These values are collected in Table II. The value of Kistiakowsky et al was excluded because it appears to be too low; the value of Tickner and Lossing was excluded because of the reported uncertainty in their temperature measurements. No measurement of the triple point pressure appears to have been made.

2. Heats of Vaporization and Fusion

a. Heat of Vaporization. Egan and Kemp[10] and Clusius and Konnertz[18] have measured the heat of vaporization at the normal boiling point. There is a discrepancy of about 36 cal/gm mole in the two values. Egan and Kemp's value has been selected as the more nearly consistent with the experimental vapor pressure data. Clusius and Konnertz also reported a value below the normal boiling point. These data are shown in Table II.

TABLE II

HEATS OF VAPORIZATION AND FUSION OF ETHYLENE

| Heat of Transition (Cal/Gm Mole) | Reported Temperature (°K) | Investigator |
|---|---|---|
| A. Heat of Vaporization | | |
| 3237 | 169.40 | Egan and Kemp[10] |
| 3201 (p = 1.002 atm) | 169.5 | Clusius and Konnertz[18] |
| 3424 (p = 0.157 atm) | 143.4 | Clusius and Konnertz[18] |
| B. Heat of Fusion | | |
| 800.8 | 103.95 | Egan and Kemp[10] |
| 699 | 103.6 | Eucken and Hauck[19] |

b. Heat of Fusion. The measurements of Egan and Kemp[10] and Eucken and Hauck[19] were the only data found for the heat of fusion of ethylene. The value of Egan and Kemp has been selected since it appears to be the more accurate and since it is found to be more nearly consistent with the measured vapor pressures below the triple point.

Ethylene exhibits no other solid phase transitions.

3. Molal Volumes of Saturated Liquid and Solid

a. Liquid Ethylene. Mathias et al,[20] Maass and Wright[21] and Maass and McIntosh[22] have measured the density of the saturated liquid near and below the normal boiling point. In addition Clusius and Wiegand[15] have measured the solid-liquid melting curve, and from the slope and the Clapeyron equation computed the change in molal volume from solid to liquid to be 4.55 ml/mole at the triple point. This change in volume has been combined with an estimated volume of the

solid to obtain a molal volume for the saturated liquid at the triple point. These data for the saturated liquid have been plotted and a smooth curve drawn through the data to obtain the values given in Table III. In drawing this curve the value of the molal volume of liquid ethylene at the triple point computed from the melting data of Clusius and Wiegand was given only a partial weight since it appeared to be somewhat inconsistent with the data of other investigators at higher temperatures.

b. Solid Ethylene. The density of solid ethylene has been measured directly by Heuse[23] at 20° K and by Stewart and LaRock[24] at 77° K. In addition the density has been determined at -175° C from the x-ray diffraction studies of Keesom and Taconis.[25] The experimental results are shown in Table IV.

The smoothed values given in Table V were obtained from a curve drawn through these data.

### 4. Heat Capacity of Saturated Liquid and Solid

The heat capacities of solid and liquid ethylene have been measured by Egan and Kemp[10] and Eucken and Hauck.[19] The data of Egan and Kemp were taken as the best available data over the range 16° to 168.71° K. These data have been assumed to apply to the saturated condensed phases. These data were fitted to a series of polynomials of the form

$$c_s' = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 \cdots \tag{23}$$

by the method of least squares. The coefficients of the polynomials used are shown in Table VI. The average per cent deviations of the polynomials from the experimental data are 0.55, 0.14, 0.98, and 0.13 per cent for polynomials 1, 2, 3 and 4, respectively.

## TABLE III

### MOLAL VOLUME OF SATURATED LIQUID ETHYLENE AT EVEN TEMPERATURES

| Temperature ($^{\circ}$K) | Molal Volume (Ml/Gm Mole) |
|---|---|
| 103.97 (t.p.) | 43.3 |
| 110 | 43.7 |
| 120 | 44.4 |
| 130 | 45.2 |
| 140 | 46.1 |
| 150 | 47.1 |
| 160 | 48.2 |
| 169.40 (n.b.p.) | 49.3 |
| 170 | 49.4 |

## TABLE IV

### DENSITY AND MOLAL VOLUME OF SOLID ETHYLENE

| Temperature | Density (Gm/Ml) | Molal Volume (Ml/Gm Mole) | Investigator |
|---|---|---|---|
| 20$^{\circ}$ K | 0.7814 | 35.9 ± 0.1 | Heuse[23] |
| 77$^{\circ}$ K | 0.732 | 38.3 ± 0.1 | Stewart and LaRock[24] |
| -175$^{\circ}$ C | 0.717 | 39.1 | Keesom and Taconis[25] |

## TABLE V

### MOLAL VOLUME OF SOLID ETHYLENE AT EVEN TEMPERATURES

| Temperature (°K) | Molal Volume (Ml/Gm Mole) |
|---|---|
| 20 | 35.9 |
| 30 | 36.3 |
| 40 | 36.8 |
| 50 | 37.2 |
| 60 | 37.6 |
| 70 | 38.0 |
| 80 | 38.4 |
| 90 | 38.8 |
| 100 | 39.2 |
| 103.97 (t.p.) | 39.3 |

## TABLE VI

### COEFFICIENTS FOR POLYNOMIALS REPRESENTING HEAT CAPACITY OF SOLID AND LIQUID ETHYLENE

| Poly-nomial | Range (°K) | $a_0$ | $a_1 \times 10^2$ | $a_1 \times 10^3$ | $a_3 \times 10^4$ | $a_4 \times 10^7$ |
|---|---|---|---|---|---|---|
| 1 | 16-65 | - 0.70919547 | - 1.7785030 | - 9.1952917 | -1.5078407 | 7.8278539 |
| 2 | 65-90 | -16.319988 | 91.832159 | - 11.799344 | 0.58423231 | 0 |
| 3 | 90-t.p. | -2184.0631 | 7122.7810 | -771.43221 | 27.925688 | 0 |
| 4 | t.p.- n.b.p. | 20.041175 | - 4.9186692 | 0.15170719 | 0 | 0 |

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### 5. Second Virial Coefficient

The equation of state for ethylene gas was assumed to be represented by Equation (3) truncated after the second virial coefficient term. The experimental data for the second virial coefficient of ethylene are given in Appendix C. In the computations for ethylene, the second virial coefficient, $B(T)$, has been represented as a function of temperature by means of the relation

$$B(T) = b_o \sum_{j=o}^{j=40} b^{(j)} \theta^{(1+2j)/4} \qquad (24)$$

given by Hirschfelder et al.[26]

In this relation $\theta = e/kT$ and $b_o$ and $e/k$ are the parameters in the 6-12 Lennard-Jones intermolecular potential. The coefficients, $b^{(j)}$, are given by Hirschfelder et al.[26] The values of $e/k$ and $b_o$ used (150.76° K and 227.06 ml/gm mole, respectively) were determined by a least squares fit of Equation (24) to the experimental data over the range 181° to 398° K. (See Appendix C.)

### 6. Thermodynamic Functions of the Ideal Gas

The thermodynamic functions $(H^O - H_o^O)''$ and $(S^O)''$, of ethylene in the ideal gas state at one atmosphere pressure were calculated assuming a rigid-rotator-harmonic oscillator model. Nuclear spin effects have been excluded. Isotope effects have been included only in the sense that the moments of inertia and molecular weight correspond to normal ethylene gas.

The enthalpy function $(H^O - H_o^O)''$ was computed from the relations

$$(H^O - H_o^O)'' = H_{trans}^O + H_{rot}^O + H_{vib}^O \qquad (25)$$

where

$$H_{trans}^O = 5\ RT/2 \qquad (26)$$

$$H^o_{rot} = RT^2 (\partial \ln Q_{rot}/\partial T) \tag{27}$$

$$H^o_{vib} = RT \sum x_i/(e^{x_i} - 1) \tag{28}$$

$$x_i = hcw_i/kT \tag{29}$$

The quantity $Q_{rot}$ in Equation (27) is the rotational partition function. In Equation (28) the sum is taken over all fundamental frequencies, $w_i$, (12 for ethylene).

The entropy $(S^o)''$ of ethylene at one atmosphere pressure was computed from the relations

$$(S^o)'' = S^o_{trans} + S^o_{rot} + S^o_{vib} \tag{30}$$

$$S^o_{trans} = R[(5/2) \ln T + (3/2) \ln M - 1.164862] \tag{31}$$

$$S^o_{rot} = RT(\partial \ln Q_{rot}/\partial T) + R\ln Q_{rot} \tag{32}$$

$$S^o_{vib} = R \sum [x_i/(e^{x_i} - 1) - \ln (1 - e^{-x_i})] \tag{33}$$

The quantity M in Equation (31) is the molecular weight of ethylene, taken to be 28.054. The sum in Equation (33) is taken over the same frequencies as Equation (28).

The fundamental frequencies and moments of inertia used in the calculations of $(H^o - H^o_o)''$ and $(S^o)''$ were those of Galloway and Barker.[27] These are shown in Table VII.

Ethylene is an asymmetric rotator. Three asymptotic expansions of the rotational partition function were examined. One of these, which we term the "classical" form, is given by Equation (34).

## TABLE VII

## MOLECULAR CONSTANTS FOR ETHYLENE

| Fundamental Frequency $(Cm^{-1})$ | | Moments of Inertia $(Gm\ Cm^{-2})$ |
|---|---|---|
| 3019.3 | 1055 | $0.5750 \times 10^{-39}\ (I_A)$ |
| 1623.3 | 3105.5 | $2.809 \times 10^{-39}\ (I_B)$ |
| 1342.4 | 995.0 | $3.384 \times 10^{-39}\ (I_C)$ |
| 2989.5 | 825 | |
| 1443.9 | 950 | |
| 3069 | 949.2 | |

$$Q_{rot} = \frac{1}{\sigma}\left(\frac{\pi}{ABC}\right)^{1/2}\left(\frac{kT}{hc}\right)^{3/2} \tag{34}$$

where A, B and C (the rotational constants) and other symbols are defined in Appendix A. A second expansion is an approximate expression for an asymmetric rotator with two moments of inertia approximately equal, formulated by Gordon[28] and given by Herzberg[29] as

$$Q_{rot} = \frac{1}{\sigma}\left[\frac{\pi}{ABC}\left(\frac{kT}{hc}\right)^3\right]^{1/2}\left[1 + \frac{1}{12}\left(1 - \frac{\sqrt{BC}}{A}\right)\sqrt{BC}\left(\frac{hc}{kT}\right)\right]\exp\left(\sqrt{BC}\frac{hc}{4kT}\right) \tag{35}$$

The rotational partition function given in Equation (35) was used in all calculations of thermodynamic properties and vapor pressures presented in this paper. A more nearly exact asymptotic expansion for the rotational partition function of the asymmetric rotator has been developed by Stripp and Kirkwood.[30] The relation came to our attention after the calculations reported in the present paper were completed.*

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*We thank Dr. H. W. Woolley of the National Bureau of Standards for pointing out this relation to us.

We have made a comparison of the differences in entropy and enthalpy result-ing from the use of the three asymptotic forms of the rotational partition func-tion over the range $20°$ to $169.40°$ K. The rotational enthalpy and entropy com-puted by Equation (35) differed by less than $0.05$ cal/gm mole (very nearly constant) and $0.001$ e.u., respectively, from those computed using the more exact relation of Stripp and Kirkwood.

The rotational enthalpy computed by Equation (35) differed by a very nearly constant amount of $0.82$ cal/gm mole from that computed using the partition func-tion given in Equation (34). The differences in rotational entropy computed using Equations (34) and (35) differed by less than $10^{-5}$ cal/gm mole $°K$.

## C. Calculation of Vapor Pressure and Heats of Vaporization and Sublimation

The vapor pressure and heats of vaporization and sublimation of ethylene have been computed from the normal boiling point ($P = 760$ mm Hg) to $20°$ K from Equations (19) and (1). The input data used are summarized in Table VIII. The calculations were made at 2 degree intervals from the normal boiling point ($169.40°$ K) to $100°$ K and at 5 degree intervals from $100°$ to $20°$ K. The computed values are shown in Table IX. The slope of the vapor pressure curve, computed as $(dP/dT)/P$, is also shown. The quantities log $P$ and $1/T$ are included to facilitate interpolation. The calculation of the pressure required iterative solution of Equation (19). In making the calculations the integral involving $v_s' dP$ was evaluated by assuming $v_s'$ to be constant over the temperature range of each $c_s'$ polynomial. The value of $v_s'$ chosen was taken to be its value at the midpoint of the temperature range covered by the $c_s'$ polynomial. The assumption that $v_s'$ is constant introduced a negligible error in the calculated vapor pres-sure and greatly simplified the calculations.

## TABLE VIII

SUMMARY OF INPUT DATA FOR VAPOR PRESSURE AND
HEATS OF VAPORIZATION AND SUBLIMATION
CALCULATIONS FOR ETHYLENE

| Item | Value Used | Table No. |
|------|-----------|-----------|
| Normal boiling point (n.b.p.) | 169.40° K | I |
| Triple point (t.p.) | 103.97° K | I |
| Heat of vaporization at n.b.p. | 3237 cal/gm mole | II |
| Heat of fusion at t.p. | 800.8 cal/gm mole | II |
| Heat capacity of saturated condensed phases | Polynomial for appropriate temperature range | VI |
| Molal volume of saturated condensed phases | Constant value for each $c_s'$ polynomial | III, V |
| Second virial coefficient parameters | $e/k = 150.76°$ K $b_o = 227.06$ ml/gm mole | |
| Molecular constants | | VII |
| Molecular weight | 28.054 | |

TABLE IX

CALCULATED VAPOR PRESSURE AND HEATS
OF VAPORIZATION AND SUBLIMATION FOR ETHYLENE

| Temperature (°K) | Pressure (Mm Hg) | Heat of Vaporization (Cal/Gm Mole) | Log P (Mm Hg) | $1/T \times 10^3$ (°K$^{-1}$) | (dP/dT)/P (°K$^{-1}$) |
|---|---|---|---|---|---|
| 169.40 | 760.000 | 3237 | | | |
| 168 | 699.197 | 3250.4 | 2.844600 | 5.95238 | 0.06011 |
| 166 | 619.005 | 3269.4 | 2.791694 | 6.02410 | 0.06172 |
| 164 | 546.207 | 3288.1 | 2.737357 | 6.09756 | 0.06340 |
| 162 | 480.317 | 3306.7 | 2.681528 | 6.17284 | 0.06516 |
| 160 | 420.865 | 3325.0 | 2.624143 | 6.25000 | 0.06699 |
| 158 | 367.396 | 3343.2 | 2.565135 | 6.32911 | 0.06890 |
| 156 | 319.468 | 3361.2 | 2.504427 | 6.41026 | 0.07089 |
| 154 | 276.664 | 3379.0 | 2.441953 | 6.49351 | 0.07298 |
| 152 | 238.575 | 3396.7 | 2.377625 | 6.57895 | 0.07516 |
| 150 | 204.815 | 3414.3 | 2.311361 | 6.66667 | 0.07744 |
| 148 | 175.013 | 3431.8 | 2.243071 | 6.75676 | 0.07982 |
| 146 | 148.822 | 3449.1 | 2.172668 | 6.84932 | 0.08231 |
| 144 | 125.907 | 3466.3 | 2.100049 | 6.94444 | 0.08492 |
| 142 | 105.951 | 3483.5 | 2.025106 | 7.04225 | 0.08766 |
| 140 | 88.662 | 3500.6 | 1.947736 | 7.14286 | 0.09052 |
| 138 | 73.758 | 3517.6 | 1.867811 | 7.24638 | 0.09353 |
| 136 | 60.984 | 3534.6 | 1.785219 | 7.35294 | 0.09668 |
| 134 | 50.098 | 3551.5 | 1.699824 | 7.46269 | 0.09998 |
| 132 | 40.878 | 3568.4 | 1.611485 | 7.57576 | 0.1035 |
| 130 | 33.117 | 3585.3 | 1.520053 | 7.69231 | 0.1071 |

(Continued)

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TABLE IX (Continued)

CALCULATED VAPOR PRESSURE AND HEATS
OF VAPORIZATION AND SUBLIMATION FOR ETHYLENE

| Temperature ($^\circ$K) | Pressure (Mm Hg) | Heat of Vaporization (Cal/Gm Mole) | Log P (Mm Hg) | $1/T \times 10^3$ ($^\circ$K$^{-1}$) | $(dP/dT)/P$ ($^\circ$K$^{-1}$) |
|---|---|---|---|---|---|
| 128 | 26.630 | 3602.2 | 1.425376 | 7.81250 | 0.1109 |
| 126 | 21.246 | 3619.0 | 1.327283 | 7.93651 | 0.1150 |
| 124 | 16.811 | 3635.9 | 1.225596 | 8.06452 | 0.1192 |
| 122 | 13.186 | 3652.7 | 1.120127 | 8.19672 | 0.1237 |
| 120 | 10.249 | 3669.6 | 1.010670 | 8.33333 | 0.1284 |
| 118 | 7.889 | 3686.5 | 0.897010 | 8.47458 | 0.1334 |
| 116 | 6.011 | 3703.5 | 0.778918 | 8.62069 | 0.1386 |
| 114 | 4.530 | 3720.4 | 0.656142 | 8.77193 | 0.1441 |
| 112 | 3.376 | 3737.4 | 0.528420 | 8.92857 | 0.1500 |
| 110 | 2.486 | 3754.5 | 0.395467 | 9.09091 | 0.1562 |
| 108 | 1.807 | 3771.6 | 0.256971 | 9.25926 | 0.1628 |
| 106 | 1.296 | 3788.7 | 0.112610 | 9.43396 | 0.1697 |
| 104 | 9.16 (-1)[a] | 3806.0 | -0.037979 | 9.61538 | 0.1771 |
| 103.97 | 9.114 (-1) | 3806.2 | -0.040286 | 9.61816 | 0.1772 |
| Solid $C_2H_4$ | | | | | |
| 103.97 | 9.11 (-1) | 4607.0 | -0.040286 | 9.61816 | |
| 102 | 5.92 (-1) | 4630.4 | -0.228026 | 9.80392 | 0.2240 |
| 100 | 3.74 (-1) | 4650.1 | -0.426894 | 10.0000 | 0.2340 |
| 95 | 1.09 (-1) | 4688.5 | -0.964113 | 10.5263 | 0.2614 |
| 90 | 2.72 (-2) | 4719.5 | -1.565347 | 11.1111 | 0.2932 |
| 85 | 5.74 (-3) | 4743.9 | -2.241299 | 11.7647 | 0.3304 |

(Continued)

TABLE IX (Continued)

CALCULATED VAPOR PRESSURE AND HEATS
OF VAPORIZATION AND SUBLIMATION FOR ETHYLENE

| Temperature ($°K$) | Pressure (Mm Hg) | Heat of Vaporization (Cal/Gm Mole) | Log P (Mm Hg) | $1/T \times 10^3$ ($°K^{-1}$) | $(dP/dT)/P$ ($°K^{-1}$) |
|---|---|---|---|---|---|
| 80 | 9.88 (-4) | 4763.9 | -3.005294 | 12.5000 | 0.3746 |
| 75 | 1.34 (-4) | 4780.0 | -3.874430 | 13.3333 | 0.4276 |
| 70 | 1.35 (-5) | 4792.8 | -4.870728 | 14.2857 | 0.4922 |
| 65 | 9.48 (-7) | 4802.4 | -6.022983 | 15.3846 | 0.5720 |
| 60 | 4.27 (-8) | 4808.8 | -7.369518 | 16.6667 | 0.6722 |
| 55 | 1.09 (-9) | 4811.9 | -8.962435 | 18.1818 | 0.8005 |
| 50 | 1.34 (-11) | 4811.3 | -10.874409 | 20.0000 | 0.9684 |
| 45 | 6.17 (-14) | 4806.6 | -13.209965 | 22.2222 | 1.1944 |
| 40 | 7.50 (-17) | 4797.4 | -16.125177 | 25.0000 | 1.5088 |
| 35 | 1.37 (-20) | 4783.4 | -19.864190 | 28.5714 | 1.9649 |
| 30 | 1.47 (-25) | 4764.3 | -24.832129 | 33.3333 | 2.6638 |
| 25 | 1.76 (-32) | 4739.9 | -31.755167 | 40.0000 | 3.8162 |
| 20 | 8.32 (-43) | 4710.3 | -42.079905 | 50.0000 | 5.9256 |

(a) Numbers in parentheses indicate powers of 10; thus 9.16 (-1) = 0.916.

D. Comparison of Computed Vapor Pressures and Heats of Vaporization with
Experimental Data

The vapor pressure of liquid ethylene has been measured by Egan and Kemp,[10]
Michels and Wassenaar,[11] Lamb and Roper,[12] Henning and Stock,[14] and Tickner and
Lossing.[17] In the solid region Lister and McDonald[31] have measured vapor pres-
sures down to 77° K and applied corrections for thermomolecular pressure effects.

Tickner and Lossing[17] have measured the vapor pressure of solid ethylene down to 79° K using a mass spectrometer technique. Liang[32] has corrected the measurements of Tickner and Lossing for thermomolecular pressure effects and has reported two additional measurements of vapor pressure. Delaplace[33] reported smoothed values for' the vapor pressure of solid ethylene over the range 86° to 100° K, but did not give the pressure units. It has been assumed that the pressure units used by Delaplace are baryes as used in his earlier papers.[34]

The vapor pressures computed using Equation (19) have been compared with the experimentally determined vapor pressure data by calculating the temperature difference $(T_{calc} - T_{obs})$, where $T_{obs}$ is the reported temperature (corrected where possible to an ice point of 273.15° K) corresponding to the experimentally determined pressure, and $T_{calc}$ is the temperature which corresponds to this same pressure as determined by interpolation in the computed vapor pressure table (Table IX).[*] These temperature differences are shown for the various sets of published data in Figures 1 and 3.

The computed vapor pressures of liquid ethylene in the range 169.40° K to 120° K agree with the data of Egan and Kemp[10] to within 0.02° K except at the normal boiling point where the difference is 0.031° K, which corresponds to the difference between the n.b.p. temperature of Egan and Kemp (169.431° K) and the selected value of the normal boiling point (169.40° K). The computed vapor pressures disagree with the limited data of Michels and Wassenaar[11] by

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[*]Values of the calculated temperature corresponding to observed vapor pressures are interpolated from the values at even intervals using Aitken's iterative method of polynomial interpolation as described by Milne.[35] This method calculates the value of the dependent variable, in this case $1/T$, corresponding to a given value of the independent variable, in this case $\ln P$, by successively interpolating with a 1, 2, 3,..., n, n+1,...degree polynomial. In the computer program used here, this successive interpolation was continued until the value of $(1/T)$ computed by the $(n+1)$-th degree polynomial differed by less than 1 part in 100,000 from the value computed by the n-th degree polynomial.
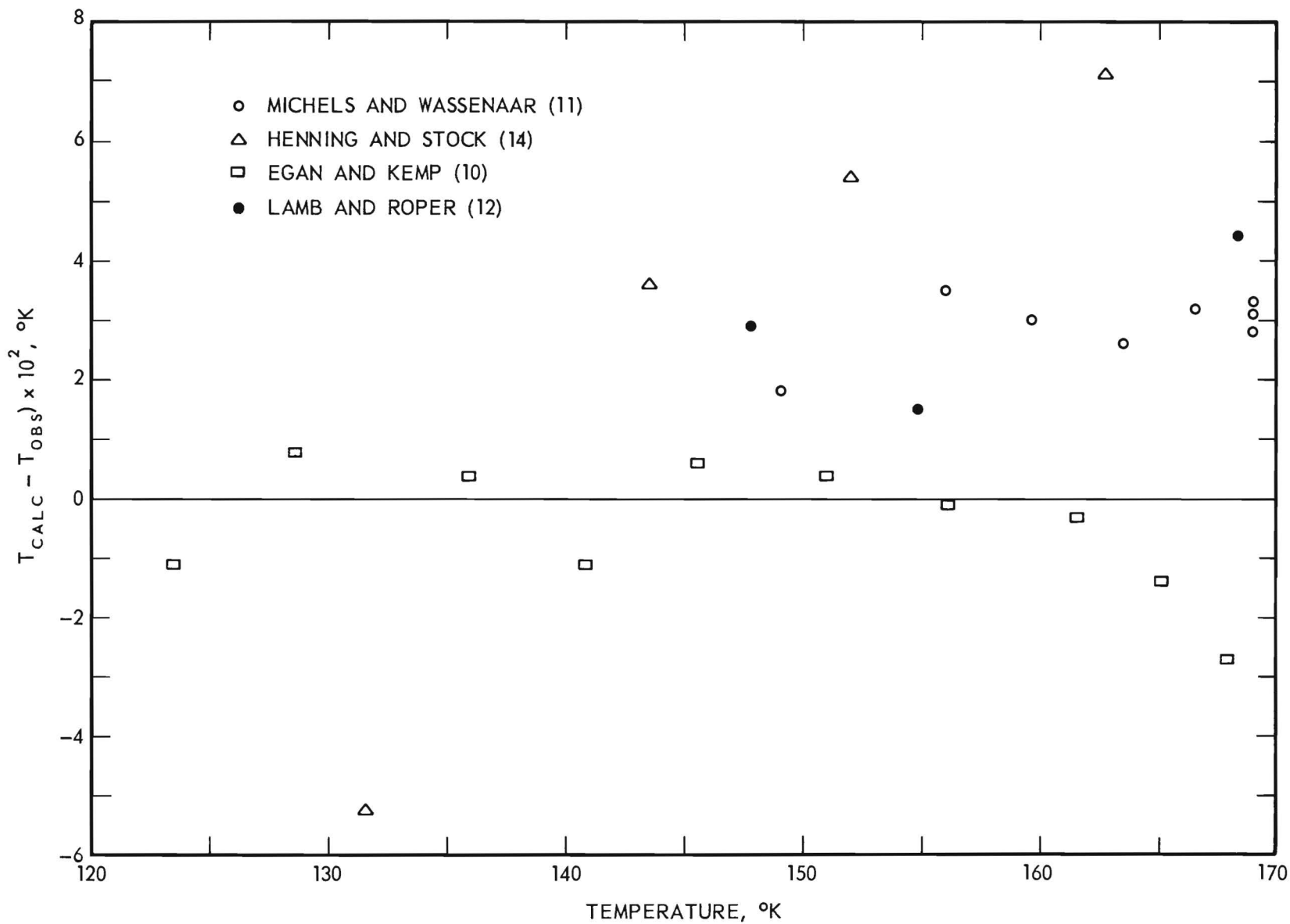
Figure 1. Comparison of Calculated and Experimental Vapor Pressures of Ethylene from 120° to 169.4° K.

an approximately constant amount of 0.03° K, which is the disagreement between the selected value of the boiling point 169.40° K and their measured value of the normal boiling point (169.37° K). The experimental data of Lamb and Roper[12] and Henning and Stock[14] show considerably larger deviations and more scatter than the data of Egan and Kemp and Michels and Wassenaar.

The good agreement obtained between the computed vapor pressures for liquid ethylene and the experimental values of Egan and Kemp[10] and Michels and Wassenaar[11] strongly suggest that the choice of Egan and Kemp's value of 3237 cal/gm mole for the heat of vaporization at the normal boiling point instead of Clusius and Konnertz' value of 3201 cal/gm mole is justified. This choice was further examined by computing $(\Delta H_v)_{T_1}$ from the experimental vapor pressure data using Equation (20). The heats of vaporization at the normal boiling point so computed are shown in Figure 2. The considerable scatter in $(\Delta H_v)_{T_1}$ near the normal boiling point is due to the sensitivity of Equation (20) to small temperature errors near the normal boiling point. It is seen from Figure 2 that a heat of vaporization of 3237 cal/gm mole is more consistent with the experimental vapor pressure data than a value of 3201 cal/gm mole. It may be noted that the heat of vaporization reported by Clusius and Konnertz at 143.4° K, namely, 3424 cal/gm mole, is smaller than the value of 3471.4 cal/gm mole interpolated from Table IX.

The agreement between the experimental vapor pressure data of Lister and McDonald[31] for solid ethylene and the computed vapor pressures is seen in Figure 3 to be good in the range 85° to 90° K but becomes increasingly poor as the temperature falls to 77.5° K where the pressure is about 0.0004 mm Hg. In this region the correction for thermal transpiration is uncertain and a pressure error of 10 per cent is approximately equivalent to a temperature error of 0.25°.
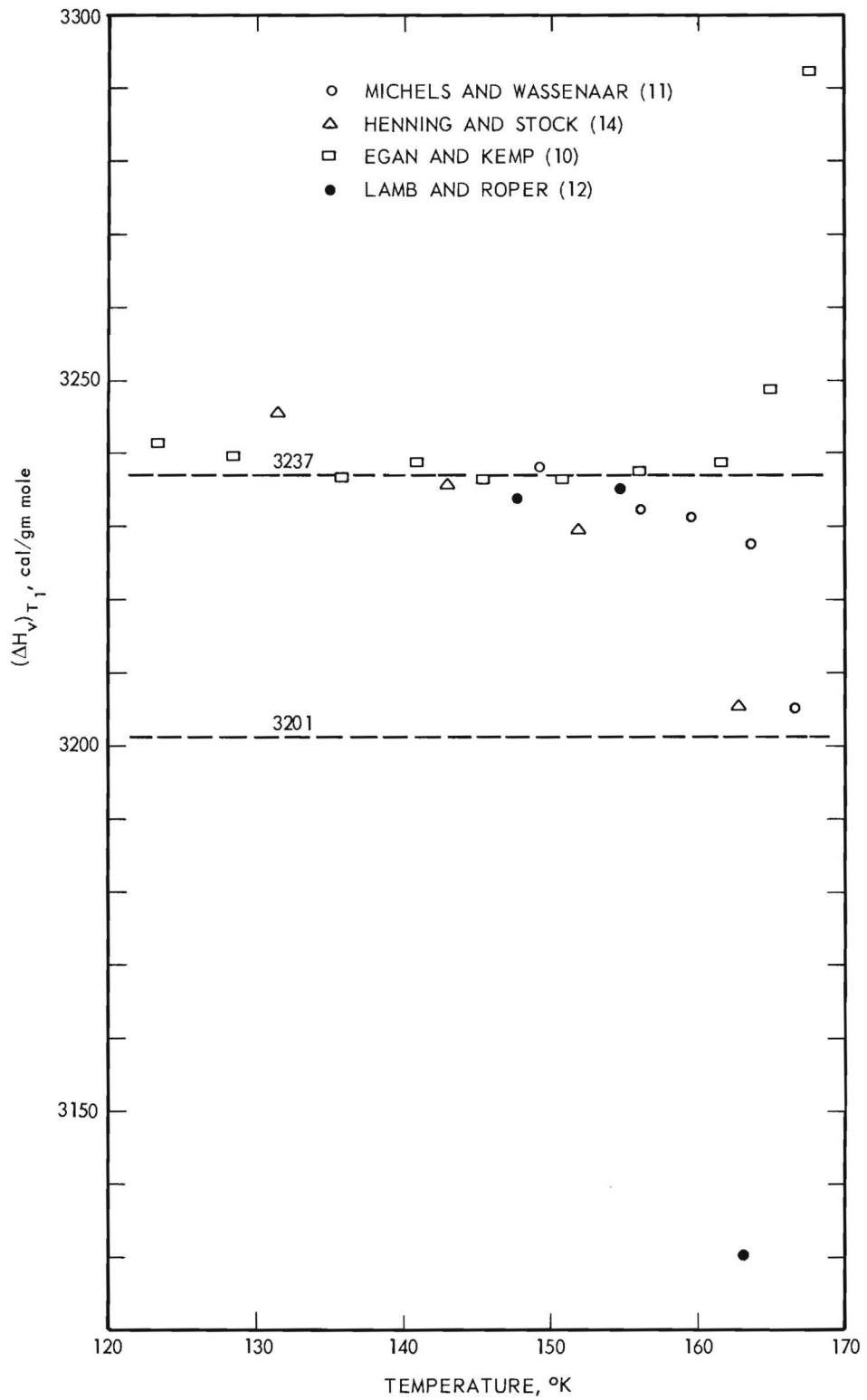
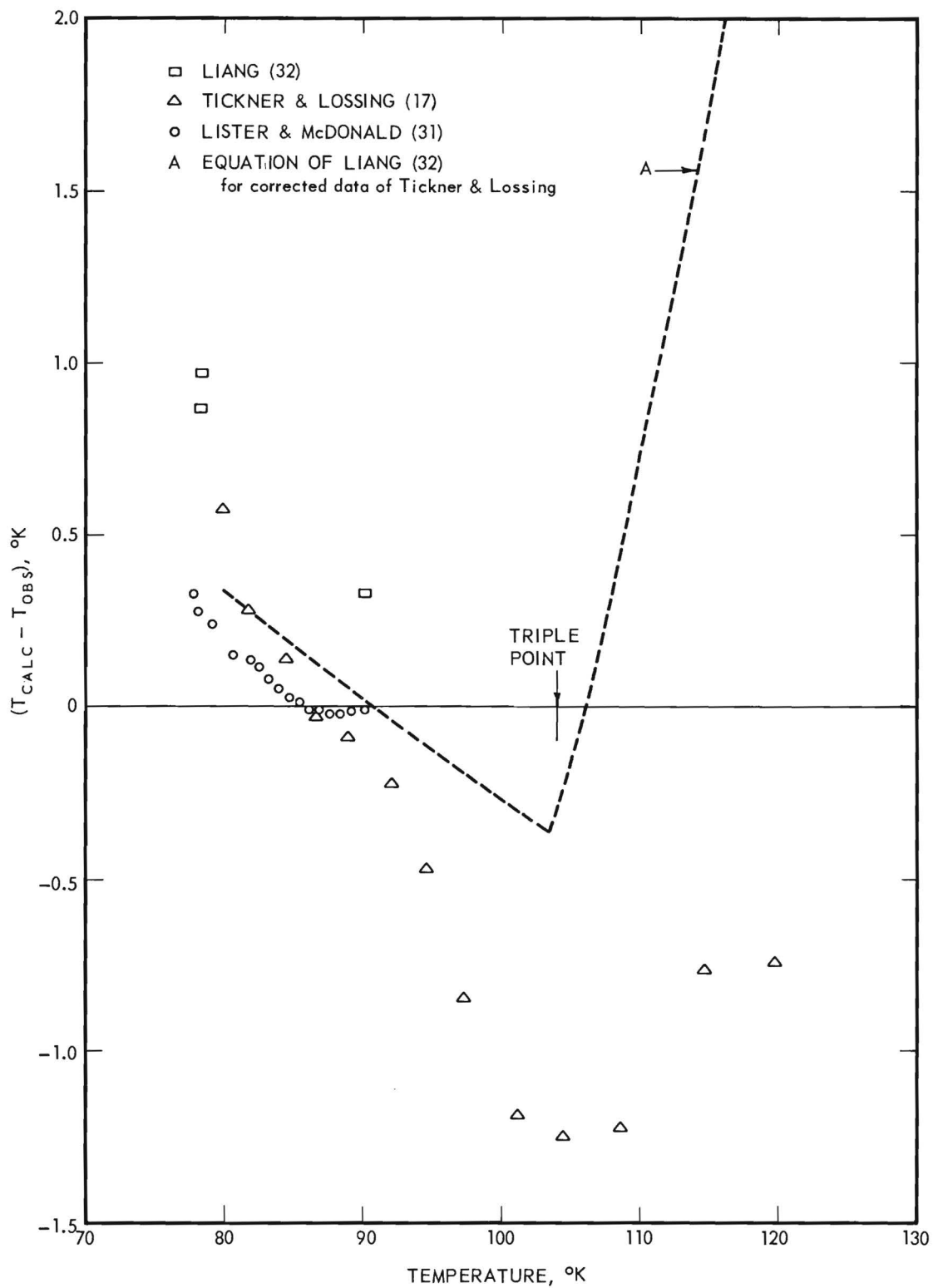Figure 2. Heat of Vaporization of Ethylene at the Normal Boiling Point Calculated from Equation (20).

Figure 3. Comparison of Calculated and Experimental Vapor Pressure of Ethylene below 120° K.

The data of Tickner and Lossing[17] and Liang[32] and Liang's correction of Tickner and Lossing's data for thermal transpiration[32] are seen to agree rather poorly with the computed vapor pressures. This may be due, at least in part, to the uncertainty in the temperatures reported by Tickner and Lossing, since they estimated that their temperatures were accurate to only about 0.3°. The vapor pressure data of Delaplace[33] (not shown) were much too low.

The triple point pressure of ethylene appears not to have been measured. The computed pressure corresponding to the selected triple point temperature of 103.97° K is 0.914 mm Hg.

The agreement between the computed and experimental vapor pressures of liquid ethylene below the normal boiling point is considered to be within the uncertaintie in the temperature scales used by the investigators. This agreement suggests that thermal data used in the calculations, including the second virial coefficient and its temperature derivative, are internally consistent.

The high degree of consistency found between the thermal and vapor pressure data of Egan and Kemp for liquid ethylene, together with the agreement found by them between the calorimetric and spectroscopic entropy of ethylene gas at its normal boiling point, strongly suggest that the thermal data obtained by them for ethylene at and below its triple point are to be relied upon. We conclude that the vapor pressures computed at and below the triple point (Table IX) are probably as accurate as the published experimental vapor pressure data for solid ethylene and provide a satisfactory set of vapor pressures down to 20° K.

The computed heats of vaporization and sublimation of ethylene given in Table IX are believed to represent these quantities within the accuracy of the thermal data now available.

E. Effect of Uncertainty in Input Data on Computed Results

A detailed analysis of the effect of uncertainty in the input data used to

compute Table IX has not been made. The good agreement found between the calculated and experimental vapor pressures of liquid ethylene suggested that the thermal data of Egan and Kemp are thermodynamically consistent with their measured vapor pressures.

One of the limitations in the applicability of Equation (19) is the uncertainty in the second virial coefficient near the normal boiling point. The effect of varying the second virial coefficient was examined by recomputing the vapor pressure of liquid and solid ethylene as a function of temperature using the set of intermolecular parameters ($e/k = 199.2^\circ$ K, $b_o = 116.7$ ml/gm mole) reported by Hirschfelder et al[26] while keeping all other input data to Equation (19) the same as given in Table VIII. Consideration of Figure 5, Appendix C, shows that these parameters give a somewhat smaller absolute value of the second virial coefficient than do the parameters used to compute Table IX.

A comparison of the vapor pressures computed with these parameters and the vapor pressures given in Table IX is shown in Figure 4. Curve A shows the difference in temperature, in a manner similar to Figure 1, between the two sets of vapor pressure calculation. It is obvious that the vapor pressures computed using the parameters $e/k = 199.2^\circ$ K, $b_o = 116.7$ ml/gm mole do not agree with the experimental vapor pressure data of Egan and Kemp and Michels and Wassenaar as well as do the pressures computed using the parameters $e/k = 150.76^\circ$ K and $b_o = 227.06$ ml/gm mole.

Curve B in Figure 4 shows the relation between the two sets of computed vapor pressures expressed as a percentage error. The vapor pressure computed using the Hirschfelder parameters is larger at each temperature than the vapor pressure at the same temperature given in Table IX. At the triple point these parameters give a triple point pressure of 0.9272 mm Hg compared with 0.9114 mm Hg computed in Table IX. The percentage difference at lower temperatures increases with decreasing temperature amounting to about 15 per cent at 20° K. It is to be noted, however, that the computed vapor pressure at this temperature is very small ($8.32 \times 10^{-43}$ mm Hg).

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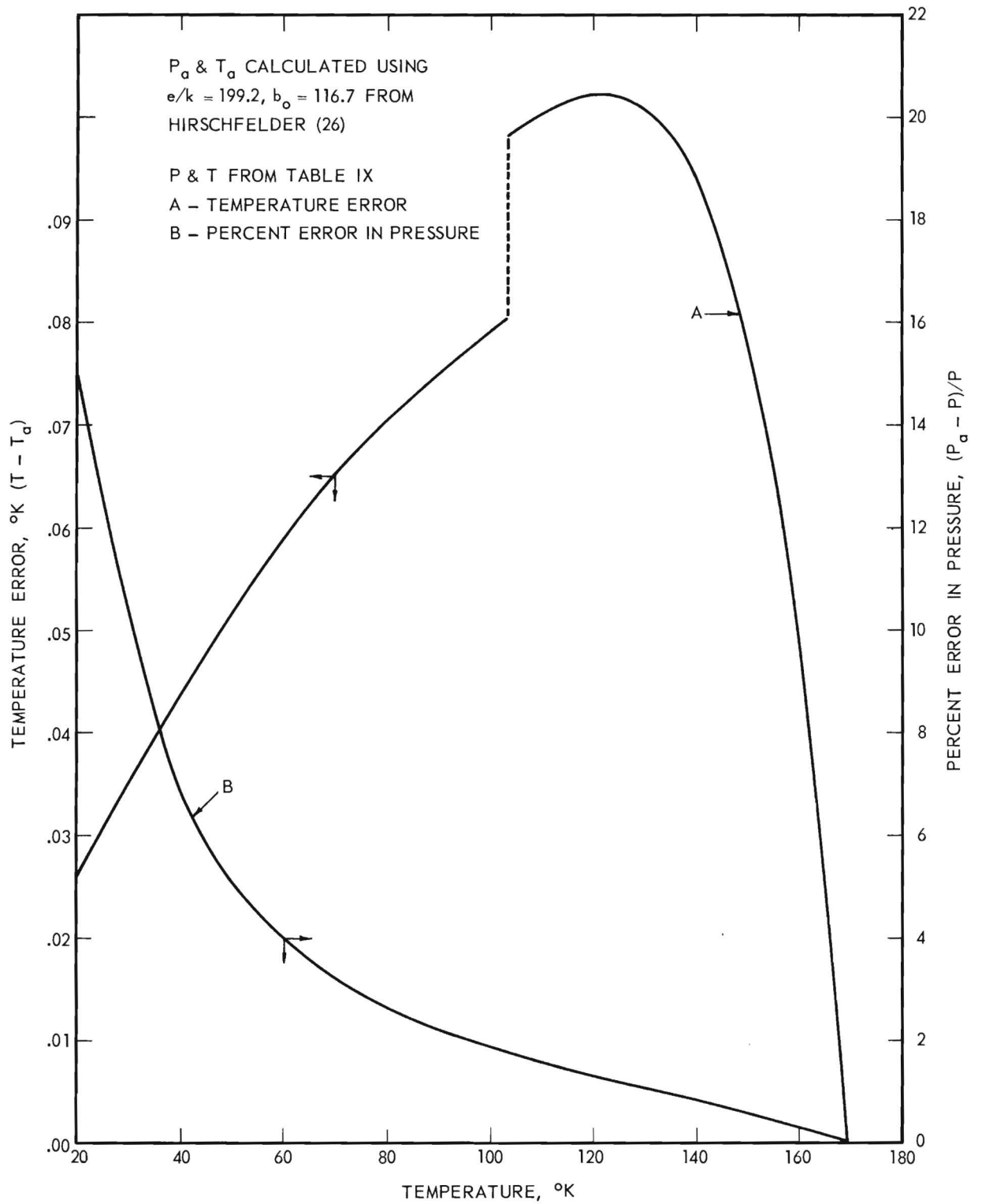Figure 4.  Effect of Varying Second Virial Coefficient on Calculated Vapor Pressures.

III. ACKNOWLEDGEMENTS

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## V.  APPENDICES

### A.  Nomenclature and Physical Constants

A, B, C  $\quad=\quad$ rotational constants, see Equation (33) $=$

$$\frac{h}{8\pi^2 c I_A}, \qquad \frac{h}{8\pi^2 c I_B}, \qquad \frac{h}{8\pi^2 c I_C},$$

B  $\quad=\quad$ second virial coefficient of gas.

$b_o$, e/k  $\quad=\quad$ parameters used in the Lennard-Jones (6-12) intermolecular potential function.

C  $\quad=\quad$ third virial coefficient of gas.

c  $\quad=\quad$ velocity of light = 2.997902 x $10^{10}$ cm/sec.

$c'_s$  $\quad=\quad$ molal heat capacity of saturated condensed phase.

G  $\quad=\quad$ Gibbs free energy.

$(G^o - H^o_o)''_T$  $\quad=\quad$ free energy function for ideal gas at P = 1 atm, T.

$(G^o - H^o_o)'$  $\quad=\quad$ free energy function of saturated condensed phase relative to $0^o$ K.

$(\Delta H_v)_T$  $\quad=\quad$ heat of vaporization (or sublimation) at T.

$(\Delta H_{tr})'$  $\quad=\quad$ heat of transition of condensed phase at transition temperature, $T_{tr}$.

$\sum\limits_{T}^{T_1} (\Delta H_{tr})'$  $\quad=\quad$ sum of all condensed phase transitions from T to $T_1$.

$\Delta H^o_o$  $\quad=\quad$ heat of sublimation at $0^o$ K.

$(H^o - H^o_o)''_T$  $\quad=\quad$ enthalpy function for ideal gas at T relative to $0^o$ K.

$(H^o - H^o_o)'_T$  $\quad=\quad$ enthalpy function of saturated condensed phase at T relative to $0^o$ K.

h  $\quad=\quad$ Planck's constant = 6.62377 x $10^{-27}$ erg sec/molecule.

$I_A$, $I_B$, $I_C$  $\quad=\quad$ principal moments of inertia of the molecule in gm $cm^2$.

| | | |
|---|---|---|
| $k$ | = | Boltzmann's constant = $1.380308 \times 10^{-16}$ erg/$^{\circ}$K molecule. |
| $M$ | = | molecular weight of ethylene = 28.054. |
| $P$ | = | pressure. |
| $P_1, T_1$ | = | pressure and temperature of a fixed point on the vapor pressure curve. For ethylene the normal boiling point was used. |
| $P_i, P_j$ | = | defined by Equation (21). |
| $Q$ | = | molecular partition function. |
| $R$ | = | gas constant = 1.98726 cal/gm mole $^{\circ}$K = 0.0820574 liter atm/gm mole $^{\circ}$K. |
| $S^*$ | = | entropy of the ideal gas. |
| $(S_o)'$ | = | entropy of solid at $0^{\circ}$ K. |
| $(S^o)''_{cal}$ | = | defined by Equation (21). |
| $(S^o)''_{spect}$ | = | statistically calculated entropy of the ideal gas at one atmosphere pressure. |
| $(S^o)''$ | = | entropy of ideal gas at $P = 1$ atm. |
| $(S^o - S_o)'$ | = | entropy of condensed phase relative to $0^{\circ}$ K. |
| $T$ | = | temperature on the thermodynamic scale with a defined ice point at $273.15^{\circ}$ K. |
| $T^*$ | = | temperature on the Kelvin Scale used by individual investigator. |
| $t^*$ | = | temperature on the Celsius Scale used by individual investigator. |
| $t$ | = | $^{\circ}$C. |
| $V$ | = | molal volume of gas. |
| $v_s'$ | = | molal volume of saturated condensed phase. |
| $w_i$ | = | wave number of the i-th frequency in cm$^{-1}$. |
| $x_i$ | = | $hcw_i/kT$. |

$\delta$    = defined by Equation (2) and Equation (4).

$\epsilon$    = defined by Equation (8) and Equation (9).

$\theta$    = e/kT.

$\sigma$    = symmetry number = 4 for ethylene.

## Superscripts

'    = condensed phase.

"    = gas phase.

*    = refers to temperature scale of individual investigator.  Also
       ideal gas state Equation (8).

## Subscripts

$O_2$    = normal boiling point of oxygen.

o    = ice point (except for $b_o$).

rot    = rotational.

s    = saturated vapor or condensed state.

trans    = translational.

vib    = vibrational.

v    = vaporization.  Also refers to sublimation for temperatures
       at and below the triple point.

c    = critical point.

## B. Conversion of Temperature Scales

The conversion of reported temperatures to a consistent thermodynamic temperature scale based on an ice point of 273.150° K has been carried out where possible. The "best" value for the normal boiling point of oxygen on this scale has been taken to be 90.168° K, the value selected by van Dijk.[9] The various methods used for making these conversions are given below. The final corrected thermodynamic temperature (in °K) used in this paper is represented by T; the temperature reported by the investigator is represented by $T^*$. In cases where the original temperatures were reported in degrees Celsius these were converted to $T^*$ by addition to the reported ice point $T_o^*$. The values of $T^*$ thus obtained were then treated by the appropriate relation given below. In the event no ice point was given the reported temperature in °C was added to 273.150 to obtain T in °K.

### 1. Method A

This method of correction was used when the ice point was given by the investigator and no other arbitrary choices of fixed points such as the oxygen point were made. The conversion relation is

$$T = T^* (T_o / T_o^*) \qquad (36)$$

where $T_o$ = 273.150° K.
This method was used for $0 < T^* < T_o^*$.

It is to be noted that this method of conversion of a thermodynamic scale from one ice point to another is strictly correct only if the ice point temperature is a <u>defined point</u>. When $T_o$ is obtained from a gas thermometer scale defined at the ice point and normal boiling point of water a more complicated

relation is required for exact conversion. (See, for instance, van Dijk[9].) Data for making the exact conversions are not always given by the investigator. Furthermore the exact relations reduce to the simple relation used in the first approximation. Henning and Otto[36] have used a somewhat different approximate method for correction than is given in Equation (36). Their relation gives the same result as Equation (36) to about 0.002°.

### 2. Method B

This method of correction, used for correction of reported temperatures where both oxygen point and ice point temperatures in °K are given by the investigator, is given by the relation

$$T = (T^* - T_{O_2}^*) \frac{(273.15 - 90.168)}{(T_o^* - T_{O_2}^*)} + 90.168 \qquad (37)$$

Equation (37) assumes a linear deviation between the reported temperature scale and the thermodynamic scale from the ice point $T_o^*$ to the oxygen point $T_{O_2}^*$.

As an example of the use of this relation we may give our method for correcting the Kelvin temperature scale used by Armstrong et. al for methane.[16] In that work temperatures above the oxygen point (-182.970° C) were measured on the International Temperature Scale. These investigators converted their measured temperatures to °K by addition of 273.16° K, their assigned ice point. The Kelvin scale thus obtained had a value of 90.190° K at the oxygen point and 273.16° K at the ice point. The Kelvin temperature scale used in our paper has an ice point of $T_o$ = 273.15° K and on this scale the "best" value of the oxygen point has been taken to be 90.168° K.[9] Thus the Kelvin temperatures reported by Armstrong et al were assumed to be 0.022° too high at 90.190° K and 0.01° too high at 273.16°. Our method assumes, for simplicity, that this difference varies linearly between the oxygen point and the ice point.

### 3. Method C

Where temperatures were given at $t^*$ °C, but were not on the International Temperature Scale, and an ice point $T_o^*$ was also given, $T^*$ was first computed from the relation

$$T^* = t^* + T_o^* \tag{38}$$

after which T was computed from $T^*$ by Method A.

## C. Second Virial Coefficient of Ethylene

Measurements of the second virial coefficient of ethylene have been made by Michels and Geldermans[38] (0° to 150° C), Eucken and Parts[39] (181° to 273° K), Cawood and Patterson[40] (0° to 21° C), Crommelin and Watts[41] (-1.36° to 20.18° C) and Roper[42] (199° to 343° K).

The data of Michels and Geldermans and Eucken and Parts shown in Table X were selected as the best data. Values of e/k and $b_o$ for the Lennard-Jones 6-12 potential function were determined by a least squares procedure using Equation (22) employing the seven values of B marked with an asterisk in Table X. These values were selected as representative of the data listed. The data of Michels and Geldermans have been corrected for $A_T = 0°$ C.[43,44] The e/k and $b_o$ values found by the least squares procedure were 150.76° K and 227.06 ml/gm mole, respectively. The agreement between the values of B computed from these parameters and the experimental data given in Table X is shown in Figure 5. Also shown is the variation of B with temperature computed from the Lennard-Jones parameters (e/k = 199.2° K, $b_o$ = 116.7 ml/gm mole) given by Hirschfelder et al,[26] based on the P-V-T data of Michels and Geldermans.[38]

TABLE X

EXPERIMENTAL VALUES OF THE SECOND VIRIAL COEFFICIENT OF ETHYLENE

| T (°K) | B (Ml/Mole) | Investigator | T (°K) | T (Ml/Mole) | Investigator |
|---|---|---|---|---|---|
| 181.13[*] | -428 | Eucken and Parts | 242.86 | -229 | Eucken and Parts |
| 191.32 | -381 | " | 250.57 | -212 | " |
| 193.01 | -374 | " | 252.99 | -207 | " |
| 201.88[*] | -339 | " | 262.08 | -192 | " |
| 203.46 | -333 | " | 273.20 | -176 | " |
| 209.92 | -312 | " | 273.15[*] | -167.84 | Michels and Geldermans |
| 212.22 | -305 | " | 298.15[*] | -140.33 | " |
| 220.13 | -280 | " | 323.15[*] | -117.97 | " |
| 223.12 | -275 | " | 348.15 | - 99.73 | " |
| 230.30 | -255 | " | 373.15 | - 84.93 | " |
| 232.38[*] | -250 | " | 398.15[*] | - 72.34 | " |
| 240.87 | -232 | " | 423.15 | - 62.29 | " |

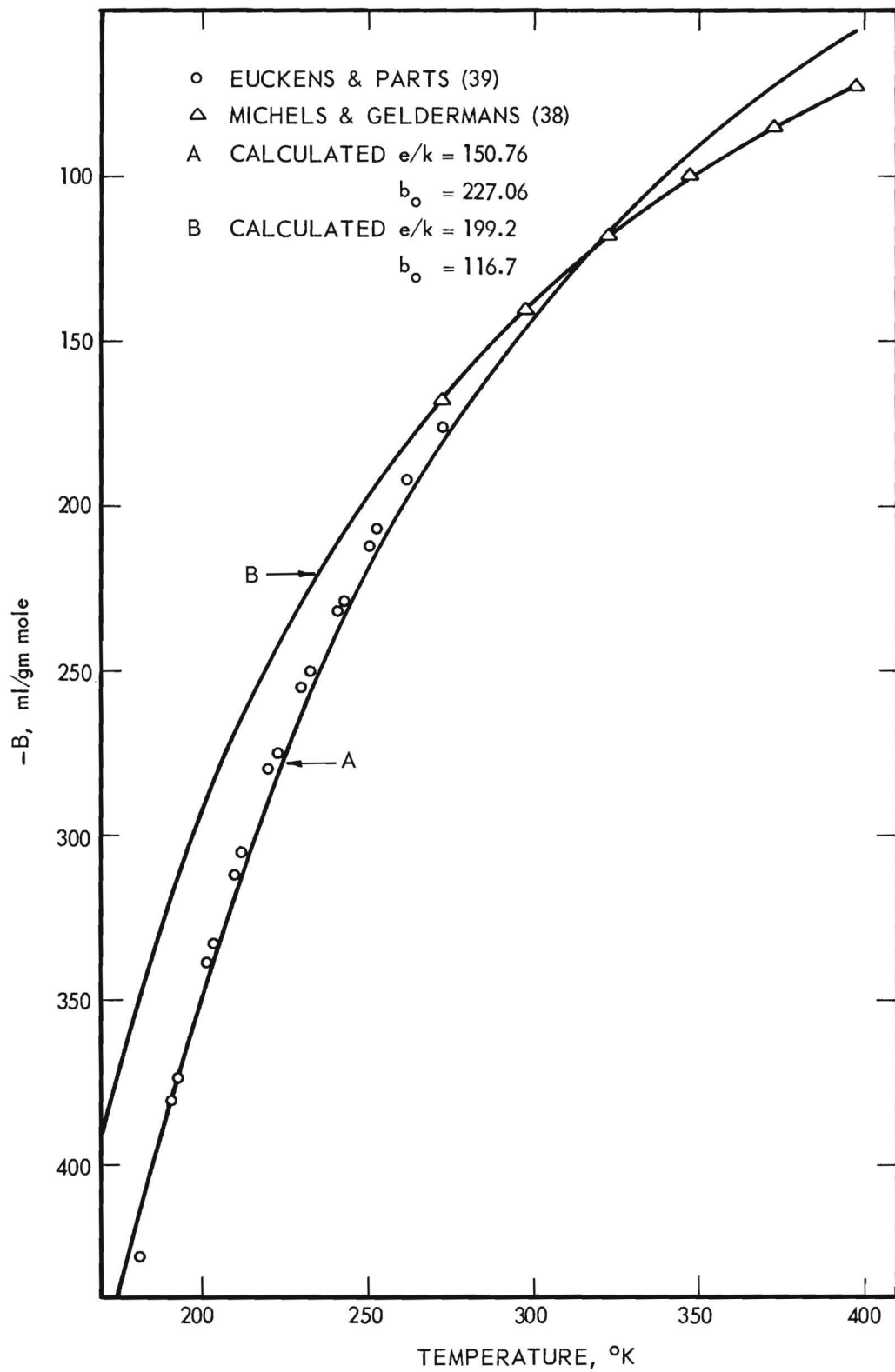[*]Data used in least squares determination of $(e/k)$ and $b_o$.

Figure 5.  Comparison of Calculated and Experimental Second Virial Coefficients for Ethylene.

TECHNICAL REPORT NO. 2

PROJECT NO. A-460


CALCULATION OF THE VAPOR PRESSURE AND HEATS OF VAPORIZATION
AND SUBLIMATION OF LIQUIDS AND SOLIDS, ESPECIALLY BELOW
ONE ATMOSPHERE PRESSURE.   II.   ARGON


By

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CONTRACT NO. CST-7238
NATIONAL BUREAU OF STANDARDS
BOULDER, COLORADO


JUNE 15, 1962


Engineering Experiment Station

Georgia Institute of Technology

Atlanta, Georgia

The values given in Table X, pages 22 and 23, should be replaced by the corrected values given below.

| Temperature (°K) | Pressure, P (Mm Hg) | | Heat of Vaporization (Cal/Gm Mole) | $1/T \times 10^2$ (°K$^{-1}$) | Log P | $(dP/dT)/P$ (°K$^{-1}$) |
|---|---|---|---|---|---|---|
| 67.0 | 2.9461 | (1) | 1904.0 | 1.49253 | 1.46925 | 0.2140 |
| 66.0 | 2.3706 | (1) | 1906.1 | 1.51515 | 1.37486 | 0.2206 |
| 65.0 | 1.8946 | (1) | 1908.1 | 1.53846 | 1.27751 | 0.2276 |
| 64.0 | 1.5033 | (1) | 1910.0 | 1.56250 | 1.17705 | 0.2350 |
| 63.0 | 1.1839 | (1) | 1911.9 | 1.58730 | 1.07333 | 0.2427 |
| 62.0 | 9.251 | | 1913.6 | 1.61290 | 0.96619 | 0.2507 |
| 61.0 | 7.169 | | 1915.3 | 1.63934 | 0.85546 | 0.2592 |
| 60.0 | 5.508 | | 1917.0 | 1.66667 | 0.74096 | 0.2681 |
| 59.0 | 4.193 | | 1918.5 | 1.69491 | 0.62249 | 0.2774 |
| 58.0 | 3.161 | | 1920.1 | 1.72413 | 0.49986 | 0.2873 |
| 57.0 | 2.360 | | 1921.5 | 1.75438 | 0.37284 | 0.2977 |
| 56.0 | 1.743 | | 1922.9 | 1.78571 | 0.24120 | 0.3086 |
| 55.0 | 1.273 | | 1924.3 | 1.81818 | 0.10468 | 0.3201 |
| 54.0 | 9.18 | (-1) | 1925.6 | 1.85185 | -0.03699 | 0.3323 |
| 53.0 | 6.54 | (-1) | 1926.8 | 1.88679 | -0.18409 | 0.3452 |
| 52.0 | 4.60 | (-1) | 1928.0 | 1.92307 | -0.33695 | 0.3588 |
| 51.0 | 3.19 | (-1) | 1929.2 | 1.96078 | -0.49588 | 0.3732 |
| 50.0 | 2.18 | (-1) | 1930.2 | 2.00000 | -0.66127 | 0.3885 |
| 48.0 | 9.71 | (-2) | 1932.2 | 2.08333 | -1.01300 | 0.4220 |

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The following data points plotted in Figure 3, page 25 and Figure 4, page 26, should be corrected. All other points in the affected temperature region are changed by less than 0.002° K.

| Temperature (°K) | $T_{calc} - T_{obs}$ (°K) | | Observer |
| | Plotted | Corrected | |
| --- | --- | --- | --- |
| 66.31 | 0.211 | 0.199 | Born (7) |
| 65.66 | 0.235 | 0.226 | Born (7) |
| 66.54 | 0.023 | 0.011 | Flubacher et al (21) |
| 66.19 | 0.085 | 0.074 | Flubacher et al (21) |

July 2, 1963

W. T. Ziegler, J. C. Mullins, and B. S. Kirk

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ABSTRACT

The vapor pressure and heats of vaporization and sublimation of argon have been calculated from 88° to 20° K using thermodynamic relations. The calculations made use of published thermal data for saturated liquid and solid argon and second virial coefficient data for the gas. Comparison of the computed vapor pressures with available experimental vapor pressure data showed that the experimental vapor pressure data were not thermodynamically consistent with the published thermal and second virial coefficient data. However, it was found that by decreasing the assigned value of the heat of vaporization at the normal boiling point by about one per cent the computed vapor pressures agreed quite well with the experimental measurements of Flubacher et al, which appear to be the most accurate data. The effects of small adjustments of the other thermal and the second virial coefficient data on the computed vapor pressure were also examined. It was found that no reasonable adjustment of these data alone could bring the computed and experimental vapor pressure data into agreement.

The adjusted heat of vaporization at the normal boiling point, together with our choice of the best experimental values for the other necessary thermal and second virial coefficient data, have been used to compute the vapor pressure and heats of vaporization and sublimation of argon at 1 degree intervals from 88° to 50° K and 2 degree intervals from 50° to 20° K.

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## I. INTRODUCTION

In a previous report[1][*] a number of thermodynamic relations were developed for the calculation of the vapor pressure and heats of vaporization and sublimation of liquids and solids. Some of these relations were then applied to the calculation of the vapor pressure and heats of vaporization and sublimation of ethylene from its normal boiling point (169.40° K) to 20° K. These relations have also been applied to parahydrogen[2] from 22° to 1° K and oxygen[3] from 100° to 20° K.

The present paper is concerned with the application to argon of the thermodynamic relations previously developed.[1] The principal thermodynamic relations used are summarized in the next section. The available thermodynamic data have been used to compute the vapor pressure and heats of vaporization and sublimation of argon from its normal boiling point (87.291°K) to 20° K. The computed results have been compared with the available experimental vapor pressure and heat of vaporization data. As in the previous reports on ethylene[1] and oxygen,[3] temperatures have been converted to the thermodynamic temperature scale with an assigned ice point of 273.15° K. On this scale the normal boiling point of oxygen has been taken to be 90.168° K. This value is based on an analysis of the various reported normal boiling points of oxygen made by van Dijk.[4]

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[*]Superscripts refer to references listed in the Bibliography.

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## II.  THERMODYNAMIC RELATIONS

### A.  Variation of Heat of Vaporization and Sublimation with Temperature

By performing an enthalpy cycle between two points, $(P,T)$ and $(P_1,T_1)$, on the vapor pressure curve of a pure substance it may be shown[1] that the heat of vaporization or sublimation may be computed as shown in Equation (1).

$$(\Delta H_v)_T = (\Delta H_v)_{T_1} + \int_T^{T_1} c_s' \, dT + \sum_T^{T_1} (\Delta H_{tr})' - \left[ (H^o - H_o^o)_{T_1}'' - (H^o - H_o^o)_T'' \right]$$

$$- RT_1 \, \delta_1 + RT\delta + \int_P^{P_1} v_s' \, dP \tag{1}$$

In this equation the quantity $\delta$ is given by the relation

$$RT\delta = \left[ H(P,T) - H^o(T) \right]'' \tag{2}$$

and $\delta_1$ is the value of $\delta$ at the point $(P_1,T_1)$.  The prime (') and double prime (") symbols refer to the condensed and vapor phases, respectively.  All other symbols are explicitly defined in Appendix A.  The evaluation of the right-hand side of Equation (2) requires an equation of state for the vapor. If a virial form of the equation of state is used, namely

$$PV = RT(1 + \frac{B}{V} + \frac{C}{V^2} + \ldots) \tag{3}$$

where the virial coefficients are assumed to be functions of temperature only, then one obtains

$$\delta = (B - T \frac{dB}{dT})/V + (C - \frac{1}{2} T \frac{dC}{dT})/V^2 + \ldots \tag{4}$$

For temperatures below the triple point, $(\Delta H_v)_T$ in Equation (1) is the

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heat of sublimation rather than the heat of vaporization. The evaluation of the last two terms of Equation (1) requires a value of the vapor pressure at T. If vapor pressure calculations are made by an iterative procedure, as described below, then this iterative procedure also provides the pressure necessary to compute the last two terms of Equation (1).

## B. Vapor Pressure Relations

From a known point $(P_1, T_1)$ on the vapor pressure curve, the vapor pressure at any other point $(P,T)$ may be calculated from the previously derived relation[1]

$$\ln P = \ln P_1 - (\Delta H_v)_{T_1}(T_1 - T)/RTT_1 + \left[ (H^O - H_o^O)''_{T_1} - (H^O - H_o^O)''_T \right]/RT$$

$$- \left[ (S^O)''_{T_1} - (S^O)''_T \right]/R - \left( \int_T^{T_1} c_s' \, dT \right)/RT$$

$$- \left( \sum_T^{T_1} (\Delta H_{tr})' \right)/RT + \left( \int_T^{T_1} c_s' \, dT/T \right)/R$$

$$+ \left( \sum_T^{T_1} (\Delta H_{tr})'/T_{tr} \right)/R + \delta_1 (T_1 - T)/T$$

$$- \varepsilon_1 + \varepsilon - \left( \int_P^{P_1} v_s' \, dP \right)/RT \tag{5}$$

where

$$\varepsilon = \left[ H^O(T) - H(P,T) \right]''/RT - \left[ S^*(P,T) - S(P,T) \right]''/R \tag{6}$$

and $\varepsilon_1$ is the value of $\varepsilon$ at $(P_1, T_I)$.

Equation (5), which may be considered to be an integration of the Clapeyron equation, may be solved if appropriate thermal data for the condensed

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phase, $(\Delta H_v)_{T_1}$, an equation of state for the real gas, and the requisite spectroscopic and molecular structure data for the ideal gas are available. Solution of Equation (5) requires iteration since the last two terms are pressure dependent.

Equation (5) can be rearranged as follows:

$$(\Delta H_v)_{T_1} = \left\{ RT \ln P_1/P + \left[ (H^o - H_o^o)''_{T_1} - (H^o - H_c^o)''_T \right] \right.$$

$$- \int_T^{T_1} c_s' \, dT - \sum_T^{T_1} (\Delta H_{tr})' - T \left[ (S^o)''_{T_1} - (S^o)''_T \right]$$

$$+ T \int_T^{T_1} c_s' \, dT/T + T \sum_T^{T_1} (\Delta H_{tr})'/T_{tr}$$

$$\left. + R(T_1 - T)\delta_1 - RT\varepsilon_1 + RT\varepsilon - \int_P^{P_1} v_s' \, dP \right\} T_1/(T_1 - T) \tag{7}$$

Equation (7) may be used to compute the heat of vaporization at a given point $(P_1, T_1)$ (say the normal boiling point or triple point) from two points $(P_1, T_1)$ and $(P, T)$ on the vapor pressure curve. It may also be used to examine the thermodynamic consistency of the experimental thermal, equation of state and vapor pressure data by computing $(\Delta H_v)_{T_1}$ for the various experimental $(P, T)$ points. Neither of these uses of Equation (7) requires an iterative procedure in the calculations. It may be shown that as $T$ approaches $T_1$ Equation (7) reduces to the Clapeyron equation.

## III. EXPERIMENTAL DATA FOR ARGON

### A. Introduction

The calculation for argon of vapor pressures from Equation (5) and heats of vaporization or sublimation from Equation (1) requires the following data: $(\Delta H_v)_{T_1}$, $P_1$, $T_1$, $(\Delta H_f)$, $T_f$ and $c_s'$ and $v_s'$ as a function of temperature. In addition a representation of the second virial coefficient as a function

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of temperature is required. In the range of interest argon may be treated as a classical monatomic gas to obtain the thermodynamic functions of the ideal gas at one atmosphere.

In calculating the vapor pressure and heats of vaporization and sublimation of a substance from the normal boiling point to some lower temperature, in this case 20° K, it is often most convenient to take $(P_1, T_1)$ as the normal boiling point since this datum point is usually well established. In the case of argon, however, the triple point was chosen as a starting point for the calculation since it appeared to be more accurately determined.

## B. Phase Transition Temperatures of Argon

### 1. Normal Boiling Point

The normal boiling point of argon has been determined by a number of investigators. The results are summarized below in Table I. From the experimental data available it appears that the normal boiling point is 87.28° K with an uncertainty of ± 0.015° K.

### 2. Triple Point

The triple point of argon has been determined by a number or investigators. The results are summarized in Table II.

The triple point temperature of Clusius and Wiegand[17] was determined using an oxygen vapor pressure thermometer. From the oxygen vapor pressure (368.2 mm Hg) we have interpolated a temperature from the oxygen vapor pressure table of Hoge[11] and then further corrected this temperature to the thermodynamic scale as outlined in Appendix B. The temperature reported by Pool et al[19] was also obtained using an oxygen vapor pressure thermometer (368.69 mm Hg). The triple point temperature of Flubacher et al[21] was

TABLE I

NORMAL BOILING POINT OF ARGON

| Reported Temperature | Ice Point (°K) | Method of Correction[a] | Corrected Temperature ($T_o$ = 273.15° K) (°K) | Year | Investigator |
|---|---|---|---|---|---|
| 86.9° K | | | | 1901 | Ramsay and Travers[5] |
| -185.84° C | 273.09 | C | 87.269 | 1913 | Crommelin[6] |
| 87.48° K | | | | 1922 | Born[7] |
| 87.29° K | | | 87.287[b] | 1943 | Clusius and Frank[8] |
| 87.29° K | | B | 87.269 | 1951 | Clark et al[9] |
| 87.25° K | 273.15 | | 87.25 | 1951 | Michels et al[9] |
| 87.28° K[c] | 90.18 | B | 87.278 | 1956 | Freeman and Halsey[10] |

a See Appendix B.

b Measured with oxygen vapor pressure thermometer, P = 555.8 mm Hg. Corrected temperature obtained by using vapor pressure of Hoge[11] and then correction by method B.

c Reported temperature based on extrapolation of Callendar-van Dusen equation with an assigned oxygen point of 90.18° K.

obtained using a platinum resistance thermometer calibrated on the NBS provisional scale with an assigned boiling point of oxygen of 90.18° K. The carefully determined triple point of Michels et al[20] was also determined using a platinum resistance thermometer with an ice point of 273.15° K. Conversion to the thermodynamic scale was made by adding 273.15° K to their reported temperature.

A value of 83.80° K has been selected as the "best" value for the triple point temperature of argon. This value is an average of the temperatures

given in Table II for the data of Clusius and Wiegand,[17] Pool et al,[19] Michels et al,[20] and Flubacher et al.[21] The temperature reported by Clark et al[9] appears to be too lov

The triple point temperature reported by Freeman and Halsey[10] was not included because it is based on an extrapolation of the Callendar-van Dusen equation which is difficult to relate to the thermodynamic temperature scale.

Clusius and coworkers[15,16,18] have reported several values for the triple point pressure of argon, of which the pressure of 516.85 mm Hg appears to us to be the most reliable value. This pressure is in excellent agreement with the values 516.82 and 516.86 mm Hg reported by Pool et al[19] and Flubacher et al,[21] respectively. The pressure 516.84 mm Hg, selected as the "best" value for the triple point pressure, is an average of these three values.

## C. Heats of Vaporization and Fusion of Argon

### 1. Heat of Vaporization

Experimental measurements of the heat of vaporization of argon have been made by Eucken,[22] Frank and Clusius,[16] and Flubacher et al.[21] These values are summarized in Table III. Flubacher et al, using their measured value of the heat of vaporization at 85.67° K, computed a value of 1555.0 ± 4.6 cal/gm mole for the heat of vaporization at their assigned value of the normal boiling point. Our method of calculation, using Equation (1), where $T_1$ is equal to 85.67° K and $P_1$ is equal to 637.20 mm Hg[*] gives a value of 1552.3 cal/gm mole for a normal boiling point of 87.291° K. The discrepancy is larger than one would expect and is unexplained.

### 2. Heat of Fusion

The heat of fusion of argon at the triple point has been determined

[*]Calculated for T = 85.67° K from the vapor pressure equation of Flubacher et al.[21]

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## TABLE II

## TRIPLE POINT OF ARGON

| Reported Temperature | Ice Point (°K) | Method of Correction[a] | Corrected Temperature (°K) | Pressure (Mm Hg) | Year | Investigator |
|---|---|---|---|---|---|---|
| -189.6° C | | | | | 1895 | Olszewski[12] |
| 85.1° K | | | | | 1902 | Ramsay and Travers[13] |
| -189.30° C | 273.09 | C | 83.808 | | 1913 | Crommelin[6] |
| 83.81° K | | | | 521.4 | 1916 | Holst and Hamburger[14] |
| 83.90° K | | | | 515.65 | 1922 | Born[7] |
| | | | | 516.5 ± 0.3 | 1936 | Clusius[15] |
| | | | | 516.8 ± 0.2 | 1939 | Frank and Clusius[16] |
| 83.78° K[b] | | B | 83.788 | | 1940 | Clusius and Wiegand[17] |
| | | | | 516.85 ± 0.06 | 1941 | Clusius and Staveley[18] |
| 83.78° K[c] | | B | 83.760 | 515.7 | 1951 | Clark et al[9] |
| 83.77° K[d] | 273.15 | | | 514.1 | 1956 | Freeman and Halsey[10] |
| -189.341° C | 273.15 | C | 83.809 | | 1957 | Michels et al[20] |
| 83.819° K[e] | 90.19 | B | 83.799 | 516.82 | 1958 | Pool et al[19] |
| 83.810° K[f] | 90.18 | B | 83.799 | 516.86 ± 0.02 | 1961 | Flubacher et al[21] |
| | Selected Value | | 83.80 | 516.84 | | |

a   See Appendix B.
b   The reported temperature was obtained with an oxygen vapor pressure thermometer (P = 368.2 mm Hg). The corrected temperature was obtained by interpolation from Hoge's oxygen vapor pressure table[11] and then further correction using method B.
c   Reported temperature was based on Hoge's oxygen vapor pressures.[11]
d   Reported temperature was based on an extrapolation of the Callendar-van Dusen equation with an assigned oxygen point of 90.18° K.
e   Reported temperature was obtained using an oxygen vapor pressure thermometer (368.69 mm Hg) and interpolation from Hoge's oxygen vapor pressure table.[11]
f   The reported temperature is based on the NBS provisional scale with an assigned oxygen point of 90.18° K.

TABLE III

HEAT OF VAPORIZATION OF ARGON

| Reported Temperature (°K) | Reported Pressure (Mm Hg) | Heat of Vaporization (Cal/Gm Mole) | Year | Investigator |
|---|---|---|---|---|
| | 760 | 1501 | 1916 | Eucken[22] |
| 87.29 | 760 | 1557.5 ± 1.5 | 1939 | Frank and Clusius[16] |
| 85.67 | | 1563.6 ± 4.6 | 1961 | Flubacher et al[21] |

by Eucken,[22] Eucken and Hauck,[23] Clusius,[15] and Flubacher et al.[21] These values are summarized in Table IV. The selected value is an average of the values of Flubacher et al and Clusius.

TABLE IV

HEAT OF FUSION OF ARGON

| Reported Temperature (°K) | Heat of Fusion (Cal/Gm Mole) | Year | Investigator |
|---|---|---|---|
| | 267.9 | 1916 | Eucken[22] |
| 83.55 | 265.2 | 1928 | Eucken and Hauck[23] |
| 83.85 | 280.8 | 1936 | Clusius[15] |
| 83.810 | 284.5 ± 0.4 | 1961 | Flubacher et al[21] |
| Selected Value | 282.6 | | |

D. Molal Volume of Saturated Liquid and Solid Argon

### 1. Saturated Liquid

The density of liquid argon has recently been determined as a function of pressure by van Itterbeek and Verbeke[24] from 86.6° to 90.5° K. These values are in good agreement with the saturation data of Mathias et al,[25] which cover the range from 90° to 168° K. The earlier density values of Baly and Donnan[26] measured over the range 84.5° to 89° K are somewhat higher than those of van Itterbeek and Verbeke. The saturated liquid data of van Itterbeek were plotted and a smooth curve drawn to obtain values of the molal volumes used in this work. Between the triple point (83.80° K) and the boiling point (87.291° K) an average molal volume was taken to be 28.30 ml/gm mole, the value corresponding to 85.5° K. The value of the molal volume extrapolated to the triple point was 28.17 ml/gm mole.

### 2. Saturated Solid

The density of solid argon has been determined by a number of investigators. A summary of the experimental results is given in Table V. The results of Dobbs et al[27] are the smoothed results of a number of determinations between 20° and 80° K. Between 20° and 60° K the values were determined from x-ray measurements. Above 60° K the density was determined by the condensation of gas into a known volume. Their results are stated to be accurate to 0.001 gm/cm$^3$. The change in volume at the triple point has been determined by Clusius and Wiegand,[17] and Simon et al[28] from the melting curve and the Clausius-Clapeyron equation. Bridgman[29] has measured the change in volume along the melting curve.

Other x-ray determinations at single points were made by de Smedt and Keesom[30] at 20° K and by Simon and von Simson[31] at 40° K. A recent determination

TABLE V

DENSITY AND MOLAL VOLUME OF SOLID ARGON

| Temperature (°K) | Density (Gm/Ml) | Molal Volume (Ml/Gm Mole) | Year | Investigator |
|---|---|---|---|---|
| 4.2 | 1.83 | 21.83 | 1958 | Henshaw[32] |
| 20 | 1.68 | 23.78 | 1925 | de Smedt and Keesom[30] |
| 20 | 1.764 ± 0.001 | 22.64 | 1956 | Dobbs et al[27] |
| 40 | 1.737 ± 0.001 | 23.00 | 1956 | Dobbs et al[27] |
| 40 | 1.65 ± 0.02 | 24.21 | 1924 | Simon and von Simson[31] |
| 60 | 1.691 ± 0.001 | 23.62 | 1956 | Dobbs et al[27] |
| 80 | 1.636 ± 0.001 | 24.42 | 1956 | Dobbs et al[27] |
| 83.80 | | 24.64[a] | 1940 | Clusius and Wiegand[17] |
| 83.80 | | 25.21[a] | 1930 | Simon, Ruhemann and Edwards[28] |
| 83.80 | | 24.99[a] | 1934 | Bridgman[29] |

a   Molal volume computed using the $\Delta V$ reported by the investigator and a value of the molal volume of the liquid of 28.17 ml/gm mole obtained by extrapolation of the data of van Itterbeek and Verbeke.[24]

of the density at 4.2° K was made by Henshaw[32] using neutron diffraction.

In determining the best values for the molal volume a smooth curve was drawn using only the values of Dobbs et al,[27] Clusius and Wiegand,[17] and Henshaw.[32] The mean molal volumes used in the calculations are given in Table VI. The values correspond to the midpoint temperature of the range.

E.  Heat Capacity of Argon

   1.  Saturated Solid

       The heat capacity of solid argon has been determined over the entire range from 2° K to the triple point by Flubacher et al,[21] from 10° K to the

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TABLE VI

MEAN MOLAL VOLUMES OF SOLID ARGON
USED IN CALCULATIONS

| Temperature Range (°K) | Mean Molal Volume (Ml/Gm Mole) |
|---|---|
| 11 - 25 | 22.39 |
| 25 - 50 | 22.91 |
| 50 - 83.80 | 23.88 |

triple point by Clusius,[15] from 17.8° K to the triple point by Eucken,[22] from 16° to 34° K by Figgins,[33] from 3° to 20° K by Hill (private communication to Figgins[33]), and from 1.2° to 20° K by Anderson.[34]

Of these data the results of Figgins agree with those of Flubacher to within $\pm$ 0.7 per cent which is about the combined, stated accuracy of these investigators. The heat capacity data of Clusius are several per cent smaller than the results of Flubacher et al over most of the range.

The data of Anderson[34] and Flubacher et al[21] have been compared by Beaumont et al[35] as follows: "Over a large part of the temperature region, particularly between 3° and 4° K and above 9° K, the two sets for both argon and krypton agree within their probable accuracies. Between 4° and 9° K Anderson's heat capacities for argon are larger by as much as 4 per cent, and for krypton smaller by as much as 5 per cent."

Figgins has presented the data of Hill in graphical form. He reported that his heat capacity measurements agreed with those of Hill to within 0.5 per cent in the temperature range 16° to 20° K where their measurements overlap.

For this work the data of Flubacher et al[21] and Figgins[33] were fitted by the method of least squares to a series of polynomials of the form

$$c_s' = a_o + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4. \tag{8}$$

The values of the coefficients are given in Table VII.

TABLE VII

COEFFICIENTS OF HEAT CAPACITY POLYNOMIALS
FOR SATURATED CONDENSED ARGON

| Range (°K) | $a_o$ | $a_1$ | $a_2 \times 10^2$ | $a_3 \times 10^3$ | $a_4 \times 10^5$ |
|---|---|---|---|---|---|
| 2.2 - 11.0 | 0 | 0 | -0.093015412 | 0.91416842 | 0 |
| 11.0 - 25.0 | -2.20200229 | 0.33244188 | -0.81945980 | 0.33859774 | -0.66588517 |
| 25.0 - 50.0 | -0.82099500 | 0.21619186 | 0.01876584 | -0.07208966 | 0.072838381 |
| 50.0 - 83.8 | -2.8014270 | 0.38832982 | -0.60113758 | 0.035483745 | 0 |
| 83.8 - 87.291 | 10.586 | 0 | 0 | 0 | 0 |

## 2. Saturated Liquid

Heat capacity of liquid argon between the triple point and boiling point has been determined by Flubacher et al,[21] Clusius,[15] and Eucken.[22] For the present work the data of Flubacher have been taken as the most reliable. Over this short range, 83.80° to 87.291° K, the heat capacity was considered constant and equal to 10.586 cal/gm mole °K.

## F. Experimental Vapor Pressure Data for Argon

The vapor pressure of argon below one atmosphere pressure has been measured by a number of investigators. A summary of the investigations is given

in Table VIII. The most recent measurements are those of Clark, Din and Robb,[9] Flubacher, Leadbetter and Morrison[21] and Freeman and Halsey.[10] The reported purity of the argon used in these studies was very high.

The measurements of Clark et al[9] are reported to be comparable in accuracy with the vapor pressure data for oxygen given by Hoge.[11] Temperature measurements of Clark et al were made by direct measurement of the vapor pressure of oxygen using the vapor pressure tables of Hoge.[11] The vapor pressure of argon was determined by a differential manometer between the oxygen and argon vapors. From the absolute pressure of oxygen (from which temperature was obtained) and the differential pressure, the vapor pressure of argon was obtained.

TABLE VIII

VAPOR PRESSURE MEASUREMENTS FOR ARGON

| Investigator | Year | Range (°K) |
|---|---|---|
| Olszewski[12] | 1895 | 86.2 - 152.0 |
| Ramsay and Travers[13] | 1902 | 77.3 - 87.8 |
| Holst and Hamburger[14] | 1916 | 83.6 - 90.0 |
| Crommelin[6] | 1913 | 67.8 - 87.2 |
| Born[7] | 1922 | 65.4 - 90.3 |
| Clark, Din and Robb[9] | 1951 | 70.0 - 150.7 |
| Freeman and Halsey[10] | 1956 | 82.0 - 88.2 |
| Flubacher, Leadbetter and Morrison[21] | 1961 | 66.1 - 86.7 |

The vapor pressure data of Flubacher et al[21] were obtained using a thermometer calibrated on the NBS provisional scale. The details of the pressure measurements were not given.

The limited data of Freeman and Halsey[10] were available only in the form of two equations. The equation for the solid range extended from 82.0° to

83.77° K. The equation for the liquid covered the range 83.77° to 88.2° K. The temperature measurements of Freeman and Halsey were made using a platinum resistance thermometer. The Callendar-van Dusen operation was used to compute the temperature from the measured resistance. Since the Callendar-van Dusen equation is only defined down to -182.97° C, an extrapolation was required. The pressure measurements of Freeman and Halsey were reported to have an absolute accuracy of $\pm$ 0.05 mm Hg.

## G. Equation of State of the Real Gas

The properties of gaseous argon below one atmosphere pressure were assumed to be adequately represented by Equation (9).

$$PV = RT \left(1 + \frac{B}{V}\right) \tag{9}$$

The value of the second virial coefficient, B, was obtained using the Lennard-Jones (6-12) intermolecular potential function. Values of B and (dB/dT) were obtained from the series relation given by Hirschfelder et al[36]

$$B(T) = b_o \sum_{j=0}^{\infty} b^{(j)} \theta^{(1 + 2j)/4} \tag{10}$$

In this relation $\theta = e/kT$, and $b_o$ and $e/k$ are the parameters in the Lennard-Jones (6-12) intermolecular potential function. The first 41 values of $b^{(j)}$ are given by Hirschfelder. The values of $e/k$ (119.3° K) and $b_o$ (50.91 ml/gm mole) used are those given by Levelt.[37] A more complete discussion of the second virial coefficient and a comparison of the computed curve with experimental data are given in Appendix C.

## H.  Thermodynamic Functions of the Ideal Gas

In the temperature range of interest, namely 20° to 88° K, the thermodynamic properties of argon at one atmosphere pressure in the ideal gas state may be calculated assuming the atom to be in its ground electronic state.  The enthalpy is given by

$$(H^o - H^o_o)'' = \frac{5}{2} RT \tag{11}$$

and the entropy by

$$(S^o)'' = R[\frac{5}{2} \ln T + \frac{3}{2} \ln M - 1.164862] \tag{12}$$

Isotope effects were included only to the extent that the molecular weight for the normal isotopic mixture of argon was used in Equation (12).

## IV.  CALCULATIONS

## A.  Introduction

The calculation of valid vapor pressures and heats of vaporization and sublimation from Equations (5) and (1) requires that the input data accurately represent the substance in question.  Consideration of the available experimental data, together with preliminary calculations made using Equations (1), (5), and (7), led to the conclusions that:  (1) the triple point pressure and temperature are more reliably known than is the normal boiling point temperature; (2) the heat capacities of the solid and liquid are known with rather high accuracy; (3) the heat of fusion is known to within perhaps $\pm$ 2 cal/gm mole; and (4) the second virial coefficient and its temperature derivative are known with considerable accuracy.

These preliminary calculations gave principal consideration to the recent vapor pressure measurements of Flubacher et al[21] and Clark et al.[9] It was noted, however, that a considerable discrepancy existed between the vapor pressure data of Flubacher et al and the data of Clark et al. The preliminary calculations further indicated that the vapor pressure data of Flubacher et al were more nearly thermodynamically consistent with the above-mentioned thermal data. These considerations led to the choice of the thermal data shown in Table IX.

TABLE IX

SUMMARY OF INPUT DATA USED IN CALCULATIONS OF THE VAPOR PRESSURE
AND HEATS OF VAPORIZATION AND SUBLIMATION OF ARGON

| Item | Value Used | Table No. |
|---|---|---|
| Triple Point (t.p.) | 83.80° K | II |
| | 516.84 mm Hg | II |
| Heat of vaporization at t.p. | 1567.4 cal/gm mole | |
| Heat of fusion at t.p. | 282.6 cal/gm mole | IV |
| Heat capacity of saturated condensed phases | Polynomial for appropriate temperature range | VII |
| Molal volume of saturated condensed phases | Constant value for each $c_s'$ polynomial | VI |
| Second virial coefficient parameters | $e/k$ = 119.3° K $b_o$ = 50.91 ml/gm mole | |
| Molecular Weight | 39.944 | |

B. Calculation of the Heat of Sublimation at the Triple Point From Experimental Vapor Pressure Data for Solid Argon

The vapor pressure data of Flubacher et al[21] and Clark et al[9] have been used, together with the appropriate data given in Table IX, to compute the heat of sublimation at the triple point by means of Equation (7). The results of

these calculations are shown in Figure 1. If the experimental vapor pressure data and other thermal data used to compute $(\Delta H_v)_{tp}$ by means of Equation (7) were thermodynamically consistent, then a single constant value of $(\Delta H_v)_{tp}$ should be found. It will be noted that the vapor pressure data of Flubacher et al do indeed give very nearly a constant value. The vapor pressure data of Clark et al give results which are approximately 50 calories smaller. This lower value is inconsistent with any reasonable choice of the thermal data. If one accepts the vapor pressure data of Flubacher as very nearly correct, then one obtains a value of about 1850 cal/gm mole for the heat of sublimation at the triple point. If one further accepts the heat of fusion of argon as being 282.6 cal/gm mole then one obtains a heat of vaporization of 1567.4 cal/gm mole for liquid argon at the triple point. These conclusions are discussed further in later sections of this paper.

C. Calculation of the Heat of Vaporization at the Triple Point From Vapor Pressure Data for Liquid Argon

The vapor pressure data of Flubacher et al,[21] Clark et al[9] and Michels et al[9] for liquid argon have been used, together with the appropriate data of Table IX, to compute the heat of vaporization at the triple point by means of Equation (7). The results of these calculations are shown in Figure 2. The limited vapor pressure data of Flubacher et al give a mean value of 1568 cal/gm mole, in excellent agreement with the value obtained from their solid vapor pressure data.

The vapor pressure data of Clark et al and Michels et al show considerable deviation from each other and do not lead to values of $(\Delta H_v)_{tp}$ which are independent of temperature. (While the calculations above one atmosphere pressure make use of an equation of state through the second virial coefficient only, extension to 100° K can be made without serious error.)
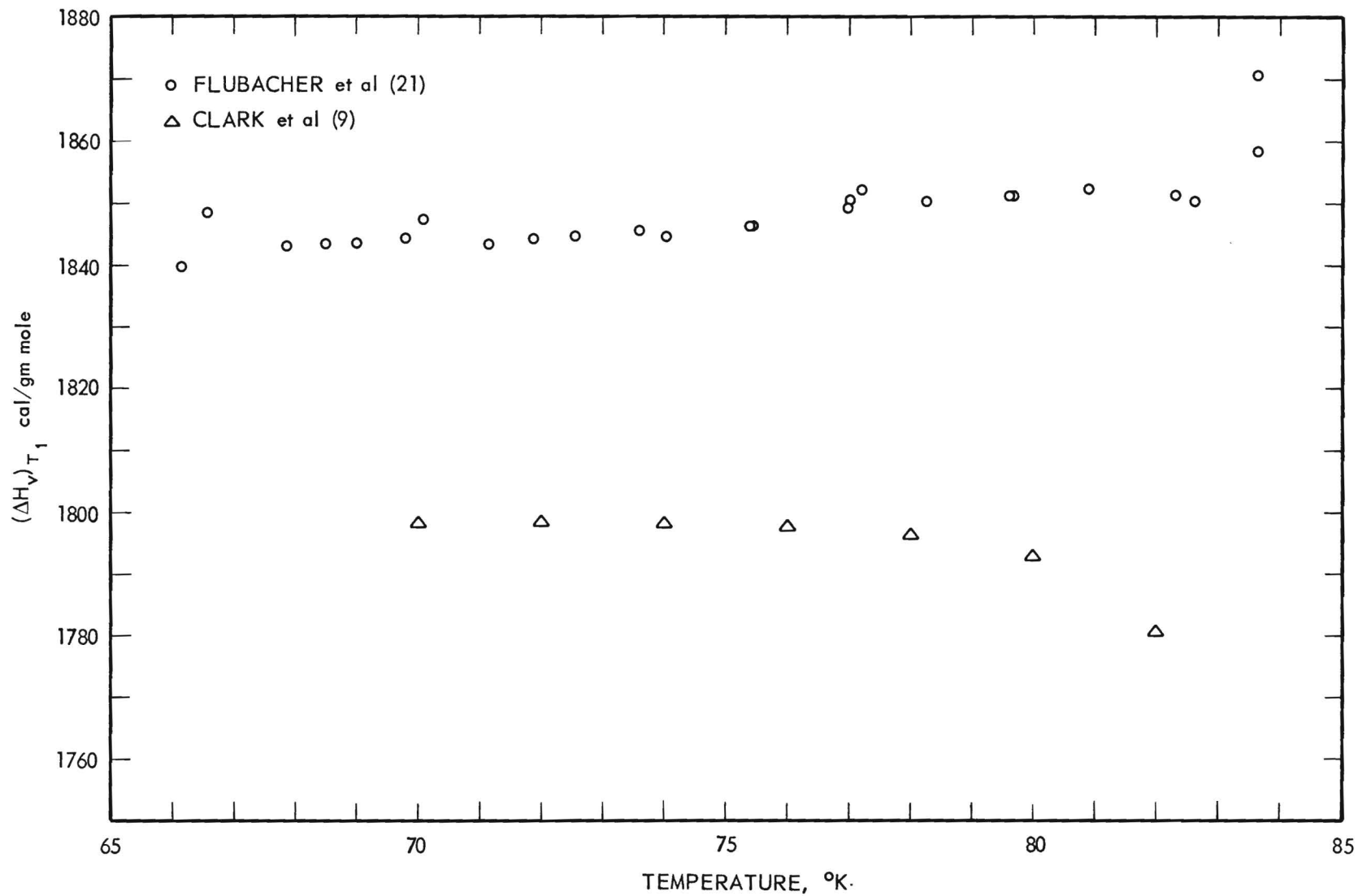
Figure 1. Heat of Sublimation of Argon at the Triple Point Calculated from
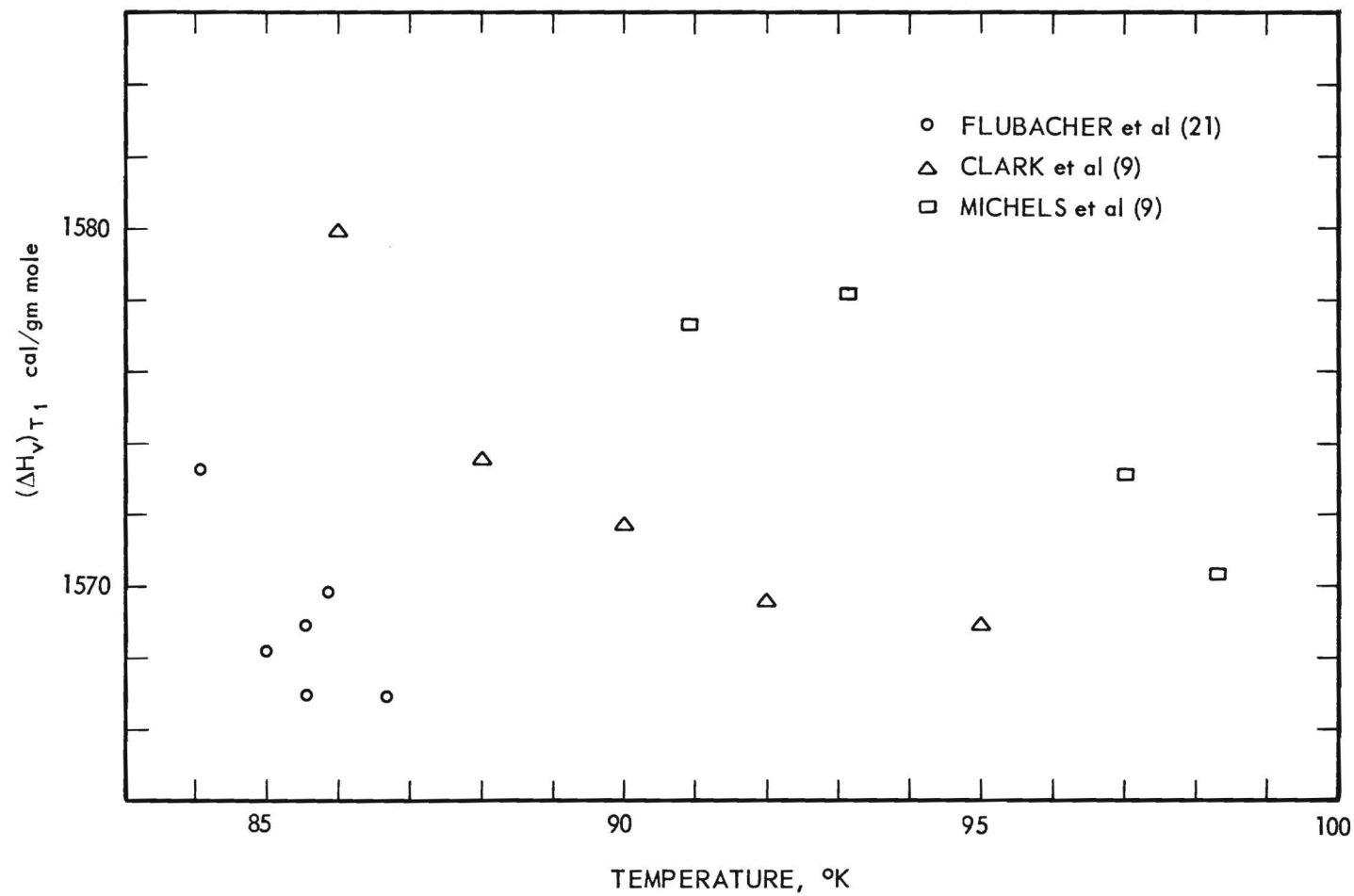Experimental Vapor Pressure Data in the Solid Region.

Figure 2.  Heat of Vaporization of Argon at the Triple Point Calculated
from Experimental Vapor Pressure Data in the Liquid Region.

Consideration of the results obtained in this and the preceding section have led us to choose values of 1850, 282.6 and 1567.4 cal/gm mole as "best" values for the heat of sublimation, heat of fusion and heat of vaporization at the triple point, respectively.

## D. Calculation of Vapor Pressure and Heats of Vaporization and Sublimation to 20° K

Vapor pressures and heats of vaporization and sublimation were calculated at one degree intervals from 88° to 20° K by means of Equations (5) and (1). The input data used are summarized in Table IX. The calculations were based on the triple point (83.80° K and 516.84 mm Hg) as the fixed point. The results of the calculations are presented in Table X.

The interpolated value of the normal boiling point (P = 760 mm Hg) corresponds to 87.291° K, which is in agreement with the experimental value 87.28° ± 0.015° K.

These calculations gave a value of 1543.4 cal/gm mole for the heat of vaporization at the normal boiling point. This value is to be compared with the experimental value of 1557.5 ± 1.5 cal/gm mole reported by Frank and Clusius[16] and a value of 1555.0 ± 4.6 cal/gm mole reported by Flubacher et al.[21] Flubacher et al have also reported a value of 1563.6 ± 4.6 cal/gm mole at 85.67° K. Our calculated value at this temperature is 1554.6 cal/gm mole.

## E. Comparison of Calculated and Experimental Vapor Pressures

The computed vapor pressures of argon given in Table X have been compared with the experimentally determined vapor pressure data by examining the temperature difference ($T_{calc} - T_{obs}$), where $T_{obs}$ is the reported temperature (corrected where possible to an ice point of 273.15° K) corresponding to the experimentally

TABLE X

CALCULATED VAPOR PRESSURE AND HEATS OF
VAPORIZATION AND SUBLIMATION FOR ARGON

| Temperature (°K) | Pressure, P (Mm Hg) | | Heat of Vaporization (Cal/Gm Mole) | $1/T \times 10^2$ (°K$^{-1}$) | Log P | (dP/dT)/P (°K$^{-1}$) |
|---|---|---|---|---|---|---|
| 88.0 | 8.1868 | (2)[a] | 1538.4 | 1.13636 | 2.91311 | 0.1039 |
| 87.291 (n.b.p.) | 7.6000 | (2) | 1543.4 | 1.14559 | 2.88081 | 0.1057 |
| 87.0 | 7.3693 | (2) | 1545.5 | 1.14942 | 2.86743 | 0.1064 |
| 86.0 | 6.6161 | (2) | 1552.4 | 1.16279 | 2.82060 | 0.1091 |
| 85.0 | 5.9237 | (2) | 1559.3 | 1.17647 | 2.77260 | 0.1119 |
| 84.0 | 5.2888 | (2) | 1566.1 | 1.19047 | 2.72336 | 0.1148 |
| 83.80 (t.p.) | 5.1684 | (2) | 1567.4 | 1.19332 | 2.71336 | 0.1154 |
| | | | SOLID | | | |
| 83.0 | 4.6302 | (2) | 1853.7 | 1.20481 | 2.66560 | 0.1387 |
| 82.0 | 4.0234 | (2) | 1858.2 | 1.21951 | 2.60459 | 0.1421 |
| 81.0 | 3.4842 | (2) | 1862.4 | 1.23456 | 2.54210 | 0.1456 |
| 80.0 | 3.0064 | (2) | 1866.5 | 1.25000 | 2.47805 | 0.1493 |
| 79.0 | 2.5845 | (2) | 1870.3 | 1.26582 | 2.41237 | 0.1531 |
| 78.0 | 2.2131 | (2) | 1873.9 | 1.28205 | 2.34500 | 0.1571 |
| 77.0 | 1.8874 | (2) | 1877.3 | 1.29870 | 2.27587 | 0.1612 |
| 76.0 | 1.6029 | (2) | 1880.6 | 1.31578 | 2.20491 | 0.1655 |
| 75.0 | 1.3553 | (2) | 1883.7 | 1.33333 | 2.13203 | 0.1700 |
| 74.0 | 1.1407 | (2) | 1886.7 | 1.35135 | 2.05715 | 0.1747 |
| 73.0 | 9.5542 | (1) | 1889.5 | 1.36986 | 1.98020 | 0.1796 |
| 72.0 | 7.9628 | (1) | 1892.2 | 1.38888 | 1.90106 | 0.1847 |
| 71.0 | 6.6018 | (1) | 1894.8 | 1.40845 | 1.81966 | 0.1901 |
| 70.0 | 5.4437 | (1) | 1897.3 | 1.42857 | 1.73589 | 0.1957 |
| 69.0 | 4.4631 | (1) | 1899.6 | 1.44927 | 1.64964 | 0.2015 |
| 68.0 | 3.6374 | (1) | 1901.9 | 1.47058 | 1.56079 | 0.2076 |
| 67.0 | 2.9388 | (1) | 1905.0 | 1.49253 | 1.46818 | 0.2135 |
| 66.0 | 2.3657 | (1) | 1906.9 | 1.51515 | 1.37396 | 0.2203 |

(Continued)

TABLE X  (Continued)

CALCULATED VAPOR PRESSURE AND HEATS OF
VAPORIZATION AND SUBLIMATION FOR ARGON

| Temperature (°K) | Pressure, P (Mm Hg) | | Heat of Vaporization (Cal /Gm Mole) | $1/T \times 10^2$ (°K$^{-1}$) | Log P | (dP/dT)/P (°K$^{-1}$) |
|---|---|---|---|---|---|---|
| 65.0 | 1.8913 | (1) | 1908.8 | 1.53846 | 1.27676 | 0.2273 |
| 64.0 | 1.5012 | (1) | 1910.6 | 1.56250 | 1.17643 | 0.2347 |
| 63.0 | 1.1825 | (1) | 1912.3 | 1.58730 | 1.07281 | 0.2424 |
| 62.0 | 9.242 | | 1914.0 | 1.61290 | 0.96577 | 0.2505 |
| 61.0 | 7.163 | | 1915.6 | 1.63934 | 0.85512 | 0.2590 |
| 60.0 | 5.504 | | 1917.2 | 1.66666 | 0.74068 | 0.2679 |
| 59.0 | 4.191 | | 1918.7 | 1.69491 | 0.62227 | 0.2773 |
| 58.0 | 3.160 | | 1920.2 | 1.72413 | 0.49968 | 0.2872 |
| 57.0 | 2.359 | | 1921.6 | 1.75438 | 0.37270 | 0.2976 |
| 56.0 | 1.742 | | 1923.0 | 1.78571 | 0.24109 | 0.3085 |
| 55.0 | 1.272 | | 1924.3 | 1.81818 | 0.10459 | 0.3201 |
| 54.0 | 9.18 | (-1) | 1925.6 | 1.85185 | -0.03705 | 0.3323 |
| 53.0 | 6.54 | (-1) | 1926.9 | 1.88679 | -0.18414 | 0.3451 |
| 52.0 | 4.60 | (-1) | 1928.0 | 1.92307 | -0.33698 | 0.3588 |
| 51.0 | 3.19 | (-1) | 1929.2 | 1.96078 | -0.49591 | 0.3732 |
| 50.0 | 2.18 | (-1) | 1930.3 | 2.00000 | -0.66129 | 0.3885 |
| 48.0 | 9.70 | (-2) | 1932.2 | 2.08333 | -1.01301 | 0.4220 |
| 46.0 | 4.02 | (-2) | 1933.9 | 2.17391 | -1.39567 | 0.4599 |
| 44.0 | 1.54 | (-2) | 1935.4 | 2.27272 | -1.81346 | 0.5030 |
| 42.0 | 5.35 | (-3) | 1936.6 | 2.38095 | -2.27136 | 0.5524 |
| 40.0 | 1.68 | (-3) | 1937.6 | 2.50000 | -2.77533 | 0.6093 |
| 38.0 | 4.65 | (-4) | 1938.2 | 2.63157 | -3.33259 | 0.6754 |
| 36.0 | 1.12 | (-4) | 1938.6 | 2.77777 | -3.95193 | 0.7527 |
| 34.0 | 2.27 | (-5) | 1938.6 | 2.94117 | -4.64420 | 0.8438 |
| 32.0 | 3.78 | (-6) | 1938.3 | 3.12500 | -5.42293 | 0.9524 |
| 30.0 | 4.95 | (-7) | 1937.5 | 3.33333 | -6.30524 | 1.0832 |

(Continued)

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TABLE X  (Continued)

CALCULATED VAPOR PRESSURE AND HEATS OF
VAPORIZATION AND SUBLIMATION FOR ARGON

| Temperature (°K) | Pressure, P (Mm Hg) | | Heat of Vaporization (Cal /Gm Mole) | $1/T \times 10^2$ (°K$^{-1}$) | Log P | (dP/dT)/P (°K$^{-1}$) |
|---|---|---|---|---|---|---|
| 28.0 | 4.86 | (-8) | 1936.3 | 3.57142 | -7.31308 | 1.2427 |
| 26.0 | 3.35 | (-9) | 1934.6 | 3.84615 | -8.47510 | 1.4400 |
| 24.0 | 1.48 | (-10) | 1932.4 | 4.16666 | -9.82941 | 1.6881 |
| 22.0 | 3.73 | (-12) | 1929.5 | 4.54545 | -11.42786 | 2.0060 |
| 20.0 | 4.54 | (-14) | 1926.0 | 5.00000 | -13.34281 | 2.4228 |

$^a$Numbers in parentheses indicate powers of 10; thus 8.1868 (2) = 8.1868 x $10^2$.

determined pressure, and $T_{calc}$ is the temperature which corresponds to this same
pressure as determined by interpolation in the computed vapor pressure table
(Table X).[*]  The results are shown in Figures 3 and 4.

Consideration of Figure 3 shows the rather considerable differences which
exist between the experimental vapor pressure measurements of the different in-
vestigators.  As is to be expected the computed values agree best with the
measurements of Flubacher et al, though disagreement with their results is found
below about 75° K.  The computed vapor pressures also agree with the limited
data of Freeman and Halsey, presented by them in the form of equations for the
temperature ranges 82.0° to 83.77° K (solid) and 83.77° to 88.2° K (liquid).  The

[*] Values of the calculated temperature corresponding to observed vapor pressures
are interpolated from the values at even intervals using Aitken's iterative meth-
od of polynomial interpolation as described by Milne.[38]  This method calculates
the value of the dependent variable, in this case 1/T, corresponding to a given
value of the independent variable, in this case ln P, by successively interpo-
lating with a 1, 2, 3, ..., n, n+1,..degree polynomial.  In the computer program
used here, this successive interpolation was continued until the value of (1/T)
computed by the (n+1)-th degree polynomial differed by less than 1 part in 100,000
from the value computed by the n-th degree polynomial.

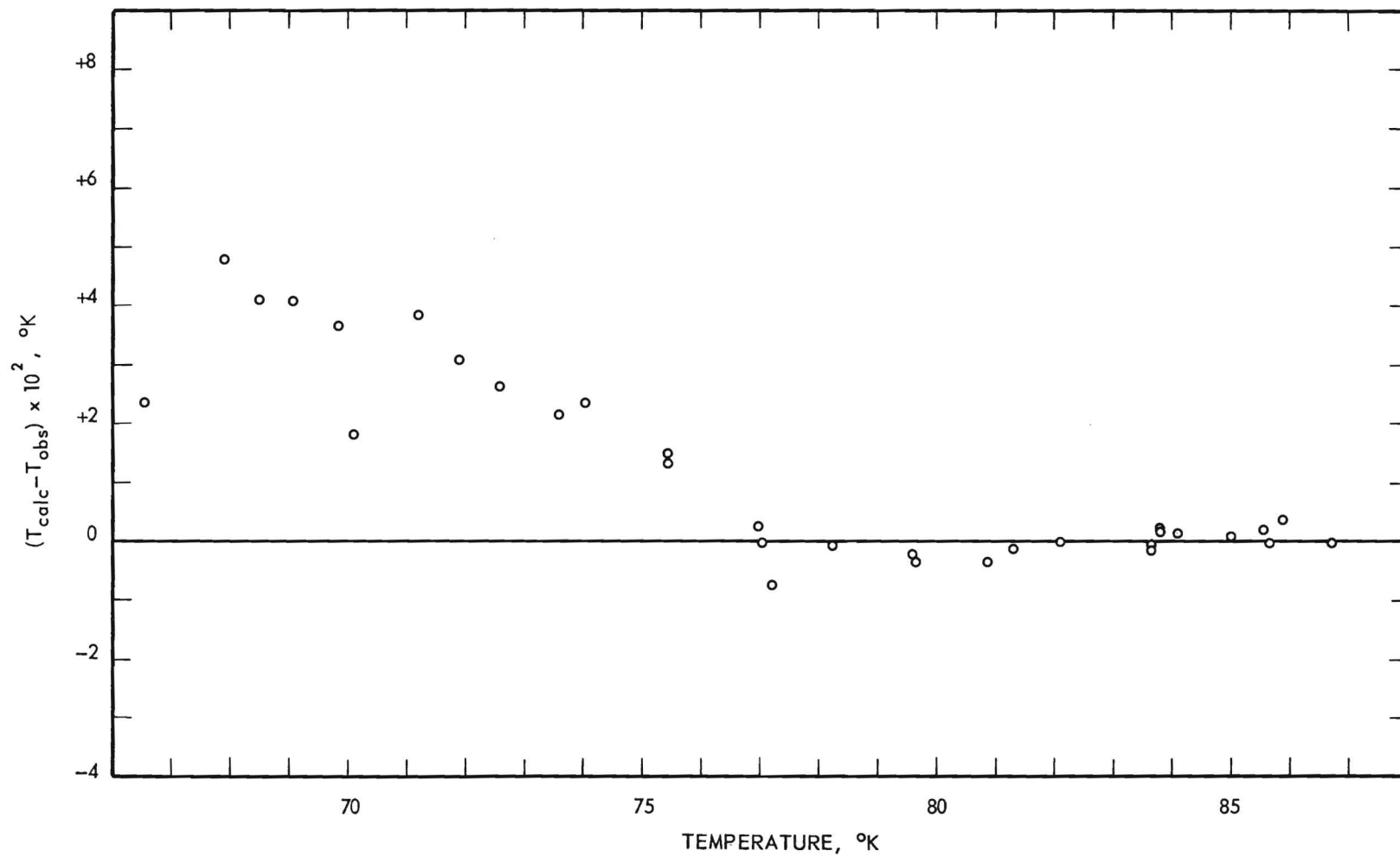Figure 3.  Comparison of Calculated and Observed Vapor Pressures.

Figure 4.  Comparison of Calculated Vapor Pressures with Data of Flubacher.

data of Clark et al agree well with the computed values in the liquid range, but show progressively larger deviations for the solid as the temperature is lowered.

A series of calculations was also made using the same input data as were used to obtain Figure 3 except that the heat of vaporization at the triple point used was consistent with the experimental heat of vaporization at the normal boiling point (1555 cal/gm mole). The discrepancy found between the vapor pressures so calculated and the experimental data of Flubacher et al and Clark et al was considerably greater than that shown in Figure 3, strongly suggesting that the value of 1555 cal/gm mole is too large.

## F. Effect of Uncertainties in Input Data on Computed Results

In order to study the effect of the input data on the computed vapor pressure, the various input parameters were each changed separately by a known amount while holding all other input data constant. These calculations extended from the normal boiling point to 20° K.

Figure 5 shows the percentage change in vapor pressure which results when the following changes in input data were made (the asterisk indicates the new value used).

Curve 1   $(n.b.p.)^* = n.b.p. - 0.01°$ K

Curve 2   $(t.p.)^* = t.p. - 0.01°$ K

Curve 3   $(c_s')^* = 0.99 \, c_s'$

Curve 4   $(\Delta H_f)^* = 0.99 \, (\Delta H_f)$

Curve 5   $(e/k)^* = 127.66°$ K; $(b_o)^* = 39.39$ ml/gm mole

Curve 6   $(\Delta H_v)^*_{T_1} = 0.99 \, (\Delta H_v)_{T_1}$

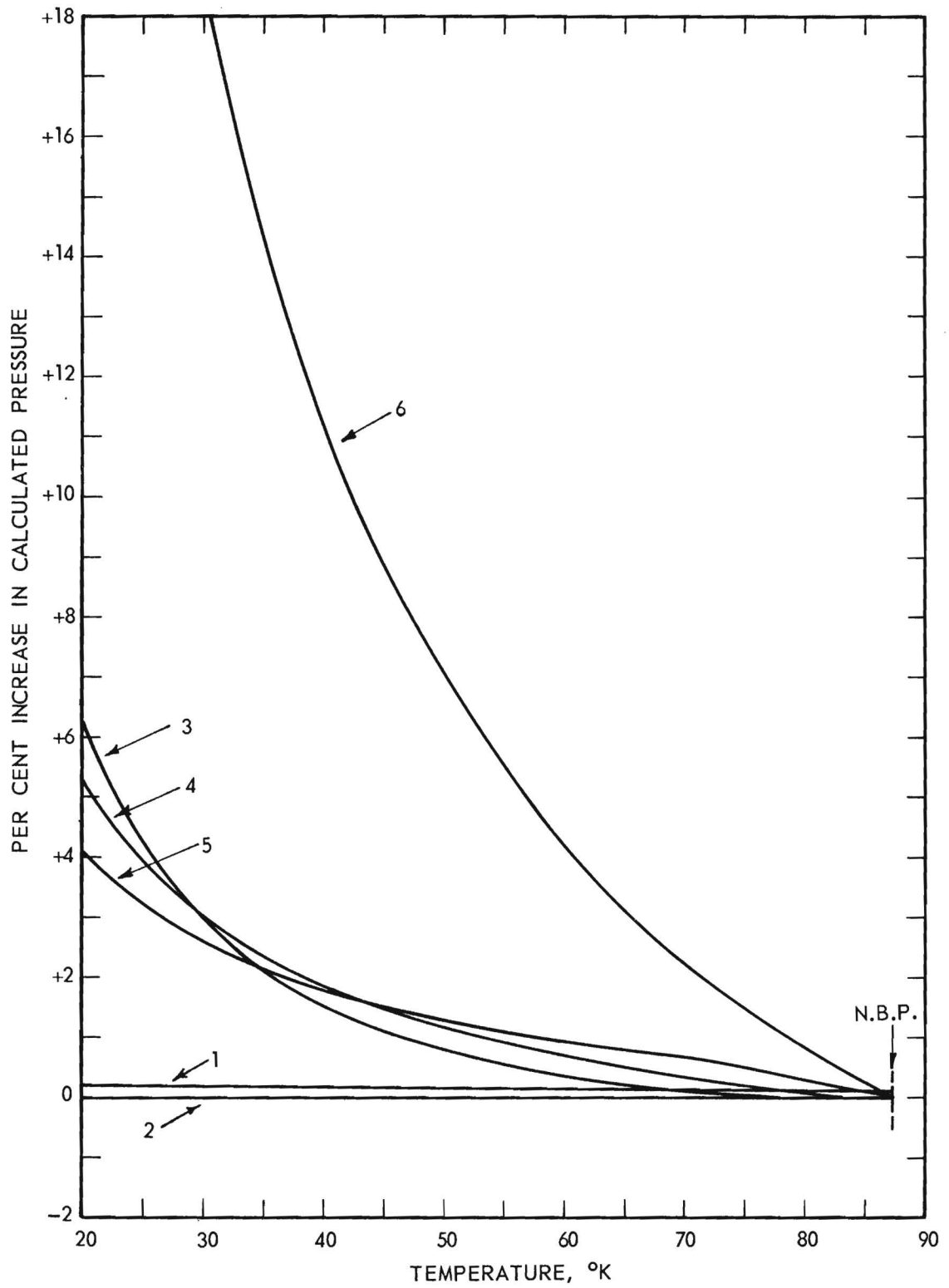Consideration of Figure 5 shows that a variation of 0.01° K in the temperature

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Figure 5. Effect of Changing Input Parameters on the Calculated Vapor Pressure.

assigned to the normal boiling point (Curve 1) and triple point (Curve 2) result in only small percentage errors in the computed vapor pressure. Since these temperatures are known experimentally to be within about 0.01° K of the values used in the computations little error is believed to arise from any uncertainty in these quantities.

The effect of an average uncertainty of one per cent in the heat capacity of the condensed phases is shown in Curve 3. Since it appears unlikely that the experimental data used for liquid and solid argon are in error by as much as one per cent, this curve may be taken to represent the maximum error arising from uncertainty in these data.

The effect of a one per cent decrease (2.8 cal/gm mole) in the heat of fusion is seen in Curve 4 of Figure 5. It appears to us unlikely that the heat of fusion of solid argon is uncertain by an amount significantly greater than one per cent.

The effect of a one per cent (15.5 cal/gm mole) decrease in the heat of vaporization at the normal boiling point is shown in Curve 6 of Figure 5. It will be noted that this decrease is nearly the same magnitude as the disagreement between our computed heat of vaporization (1543.4 cal/gm mole, Table X) and the "best" experimental value (1555 cal/gm mole).

Consideration of Curves 4 and 6 shows that satisfactory calculations of vapor pressures can only be made if the uncertainty in the heat of fusion and vaporization is of the order of a few calories per mole.

## G. Third Law Calculation

In order to examine further the consistency of the thermal data used to compute the vapor pressure and heats of vaporization and sublimation in Table X

these thermal data were used to compute the calorimetric entropy of the ideal

gas at the normal boiling point (87.291° K), assuming that the entropy of solid

argon at 0° K is zero.  The results of the calculation are shown in Table XI.

TABLE XI

COMPARISON OF THE CALORIMETRIC AND SPECTROSCOPIC ENTROPY
OF ARGON AT 87.291° K AND ONE ATMOSPHERE PRESSURE

| Temperature Range (°K) | Entropy Change (Cal/Gm Mole °K) | Comments |
|---|---|---|
| 0 - 11 | 0.349 | Integration of $c_s'/T$ using polynomial given in Table VII |
| 11 - 83.80 | 8.936 | Integration of $c_s'/T$ using polynomials given in Table VII |
| 83.80 (t.p.) | 3.372 | Fusion, 282.6/83.80 |
| 83.80 - 87.291 | 0.433 | Integration, $c_s' = 10.586$ cal/gm mole °K |
| 87.291 (n.b.p.) | 17.681 | Vaporization, 1543.4/87.291 |
| 87.291 | 0.112 | Correction for nonideality, using Equation (9) and L-J parameters of Table IX |
| | $(S^o_{cal})'' = 30.883$ | |
| | $(S^o_{spect}) = 30.881$ | Calculated using Equation (12) |

It is seen that the entropy calculated from the thermal data $(S^o_{cal})''$ is in ex-

cellent agreement with the entropy of the ideal gas $(S^o_{spect})''$ computed by means

of statistical mechanics (Equation (12)).  If the larger values of the heat of

vaporization of Frank and Clusius (1557.5 ± 1.5 cal/gm mole) and Flubacher et al

(1555.0 ± 4.6 cal/gm mole) are used to compute the entropy of vaporization, then

the difference in entropy, $(S^o_{cal})'' - (S^o_{spect})''$, becomes 0.16 and 0.13 cal/gm mole °K, respectively.

## V. CONCLUSIONS

The available thermal, equation of state, and vapor pressure data for argon below its normal boiling point have been examined for thermodynamic consistency by comparing the vapor pressure computed from the thermal and equation of state data with experimental vapor pressures. The vapor pressures computed from the "best" experimental thermal and equation of state data were found to deviate considerably from the experimental vapor pressure data, indicating that the thermal and equation of state data were not thermodynamically consistent with the available vapor pressure data. It was found, furthermore, that the vapor pressure data were not consistent with each other. However, the vapor pressure data of Flubacher et al most nearly approached thermodynamic consistency.

Analysis of the possible sources of discrepancy suggested that the second virial coefficient, the heat of vaporization or both might be somewhat in error. However, the second virial coefficient of argon appears to be known to within several per cent near the normal boiling point and no reasonable adjustment of the second virial coefficient resulted in agreement between the computed and experimental vapor pressures.

It was found that by lowering the heat of vaporization at the normal boiling point by about one per cent, the computed vapor pressures could be brought into agreement with the experimental vapor pressure measurements of Flubacher et al to within experimental error from 87.291° K (the normal boiling point) to about 75° K. Below this temperature the computed values deviated somewhat more than the estimated experimental error. No reasonable adjustment of the heat of vaporization could be found which would result in an equally good fit

for other published vapor pressure data. On the other hand, the experimental errors assigned to the measured heat of vaporization at the normal boiling point by Frank and Clusius and Flubacher et al are 0.1 per cent and 0.3 per cent, respectively. Thus the adjustment of this value by one per cent is not justified by the experimental investigations. It is to be noted, however, that the third law calculation made using these heats of vaporization gave slightly poorer agreement with the statistically calculated entropy than did the adjusted value.

It is possible that small adjustments in experimental heat capacities, heat of fusion, equation of state (second virial coefficient) and experimental vapor pressure data, taken together, could reduce the adjustment of the heat of vaporization which is necessary to bring about thermodynamic consistency. More precise measurements of the various quantities involved are required to resolve these discrepancies.

It is believed that the computed values of vapor pressure given in Table X represent a reasonable extrapolation of the experimental data below about 60° K, the lowest temperature for which experimental data are now available. The error in the computed pressures increases with decreasing temperature and may be as large as 25 per cent at 20° K.

## VI.  ACKNOWLEDGEMENTS

Respectfully submitted:


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## VIII.  APPENDIXES

### A.  Nomenclature and Physical Constants

$B$ = second virial coefficient of gas.

$b_o$, $e/k$ = parameters used in the Lennard-Jones (6-12) intermolecular potential function.

$C$ = third virial coefficient of gas.

$c$ = velocity of light = $2.997902 \times 10^{10}$ cm/sec.

$c_s'$ = molal heat capacity of saturated condensed phase.

$(\Delta H_v)_T$ = heat of vaporization (or sublimation) at T.

$(\Delta H_{tr})'$ = heat of transition of condensed phase at transition temperature, $T_{tr}$.

$\sum\limits_{T}^{T_1} (\Delta H_{tr})'$ = sum of all condensed phase transitions from T to $T_1$.

$(H^o - H_o^o)_T''$ = enthalpy function for ideal gas at T relative to $0^o$ K.

$(H^o - H_o^o)_T'$ = enthalpy function of saturated condensed phase at T relative to $0^o$ K.

$M$ = molecular weight of argon = 39.944.

$P$ = pressure.

$P_1, T_1$ = pressure and temperature of a fixed point on the vapor pressure curve.  For argon the triple point was used.

$R$ = gas constant = 1.98726 cal/gm mole $^o$K = 0.0820574 liter atm/gm mole $^o$K. (1 cal. = 4.1840 ab. joules = 4.1833 int. joules.)

$S^*$ = entropy of the ideal gas.

$(S^o)_{cal}''$ = calorimetric entropy of the ideal gas at one atmosphere pressure.

$(S^\circ)''_{spect}$ = statistically calculated entropy of the ideal gas at one atmosphere pressure.

$(S^\circ)''$ = entropy of ideal gas at P = 1 atm.

$T$ = temperature on the thermodynamic scale with a defined ice point of 273.15° K.

$T^*$ = temperature on the Kelvin Scale used by individual investigator.

$t^*$ = temperature on the Celsius Scale used by individual investigator.

$t$ = °C.

$V$ = molal volume of gas.

$v'_s$ = molal volume of saturated condensed phase.

$\delta$ = defined by Equation (2) and Equation (4).

$\varepsilon$ = defined by Equation (6).

$\theta$ = e/kT

Superscripts

' = condensed phase

" = gas phase

* = refers to temperature scale of individual investigator. Also ideal gas state Equation (6).

Subscripts

$0_2$ = normal boiling point of oxygen.

o = ice point (except for $b_o$).

s = saturated vapor or condensed state.

v = vaporization. Also refers to sublimation for temperatures at and below the triple point.

B.  Conversion of Temperature Scales

The conversion of reported temperatures to a consistent thermodynamic temperature scale based on an ice point of 273.150° K has been carried out where possible.  The "best" value for the normal boiling point of oxygen on this scale has been taken to be 90.168° K, the value selected by van Dijk.[4] The various methods used for making these conversions are given below.  The final corrected thermodynamic temperature (in °K) used in this paper is represented by $T$; the temperature reported by the investigator is represented by $T^*$. In cases where the original temperatures were reported in degrees Celsius these were converted to $T^*$ by addition to the reported ice point $T_o^*$.  The values of $T^*$ thus obtained were then treated by the appropriate relation given below.  In the event no ice point was given the reported temperature in °C was added to 273.150 to obtain $T$ in °K.

1.  Method A

This method of correction was used when the ice point was given by the investigator and no other arbitrary choices of fixed points such as the oxygen point were made.  The conversion relation is

$$T = T^* (T_o/T_o^*) \tag{13}$$

where $T_o$ = 273.150° K.
This method was used for $0 < T^* < T_o^*$.

It is to be noted that this method of conversion of a thermodynamic scale from one ice point to another is strictly correct only if the ice point temperature is a <u>defined point</u>.  When $T_o$ is obtained from a gas thermometer scale defined at the ice point and normal boiling point of water, a more complicated relation

is required for exact conversion. (See, for instance, van Dijk.[4]) Data for making the exact conversions are not always given by the investigator. Furthermore the exact relations reduce to the simple relation used in the first approximation. Henning and Otto[39] have used a somewhat different approximate method for correction than is given in Equation (13). Their relation gives the same result as Equation (13) to about 0.002°.

### 2. Method B

All reported temperatures based on an assigned oxygen point $T^*_{O_2}$ have been converted to the temperature scale used in this paper by the relation

$$T = T^*\left(\frac{90.168}{T^*_{O_2}}\right) \tag{14}$$

### 3. Method C

Where temperatures were given as $t^*$ °C, but were not on the International Temperature Scale, and an ice point $T^*_o$ was also given, $T^*$ was first computed from the relation

$$T^* = t^* + T^*_o \tag{15}$$

after which $T$ was computed from $T^*$ by Method A.

## C. Second Virial Coefficient of Argon

Whalley, Lupien and Schneider[40] have measured the second virial coefficient of argon over the range 0° to 600° C. In addition they analysed all P-V-T data and second virial coefficients determined from P-V-T data prior to 1953. In a later paper Whalley and Schneider[41] investigated various potential functions using the selected values of the second virial coefficients given in their previous paper. We have assumed that their selected values adequately

represent the data from P-V-T measurements up to 1953.

The analysis of Whalley et al[40] did not include the sound velocity deter-
minations of van Itterbeek and van Paemel[42] and the gas thermometer measurements
of Cath and Onnes.[43] Van Itterbeek's method of determination of the second
virial coefficient from sound velocity data requires a knowledge of the second
virial coefficient at higher temperatures. He reported two sets of values, one
based on the Berlin data[44] and the other based on older Leiden data.[45]

Subsequent to the evaluation of the available P-V-T data by Whalley et al,[40]
Michels et al[46] determined the compressibility isotherms of argon between -25°
and -155° C and reported the data in virial form. Michels et al[47] also deter-
mined the compressibility isotherms between 0° and 150° C and obtained values
of $e/k$ and $b_o$ for the Lennard-Jones (6-12) intermolecular potential function
which fit to this range. The second virial coefficients computed from their
values of $e/k$ and $b_o$ (119.8° K, 49.81 ml/gm mole) agree well with their low
temperature data down to -70° C; below this temperature the calculated values
are smaller (in absolute magnitude) than their experimental values. Kerr[48]
reported values of the second virial coefficient from 100° to 303° K.

Recently Levelt[37] has studied the reduced equation of state of argon and
xenon using the parameters of the Lennard-Jones (6-12) potential function.
After due consideration of the previously determined values of the Lennard-Jones
(6-12) parameters of Whalley and Schneider[41] and Michels et al,[47] Levelt found
that the slightly adjusted values of 119.3° K and 50.91 ml/gm mole gave better
agreement in the low temperature region. For this reason, the $e/k$ and $b_o$
values of Levelt have been used for the calculations made in the paper. A
comparison between the second virial coefficients calculated using these values
of $e/k$ and $b_o$ (Curve A) and the experimental data is shown in Figure 6. The
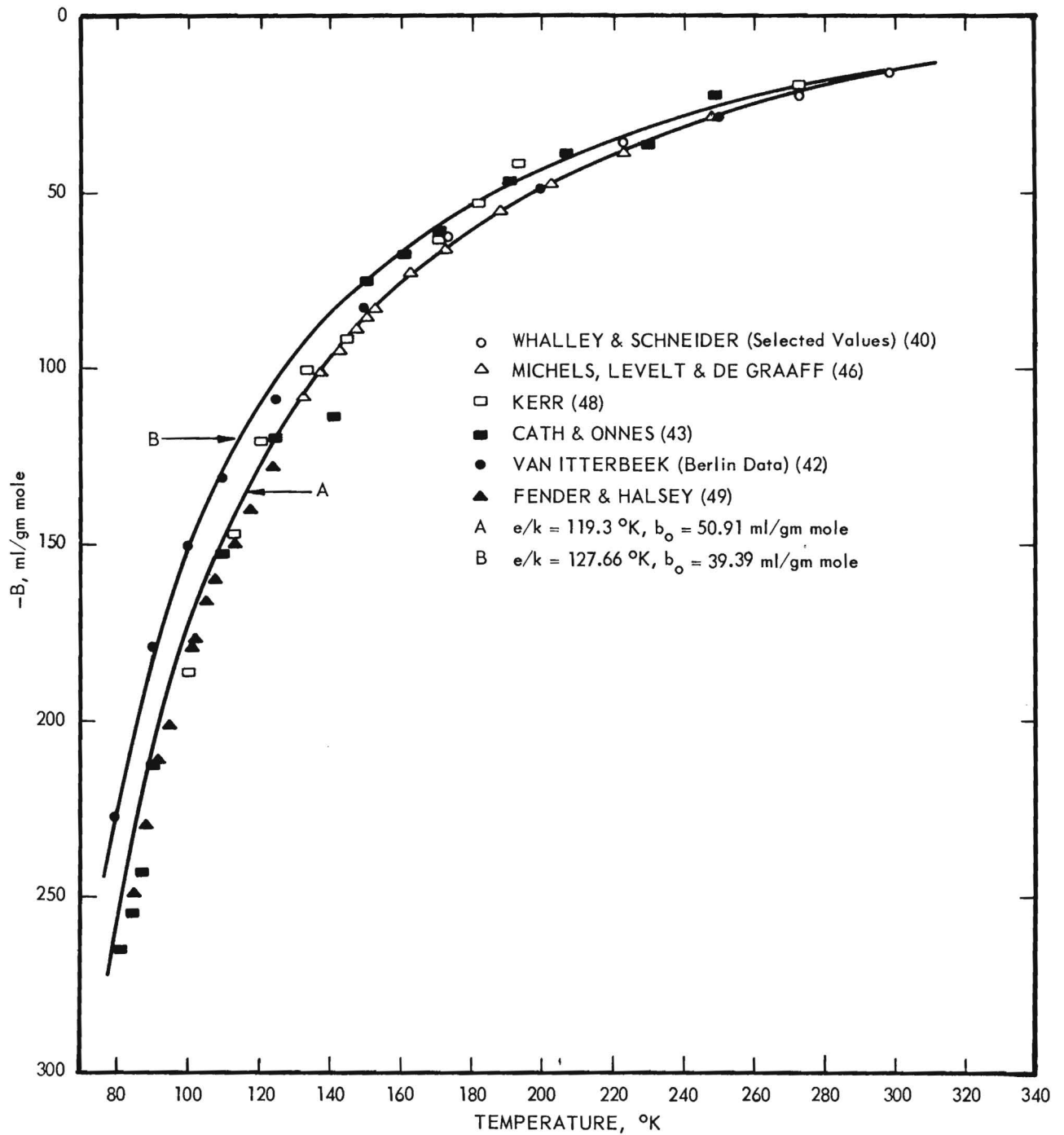
Figure 6.   Comparison of Calculated and Experimental Second Virial Coefficient of Argon.

recently published experimental values of Fender and Halsey[49] are also shown.*

Also shown in Figure 6 is a curve (Curve B) computed from a set of parameters which were arbitrarily adjusted to give better agreement with the second virial coefficient data of van Itterbeek et al.[42] These parameters were used to examine the effect of changes in the second virial coefficient on the calculated vapor pressures as discussed in Section IV-F.

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*These data came to our notice after the calculations reported in this paper were completed. They support the earlier measurements of Cath and Onnes[43] and are in agreement with our choice of $e/k$ and $b_o$.

TECHNICAL REPORT NO. 3 [Final]

PROJECT NO. A-460

CALCULATION OF THE VAPOR PRESSURE AND HEATS OF VAPORIZATION
AND SUBLIMATION OF LIQUIDS AND SOLIDS, ESPECIALLY BELOW
ONE ATMOSPHERE PRESSURE. III. METHANE.

By

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NATIONAL BUREAU OF STANDARDS
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AUGUST 31, 1962

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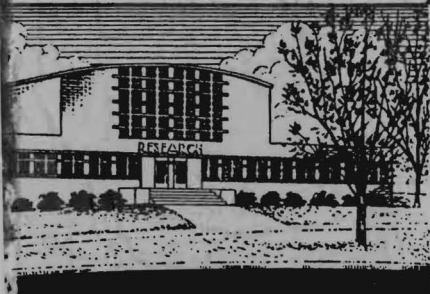
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Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
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## ABSTRACT

The vapor pressure and heats of vaporization and sublimation of methane have been calculated at 2 degree  intervals from the normal boiling point to the triple point and at 5 degree intervals from the triple point to 20.4° K by a thermodynamic method.  Two sets of calculations were made.  One calculation, given in Table VII, made use of a selected set of "best" experimental values for the necessary physical and thermal data.  The other calculation, given in Table VIII, made use of the same input data except for slight adjustments in the heat of vaporization and temperature of the normal boiling point.  The calculated vapor pressures have been compared with the available experimental data.

It was found that the computed vapor pressures agreed quite well with the smoothed experimental data of Brickwedde and Scott[8] down to about 70° K.  Below 70° K the agreement, while progressively poorer, still appears to be within the uncertainty of the experimental measurements.

There appears to be little basis on which to choose between the computed values given in Tables VII and VIII.  Uncertainties in the "best" values of thermal data used, as well as uncertainty in the temperature scale corrections, no doubt still exist.  However, since the computed vapor pressures given in Table VIII agree slightly better with the extensive and careful measurements of Brickwedde and Scott,[8] the vapor pressures and heats of vaporization and sublimation given in Table VIII are recommended for use.  A table of vapor pressures interpolated to one degree intervals is included for convenience.

The thermodynamic functions $(H^o - H^o_0)/T$, $S^o/R$ and $-(F^o - H^o_0)/T$ for methane in the ideal gas state at one atmosphere have been computed at 2 degree intervals from the normal boiling point to 90° K and at 5 degree intervals from 90° to

20° K, assuming a rigid rotator, harmonic oscillator model, using a summation procedure for the rotational partition function which takes into account nuclear spin. These functions have been used in the calculation of the vapor pressure and heats of vaporization and sublimation mentioned above, assuming that no interconversion of the nuclear spin species occurs (i.e. the room temperature equilibrium state is "frozen in").

The vapor pressure and heats of vaporization and sublimation have also been computed assuming the classical statistical mechanical form of the rotational partition function.

The rotational contribution to the ideal gas thermodynamic functions of methane $(E^o - H^o_o)_{rot}$, $(S^o)_{rot}/R$ and $(C^o_{rot})/R$ for the individual nuclear spin species A, E, and F and the "frozen" high temperature equilibrium mixture (A: E: F = 5: 2: 9) have been computed down to 5° K.

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(Continued)

## TABLE OF CONTENTS (Continued)

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## I.   INTRODUCTION

In a previous report[1*] a number of thermodynamic relations were presented for the calculation of the vapor pressure and heats of vaporization and sublimation of liquids and solids.  These relations have been used to compute the vapor pressure and heats of vaporization and sublimation of ethylene,[1] oxygen,[2] and argon[3] from approximately the normal boiling point to 20° K and of parahydrogen[4] from 22° to 1° K.

The present report is concerned with the application to methane of the thermodynamic relations previously developed.[1]  The principal thermodynamic relations used are summarized in the next section.  The necessary available thermodynamic data have been used to compute the vapor pressure and heats of vaporization and sublimation of methane from its normal boiling point to 20.4° K.  The computed results have been compared with the available experimental vapor pressure and heat of vaporization data.  As in the previous reports on ethylene, oxygen and argon, the temperatures reported by different investigators have been converted to the thermodynamic temperature scale with an assigned ice point of 273.15° K.  On this scale the normal boiling point of oxygen has been taken to be 90.168° K.  This value is based on an analysis of the various reported normal boiling points of oxygen made by van Dijk.[5**] The energy quantities appearing in the calculations are expressed in terms of the defined calorie (1 calorie = 4.1840 ab. joule = 4.1833 int. joules).  No

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[*]Superscripts refer to references listed in the Bibliography.

[**]Barber (Brit. J. Appl. Phys. 13, 235 (1962)) has recently redetermined the oxygen point and reported a value of 90.177 ± 0.006° K.  He has combined this value with existing data to obtain an average value of 90.170° K.  There still appears to be an uncertainty of about 0.01° in the oxygen point.

attempt was made, however, to correct experimental thermal data to a uniform energy unit basis.

One interesting feature of the calculations is the treatment of the rotational contributions to the ideal gas thermodynamic functions of methane. This treatment demonstrates a significant deviation from classical behavior within the temperature range considered. This deviation is reflected in the computed values of the vapor pressure and heat of sublimation below 50° K.

## II. THERMODYNAMIC RELATIONS

### A. Variation of Heat of Vaporization and Sublimation with Temperature

By performing an enthalpy cycle between two points, $(P,T)$ and $(P_1,T_1)$, on the vapor pressure curve of a pure substance it can be shown[1] that the heat of vaporization or sublimation can be computed from Equation (1).

$$(\Delta H_v)_T = (\Delta H_v)_{T_1} + \int_T^{T_1} c_s' \, dT + \sum_T^{T_1} (\Delta H_{tr})' - \left[ (H^o - H_o^o)_{T_1}'' - (H^o - H_o^o)_{T}'' \right]$$

$$- RT_1 \, \delta_1 + RT\delta + \int_P^{P_1} v_s' \, dP \qquad (1)$$

In this equation the quantity $\delta$ is given by the relation

$$RT\delta = \left[ H(P,T) - H^o(T) \right]'' \qquad (2)$$

and $\delta_1$ is the value of $\delta$ at the point $(P_1,T_1)$. The prime (') and double prime ('') symbols refer to the condensed and vapor phases, respectively. All symbols are defined in Appendix A. The evaluation of the right-hand side of Equation (2) requires an equation of state for the vapor. If a virial form of the equation of state is used, namely,

$$PV = RT \left( 1 + \frac{B}{V} \right) \qquad (3)$$

where the second virial coefficient, $B$, is assumed to be a function of temperature only, then one obtains

$$\delta = \left( B - T \frac{dB}{dT} \right) / V \qquad (4)$$

For temperatures below the triple point, $(\Delta H_v)_T$ in Equation (1) is the heat of sublimation rather than the heat of vaporization. The evaluation of the last two terms of Equation (1) requires a value of the vapor pressure at T. If vapor pressure calculations are made by an iterative procedure, then this iterative procedure also provides the pressure necessary to compute the last two terms of Equation (1).

B. Vapor Pressure Relations

From a known point $(P_1, T_1)$ on the vapor pressure curve, the vapor pressure at any other point $(P,T)$ can be calculated from the previously derived relation[1]

$$\ln P = \ln P_1 - (\Delta H_v)_{T_1} (T_1 - T)/RTT_1 + \left[ (H^o - H_o^o)_{T_1}^{''} - (H^o - H_o^o)_T^{''} \right]/RT$$

$$- \left[ (S^o)_{T_1}^{''} - (S^o)_T^{''} \right]/R - \left( \int_T^{T_1} c_s^{'} \, dT \right)/RT$$

$$- \left( \sum_T^{T_1} (\Delta H_{tr})^{'} \right)/RT + \left( \int_T^{T_1} c_s^{'} \, dT/T \right)/R$$

$$+ \left( \sum_T^{T_1} (\Delta H_{tr})^{'}/T_{tr} \right)/R + \delta_1 (T_1 - T)/T$$

$$- \varepsilon_1 + \varepsilon - \left( \int_P^{P_1} v_s^{'} \, dP \right)/RT \tag{5}$$

where

$$\varepsilon = \left[ H^o(T) - H(P,T) \right]^{''}/RT - \left[ S^o(P,T) - S(P,T) \right]^{''}/R \tag{6}$$

and $\varepsilon_1$ is the value of $\varepsilon$ at $(P_1, T_1)$. If the virial form of the equation of

state is assumed, i.e., Equation (3), then $\varepsilon$ becomes

$$\varepsilon = \ln(PV/RT) - 2B/V \tag{7}$$

Equation (5), which may be considered to be an integration of the Clapeyron equation, can be solved if appropriate thermal data for the condensed phase, $(\Delta H_v)_{T_1}$, an equation of state for the real gas, and the requisite molecular structure data for the ideal gas are available. Solution of Equation (5) requires iteration since the last two terms are pressure dependent.

5

III.  REVIEW OF EXPERIMENTAL DATA FOR METHANE

A.  Introduction

The calculation for methane of vapor pressure from Equation (5) and heats of vaporization and sublimation from Equation (1) in the temperature range from the normal boiling point to 20.4° K requires the following data: $(\Delta H_v)_{T_1}$; $P_1$; $T_1$; $(\Delta H_f)$; $T_f$; and $c_s'$ and $v_s'$ as a function of temperature. A representation of the second virial coefficient as a function of temperature is also required. The effect of higher virial coefficients is assumed to be negligible. In addition, the appropriate molecular structure data are required to permit calculation of the thermodynamic properties of the ideal gas.

From a survey of the literature, a selection has been made of the "best" values of these thermal and related properties of methane. These selected values are summarized in Table I. The reasons for selecting them are discussed in the following sections. The temperature range of principal interest has been from the normal boiling point to 20.4° K, at which temperature solid methane exhibits a lambda-type phase transition. The available experimental data for the vapor pressure of liquid and solid methane below one atmosphere have also been assembled for comparison with the computed quantities.

The temperatures of all transition points and vapor pressure data have been corrected, wherever possible, to a thermodynamic scale with an ice point of 273.15° K. Methods of temperature correction used are given in Appendix B. No temperature corrections have been applied to heat capacity, equation of state or heat of transition data since such changes are believed to be within the experimental error of the data. No corrections have been applied to energy quantities to bring them to a uniform base. However, all calculations have been

TABLE I

SUMMARY OF SELECTED PHYSICAL PROPERTIES OF METHANE

| Property | Selected Value | Table No. |
|---|---|---|
| Normal boiling point (n.b.p.) (P = 760 mm Hg) | 111.67° K[a] | II |
| Triple point (t.p.) | 90.64° K | III |
| Heat of vaporization (n.b.p.) | 1953 cal/gm mole[a] | |
| Heat of fusion (t.p.) | 224 cal/gm mole | |
| Heat capacity of saturated condensed phases | Polynomial for appropriate temperature range | IV |
| Mean molal volume of liquid (90.64 - 111.67° K) | 37.35 ml/gm mole at 108° K | |
| Mean molal volume of solid (20.4 - 90.64° K) | 32.6 ml/gm mole at 85° K | |
| Lennard-Jones (6-12) parameters for second virial coefficient | $e/k$ = 114.39° K $b_o$ = 126.40 ml/gm mole | |
| Molecular parameters Moment of inertia | $5.327 \times 10^{-40}$ gm cm$^2$ | V |
| Fundamental frequencies | $\nu_1$ = 2917 cm$^{-1}$ $\nu_2$ = 1534 cm$^{-1}$ $\nu_3$ = 3019 cm$^{-1}$ $\nu_4$ = 1306 cm$^{-1}$ | VI |
| Molecular weight | 16.043 | |

[a]However, see discussion regarding adjustment of these values for use in calculation of Table VIII, Section IV-B.

made assuming the quantities to be given in defined calories (1 defined calorie = 4.1840 ab. joules = 4.1833 int. joules).

## B. Phase Transition Temperatures of Methane

### 1. Normal Boiling Point

Experimental data for the normal boiling point of methane ($P = 760$ mm Hg) are summarized in Table II. Henning and Stock[6] extrapolated their measured vapor pressure curve from a largest measured pressure of 696.1 mm Hg to obtain a $T_{nbp}$ of 111.73° K (-161.37° C). Keyes, Taylor and Smith[7] reported a $T_{nbp}$ of 111.52° K. Their empirical equation fitted to their experimental data yields 111.516° K. However, a detailed examination of the deviation of their measured vapor pressures in the vicinity of one atmosphere from their equation leads to a $T_{nbp}$ of 111.503° K with a scatter of 0.020° K. Brickwedde and Scott[8*] obtained a $T_{nbp}$ of 111.669 ± 0.01° K by fitting an equation to their measured vapor pressure data. Bloomer and Parent[9] obtained a $T_{nbp}$ of 111.71° K by interpolation of their measured vapor pressure data. Hestermans and White[10] interpolated their vapor pressure data (of which only one point was below one atmosphere) to obtain a $T_{nbp}$ of 111.42° K.

The rather large deviation of these reported boiling points may be partially explained from considerations noted by Bloomer and Parent. Apparently it is quite difficult to remove all of the nitrogen impurity from a methane sample and even a few hundredths of a mole per cent of this impurity appears to produce a sizeable difference between the dew point and bubble point of the sample. Only Bloomer and Parent[9] and Hestermans and White[10] give quantitative purity data for their samples; these were 99.97 and 99.96 mole per cent methane, respectively.

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*The paper by Armstrong, Brickwedde and Scott[8] contains a section in which previously unpublished vapor pressure measurements of Brickwedde and Scott are described. Specific reference to these measurements is implied when the reference Brickwedde and Scott[8] is given.

TABLE II

NORMAL BOILING POINT OF METHANE

| Reported Temperature ($^\circ$ K) | Method of Temperature Correction[a] (Equation No.) | Corrected Temperature $T_o = 273.15^\circ$ ($^\circ$ K) | Year | Investigator |
|---|---|---|---|---|
| 111.73 | 18 | 111.75 | 1921 | Henning and Stock[6] |
| $111.50_3$[b] | 24 | $111.48_1$ | 1922 | Keyes et al[7] |
| $111.66_9$ | 23 | $111.64_8$ | 1937 | Brickwedde and Scott[8] |
| 111.71 | 23 | 111.69 | 1952 | Bloomer and Parent[9] |
| 111.42 | 17 | $111.41_6$ | 1961 | Hestermans and White[10] |
| | Selected value | 111.67 | | |

[a]See Appendix B

[b]Based on reexamination of data by present authors.

From approximate calculations using the K-factor charts for nitrogen in methane shown by Bloomer and Parent,[9] it appears that samples of this purity would exhibit 0.1$^\circ$ K or more difference between the dew point and the bubble point near one atmosphere.

An arithmetic average of the values reported by Brickwedde and Scott and Bloomer and Parent was selected as the "best" value.

2. Triple Point

The triple point temperature and pressure of methane have been determined by a number of investigators as shown in Table III. The only recently reported value  of the triple point temperature which used other than vapor

pressure thermometry is that of Brickwedde and Scott[8] of 90.660 ± 0.005° K, determined with a platinum resistance thermometer calibrated _in situ_ against the oxygen boiling point. Clusius and co-workers[11,12] reported 90.67° K using vapor pressure thermometers (oxygen and methane). The value reported by Brickwedde and Scott was selected.

The triple point pressure has been carefully measured by a number of investigators. A detailed summary is given by Armstrong, et al.[8] The more recently reported pressures are shown in Table III. The selected "best" value of 87.68 mm Hg is an average of the values listed, excluding the earlier value of Clusius and Wiegand (see Ref. (12)).

TABLE III

TRIPLE POINT OF METHANE

| Reported Temperature (°K) | Method of Temperature Correction[a] (Equation No.) | Corrected Temperature $T_o = 273.15°$ (°K) | Reported Pressure (Mm Hg) | Year | Investigator |
|---|---|---|---|---|---|
| 90.660 | 23 | $90.63_8$ | 87.60 | 1937 | Brickwedde and Scott[8] |
| $(90.67_5)$[b] | | | 87.4 | 1940 | Clusius and Wiegand[11] |
| | | | 87.75 | 1949 | Staveley and Gupta[13] |
| | | | 87.69 | 1954 | Clusius and Bühler[14] |
| | | | 87.75 | 1959 | Clusius, Piesbergen and Varde[15] |
| $(90.67)$[c] | | | 87.73 | 1960 | Clusius, Endtinger and Schleich[12] |
| | | | 87.58 | 1960 | Thomaes and Van Steenwinkel[28] |
| | Selected Value | 90.64 | 87.68 | | |

[a]See Appendix B

[b]Average of measurements made with oxygen and methane vapor pressure thermometers.

[c]Temperature measured by methane vapor pressure using equation of Brickwedde and Scott.[8]

### 3. Solid Phase Transition

Methane exhibits a lambda-type phase transition near 20° K. Clusius[16] has reported a transition temperature of 20.44° K, Clusius and Perlick[17] reported a temperature of 20.40° K. A number of other studies of this transition have been made in recent years. These studies gave essentially the same temperature for the transition. Since the calculations in the present report did not involve this temperature directly, a detailed study of the literature was not made. The value selected was 20.4° K.

## C. Heats of Vaporization, Fusion and Transition

### 1. Heat of Vaporization

Only Hestermans and White[10] have published experimental values for the heat of vaporization near the normal boiling point. Their lowest temperature was 111.85° K. Apparently by using the value 2036 ± 2 cal/mole at 99.54° K quoted by Frank and Clusius[18] to guide their extrapolation, they obtained a smoothed table of heats of vaporization at even temperatures from 100° to 190° K. From a large scale graph of this smoothed data, the value 1953 cal/gm mole was read at 111.41° K, the normal boiling point reported by these investigators. The experimental points showed a spatter of about 3 cal/mole in this region.

Rossini et al[19] reported a value of 121.87 cal/gm (1955.2 cal/gm mole) at the normal boiling point which they attributed to unpublished data of Osborne and others.

The value selected was 1953 cal/mole at an assigned normal boiling point of 111.67° K.

## 2. Heat of Fusion

The heat of fusion of methane appears to have been determined only by Clusius.[16] The average of four determinations was 224.0 cal/gm mole. This value was selected.

## D. Heat Capacity of Saturated Condensed Methane

### 1. Heat Capacity of Saturated Liquid

The experimental data, between the triple point and the boiling point, of Clusius[16] and Wiebe and Brevoort[20] were plotted. Two points appeared to fall well off any smooth curve through these points (Clusius' point at 102.1° K and Wiebe and Brevoort's point at 102.27° K). These two points were discarded and a straight line fitted to the remaining data by a least squares procedure for the range 90.64° to 112° K. The coefficients found are given in Table IV. The resulting equation represents the data to better than 0.5 per cent.

### 2. Heat Capacity of Saturated Solid

The experimental data of Clusius[16] and Frank and Clusius[21] for the range 21.06° to 87.20° K were fitted by a fourth degree polynomial in temperature by the method of least squares. The general form of the equation used was

$$c_s' \; (cal/gm \; mole \; °K) \; = a_o + a_1 \, T + a_2 \, T^2 + a_3 \, T^3 + a_4 \, T^4 \qquad (8)$$

The coefficients calculated are also given in Table IV. The older data of Eucken and Karwat,[22] which exhibit considerably more scatter, were not used. The resulting equation was assumed to be valid for the range 20.4° K to 90.64° K. The deviation of the experimental points from this equation was less than 0.5 per cent except within a few degrees of either end of the range.

At the lower temperatures, in the vicinity of the solid transition point, the deviation reached several per cent. Near the melting point, the deviation did not exceed one per cent.

E. Molal Volumes of Saturated Condensed Methane

Smoothed values of the molal volume of saturated liquid and solid methane have been presented by Kirk, Ziegler, and Mullins.[23] Calculations using Equations (1) and (5) were made using a constant mean value of 32.6 ml/gm mole at 85° K for the solid range (20.4° to 90.64° K) and a constant mean value of 37.35 ml/gm mole at 108° K for the liquid range (90.64° to 111.67° K).

TABLE IV

COEFFICIENTS OF HEAT CAPACITY POLYNOMIALS FOR METHANE

| Range, (° K) | $a_o$ | $a_1 \times 10^1$ | $a_2 \times 10^3$ | $a_3 \times 10^6$ | $a_4 \times 10^8$ |
|---|---|---|---|---|---|
| 20.4 - 90.64 | - 0.20886034 | 2.6832881 | - 2.5279477 | 5.3954182 | 4.5923201 |
| 90.64 - 111.67 | 10.847935 | 0.20795292 | | | |

F. Second Virial Coefficient and Lennard-Jones (6-12) Parameters

The second virial coefficient of methane has been measured by Schamp et al[24] (273° to 423° K), Michels and Nederbragt[25] (0° to 150° C), Kanda[26] (150° to 450° K), Mueller[27] (144° to 283° K) and Thomaes and Van Steenwinkel[28] (108° to 250° K). These measurements were used to obtain the Lennard-Jones (6-12) parameters, $e/k = 114.39$° K with $b_o = 126.40$ ml/gm mole by a least squares procedure as discussed in Appendix C. Hirchfelder et al[29] give values of $e/k = 148.2$° K and $b_o = 70.16$ ml/gm mole, based on the data of Michels and

and Nederbragt. Schamp et al[24] give values of $e/k = 148.1°$ K and $b_o = 69.75$ ml/gm mole (computed from their value of $r_m = 4.276$ $\overset{o}{A}$).

## G. Experimental Vapor Pressure Data for Methane

Armstrong, Brickwedde, and Scott[8] have presented a review of the literature of the experimental determinations of the vapor pressure of methane.

Vapor pressures of less than one atmosphere have been reported by Freeth and Verschoyle[30] from -208.32° to -182.47° C. These authors give no information about their temperature scale. Their values, determined when their vapor pressure bulb was nearly empty, were taken to be the vapor pressure of methane.

Tickner and Lossing[31] published smoothed vapor pressure data from 0.001 to 10 mm Hg which were determined by using a mass spectrometer; however, their stated temperature accuracy was only 0.3° K.

Henning and Stock[6] have reported values from -192.89° to -162.45° C.

Karwat[32] has determined vapor pressures of solid methane from 76.89° to 87.25° K. Karwat suspected a volatile impurity in his sample and, so, subtracted 0.2 mm from all of his experimental values of vapor pressure.

Keyes, Taylor, and Smith[7] reported values from 97.293° K to well beyond the normal boiling point.

Bloomer and Parent[9] have reported two points below the boiling point, using a sample quoted as 99.97 per cent pure as determined by mass spectrometer analysis. These authors also note a difference in the bubble point and the dew point pressures and report the dew point pressures as the vapor pressure of pure methane.

Hestermans and White[10] report one point below the boiling point, using a sample quoted as 99.96 per cent pure as determined by mass spectrometer analysis.

Liang[33] has corrected the results of Tickner and Lossing for the thermo-molecular pressure effects using semiempirical relations. His results are presented only as an equation which is stated to be valid for temperatures below 90° K.

The most extensive measurements in the region below the boiling point have been made by Brickwedde and Scott.[8] These investigators present their results only in the form of equations fitted to their data and a very small deviation plot. An examination of this plot, which shows pressure deviation as a function of temperature, indicates that these data have an equivalent temperature uncertainty of, very approximately, 0.003° K at 110° K, 0.004° K at 100° K, 0.01° K at 90° K, 0.2° K at 70° K, and several degrees at 55° K.

A tabulation of all of these experimental data is included in Appendix D.

## H.  Thermodynamic Functions of the Ideal Gas

The thermodynamic functions $(H^o - H^o_0)''$ and $(S^o)''$ and $-(F^o - H^o_0)''$ of methane in the ideal gas state at one atmosphere pressure were calculated assuming a rigid-rotator, harmonic-oscillator model. The enthalpy function was computed from the relations

$$(H^o - H^o_0)'' = H^o_{trans} + H^o_{rot} + H^o_{vib} \tag{9}$$

where

$$H^o_{trans} = 5\,RT/2 \tag{10}$$

$$H^o_{vib} = RT \sum x_i/(e^{x_i} - 1) \tag{11}$$

$$x_i = hc\nu_i/kT \tag{12}$$

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In Equation (11) the sum is taken over all fundamental frequencies, $\nu_i$, (9 for methane). The rotational contribution to the enthalpy, $H^o_{rot}$, was computed as outlined in Appendix E.

The entropy $(S^o)'''$ of methane at one atomsphere pressure was computed from the relations

$$(S^o)''' = S^o_{trans} + S^o_{rot} + S^o_{vib} \tag{13}$$

$$S^o_{trans} = R\left[(5/2)\ln T + (3/2)\ln M - 1.164862\right] \tag{14}$$

$$S^o_{vib} = R\sum \left[x_i/(e^{x_i} - 1) - \ln(1 - e^{-x_i})\right] \tag{15}$$

The quantity M in Equation (14) is the molecular weight of methane, taken to be 16.043. The sum in Equation (15) is taken over the same frequencies as Equation (11). The rotational contribution to the entropy was computed as outlined in Appendix E.

Since methane is spherically symmetric, its moment of inertia, I, is independent of the reference axis direction. The recently reported values of I from spectroscopic measurements are summarized in Table V. The value of I used in the calculations is an average of the values listed. In this table, $B_o(cm^{-1})$ is defined as $h/8\pi^2 cI$ or $2.79832 \times 10^{-39}/I$.

The high symmetry of the methane molecule, its relatively low moment of inertia, and the nuclear spin of the four hydrogen atoms cause anomalous behavior of the rotational partition function of methane at low temperatures. This has been described by Villars and Schultze,[38] MacDougall,[39] and Herzberg.[40] This behavior is analogous to the ortho- and para- modifications of hydrogen; however, there are three nuclear spin species for methane; the singlet or E, the triplet or F, and the quintet or A species.

TABLE V

MOMENT OF INERTIA OF METHANE

| Method of Determination | $B_o$ ($Cm^{-1}$) | $I \times 10^{40}$ ($Gm-Cm^2$) | Date | Reference |
|---|---|---|---|---|
| IR | 5.252 | 5.328 | 1940 | 34 |
| Raman | 5.253 | 5.327 | 1952 | 35 |
| IR | 5.249 | 5.331 | 1952 | 35 |
| Raman | 5.270 | 5.310 | 1955 | 36 |
| IR | 5.241 | 5.339 | 1957 | 37 |
| | Selected | 5.327 | | |

In these calculations, the rotational contributions to the ideal gas energy and entropy functions were calculated by direct summation of the rotational partition function and its derivative assuming a rigid rotor and using the statistical weights for the rotational energy levels as given by Wilson.[41] The concentration of the nuclear spin species were assumed to be "frozen" at the high (room) temperature values; that is, the relative amounts of the A, E, and F species were taken to be in the ratio 5:2:9. Appendix E contains a more detailed discussion of this calculation.

The calculated rotational contributions, to the ideal gas energy, entropy, and heat capacity functions for the three nuclear spin species and for the "frozen" spin species ratio are shown in Tables XIV, XV, and XVI of Appendix E. For comparison, values of the entropy function computed by the classical approximation are also shown. Only the values for the heat capacity function using older constants appear to have been published.[39]

The fundamental frequencies and the calculations are those published by Jones and McDowell.[42] They differ only slightly from values reported by others, as may be seem from Table VI.

TABLE VI

FUNDAMENTAL FREQUENCIES OF METHANE

| Designation | Frequency ($cm^{-1}$) | | |
|---|---|---|---|---|---|---|
| | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | | |
| Degeneracy | 1 | 2 | 3 | 3 | Date | Reference |
| | 2914.2 | 1526 | 3020.3 | 1306.2 | 1945 | 40 |
| | 2916.5 | 1533.6 | 3018.8 | 1306 | 1955 | 36 |
| | 2915 | 1534 | 3019 | 1306.2 | 1958 | 43 |
| | 2917 | 1534 | 3019 | 1306 | 1959 | 42 |

IV.  CALCULATION OF VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION

A.  Calculations Based on Selected "Best" Values of Thermal Properties

The vapor pressure and heats of vaporization and sublimation of methane were computed, using Equations (5) and (1) and the physical data shown in Table I, from the normal boiling point to 20.4° K at 2 degree intervals in the liquid range and at 5 degree intervals in the solid range.  The results are summarized in Table VII.

The published experimental vapor pressure data for methane have been compared with the computed values given in Table VII by examining the temperature difference ($T_{calc} - T_{obs}$), where $T_{obs}$ is the reported temperature (corrected where possible to an ice point of 273.15° K) corresponding to the experimentally determined pressure and $T_{calc}$ is the temperature which corresponds to this same pressure as determined by interpolation in Table VII.[*]  A detailed summary of these comparisons is given in Appendix D.

The experimental vapor pressure data of Henning and Stock,[6] Bloomer and Parent[9] and the experimental data of Brickwedde and Scott[8] for the liquid range below the normal boiling point are compared with the computed vapor pressures in Figure 1.  The limited measurements of Keyes et al[7] and Hestermans and White[10] are not shown since they deviate by more than 0.1° from the more precise measurements of Brickwedde and Scott.  The agreement between the computed vapor pressures

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[*]Values of the calculated temperature corresponding to observed vapor pressures are interpolated from the values shown in Table VII using Aitken's iterative method of polynomial interpolation as described by Milne.[47]  This method calculates the value of the dependent variable, in this case $1/T$, corresponding to a given value of the independent variable, in this case ln P, by successively interpolating with a 1, 2, 3, . . ., n, n+1, . . . degree polynomial.  In the computer program used here, this successive interpolation was continued until the value of $(1/T)$ computed by the (n+1)-th degree polynomial differed by less than 1 part in 100,000 from the value computed by the n-th degree polynomial.

Figure 1.   Comparison of Experimental Vapor Pressure Data for Liquid Methane
with Computed Values.

## TABLE VII

CALCULATED VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF
METHANE BASED ON SELECTED VALUES OF PHYSICAL PROPERTIES GIVEN IN TABLE I

| Temperature (°K) | Pressure (Mm Hg) | Heat of Vaporization (Cal/Gm Mole) | log P | $(dP/dT)/P$ (°K$^{-1}$) |
|---|---|---|---|---|
| 111.67 | 760.000 | 1953.00 | 2.880814 | |
| 110.00 | 660.996 | 1964.38 | 2.820199 | 0.0849 |
| 108.00 | 555.918 | 1977.63 | 2.745010 | 0.0882 |
| 106.00 | 464.329 | 1990.49 | 2.666826 | 0.0918 |
| 104.00 | 384.992 | 2002.98 | 2.585452 | 0.0956 |
| 102.00 | 316.726 | 2015.12 | 2.500684 | 0.0996 |
| 100.00 | 258.403 | 2026.93 | 2.412298 | 0.1039 |
| 98.00 | 208.955 | 2038.43 | 2.320053 | 0.1085 |
| 96.00 | 167.373 | 2049.64 | 2.223686 | 0.1134 |
| 94.00 | 132.713 | 2060.57 | 2.122913 | 0.1186 |
| 92.00 | 104.094 | 2071.25 | 2.017424 | 0.1242 |
| 90.64 | 87.665 | 2078.37 | 1.942829 | 0.1283 |
| - - - - SOLID - - - - | | | | |
| 90.64 | 87.665 | 2302.37[a] | 1.942829 | |
| 90.00 | 79.989 | 2304.25 | 1.903030 | 0.1442 |
| 85.00 | 37.245 | 2317.32 | 1.571073 | 0.1620 |
| 80.00 | 15.730 | 2327.91 | 1.196725 | 0.1833 |
| 75.00 | 5.9070 | 2336.47 | 0.771370 | 0.2092 |
| 70.00 | 1.9233 | 2343.31 | 0.284037 | 0.2407 |
| 65.00 | 0.5254 | 2348.54 | -.279509 | 0.2797 |
| 60.00 | 0.1153 | 2352.16 | -.938122 | 0.3287 |
| 55.00 | 1.917(-2)[b] | 2354.07 | -1.717358 | 0.3916 |

(Continued)

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TABLE VII (Continued)

CALCULATED VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF
METHANE BASED ON SELECTED VALUES OF PHYSICAL PROPERTIES GIVEN IN TABLE I

| Temperature (°K) | Pressure (Mm Hg) | Heat of Vaporization (Cal/Gm Mole) | log P | $(dP/dT)/P$ ($°K^{-1}$) |
|---|---|---|---|---|
| 50.00 | 2.224(-3) | 2354.01 | -2.652793 | 0.4738 |
| 45.00 | 1.601(-4) | 2351.68 | -3.795515 | 0.5844 |
| 40.00 | 6.002(-6) | 2346.67 | -5.221675 | 0.7380 |
| 35.00 | 8.909(-8) | 2338.59 | -7.050163 | 0.9606 |
| 30.00 | 3.327(-10) | 2327.25 | -9.477928 | 1.3012 |
| 25.00 | 1.387(-13) | 2312.96 | -12.857832 | 1.8622 |
| 20.40 | 3.967(-18) | 2298.11 | -17.401535 | 2.7788 |

[a]Heat of sublimation if condensed phase is solid.

[b]Numbers in parentheses are powers of ten by which entry must be multiplied.

and experimental measurements of Brickwedde and Scott[8] (Curve A) as computed from their equation representing their data, is seen to be within about 0.01° except near the boiling point where the discrepancy amounts to about 0.02°. This relatively large deviation near the boiling point is due primarily to the fact that the selected boiling point temperature (111.67° K) differs from their value (111.648° K). The effect of the difference is discussed further in the next section.

A similar comparison of the vapor pressures computed in Table VII with the tabulated data of Armstrong, Brickwedde, and Scott[8] (their Table 4) showed very nearly the same agreement, as can be seen by comparing Tables XI and XII, Appendix D.

The calculated vapor pressures for solid methane are compared with the available experimental data in Figure 2. The agreement between the computed and experimental data is seen to be generally poorer than for the liquid range. The large deviation of the experimental equation of Brickwedde and Scott in the low pressure region is not surprising considering the uncertainty of their pressure measurements in this region. The deviations of their data from the computed values near the triple point are approximately within their estimated error (±0.005°) in temperature measurement at 90° K. The agreement is further aided by the fact that the selected triple point temperature used in the calculations (90.640° K) agreed closely with their triple point temperature (corrected) of 90.638° K (see Table III). The triple point pressure computed for 90.640° K was 87.665 mm Hg (see Table VII) which agrees very well with the measured value 87.60 ± 0.10 mm Hg reported by Brickwedde and Scott[8] and the selected "best" value of 87.68 mm Hg (Table III).

A comparison (see Table XII, Appendix D) of the tabulated vapor pressures of Armstrong, et al[8] and those computed in Table VII was also made. These tabulated values agree somewhat better with the computed values, especially below about 70° K, than do the vapor pressures computed from the experimental equation (Equation (26), Appendix D) of Brickwedde and Scott.[8]

The data of Henning and Stock[6] and Karwat[32] deviate somewhat more from the computed vapor pressures than the data of Brickwedde and Scott[8] and Freeth and Verschoyle.[30] The smoothed data reported by Tickner and Lossing[31] agree with computed results approximately within the uncertainty of their temperature measurements (±0.3°). The correction of their data for thermomolecular pressure effects proposed by Liang,[33] while improving the agreement in the low pressure region, results in serious disagreement above 70° K.
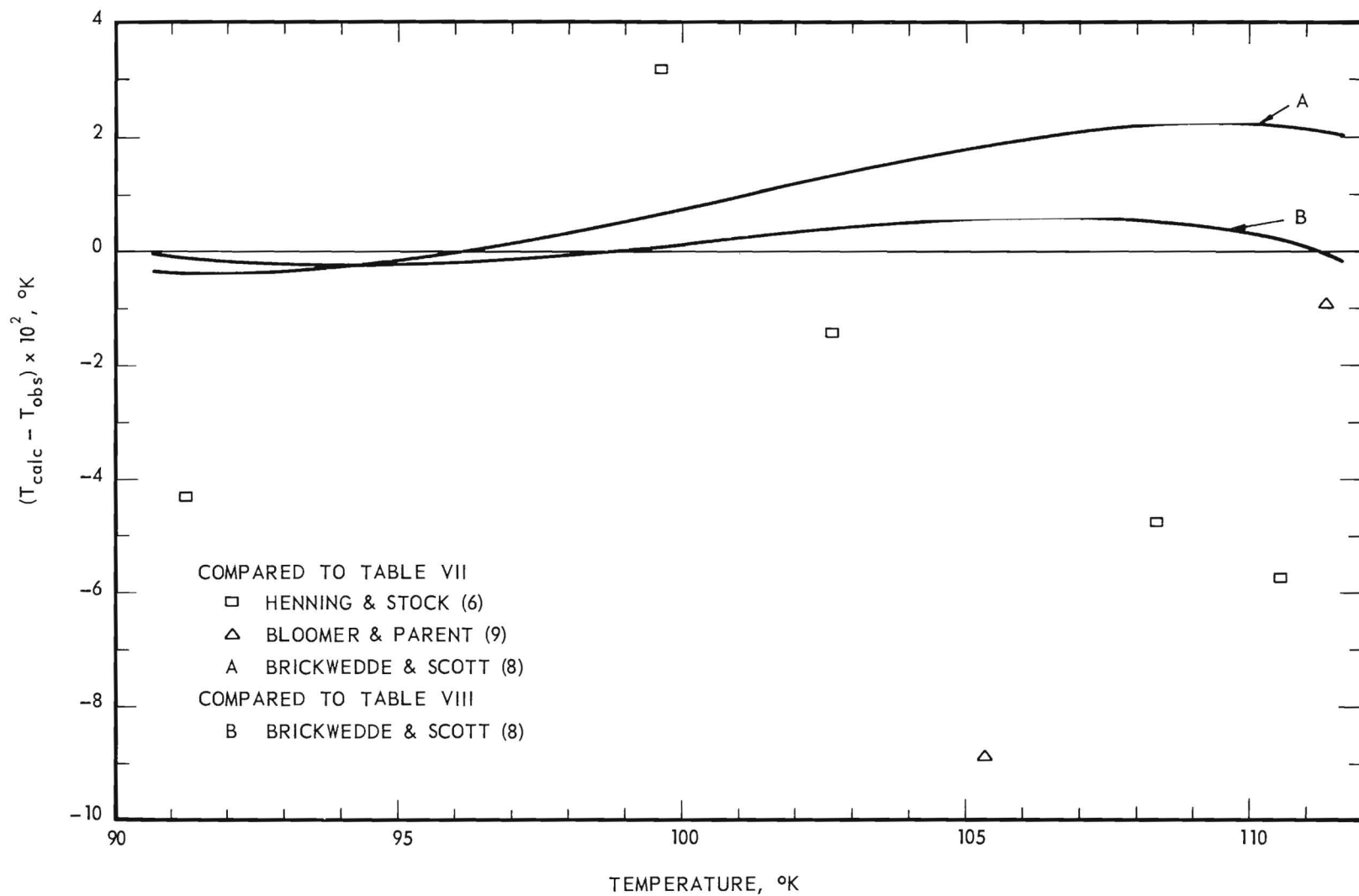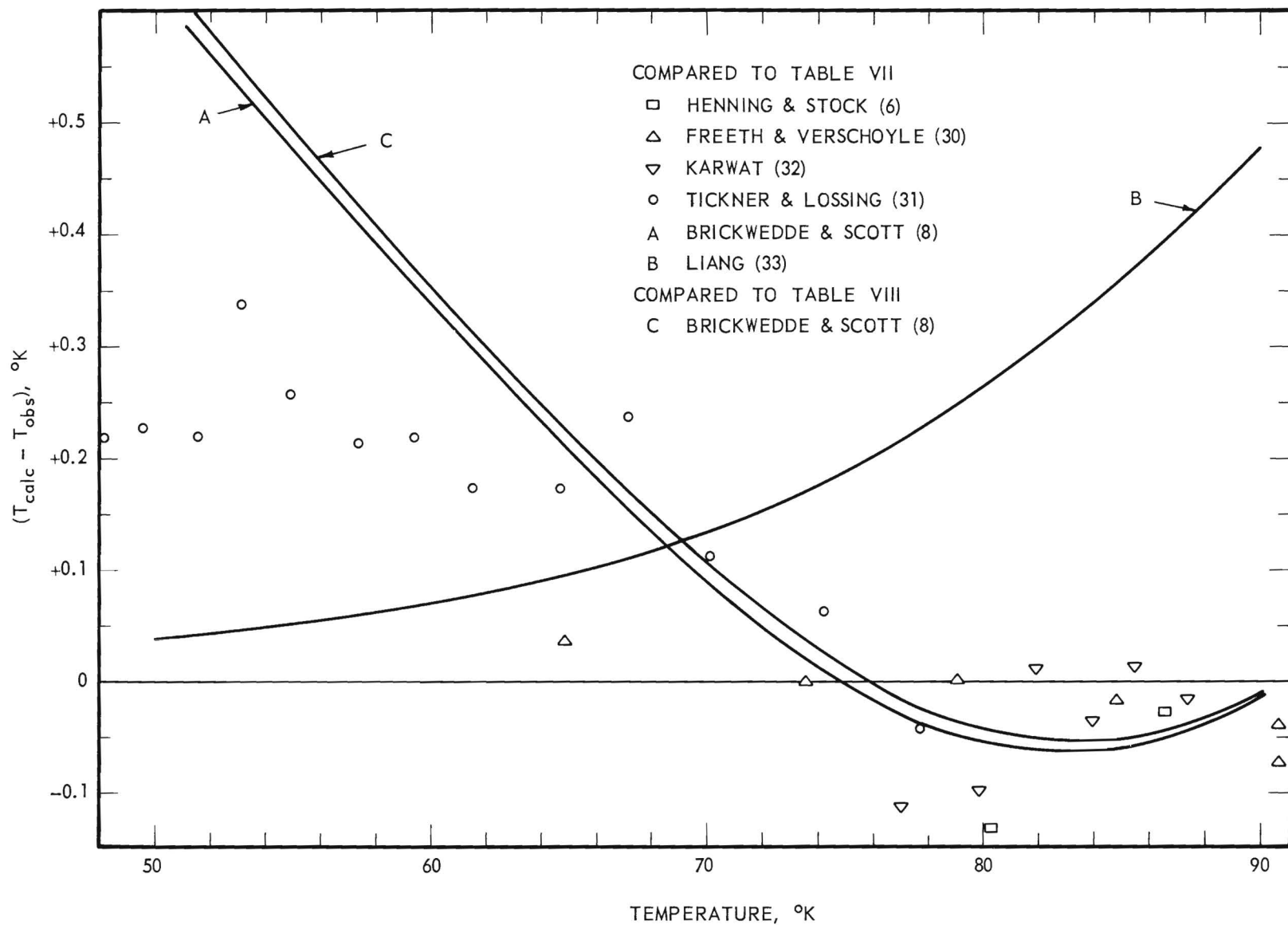
Figure 2.   Comparison of Experimental Vapor Pressure Data for Solid Methane
with Computed Values.

The computed heats of vaporization of liquid methane listed in Table VII have been compared in Figure 3 with the available experimental data. The selected value (1953 cal/gm mole) at the normal boiling point (111.67° K) agrees quite closely with the unpublished value of Osborne et al (121.87 cal/gm = 1955.2 cal/gm mole) as reported by Rossini et al.[19] At 99.54° K the computed heat of vaporization is somewhat smaller than the experimental value (2036 ± 2 cal/gm mole) reported by Frank and Clusius.[18] The computed values agree quite well with the smoothed values of heat of vaporization presented by Hestermans and White.[10] The value computed by them at 110° K from their vapor pressure data appears to be somewhat too large.

## B. Calculations Based on "N. B. S." Parameters

In order to further examine the agreement between these methods of calculating vapor pressures and the equations representing the extensive data of Brickwedde and Scott[8] and to demonstrate the effects of small changes of the input parameters, vapor pressures and heats of vaporization and sublimation were computed over the same range described above. All of the selected properties given in Table I were employed except that the normal boiling point of Brickwedde and Scott,[8] 111.648° (corrected) and the heat of vaporization at the normal boiling point of Osborne et al,[19] 1955.2 cal/gm mole, were used. For convenience, these are referred to as the "N. B. S." parameters. The vapor pressure and heats of vaporization and sublimation so computed are given in Table VIII. These computed vapor pressures for the liquid range have been compared with the experimental data of Brickwedde and Scott[8] in Figure 1 as Curve B. Comparison of Curves A and B in Figure 1 shows that the principal effect of the change in parameters is to improve the agreement between the computed and experimental data above 100° K so that the differences are now within the estimated uncertainty of ± 0.005° near 90° K and ± 0.010° at 111.6° K given by Armstrong, et al.[8]

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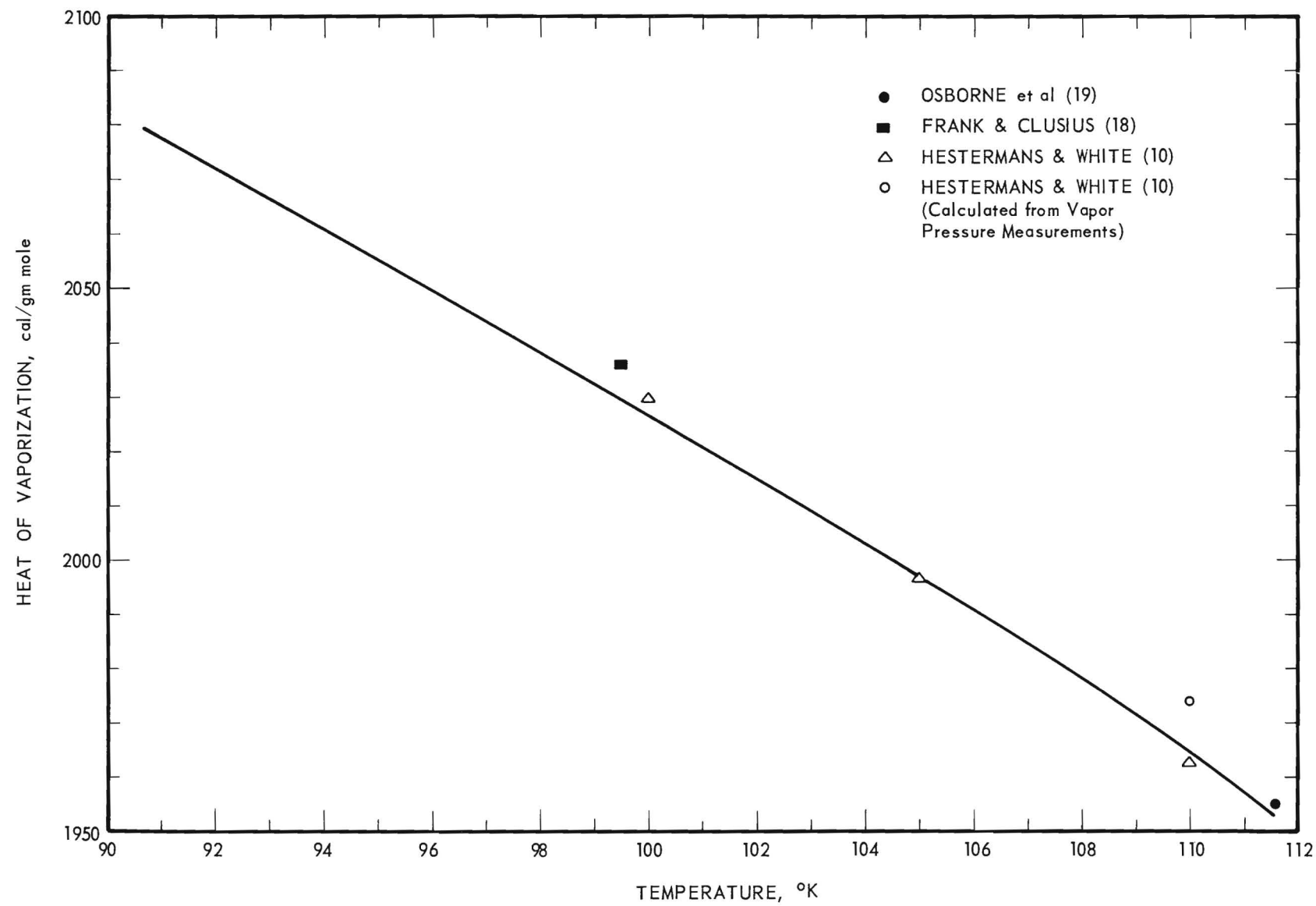
Figure 3.   Comparison of Experimental Heal of Vaporization Data with Values
Computed Using Selected Physical Data.

A similar comparison has been made in the solid region between the experimental vapor pressure equation of Brickwedde and Scott (Equation (26), Appendix D) and the vapor pressures computed in Table VIII. The comparison is shown in Figure 2 as Curve C. Comparison of Curve A, obtained using Table VII, and Curve C shows that the "N. B. S." parameters provide no significant improvement.

A comparison has also been made between the vapor pressure table of Armstrong, Brickwedde, and Scott[8] (their Table 4) and the vapor pressures computed in Table VIII. Details of the comparison are shown in Table XII, Appendix D. It was found that the vapor pressures computed in Table VIII agreed slightly better with the tabulated vapor pressures of Armstrong, et al than with the equations of Brickwedde and Scott, especially below 70° K. However, the disagreement is considered to be within the estimated uncertainty in the vapor pressure data.

Comparison of Tables VII and VIII shows that the differences in computed vapor pressures are small except at the lowest temperatures where the difference amounts to several per cent. The computed heats of vaporization and sublimation differ by about 2.2 cal/gm mole.

There appears to be little basis on which to choose between the computed values given in Tables VII and VIII. Uncertainties in the "best" values of the thermal data, as well as uncertainty in the temperature scale corrections, no doubt still exist. However, since the computed vapor pressures given in Table VIII agree slightly better with the extensive and careful measurements of Brickwedde and Scott,[8] the values of this table are recommended for use. For convenience a table of vapor pressures at one degree intervals, obtained by interpolation in Table VIII, is given as Table XVIII in Appendix D.

## C. Calculations Based on Selected Values of Thermal Properties but Assuming a Constant Rotational Heat Capacity of (3/2)R

In order to examine the effect of the nonclassical behavior of the rotation

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of the methane molecule on vapor pressures and heats of vaporization and subli-
mation, these quantities were computed assuming a constant rotational heat
capacity of $(3/2)R$ (that is, classical rotation) using the selected physical
parameters of Table I. A comparison of the results of this calculation with
the computed values given in Table VII is given in Table IX.

## D. Third Law Calculation

Frank and Clusius[21] have computed the calorimetric entropy of methane
in the ideal gas state at their selected value of the normal boiling point
($111.5^\circ$ K) to be $36.531 \pm$ e.u. (cal/gm mole $^\circ$K), based on the assumption that
the third law of thermodynamics is applicable. This calculation involved an
extrapolation of the thermal data below $11^\circ$ K. This result they found to be
in good agreement with a value of $36.616$ e.u. for the virtual entropy calcu-
lated from statistical mechanics.

The calorimetric entropy of methane in the ideal gas state has been recom-
puted by us, using the calorimetric data of Clusius,[16] Clusius and Perlick,[17]
and Frank and Clusius[21] in the range below $21^\circ$ K and the selected values of
Table I above $21^\circ$ K, to obtain a calorimetric entropy of $36.357$ e.u. at our
assigned value of the normal boiling point ($111.67^\circ$ K). A similar calculation
employing the "N.B. S." parameters used to compute Table VIII resulted in a
calorimetric entrophy of $36.378$ e.u. at $111.648^\circ$ K. The corresponding values
for the statistical entropy (virtual) of the ideal gas were $36.593$ e.u. at
$111.67^\circ$ K and $36.591$ e.u. at $111.648^\circ$ K.

The entropy difference ($S^\circ_{stat} - S^\circ_{cal}$) computed using these two sets of
data, namely, $0.236$ e.u. and $0.213$ e.u., is considerably larger than that of
$0.085 \pm 0.1$ e.u. computed by Frank and Clusius.[21] Our computed calorimetric entropy

## TABLE VIII

CALCULATED VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION
OF METHANE USING "N. B. S." PARAMETERS

| Temperature ($^\circ$K) | Pressure, P (Mm Hg) | Heat of Vaporization[a] (Cal/Gm Mole) | Log P | (dP/dT)/P ($^\circ$K$^{-1}$) |
|---|---|---|---|---|
| 111.648 | 760.000 | 1955.20 | 2.880814 | |
| 110.00 | 662.090 | 1966.44 | 2.820917 | 0.0850 |
| 108.00 | 556.732 | 1979.70 | 2.745646 | 0.0883 |
| 106.00 | 464.917 | 1992.56 | 2.667376 | 0.0919 |
| 104.00 | 385.403 | 2005.06 | 2.585915 | 0.0957 |
| 102.00 | 316.998 | 2017.20 | 2.501057 | 0.0997 |
| 100.00 | 258.570 | 2029.02 | 2.412579 | 0.1040 |
| 98.00 | 209.044 | 2040.52 | 2.320238 | 0.1086 |
| 96.00 | 167.406 | 2051.73 | 2.223772 | 0.1135 |
| 94.00 | 132.708 | 2062.66 | 2.122896 | 0.1187 |
| 92.00 | 104.064 | 2073.34 | 2.017301 | 0.1244 |
| 90.64 | 87.625 | 2080.47 | 1.942630 | 0.1284 |
| | | - - - - SOLID - - - - | | |
| 90.64 | 87.625 | 2304.47 | 1.942630 | |
| 90.00 | 79.946 | 2306.35 | 1.902796 | 0.1443 |
| 85.00 | 37.200 | 2319.41 | 1.570539 | 0.1621 |
| 80.00 | 15.698 | 2330.00 | 1.195855 | 0.1835 |
| 75.00 | 5.890 | 2338.57 | 0.770119 | 0.2093 |
| 70.00 | 1.916 | 2345.40 | 0.282351 | 0.2409 |
| 65.00 | 0.5228 | 2350.63 | -0.281697 | 0.2799 |
| 60.00 | 0.1146 | 2354.26 | -0.940897 | 0.3290 |

(Continued)

TABLE VIII (Continued)

CALCULATED VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION
OF METHANE USING "N. B. S." PARAMETERS

| Temperature ($^\circ$K) | Pressure, P (Mm Hg) | Heat of Vaporization[a] (Cal/Gm Mole) | Log P | (dP/dT)/P ($^\circ$K$^{-1}$) |
|---|---|---|---|---|
| 55.00 | 1.902(-2)[b] | 2356.16 | -1.720825 | 0.3919 |
| 50.00 | 2.202(-3) | 2356.10 | -2.657092 | 0.4742 |
| 45.00 | 1.582(-4) | 2353.77 | -3.800831 | 0.5849 |
| 40.00 | 5.912(-6) | 2348.76 | -5.228262 | 0.7386 |
| 35.00 | 8.742(-8) | 2340.69 | -7.058384 | 0.9615 |
| 30.00 | 3.248(-10) | 2329.35 | -9.488327 | 1.3023 |
| 25.00 | 1.345(-13) | 2315.05 | -12.871280 | 1.8639 |
| 20.40 | 3.810(-18) | 2300.20 | -17.419108 | 2.7813 |

[a] Heat of sublimation if condensed phase is solid.
[b] Numbers in parentheses are powers of ten by which entry must be multiplied.

for the saturated solid at 90.64$^\circ$ K is 13.563 e.u. which may be compared with
values of 13.656 e.u. at 90.6$^\circ$ K reported by Frank and Clusius[21] and 13.63 e.u.
reported by Kelley and King[46] at 90.60$^\circ$ K. An additional 0.07 e.u. of the
discrepancy between our calorimetric entropy and that computed by Frank and
Clusius arises from our choice of a slightly smaller heat of vaporization. The
good agreement between the vapor pressures computed in Tables VII and VIII and
the experimental data of Brickwedde and Scott[8] in the liquid state appear to
support the choice of this smaller value for the heat of vaporization.

More precise measurements of the thermal properties of methane are needed
to resolve these discrepancies between the calorimetric and statistically
calculated entropy.

## TABLE IX

### EFFECT OF NONCLASSICAL ROTATION ON COMPUTED PROPERTIES

| Temperature | Vapor Pressure | | Heat of Vaporization (or Sublimation) | |
|---|---|---|---|---|
| | Classical | Quantum[a] | Classical | Quantum[a] |
| (°K) | (Mm Hg) | (Mm Hg) | (Cal/Gm Mole) | (Cal/Gm Mole) |
| 111.67 | 760 | 760 | 1953.00 | 1953.00 |
| 110.00 | 660.996 | 660.996 | 1964.38 | 1964.38 |
| 100.00 | 258.404 | 258.403 | 2026.93 | 2026.93 |
| 90.64 | 87.665 | 87.665 | 2078.38 | 2078.37 |
| 90.00 | 79.989 | 79.989 | 2304.27 | 2304.25 |
| 80.00 | 15.730 | 15.730 | 2327.95 | 2327.91 |
| 70.00 | 1.923 | 1.923 | 2343.44 | 2343.31 |
| 60.00 | 0.1153 | 0.1153 | 2352.58 | 2352.16 |
| 50.00 | 2.221(-3)[b] | 2.224(-3)[b] | 2355.23 | 2354.01 |
| 40.00 | 5.960(-6) | 6.002(-6) | 2349.90 | 2346.67 |
| 30.00 | 3.233(-10) | 3.327(-10) | 2334.14 | 2327.25 |
| 20.40 | 3.614(-18) | 3.967(-18) | 2306.19 | 2298.11 |

[a] From Table VII.

[b] Numbers in parentheses are powers of ten by which entry must be multiplied.

## V.  ACKNOWLEDGEMENTS

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Approved:


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## VII.  APPENDIXES

### A.  Nomenclature and Physical Constants*

| | | |
|---|---|---|
| $B$ | $=$ | second virial coefficient of gas. |
| $B_0$ | $=$ | $h/8\pi^2 cI = 2.79832 \times 10^{-39}/I$ (gm cm$^2$). |
| $b_0$, $e/k$ | $=$ | parameters used in the Lennard-Jones (6-12) intermolecular potential function. |
| $C$ | $=$ | heat capacity of ideal gas. |
| $c$ | $=$ | velocity of light $= 2.997902 \times 10^{10}$ cm/sec. |
| $c_s'$ | $=$ | molal heat capacity of saturated condensed phase. |
| $h$ | $=$ | Planck constant $= 6.62377 \times 10^{-27}$ erg sec. |
| $(\Delta H_v)_T$ | $=$ | heat of vaporization (or sublimation) at T. |
| $(\Delta H_{tr})'$ | $=$ | heat of transition of condensed phase at transition temperature, $T_{tr}$. |
| $\sum_T^{T_1} (\Delta H_{tr})'$ | $=$ | sum of all condensed phase transitions from T to $T_1$. |
| $(H^o - H_o^o)_T''$ | $=$ | enthalpy function for ideal gas at T relative to the J = 0 rotational quantum state at 0° K. |
| $I$ | $=$ | moment of inertia of methane molecule. |
| $J$ | $=$ | rotational quantum number. |
| $k$ | $=$ | Boltzmann constant $= 1.380308 \times 10^{-16}$ erg/°K. |
| $M$ | $=$ | molecular weight of methane $= 16.043$. |
| $P$ | $=$ | pressure. |

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*The physical constants used were those of Rossini et al, _J. Am. Chem. Soc._ 74, 2699 (1952) adjusted to an ice point of 273.150° K.

$P_1, T_1$ = pressure and temperature of a fixed point on the vapor pressure curve. For methane the normal boiling point was used.

$Q_s$ = rotational partition function defined by Equation (32).

$R$ = gas constant = 1.98726 cal/gm mole °K = 0.0820574 liter atm/gm mole °K. (1 calorie = 4.1840 ab. joules = 4.1833 int. joules.)

$S°(P,T)''$ = entropy of the ideal gas at P and T.

$(S°)''_{cal}$ = calorimetric entropy of the ideal gas at one atmosphere pressure.

$(S°)''_{stat}$ = statistically calculated entropy of the ideal gas at one atmosphere pressure.

$(S°)''_T$ = entropy of ideal gas at P = 1 atm and T.

$T$ = temperature on the thermodynamic scale with a defined ice point of 273.15° K.

$T^*$ = temperature on the Kelvin Scale used by individual investigator.

$t^*$ = temperature on the Celsius Scale used by individual investigator.

$t$ = degree Celsius.

$V$ = molal volume of gas.

$v'_s$ = molal volume of saturated condensed phase.

$w^s$ = weighting factor defined by Equation (28).

$\delta$ = defined by Equation (2) and Equation (4).

$\epsilon$ = defined by Equation (6) and Equation (7).

$\theta$ = $h^2/8I\pi^2 k$.

$\nu$ = fundamental frequency of methane molecule.

Superscripts

    s             = designation for particular nuclear spin species.

    '             = condensed phase. Also used to designate first derivative of $Q_s$ with respect to $1/T$ in Equation (34).

    "             = gas phase. Also used to designate second derivative of $Q_s$ with respect to $1/T$ in Equation (36).

    *             = refers to temperature scale of individual investigator.

Subscripts

    $O_2$           = normal boiling point of oxygen.

    o             = ice point (except for $b_o$).

    s             = saturated vapor or condensed state. Also used to designate particular nuclear spin species.

    v             = vaporization. Also refers to sublimation for temperatures at and below the triple point.

    f             = fusion.

    nbp          = normal boiling point.

    tp           = triple point.

## B. Conversion of Temperature Scales

The conversion of temperatures reported by a given investigator to a consistent thermodynamic scale based on an ice point of 273.150° K has been made where possible. The "best" value for the normal boiling point of oxygen on this scale has been taken to be 90.168° K, the value selected by van Dijk.[5] The various methods used for making these corrections are given below. The final corrected thermodynamic temperature (in °K) used in this paper is reported by T; the temperature reported by the investigator is represented by $T^*$. In cases where the original temperatures were reported in °C, these were converted to $T^*$ by addition to the reported ice point $T_o^*$. When no ice point was given, the reported temperature in °C was added to 273.150° to obtain T in °K.

The relations used for making temperature scale conversions were:

1. <u>Methods involving only ice point ratios</u>

$$T = T^*(T_o/T_o^*) \tag{16}$$

$$T = T^*(273.15/273.16) \tag{17}$$

$$T = T^*(273.15/273.10) \tag{18}$$

$$T = T^*(273.15/273.09) \tag{19}$$

This method of conversion of a thermodynamic temperature scale from one ice point to another is strictly correct only if the ice point temperature is a <u>defined</u> <u>point</u>. When $T_o$ is obtained from a gas thermometer scale defined at the ice point and normal boiling point of water, a more complicated relation is required for exact conversion. (See, for instance, van Dijk.[5]) Data for making the exact conversions are not always given by the investigator. However, the exact relations reduce to the simple relation used here in the first approximation. Henning and Otto[44] have used a somewhat different approximate method for correction. Their relation gave the same results as Equation (16) to about 0.002°.

2.  Methods involving only oxygen point

$$T = T^* (T_{O_2}/T^*_{O_2}) \tag{20}$$

$$T = T^* (90.168/90.190) \tag{21}$$

3.  Methods involving both ice point and oxygen point

This method of correction, used for correction of reported tempera-
tures where both oxygen point and ice point temperatures in °K are given by
the investigator, is given by the relation

$$T = (T^* - T^*_{O_2}) \frac{(273.15 - 90.168)}{(T^*_{O} - T^*_{O_2})} + 90.168 \tag{22}$$

For specific choices of $T^*_{O}$ and $T^*_{O_2}$ the relation becomes

$$T = (T^* - 90.190) \frac{(273.15 - 90.168)}{(273.16 - 90.190)} + 90.168 \tag{23}$$

$$T = (T^* - 90.190) \frac{(273.15 - 90.168)}{(273.13 - 90.190)} + 90.168 \tag{24}$$

Equations (22) through (24) assume a linear deviation between the reported
temperature scale and the thermodynamic scale from the ice point $T^*_{O}$ to the
oxygen point $T^*_{O_2}$.

As an example of the use of Equation (22) we may give our method for cor-
recting the Kelvin temperature scale used by Armstrong et al for methane.[8] In
that work temperatures above the oxygen point (-182.970° C) were measured on
the International Temperature Scale. These investigators converted their measured
temperatures to °K by addition of 273.16° K, their assigned ice point. The Kelvin
scale thus obtained had a value of 90.190° K at the oxygen point and 273.16° K

at the ice point. The Kelvin temperature scale used in our paper has an ice point of $T_0 = 273.15°$ K and on this scale the "best" value of the oxygen point has been taken to be $90.168°$ K.[5] Thus the Kelvin temperatures reported by Armstrong et al were assumed to be $0.022°$ too high at $90.190°$ K and $0.01°$ too high at $273.16°$ K. Equation (23) shows how the corrected temperature was obtained from their reported temperatures.

## C. Second Virial Coefficient and Lennard-Jones (6-12) Parameters

Schamp et al[24] have measured the second virial coefficient from $273°$ to $423°$ K and have obtained $e/k = 148.1°$ K and $r_m = 4.276$ Å ($b_0 = 69.75$ ml/gm mole) from these data. Michels and Nederbragt[25] have measured the second virial coefficient from $0°$ to $150°$ C for which Hirschfelder et al[29] give $e/k = 148.2°$ K and $b_0 = 70.16$ ml/gm mole.

Kanda[26] has measured the second virial coefficient by an isothermal expansion technique and reports values at even temperatures from $150°$ to $450°$ K. Mueller[27] has determined the second virial coefficients from $144°$ to $283°$ K by the Burnett method. Thomaes and Van Steenwinkel[28] have measured the second virial coefficient from $108°$ to $250°$ K by a differential technique using hydrogen as a reference substance.

In the region below the ice point, the values reported by Kanda are less negative than those reported by Thomaes and Van Steenwinkel which are, in turn, less negative than those reported by Mueller.

These data were plotted on a large scale graph and a smooth curve drawn. This curve rather heavily weighted the data of Thomaes and Van Steenwinkel. Eight points were selected from this curve in the interval $108.45°$ to $280°$ K and values of $e/k$ and $b_0$ were fitted to these points by a method of least squares.

This least squares procedure, which minimizes the sum of the squares of the deviations, weights the fit towards the low temperature end of the curve since B increases greatly in magnitude as the temperature is reduced. Unfortunately, this trial and error solution of the normal equations can produce mathematically correct but physically incorrect solutions due, apparently, to the existence of relative maxima and minima in the sum of the squares of the deviations.

In this case, however, the solution $e/k = 114.39°$ K and $b_0 = 126.40$ ml/gm mole appears to be the true minimum for the eight points fitted. These parameters yield a value of B which is about 3 per cent less negative than that reported by Thomaes and Van Steenwinkel at $108.45°$ K and fits well over the entire range.

No attempts were made to apply quantum corrections to these calculations other than to determine that using the parameters fitted here, the effect would be on the order of one per cent at $115°$ K and would increase at lower temperatures. These data and Lennard-Jones functions are shown in Figure 4.

D. Comparison of Experimental and Calculated Vapor Pressures

The experimentally determined vapor pressure data of Henning and Stock;[6] Freeth and Verschoyle;[30] Karwat;[32] Keyes, Taylor and Smith;[7] Bloomer and Parent;[9] Hestermans and White;[10] Tickner and Lossing;[31] and Liang[33] are shown in Table X. The data of Tickner and Lossing were smoothed by them. The data of Liang were computed from his equation log P (mm Hg) = 7.655 - 515/T which was stated to be applicable below $90°$ K. All reported temperatures, unless otherwise stated, have been corrected to a thermodynamic scale based on an ice point of $273.15°$ K as outlined in Appendix B. No corrections have been applied to the reported pressures.

The computed vapor pressures of methane given in Table VII are compared with the experimentally determined vapor pressure data in Table X by examining

42
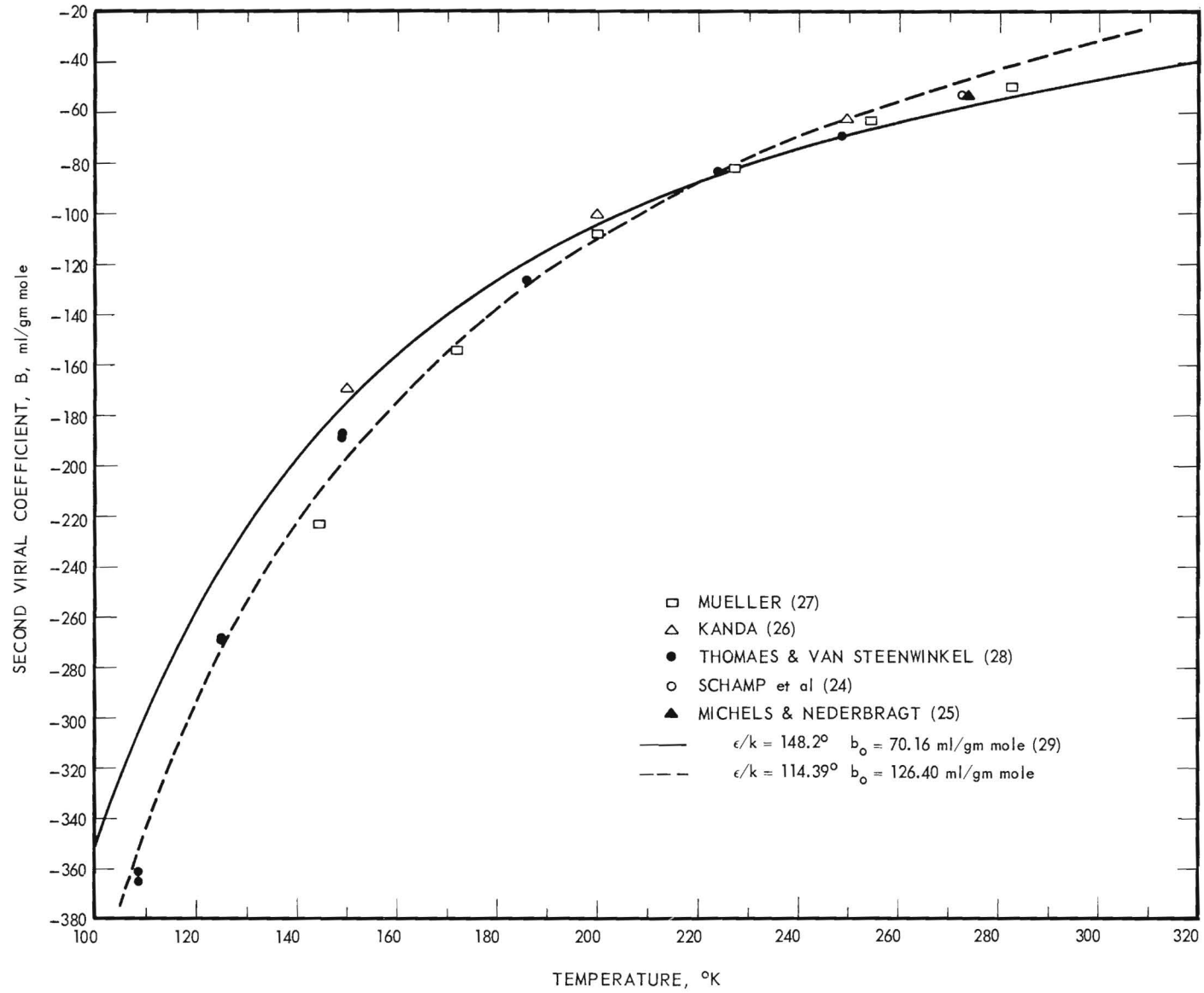
Figure 4.  Second Virial Coefficient of Methane.

TABLE X

COMPARISON OF EXPERIMENTAL VAPOR PRESSURES WITH CALCULATED VAPOR
PRESSURES PRESENTED IN TABLE VII

| Investigator | Reported Temperature ($^{\circ}$K) | Corrected Temperature, $T_{obs}$ ($T_o = 273.15^{\circ}$) ($^{\circ}$K) | Reported Pressure (Mm Hg) | $T_{calc} - T_{obs}$ ($^{\circ}$K) |
|---|---|---|---|---|
| Henning and Stock[6] | 110.65 | 110.670[a] | 696.1 | -0.0572 |
| | 108.33 | 108.350 | 570.9 | -0.0476 |
| | 102.61 | 102.629 | 336.6 | -0.0140 |
| | 99.61 | 99.628 | 249.4 | 0.0318 |
| | 91.23 | 91.247 | 94.2 | -0.0428 |
| | 86.43 | 86.446 | 46.7 | -0.0260 |
| | 80.21 | 80.225 | 16.0 | -0.1317 |
| Karwat[32] | 87.25 | 87.269[b] | 53.15 | -0.0154 |
| | 85.42 | 85.439 | 40.06 | 0.0132 |
| | 83.82 | 83.838 | 30.58 | -0.0377 |
| | 81.74 | 81.758 | 21.60 | 0.0103 |
| | 79.75 | 79.768 | 14.80 | -0.0984 |
| | 76.89 | 76.907 | 8.52 | -0.1134 |
| Freeth and Verschoyle[30] | 90.68 | 90.68[c] | 87.67 | -0.0396 |
| | 90.69 | 90.69 | 87.37 | -0.0737 |
| | 84.66 | 84.66 | 35.13 | -0.0193 |
| | 78.99 | 78.99 | 13.04 | 0.0006 |
| | 73.45 | 73.45 | 4.24 | -0.0016 |
| | 64.83 | 64.83 | 0.506 | 0.0358 |
| Keyes, Taylor and Smith[7] | 110.023 | 110.000[d] | 671.84 | 0.1920 |
| | 106.003 | 106.800 | 471.81 | -0.6256 |
| | 100.902 | 100.878 | 287.28 | 0.1525 |
| | 97.293 | 97.268 | 195.62 | 0.1283 |
| Bloomer and Parent[9] | 111.36 | 111.339[e] | 738.95 | -0.0093 |
| | 105.38 | 105.359 | 434.04 | -0.0884 |
| Hestermans and White[10] | 109.38 | 109.376[f] | 643.72 | 0.3130 |
| Tickner and Lossing[31] | 77.65 | 77.65[c] | 10.0 | -0.0445 |
| | 74.15 | 74.15 | 5.0 | 0.0617 |
| | 70.05 | 70.05 | 2.0 | 0.1129 |
| | 67.15 | 67.15 | 1.0 | 0.2361 |
| | 64.65 | 64.65 | 0.50 | 0.1733 |

(Continued)

TABLE X (Continued)

COMPARISON OF EXPERIMENTAL VAPOR PRESSURES WITH CALCULATED VAPOR
PRESSURES PRESENTED IN TABLE VII

| Investigator | Reported Temperature ($^\circ$K) | Corrected Temperature, $T_{obs}$ ($T_o = 273.15^\circ$) ($^\circ$K) | Reported Pressure (Mm Hg) | $T_{calc} - T_{obs}$ ($^\circ$K) |
|---|---|---|---|---|
| Tickner and Lossing[31] | 61.55 | 61.55 | 0.20 | 0.1733 |
| | 59.35 | 59.35 | 0.10 | 0.2197 |
| | 57.35 | 57.35 | 0.05 | 0.2123 |
| | 54.85 | 54.85 | 0.02 | 0.2583 |
| | 53.05 | 53.05 | 0.01 | 0.3367 |
| | 51.55 | 51.55 | 0.005 | 0.2195 |
| | 49.55 | 49.55 | 0.002 | 0.2265 |
| | 48.15 | 48.15 | 0.001 | 0.2174 |
| Liang[33] | 90.0 | 90.0[c] | 85.660 | 0.4775 |
| | 85.0 | 85.0 | 39.462 | 0.3583 |
| | 80.0 | 80.0 | 16.501 | 0.2617 |
| | 75.0 | 75.0 | 6.142 | 0.1871 |
| | 70.0 | 70.0 | 1.985 | 0.1324 |
| | 65.0 | 65.0 | 0.5394 | 0.0942 |
| | 60.0 | 60.0 | 0.1179 | 0.0686 |
| | 55.0 | 55.0 | 0.0196 | 0.0513 |
| | 50.0 | 50.0 | $2.264 \times 10^{-3}$ | 0.0379 |
| | 45.0 | 45.0 | $1.624 \times 10^{-4}$ | 0.0239 |

[a]Reported temperatures corrected by Equation (18), Appendix B.

[b]Reported temperatures corrected by Equation (19), Appendix B.

[c]No temperature corrections applied.

[d]Reported temperatures corrected by Equation (24), Appendix B.

[e]Reported temperatures corrected by Equation (23), Appendix B.

[f]Reported temperatures corrected by Equation (17), Appendix B.

the temperature difference $(T_{calc} - T_{obs})$ where $T_{obs}$ is the corrected reported

temperature corresponding to the experimentally determined pressure, and $T_{calc}$

is the temperature which corresponds to this same pressure as determined by

interpolation in the computed vapor pressure given in Table VII.

Brickwedde and Scott[8] represented their experimental vapor pressure data for methane above the triple point by the equation

$$\log P \text{ (mm Hg)} = 7.55073 - 483.22/T^* - 0.0030686 \; T^* \qquad (25)$$

and below the triple point by the equation

$$\log P \text{ (mm Hg)} = 6.7838 - 477.46/T^* + 0.00469 \; T^* \qquad (26)$$

In these equations $T^*$ represents the temperature in °K as used by these investigators. A comparison of the experimental data of Brickwedde and Scott,[8] as represented by these equations, with the calculated vapor pressures given in Tables VII and VIII is shown in Table XI. The temperature difference $(T_{calc} - T_{obs})$ was computed in the same manner as for Table X. It is noted that the vapor pressures given in Table VIII agree within the estimated uncertainly of the experimental data in the liquid range (111.67° to 90.64° K). There is no significant difference between the results obtained for Tables VII and VIII in the solid range.

In addition to the vapor pressure equations of Brickwedde and Scott cited above, Armstrong, Brickwedde, and Scott[8] presented a second set of equations which represented slight adjustments of Equations (25) and (26). These adjusted equations were used to compute a vapor pressure table for methane at one degree intervals down to 51° K. This tabulated set of vapor pressures (their Table 4) has been compared with the vapor pressures computed in Tables VII and VIII in Table XII, the temperature difference, $(T_{calc} - T_{obs})$, being calculated as in Table XI. Comparison of Tables XI and XII shows that in the liquid range (110° to 92° K) the computed vapor pressures given in Table VIII agree very well with

## TABLE XI

### COMPARISON OF CALCULATED VAPOR PRESSURES WITH SMOOTHED EXPERIMENTAL DATA OF BRICKWEDDE AND SCOTT[8]

| Reported Temperature, $T^*$ ($^\circ$K) | Corrected Temperature, $T_{obs}$ ($T_o = 273.15^\circ$ K) ($^\circ$K) | Reported Pressure (Mm Hg) | $(T_{calc} - T_{obs})^a$ ($^\circ$K) | $(T_{calc} - T_{obs})^b$ ($^\circ$K) |
|---|---|---|---|---|
| 111.67 | 111.649 | 760.000 | 0.0205 | −0.0014 |
| 110.00 | 109.979 | 661.111 | 0.0227 | 0.0033 |
| 108.00 | 107.979 | 555.983 | 0.0221 | 0.0056 |
| 106.00 | 105.979 | 464.279 | 0.0198 | 0.0060 |
| 104.00 | 103.979 | 384.812 | 0.0162 | 0.0051 |
| 102.00 | 101.979 | 316.433 | 0.0119 | 0.0033 |
| 100.00 | 99.979 | 258.029 | 0.0074 | 0.0012 |
| 98.00 | 97.978 | 208.540 | 0.0032 | −0.0006 |
| 96.00 | 95.978 | 166.956 | −0.0003 | −0.0020 |
| 94.00 | 93.978 | 132.325 | −0.0028 | −0.0024 |
| 92.00 | 91.978 | 103.759 | −0.0039 | −0.0016 |
| 90.64 | 90.618 | 87.376 | −0.0038 | −0.0002 |
| 90.00 | 89.978 | 79.577 | −0.0137 | −0.0100 |
| 85.00 | 84.979 | 36.751 | −0.0614 | −0.0538 |
| 80.00 | 79.980 | 15.515 | −0.0553 | −0.0443 |
| 75.00 | 74.982 | 5.881 | −0.0031 | 0.0105 |
| 70.00 | 69.983 | 1.955 | 0.0861 | 0.1022 |
| 65.00 | 64.984 | 0.5535 | 0.2027 | 0.2207 |
| 60.00 | 59.985 | 0.1281 | 0.3363 | 0.3556 |
| 55.00 | 54.986 | 2.294(−2) | 0.4761 | 0.4964 |
| 51.00 | 50.988 | 4.582(−3) | 0.5853 | 0.6061 |

[a] $T_{calc}$ obtained by interpolation at reported pressure in Table VII

[b] $T_{calc}$ obtained by interpolation at reported pressure in Table VIII

[c] Reported temperatures corrected by Equation (23), above 90.19$^\circ$ K and Equation (21) below 90.19$^\circ$ K.

TABLE XII

COMPARISON OF CALCULATED VAPOR PRESSURES WITH TABULATED VALUES
OF ARMSTRONG, BRICKWEDDE AND SCOTT[8]

| Tabulated Temperature, $T*$ | Corrected Temperature, $T_{obs}$ ($T_o$ = 273.15°)[c] | Tabulated Pressure | $(T_{calc} - T_{obs})$[a] | $(T_{calc} - T_{obs})$[b] |
|---|---|---|---|---|
| (°K) | (°K) | (Mm Hg) | (°K) | (°K) |
| 110.0 | 109.979 | 661.01 | 0.0209 | 0.0015 |
| 108.0 | 107.979 | 555.93 | 0.0210 | 0.0045 |
| 106.0 | 105.979 | 464.28 | 0.0198 | 0.0060 |
| 104.0 | 103.979 | 384.85 | 0.0172 | 0.0061 |
| 102.0 | 101.979 | 316.51 | 0.0143 | 0.0057 |
| 100.0 | 99.979 | 258.12 | 0.0108 | 0.0046 |
| 98.0 | 97.979 | 208.62 | 0.0067 | 0.0028 |
| 96.0 | 95.978 | 167.00 | 0.0019 | 0.0002 |
| 94.0 | 93.978 | 132.32 | -0.0031 | -0.0028 |
| 92.0 | 91.978 | 103.70 | -0.0085 | -0.0062 |
| 90.0 | 89.978 | 79.55 | -0.0161 | -0.0123 |
| 85.0 | 84.979 | 36.90 | -0.0366 | -0.0290 |
| 80.0 | 79.980 | 15.58 | -0.0325 | -0.0216 |
| 75.0 | 74.982 | 5.88 | -0.0035 | 0.0101 |
| 70.0 | 69.983 | 1.939 | 0.0510 | 0.0671 |
| 65.0 | 64.984 | 0.541 | 0.1207 | 0.1386 |
| 60.0 | 59.985 | 0.1229 | 0.2092 | 0.2285 |
| 55.0 | 54.987 | 0.0215 | 0.3078 | 0.3282 |
| 51.0 | 50.988 | 0.0042 | 0.3907 | 0.4115 |

[a]$T_{calc}$ obtained by interpolation at reported pressure in Table VII.

[b]$T_{calc}$ obtained by interpolation at reported pressure in Table VIII.

[c]Reported temperatures corrected by Equation (23) above 90.19° K and by Equation (21) below 90.19° K.

both the tabulated data of Armstrong et al[8] and the equations of Brickwedde and Scott.[8] In the solid range the computed values in Table VIII agree somewhat better with the table of Armstrong et al.[8]

## E. Evaluation of the Rotational Contributions to the Ideal Gas Thermodynamic Functions for Methane

Methane is a spherical rotor. The moment of inertia, I, is comparatively small. This fact, together with the high symmetry of the molecule, results in considerable deviation from the classical statistical mechanical approximation of the partition function within the temperature range for which these vapor pressure calculations have been made.

If one ignores the problem of nuclear spin of the four hydrogen atoms, each rotational level of quantum number J should have[40] a statistical weight of $(2J + 1)^2$. When one considers the spins of the nuclei, it follows that there exist three separate species of the methane molecule which are distinguished by the symmetry properties of the nuclear spins of the four hydrogen atoms. These have been called by various authors; singlet, triplet and quintet;[38] ortho, para and meta;[38] E, T, and A;[41] or E, F, and A.[40] Hereafter, the last listed nomenclature will be used.

As is the case with the ortho- and para- nuclear spin species of hydrogen, the conversion from one spin species to another is presumably a very slow process. The high temperature ratio of these spin species is[40] A:E:F::5:2:9. Since the attainment of equilibrium among these species at low temperatures was assumed to take place slowly, the thermodynamic properties of ideal gaseous methane have been computed for the purposes of this work on the basis of the "frozen" or "meta-stable" high temperature ratio of the spin species.

From symmetry arguments, it has been shown that the statistical weights for the J-th rotational level are different for each of the nuclear spin species.

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Villars and Schultze[38] give these statistical weights up to J = 10; Herzberg[40] gives them up to J = 15. Wilson[41] presents a general table of statistical weighting functions for the molecule $XY_4$ and for nuclear spins of the four identical atoms equal to 0, 1/2, and 1.

Wilson[41] shows that these statistical weighting functions also depend upon the symmetry properties of the combined electronic and vibrational wave functions. We have used the case where this combined wave function is of symmetry A; this is in agreement with the values used by Villars and Schultze[38] and MacDougall.[39]

The weighting functions given by Wilson have a periodicity in J of six; therefore, dummy variables $\underline{u}$ and $\underline{v}$ have been introduced for computational purposes. Using these variables, J may be represented by Equation (27).

$$J = 6u + v \tag{27}$$

where

$$u = 0, 1, 2, 3, \ldots$$
$$v = 0, 1, 2, 3, 4, \text{ and } 5.$$

The statistical weight of rotational level J for the nuclear spin species $\underline{s}$ (i.e., A, E, or F) can be expressed as the product $w^s (2J + 1)$ where $w^s$ is defined by Equation (28).

$$w^s = m^s(u + n_v^s) \tag{28}$$

The values of $m^s$ and $n_v^s$ as deduced from Wilson's table[41] of weighting functions are shown in Table XIII.

The energy, $e_J$, assigned to the J-th rotational level is given below.

$$e_J = J(J + 1)\theta_r/T \tag{29}$$

## TABLE XIII

### VALUES OF $m^S$ AND $n_v^S$ FOR METHANE IN EQUATION (28)

| | Nuclear Spin Species | | |
| | A(quintet) $m^A = 5$ | E(singlet) $m^E = 2$ | F(triplet) $m^F = 9$ |
| v | $n_v^A$ | $n_v^E$ | $n_v^F$ |
|---|---|---|---|
| 0 | 1 | 0 | 0 |
| 1 | 0 | 0 | 1/3 |
| 2 | 0 | 1 | 1/3 |
| 3 | 1 | 0 | 2/3 |
| 4 | 1 | 1 | 2/3 |
| 5 | 0 | 1 | 1 |

where

$$\theta_r = h^2/8\pi^2 Ik \tag{30}$$

The rotational partition function for each species, $Q_s$, is given by

$$Q_s = \sum_{J=0}^{J} w^s (2J + 1) \exp\left[-J(J + 1)\,\theta_r/T\right] \tag{31}$$

The rotational partition functions for each species were computed* from Equation (32).

$$Q_s = \sum_{u=0}^{u} \sum_{v=0}^{v=5} \frac{m^s(u + n_v^s)[2(6u + v) + 1]}{\exp[(6u + v)(6u + v + 1)\theta_r/T]} \tag{32}$$

Equation (32) can also be written as

---

*The summation was continued until the last summation over v was less than $1 \times 10^{-6}$ of the accummulated summation over u.

$$Q_s = \sum_{J=0}^{J} q_s(J,T) \tag{33}$$

In order to compute the energy and heat capacity functions the quantities $Q_s'$ and $Q_s''$ are needed. The quantities are

$$Q_s' = dQ_s/d(1/T) \tag{34}$$

$$Q_s' = -\sum_{J=0}^{J} J(J+1)\theta_r q_s(J,T) \tag{35}$$

$$Q_s'' = d^2 Q_s/[d(1/T)]^2 \tag{36}$$

$$Q_s'' = \sum_{J=0}^{J} [J(J+1)\theta_r]^2 q_s(J,T) \tag{37}$$

Having computed the quantities of Q, Q', and Q'' for each species as a function of temperature, the rotational contributions to the ideal gas thermodynamic functions for each nuclear spin species were computed from Equations (38), (39), and (40).[45]

$$(H_{rot}^o/R)_s = (E_{rot}^o/R)_s = -Q_s'/Q_s \tag{38}$$

$$(S_{rot}^o/R)_s = (E_{rot}^o/RT)_s + \ln Q_s \tag{39}$$

$$(C_{rot}^o/R)_s = (1/T^2)\left[(Q_s''/Q_s) - (Q_s'/Q_s)^2\right] \tag{40}$$

The entropy function computed from Equation (39) includes the nuclear spin entropy. In order to convert this to virtual entropy, the natural logarithm of the nuclear spin degeneracy must be subtracted. These degeneracies are 5,

2, and 9 for species A, E, and F, respectively.

The rotational contributions to the ideal gas thermodynamic functions for the "frozen" ratio of the spin species were computed from Equations (41), (42), (43), and (44), in which $x_s$ represents the mole fraction of the given spin species.

$$E^o_{rot} = \sum_s x_s (E^o_{rot})_s \tag{41}$$

$$C^o_{rot} = \sum_s x_s (C^o_{rot})_s \tag{42}$$

$$(S^o_{rot}/R)(virtual) = \sum_s x_s (S^o_{rot}/R)_s - \Delta^* S/R \tag{43}$$

where

$$\Delta^* S/R = (5/16)\ln 5 + (2/16)\ln 2 + (9/16)\ln 9 = 1.8255314 \tag{44}$$

The calculated rotational contributions to the ideal gas energy, entropy, and heat capacity functions for the three nuclear spin species for the "frozen" high temperature equilibrium mixture are shown in Tables XIV, XV, and XVI.

MacDougall[39] has carried out similar calculations of $C^o_{rot}/R$. The values given in Table XVI agree closely with those of MacDougall, the small differences observed presumably arising from slight differences in the values of the moment of inertia and fundamental constants chosen.

The thermodynamic functions $(H^o - H^o_0)/T$, $-(F^o - H^o_0)/T$ and $S^o/R$ of the frozen high temperature equilibrium mixture of methane at one atmosphere are given in Table XVII.

## TABLE XIV

### ROTATIONAL CONTRIBUTION TO ENERGY FUNCTION OF IDEAL GAS

| Temperature | $(E^{\circ} - H_o^{\circ})$ | | | |
|---|---|---|---|---|
| ($^{\circ}$K) | (Cal/Gm Mole) | | | |
| | A species | E species | F species | Frozen Ratio |
| 5 | 1.675(-5) | 90.108 | 30.272 | 28.292 |
| 7.5 | 7.077(-3) | 90.109 | 31.792 | 29.149 |
| 10 | 1.460(-1) | 90.118 | 34.872 | 30.926 |
| 12.5 | 0.902 | 90.189 | 39.184 | 33.596 |
| 15 | 3.049 | 90.440 | 44.464 | 37.269 |
| 20 | 13.849 | 92.091 | 57.058 | 47.934 |
| 20.4 | | | | 48.970 |
| 25 | 33.116 | 96.028 | 75.105 | 62.363 |
| 30 | 56.689 | 102.556 | 85.774 | 78.783 |
| 35 | 80.430 | 111.461 | 100.603 | 95.657 |
| 40 | 102.388 | 122.286 | 115.488 | 112.241 |
| 45 | 122.252 | 134.530 | 130.387 | 128.363 |
| 50 | 140.396 | 147.760 | 145.290 | 144.069 |
| 60 | 173.439 | 175.930 | 175.098 | 174.684 |
| 70 | 204.378 | 205.172 | 204.907 | 204.775 |
| 80 | 234.554 | 234.797 | 234.716 | 234.676 |
| 90 | 264.477 | 264.549 | 264.525 | 264.513 |
| 100 | 294.320 | 294.341 | 294.334 | 294.331 |
| 110 | 324.139 | 324.145 | 324.143 | 324.142 |
| 111.67 | | | | 329.120 |

TABLE XV

ROTATIONAL CONTRIBUTION TO ENTROPY FUNCTION OF IDEAL GAS

| Temperature | $(S^o/R)_{rot}$ | | | | | |
|---|---|---|---|---|---|---|
| (°K) | | | | | "Frozen Ratio" | |
| | A Species* | E Species* | F Species* | Absolute** | Virtual | Classical |
| 5 | 1.60944 | 2.30259 | 2.22495 | 2.04231 | | |
| 7.5 | 1.60995 | 2.30261 | 2.34440 | 2.10966 | | |
| 10 | 1.61759 | 2.30315 | 2.52081 | 2.21134 | | |
| 12.5 | 1.65074 | 2.30619 | 2.71358 | 2.33052 | | |
| 15 | 1.72854 | 2.31526 | 2.90689 | 2.46470 | | |
| 20 | 2.03471 | 2.36176 | 3.27000 | 2.77044 | 0.94491 | 1.04730 |
| 20.4 | | | | | 0.97071 | 1.07701 |
| 25 | 2.46455 | 2.44910 | 3.58566 | 3.09324 | 1.26771 | |
| 30 | 2.89655 | 2.56817 | 3.85426 | 3.39422 | 1.56868 | 1.65550 |
| 35 | 3.26511 | 2.70589 | 4.08431 | 3.65601 | 1.83048 | |
| 40 | 3.56051 | 2.85111 | 4.28433 | 3.87898 | 2.05345 | 2.08702 |
| 45 | 3.79621 | 2.99612 | 4.46094 | 4.07011 | 2.24458 | |
| 50 | 3.98874 | 3.13632 | 4.61897 | 4.23669 | 2.41116 | 2.42174 |
| 60 | 4.29234 | 3.39454 | 4.89244 | 4.51767 | 2.69214 | 2.69522 |
| 70 | 4.53245 | 3.62131 | 5.12367 | 4.75111 | 2.92559 | 2.92645 |
| 80 | 4.73525 | 3.82036 | 5.32397 | 4.95204 | 3.12651 | 3.12674 |
| 90 | 4.91261 | 3.99669 | 5.50064 | 5.12889 | 3.30336 | 3.30342 |
| 90.64 | | | | | 3.31399 | 3.31405 |
| 100 | 5.07083 | 4.15464 | 5.65868 | 5.28697 | 3.46144 | 3.46146 |
| 110 | 5.21384 | 4.29758 | 5.80165 | 5.42995 | 3.60442 | 3.60442 |
| 111.67 | | | | | 3.62702 | 3.62702 |

*These values are absolute entropy, which includes the entropy of nuclear spin. To convert to virtual entropy, subtract the natural logarithm of the spin degeneracy, which is 5, 2, and 9 for A, E, and F, respectively.
**To obtain virtual entropy subtract 1.82553 (see Eq. (44)).

TABLE XVI

ROTATIONAL CONTRIBUTION TO THE HEAT CAPACITY OF IDEAL GAS

| Temperature (°K) | $C^{\circ}_{rot}/R$ | | | |
|---|---|---|---|---|
| | A Species | E Species | F Species | Frozen Ratio |
| 5 | 0.00003 | 0.00000 | 0.14340 | 0.08067 |
| 7.5 | 0.00574 | 0.00027 | 0.47257 | 0.26765 |
| 10 | 0.06678 | 0.00513 | 0.75447 | 0.44590 |
| 12.5 | 0.26510 | 0.02741 | 0.97299 | 0.63358 |
| 15 | 0.62308 | 0.07898 | 1.14543 | 0.84889 |
| 20 | 1.55862 | 0.27037 | 1.36288 | 1.28748 |
| 25 | 2.23942 | 0.52679 | 1.45484 | 1.58402 |
| 30 | 2.43270 | 0.78310 | 1.48663 | 1.69433 |
| 35 | 2.31490 | 1.00135 | 1.49631 | 1.69025 |
| 40 | 2.10133 | 1.16890 | 1.49903 | 1.64599 |
| 45 | 1.90416 | 1.28834 | 1.49975 | 1.59971 |
| 50 | 1.75651 | 1.36885 | 1.49994 | 1.56373 |
| 60 | 1.59315 | 1.45318 | 1.49999 | 1.52325 |
| 70 | 1.53106 | 1.48445 | 1.50000 | 1.50776 |
| 80 | 1.50980 | 1.49510 | 1.50000 | 1.50245 |
| 90 | 1.50297 | 1.49851 | 1.50000 | 1.50074 |
| 100 | 1.50087 | 1.49956 | 1.50000 | 1.50022 |
| 110 | 1.50025 | 1.49987 | 1.50000 | 1.50006 |

## TABLE XVII

CALCULATED THERMODYNAMIC FUNCTIONS OF METHANE AS IDEAL GAS
AT ONE ATMOSPHERE PRESSURE[a]

| Temperature (°K) | $(H^o - H^o_o)/T$ (Cal/Gm Mole °K·) | $-(F^o - H^o_o)/T$ (Cal/Gm Mole °K) | $S^o/R$ |
|---|---|---|---|
| 111.67 | 7.915416 | 28.67787 | 18.41394 |
| 110.00 | 7.914903 | 28.55861 | 18.35367 |
| 108.00 | 7.914267 | 28.41339 | 18.28027 |
| 106.00 | 7.913606 | 28.26546 | 18.20550 |
| 104.00 | 7.912920 | 28.11472 | 18.12930 |
| 102.00 | 7.912206 | 27.96108 | 18.05163 |
| 100.00 | 7.911461 | 27.80440 | 17.97242 |
| 98.00 | 7.910683 | 27.64458 | 17.89159 |
| 96.00 | 7.909871 | 27.48147 | 17.80912 |
| 94.00 | 7.909020 | 27.31495 | 17.72489 |
| 92.00 | 7.908128 | 27.14487 | 17.63886 |
| 90.00 | 7.907189 | 26.97107 | 17.55093 |
| 85.00 | 7.904608 | 26.51918 | 17.32223 |
| 80.00 | 7.901601 | 26.04005 | 17.07962 |
| 75.00 | 7.897998 | 25.53021 | 16.82125 |
| 70.00 | 7.893511 | 24.98545 | 16.54487 |
| 65.00 | 7.887650 | 24.40069 | 16.24767 |
| 60.00 | 7.879554 | 23.76965 | 15.92605 |
| 55.00 | 7.867720 | 23.08452 | 15.57534 |
| 50.00 | 7.849544 | 22.33547 | 15.18926 |
| 45.00 | 7.820664 | 21.50986 | 14.75928 |
| 40.00 | 7.774253 | 20.59130 | 14.27370 |
| 35.00 | 7.701206 | 19.55782 | 13.71689 |
| 30.00 | 7.594249 | 18.37869 | 13.06972 |
| 25.00 | 7.462704 | 17.00633 | 12.31295 |
| 20.00 | 7.364891 | 15.49992 | 11.43229 |

[a]The calculation is for the "frozen" high temperature equilibrium mixture.

## F. Vapor Pressure of Methane at One Degree Intervals

For convenience the vapor pressures given in Table VIII have been tabulated at one degree intervals using Aitken's method of interpolation (see footnote, page 19). The independent variable used was $1/T$.

TABLE XVIII

VAPOR PRESSURE OF METHANE AT ONE DEGREE INTERVALS
FROM INTERPOLATION IN TABLE VIII

| Temperature (°K) | Pressure, P (Mm Hg) | $1/T \times 10^3$ (°K$^{-1}$) | log P |
|---|---|---|---|
| 111.648(n.b.p.) | 760.000 | 8.95672 | 2.88081 |
| 111.0 | 720.235 | 9.00901 | 2.85747 |
| 110.0 | 662.090 | 9.09091 | 2.82092 |
| 109.0 | 607.612 | 9.17431 | 2.78363 |
| 108.0 | 556.732 | 9.25926 | 2.74565 |
| 107.0 | 509.186 | 9.34579 | 2.70688 |
| 106.0 | 464.917 | 9.43396 | 2.66738 |
| 105.0 | 423.675 | 9.52381 | 2.62703 |
| 104.0 | 385.403 | 9.61538 | 2.58592 |
| 103.0 | 349.884 | 9.70874 | 2.54392 |
| 102.0 | 316.999 | 9.80392 | 2.50106 |
| 101.0 | 286.606 | 9.90099 | 2.45728 |
| 100.0 | 258.570 | 10.00000 | 2.41258 |
| 99.0 | 232.759 | 10.10101 | 2.36691 |
| 98.0 | 209.044 | 10.20408 | 2.32024 |
| 97.0 | 187.300 | 10.30928 | 2.27254 |
| 96.0 | 167.406 | 10.41667 | 2.22377 |
| 95.0 | 149.246 | 10.52632 | 2.17390 |
| 94.0 | 132.708 | 10.63830 | 2.12290 |
| 93.0 | 117.682 | 10.75269 | 2.07071 |
| 92.0 | 104.064 | 10.86957 | 2.01730 |
| 91.0 | 91.752 | 10.98901 | 1.96261 |
| 90.64(t.p.) | 87.625 | 11.03266 | 1.94263 |
| 90.0 | 79.946 | 11.11111 | 1.90280 |
| 89.0 | 69.085 | 11.23596 | 1.83939 |
| 88.0 | 59.499 | 11.36364 | 1.77451 |
| 87.0 | 51.063 | 11.49425 | 1.70811 |
| 86.0 | 43.666 | 11.62791 | 1.64014 |
| 85.0 | 37.200 | 11.76471 | 1.57054 |
| 84.0 | 31.568 | 11.90476 | 1.49924 |
| 83.0 | 26.681 | 12.04819 | 1.42619 |

(Continued)

TABLE XVIII (Continued)

VAPOR PRESSURE OF METHANE AT ONE DEGREE INTERVALS
FROM INTERPOLATION IN TABLE VIII

| Temperature (°K) | Pressure, P (Mm Hg) | $1/T \times 10^3$ (°K$^{-1}$) | log P |
|---|---|---|---|
| 82.0 | 22.456 | 12.19512 | 1.35133 |
| 81.0 | 18.818 | 12.34568 | 1.27457 |
| 80.0 | 15.698 | 12.50000 | 1.19586 |
| 79.0 | 13.035 | 12.65823 | 1.11511 |
| 78.0 | 10.771 | 12.82051 | 1.03225 |
| 77.0 | 8.855 | 12.98701 | 0.94718 |
| 76.0 | 7.242 | 13.15789 | 0.85984 |
| 75.0 | 5.890 | 13.33333 | 0.77012 |
| 74.0 | 4.764 | 13.51351 | 0.67793 |
| 73.0 | 3.830 | 13.69863 | 0.58317 |
| 72.0 | 3.060 | 13.88889 | 0.48573 |
| 71.0 | 2.429 | 14.08451 | 0.38550 |
| 70.0 | 1.916 | 14.28571 | 0.28235 |
| 69.0 | 1.500 | 14.49275 | 0.17617 |
| 68.0 | 1.166 | 14.70588 | 0.06682 |
| 67.0 | 8.998(-1)[a] | 14.92537 | -0.04584 |
| 66.0 | 6.887(-1) | 15.15152 | -0.16196 |
| 65.0 | 5.228(-1) | 15.38462 | -0.28170 |
| 64.0 | 3.934(-1) | 15.62500 | -0.40522 |
| 63.0 | 2.933(-1) | 15.87302 | -0.53270 |
| 62.0 | 2.166(-1) | 16.12903 | -0.66434 |
| 61.0 | 1.584(-1) | 16.39344 | -0.80033 |
| 60.0 | 1.146(-1) | 16.66667 | -0.94090 |
| 59.0 | 8.199(-2) | 16.94915 | -1.08625 |
| 58.0 | 5.799(-2) | 17.24138 | -1.23665 |
| 57.0 | 4.052(-2) | 17.54386 | -1.39236 |
| 56.0 | 2.795(-2) | 17.85714 | -1.55365 |
| 55.0 | 1.902(-2) | 18.18182 | -1.72083 |
| 54.0 | 1.276(-2) | 18.51852 | -1.89420 |
| 53.0 | 8.431(-3) | 18.86792 | -2.07413 |
| 52.0 | 5.483(-3) | 19.23077 | -2.26098 |
| 51.0 | 3.506(-3) | 19.60784 | -2.45516 |
| 50.0 | 2.202(-3) | 20.00000 | -2.65709 |
| 49.0 | 1.358(-3) | 20.40816 | -2.86722 |
| 48.0 | 8.201(-4) | 20.83333 | -3.08611 |
| 47.0 | 4.850(-4) | 21.27660 | -3.31426 |
| 46.0 | 2.804(-4) | 21.73913 | -3.55229 |
| 45.0 | 1.582(-4) | 22.22222 | -3.80083 |
| 44.0 | 8.699(-5) | 22.72727 | -4.06055 |
| 43.0 | 4.653(-5) | 23.25581 | -4.33230 |
| 42.0 | 2.416(-5) | 23.80952 | -4.61686 |
| 41.0 | 1.216(-5) | 24.39024 | -4.91514 |

(Continued)

TABLE XVIII (Continued)

VAPOR PRESSURE OF METHANE AT ONE DEGREE INTERVALS
FROM INTERPOLATION IN TABLE VIII

| Temperature ($^\circ$K) | Pressure, P (Mm Hg) | $1/T \times 10^3$ ($^\circ$K$^{-1}$) | log P |
|---|---|---|---|
| 40.0 | 5.912(-6) | 25.00000 | -5.22826 |
| 39.0 | 2.772(-6) | 25.64103 | -5.55717 |
| 38.0 | 1.250(-6) | 26.31579 | -5.90319 |
| 37.0 | 5.399(-7) | 27.02703 | -6.26769 |
| 36.0 | 2.227(-7) | 27.77778 | -6.65219 |
| 35.0 | 8.742(-8) | 28.57143 | -7.05838 |
| 34.0 | 3.251(-8) | 29.41176 | -7.48804 |
| 33.0 | 1.139(-8) | 30.30303 | -7.94335 |
| 32.0 | 3.744(-9) | 31.25000 | -8.42666 |
| 31.0 | 1.146(-9) | 32.25806 | -8.94065 |
| 30.0 | 3.248(-10) | 33.33333 | -9.48833 |
| 29.0 | 8.449(-11) | 34.48276 | -10.07317 |
| 28.0 | 2.000(-11) | 35.71429 | -10.69891 |
| 27.0 | 4.263(-12) | 37.03704 | -11.37028 |
| 26.0 | 8.084(-13) | 38.46154 | -12.09240 |
| 25.0 | 1.345(-13) | 40.00000 | -12.87128 |
| 24.0 | 1.932(-14) | 41.66667 | -13.71394 |
| 23.0 | 2.353(-15) | 43.47826 | -14.62845 |
| 22.0 | 2.37 (-16) | 45.45455 | -15.6250 |
| 21.0 | 1.93 (-17) | 47.61905 | -16.7147 |
| 20.0 | 3.810(-18) | 49.01961 | -17.41911 |

[a]Numbers in parentheses are power of ten by which entry must be multiplied.