GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station
Atlanta, Georgia 30332

Progress Letter No. 1

July 13, 1964

TO: Dr. Edward L. Brady, Scientific Officer

FROM: W. T. Ziegler, Project Director

SUBJECT: Progress on Contract No. CST-1154 (our Project No. A-764) for the period 1 January 1964 through 30 June 1964.

1. Thermodynamic Calculation of Vapor Pressure and Heats of Vaporization and Sublimation of Substances of Cryogenic Interest.

The objectives of this phase of the subject contract are to "calculate, by thermodynamic procedures, the vapor pressure and heats of vaporization and sublimation of krypton, ethane and, if time permits, acetylene, from the normal boiling point to temperatures at which the vapor pressure is approximately 10^{-20} atm. These calculations shall be based on an analysis of the available published data."

a. Krypton

The literature search, analysis of the available data and computations of the vapor pressure and heats of vaporization and sublimation of krypton have been completed. The computations cover the range 119.786° K (nbp) to 12° K. A technical report covering this work is in the final stages of preparation and will be issued in August, 1964.

b. Ethane

The literature search and analysis of the available data have been completed. Computations of the vapor pressure and heats of vaporization and sublimation from 184.52° K (nbp) to about 20° K are in progress. It is expected that a technical report covering ethane will be issued by about 1 October 1964.

2. Correlation of Phase Equilibrium Data

The objectives of this phase of the contract are to correlate the available phase equilibrium data for the helium-argon system and to make such calculations, based on theoretical models, as may be helpful in making the correlation.

The principal available experimental data are those obtained in this laboratory by W. D. McCain, Jr. (100 to 145° K and pressures up to 70 atm., Ph.D. thesis, 1964) and J. C. Mullins (68 to 108° K and pressures up to 120 atm., unpublished, 1964). Correlation of these data using certain theoretical models is in progress.

3. Personnel

Personnel associated with the project during the period covered by this letter have been J. C. Mullins, B. S. Kirk, D. W. Yarbrough, A. R. Berquist and W. T. Ziegler.

W. T. Ziegler
Regents' Professor
Chemical Engineering

WTZ:js

cc: G. B. Kefover (2 copies)

TECHNICAL REPORT NO. 1

PROJECT NO. A-764

CALCULATION OF THE VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF LIQUIDS AND SOLIDS BELOW ONE ATMOSPHERE PRESSURE. VI. KRYPTON

by

W. T. Ziegler, D. W. Yarbrough and J. C. Mullins

Contract No. CST-1154
National Standard Reference Data Program
National Bureau of Standards
U. S. Department of Commerce
Washington, D. C.

1964

July 15, 1964

Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

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ABSTRACT

The "best" available experimental thermal and second virial coefficient data, together with suitable thermodynamic relations have been used to compute the vapor pressure and heats of vaporization and sublimation of krypton at one degree intervals from 119.786° K (normal boiling point) to 12° K.

The effect on the computed results of varying separately the heat of vaporization at the normal boiling point and the second virial coefficient of krypton was examined. In order to obtain reasonably good agreement between the experimental and computed vapor pressures it was found necessary to use a heat of vaporization at the normal boiling point of 2154 cal/gm mole, a value approximately 0.35 per cent smaller than the best experimental value.

The input data for the calculations were used to compute the heat of sublimation of krypton at 0° K and the calorimetric entropy of krypton in the ideal gas state at 119.786° K.

The computed vapor pressures are believed to represent the vapor pressure of krypton as a function of temperature below 119.786° K very nearly within the uncertainty of the experimental data. They are especially recommended for use below 75° K where experimental data are scanty or lacking.

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I. INTRODUCTION

In a previous report[41] a number of thermodynamic relations were presente for the calculation of the vapor pressure and heats of vaporization and subli tion of liquids and solids. These thermodynamic relations are similar in pri ciple to relations developed or used by other investigators.[18, 19, 16, 34, 3 26, 27] These relations have been used to compute the vapor pressures and hea of vaporization and sublimation of parahydrogen,[29] oxygen,[30] ethylene,[41] argo methane,[43] nitrogen,[44] fluorine,[44] carbon monoxide[31] and carbon dioxide[31] fro approximately their normal boiling point to or below 20° K. In the case of parahydrogen the calculations were made to 1° K.

The present report is concerned with the application to krypton of the thermodynamic relations previously developed. The thermodynamic data needed fo the computations are: (1) the heat capacity and volume of the saturated condens phase as a function of temperature over the range of interest; (2) the heat of fusion and one heat of vaporization or sublimation at a known temperature and pressure (e.g., the normal boiling point); (3) the triple point temperature; (4) the heat capacity of the gas phase or thermodynamic functions of the ideal gas calculated from statistical mechanics; (5) an equation of state for the gas phase. These thermodynamic data have been used to compute the vapor pressure and heats of vaporization and sublimation of krypton from its normal boiling point (119.786° K) to 12° K, where its vapor pressure is computed to be 1.73×10^{-42} mm Hg. The computed results have been compared with the available experimental vapor pressure and heats of vaporization and sublimation. In addition a comparison has been made between the "third law" entropy calculated from calorimetric data and the entropy calculated using statistical mechanics.

Naturally occurring krypton consists of a mixture of six isotopes. The calculations made in this paper have taken this fact into account only in that an average atomic weight has been used.

The temperature scales used by different investigators have been converted, where possible, to a thermodynamic scale on which the ice point is 273.15° K and the oxygen point is 90.168° K.

The thermodynamic relations used are presented in Section II. The experimental data for krypton are reviewed in Section III and the best values selected for the various physical quantities needed in the calculations are given. The calculations of vapor pressure and heats of vaporization and sublimation are presented in Section IV, together with a discussion of the agreement between the computed and experimental data. Conclusions and recommendations regarding the use of the computed results are given in Section V.

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[41] that the heat of vaporization or sublimation at the temperature T can be computed from Equation (1).*

$$(\Delta H_v)_T = (\Delta H_v)_{T_1} + \int_T^{T_1} c_s' \, dT + \sum_T^{T_1} (\Delta H_{tr})' - \left[(H^o - H_o^o)''_{T_1} - (H^o - H_o^o)''_T \right] - RT_1\delta_1 + RT\delta + \int_P^{P_1} v_s' \, dP \qquad (1)$$

---

* All symbols are defined in Appendix A.

In this equation the quantity δ is given by the relation,

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

and δ_1 is the value of δ at the point (P_1,T_1). The prime (') and double prime (") symbols refer to the condensed and vapor phases, respectively. 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,

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

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

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

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[41]

$$\begin{aligned}\ln P = {} & \ln P_1 - (\Delta H_v)_{T_1} \; (T_1 - T)/RTT_1 + \left[(H^o - H^o_o)''_{T_1} - (H^o - H^o_o)''_T \right] /RT \\ & - \left[(S^o)''_{T_1} - (S^o)''_T \right] /R - \left(\int_T^{T_1} c_s' \, dT \right) /RT - \left(\sum_T^{T_1} (\Delta H_{tr})' \right) /RT \\ & + \left(\int_T^{T_1} c_s' \, dT/T \right) /R + \left(\sum_T^{T_1} (\Delta H_{tr})'/T_{tr} \right) /R + \delta_1 (T_1 - T)/T \\ & - \epsilon_1 + \epsilon - \left(\int_P^{P_1} v_s' \, dP \right) /RT \end{aligned} \tag{5}$$

where

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

and ϵ_1 is the value of ϵ at (P_1, T_1). If the virial form of the equation of state is assumed, i.e., Equation (3), then ϵ becomes,

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

Equation (5), which may be considered to be an integration of the Clapeyron equation, can be solved if appropriate data are available: thermal data for the condensed phase; $(\Delta H_v)_{T_1}$ at (P_1, T_1); an equation of state for the real gas; and the requisite molecular structure data for the ideal gas. Solution of Equation (5) requires iteration since the last two terms are pressure dependent.

Equation (5) can be rearranged as follows:

$$\begin{aligned}(\Delta H_v)_{T_1} = {} & \Bigg\{ RT \ln P_1/P + \left[(H^o - H^o_o)''_{T_1} - (H^o - H^o_o)''_T \right] \\ & - \int_T^{T_1} c_s' \, dT - \sum_T^{T_1} (\Delta H_{tr})' - T \left[(S^o)''_{T_1} - (S^o)''_T \right] \end{aligned}$$

(Equation Continued)

$$+ \; T\int_{T}^{T_1} c_s' \, dT/T \; + \; T\sum_{T}^{T_1} (\Delta H_{tr})' \, /T_{tr}$$

$$+ \; R(T_1 - T)\delta_1 - RT\epsilon_1 + RT\epsilon - \int_{P}^{P_1} v_s' \, dP \Big\} \; T_1/(T_1 - T) \tag{8}$$

Equation (8) may 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. It may also 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. Neither of these uses of Equation (8) requires an iterative procedure in the calculations.

III. EXPERIMENTAL DATA FOR KRYPTON

A. Introduction

The calculation of the vapor pressure from Equation (5) and heats of vaporization and sublimation from Equation (1) from the normal boiling point (119.786° K) to 12° K required the following data: molecular weight, the temperature of the normal boiling point and triple point; the heat of vaporization at the normal boiling point; and the heat capacity and molal volume of the saturated condensed phase. The second virial coefficient of the gas was also required. The contribution of higher virial coefficients was assumed to be negligible at pressures below one atmosphere.

From a survey of the literature a selection was made of the "best" values of these thermal and related data of krypton. These selected values are summarized in Table I. The reasons for making these selections are given below. The temperatures of all transition points and vapor pressure data have been corrected where possible to a thermodynamic temperature scale having an assigned triple point of ice of 273.16° K (ice point of 273.15° K). A further discussion of this scale and the methods of temperature correction used are given in Appendix B. No temperature corrections have been applied to heat capacity and molal volume of the condensed phase or second virial coefficient data since such corrections are believed to be smaller than the experimental error of these data. All calculations have been made on the basis of the defined calorie (1 defined calorie = 4.1840 ab. joules = 4.1833 int. joules). No corrections have been applied to energy quantities to bring them to this uniform base.

TABLE I

SELECTED PHYSICAL PROPERTIES OF KRYPTON

Property	Selected Value	Table No. or Section
Molecular Weight	83.80	Section B
Normal Boiling Point (nbp)	119.786° K	II
Triple Point (tp)	115.76° K - 548.7 mm Hg	III
Heat of Vaporization (nbp)	2154 cal/gm mole	Section E
Heat of Fusion	392 cal/gm mole	Section E
Heat Capacity of Condensed Phases	Polynomial expression for different temperature intervals	IV
Mean Molal Volumes of Condensed Phases		V
Second Virial Coefficient	Prausnitz-Myers parameters, Kihara Core Model	Section H

B. Molecular Weight

Naturally occurring krypton consists of a mixture of isotopes in the following proportions:[7]

Isotope Mass Number	Abundance Per cent
78	0.354
80	2.27
82	11.56
83	11.55
84	56.90
86	17.37
Avg. atomic weight	83.80

The presence of these different isotopes will be expected to have some effect on the equilibrium vapor pressure of naturally occurring krypton. These effects have not been taken into account in the present computation except insofar as the use of the average molecular weight of 83.80 provides some compensation.

C. Normal Boiling Point

The normal boiling point of krypton as reported by a number of investigators is given in Table II. The "best" value for the normal boiling point was taken to be 119.786° K, the average of the corrected normal boiling points of Michels et al.,[25] Freeman and Halsey,[17] and Lovejoy.[22]

D. Triple Point Temperature and Pressure

The triple point temperature of krypton reported by a number of investigators is presented in Table III. The "best" value of the triple point temperature has been selected as 115.76° K, based on the careful work of Beaumont, et al,[6] and Lovejoy.[22] The temperature reported by Beaumont has been decreased by 0.006° K as suggested by Lovejoy.[22]

TABLE II

NORMAL BOILING POINT OF KRYPTON

Reported Temperature °K	Method of Correction[a]	Corrected Temperature °K	Investigator	Year
122.0			Peters and Weil[32]	1930
(-152.90° C)	None	(120.25)	Allen and Moore[1]	1931
119.93	Eq. (15)	119.93	Meihuizen and Crommelin[24]	1937
119.75	None	119.75	Michels, et al[25]	1952
119.82	Eq. (17)	119.81	Freeman and Halsey[17]	1956
119.8084	Eq. (17)	119.7983	Lovejoy[22]	1963
Selected value		119.786		

a) See Appendix B for method of temperature correction

Values for the triple point pressure of krypton are also tabulated in Table III. These values are in much closer agreement among themselves than the corresponding triple point temperatures. The "best" value of the triple

TABLE III

TRIPLE POINT TEMPERATURE AND PRESSURE OF KRYPTON

Reported Temperature °K	Method of Temperature Correction[a]	Corrected Temperature $(T_o = 273.15^\circ)$ °K	Reported Pressure mm Hg	Investigator	Year
116.0			549.5(± 1)	Clusius[8]	1936
115.94	Eq. (15)	115.94	549.5(± 1.5)	Keesom, et al[20]	1935
115.97	Eq. (15)	115.97	549 (± 1.5)	Meihuizen and Crommelin[24]	1937
115.95	Eq. (16)	115.95	548.7 (± 1.5)	Clusius, et al[9]	1938
115.95	b	115.71	549 (± 1.5)	Clusius and Weigand[10]	1940
115.6	Eq. (17)	115.6	538.1	Freeman and Halsey[17]	1956
115.776[c]	Eq. (17)	115.76	548.7(± 0.1)	Beaumont, et al[6]	1961
115.7701	Eq. (17)	115.76		Lovejoy[22]	1963
Selected Value		115.76	548.7		

a) See Appendix B for method of temperature correction.

b) Recomputed using methane vapor pressure data of Armstrong, et al.[3] and Eq. (

c) This temperature was decreased by 0.006° before correction (see Lovejoy[22]).

point pressure appears to be 548.7 ± 0.1 mm Hg as reported by Beaumont, et al.[6] This value is in good agreement with that found by Clusius, et al[9] and except for the value given by Freeman and Halsey[17] agrees with the other data listed to within the estimated uncertainty in these data.

E. Heats of Vaporization and Fusion

1. Heat of Vaporization

Two direct measurements of the heat of vaporization of krypton were found.[9, 6] Clusius, et al[9] reported a value of 2158 ± 3 cal/gm mole for the heat of vaporization of the normal boiling point based on an atomic weight of 83.66. After correction to the currently accepted atomic weight of 83.80, the value of Clusius, et al becomes 2161.6 ± 3 cal/gm mole.

More recently Beaumont, et al[6] obtained a value of 2179.2 ± 0.9 cal/gm mole for the heat of vaporization at 116.85° K. These investigators reported a computed value of 2161.6 ± 1 cal/gm mole at the normal boiling point. The method by which this value was obtained was not given. An independent extrapolation based on Equation (1) using the experimental value of 2179.2 cal/gm mole at 116.85° K, together with the thermodynamic data of Table I, yielded a value of 2158.6 ± 1 cal/gm mole at 119.786° K (nbp).

The experimental vapor pressure data were examined for thermodynamic consistency by means of Equation (8) using the necessary input data given in Table I. This analysis led to the selection of $\Delta H_v = 2154$ cal/gm mole at 119.786° as the value most nearly consistent with the available experimental vapor pressure data. This choice is discussed further in connection with the agreement between computed and experimental results. (See Sections IV A and IV C.)

2. Heat of Fusion

The heat of fusion of krypton has been measured by Clusius[8] and Beaumont, et al[6] who reported values of 390.7 and 392.0 ± 2.3 cal/gm mole, respectively. The value 392 ± 2.3 has been selected as the best value, largely because this choice is consistent with the use made in these calculations of the heat capacity data reported by Beaumont, et al.[6]

F. Heat Capacity of Liquid and Solid Krypton

1. Heat Capacity of Saturated Liquid

The heat capacity of saturated liquid krypton has been measured by Clusius,[8] Clusius, et al,[9] and Beaumont, et al[6] from the triple point to somewhat above the normal boiling point. The sets of data deviate somewhat from each other and show some internal scatter. A constant value of 10.567 cal/gm mole °K was chosen as representative of the data over the range 115.76 to 120.5° K.

2. Heat Capacity of Saturated Solid

The heat capacity of solid krypton has been measured over the indicated temperature ranges: Veith (as reported by Eucken and Veith),[12] 10 to 80°K; Clusius,[8] 10.5 to 112.5°K; Clusius, et al,[9] 63 to 123° K; and Beaumont, et al,[6] 2.3 to 114.4° K. Beaumont, et al have made a detailed comparison of their extensive measurements with the data of Clusius[8] and Clusius, et al.[9] From 30° K to the triple point, the data of Clusius[8, 9] deviate by less than 2 per cent from a smooth curve through the data of Beaumont, et al. Below 30° K the data of Clusius[8] showed larger deviations.

Beaumont, et al compared their results with the unpublished data of Anderson[2] in the range 1.2 to 20° K. They reported agreement to within the probable accuracy of both sets of measurements over the range 3° to 20° K except in the region 4° to 9° K where Anderson's results for krypton were about

5 per cent smaller. Below 3° K Anderson's results were reported to be about 3 per cent higher than those of Beaumont, et al.

On the basis of an independent analysis of the results of Beaumont, et al[6] Clusius,[8] Clusius, et al,[9] and Veith[12] it appeared that the data of Beaumont, et al best represented the experimental values for solid krypton. The heat capacity data of Beaumont, et al were fitted over specific temperature intervals by the method of least squares to polynomials of the form given in Equation (9).

$$c_s' = A_o + A_1T + A_2T^2 + A_3T^3 + A_4T^4 + A_5T^5 \qquad (9)$$

The temperature range from the triple point to 8° K was divided into three intervals 8 to 30° K, 30 to 70° K and 70 to 115.76° K. Sufficient overlap was allowed so that the heat capacity relationships were very nearly continuous at 30° and 70° K.

In the range 2.5 to 8° K that data of Beaumont, et al were fitted to Equation (10).

$$c_s'/T^2 = A_2 + A_3T \qquad (10)$$

Below 2.5° K the Debye T^3-law was assumed, the value of A_3 being an average of the values obtained from the data of Beaumont, et al at 2.317, 2.309, 2.500 and 2.697° K.

A summary of the coefficients for the several heat capacity polynomials is given in Table IV.

G. Molal Volumes of Saturated Liquid and Solid Krypton

1. Molal Volume of Saturated Solid

An extensive tabulation of experimental data for the density of solid krypton has been made by Cook.[11] More recently Figgins and Smith[15] have reported additional data over the range 20 to 90° K which agree well with earlier work.

In all calculations made using Equations (1), (5) and (8) the integral involving the volume of the solid, v_s' , was evaluated assuming v_s' to be constant over the temperature range of each heat capacity polynomial. The mean values of v_s' selected are shown in Table V. They are based on the above mentioned experimental data.

2. Molal Volume of Saturated Liquid

The density of saturated liquid krypton has been measured by Mathias, et al[23] from 125.96 to 208.20° K. Cook[11] has extrapolated these data to 116° K as shown in Table VI.

Clusius and Weigand[10] found V(liq) - V(solid) = 4.48 cc/gm mole at the triple point. Combining this with their value of the molal volume of solid krypton at the triple point, 29.65 cc/gm mole, they reported the molal volume of the liquid at the triple point to be 34.13 cc/gm mole. A mean value of 34.54 ml/gm mole between the triple point and normal boiling point has been used in all calculations involving v_s' over this temperature range.

H. Second Virial Coefficient

The second virial coefficient of krypton above 273° K has been measured by Whalley and Schneider[40] and Beattie, et al.[5] Thomaes and van Steenwinkel[36]

TABLE IV

COEFFICIENTS OF HEAT CAPACITY POLYNOMIALS FOR LIQUID AND SOLID KRYPTON

Coefficient (Equation 9)	Liquid	Solid				
A_o	10.567	-1.4042117(+2)[a]	-2.3334177	2.51191(-2)	0	0
A_1	0	8.3736765	5.1018908(-1)	-2.0256056(-1)	0	0
A_2	0	-1.9017186(-1)	-1.3171915(-2)	5.9672403(-2)	-1.5954(-3)	1.329(-3)
A_3	0	2.1473093(-3)	1.7352529(-4)	-3.2142241(-3)	-1.9381(-3)	0
A_4	0	-1.2036240(-5)	-1.0695472(-6)	7.2875074(-5)	0	0
A_5	0	2.6866606(-8)	2.3244582(-9)	-6.1367061(-7)	0	0
Temperature range used in L.S. fit °K		67.237 to 114.444	25.714 to 78.498	6.683 to 35.96	2.317 to 7.743	-
Temperature range used in vapor pressure calculations, °K	115.76 to 119.786	70 to 115.76	30 to 70	8 to 30	2.5 to 8	0 to 2.5

[a] Number in parentheses indicates power of 10 by which entry is to be multiplied.

TABLE V

MEAN MOLAL VOLUMES OF SATURATED CONDENSED KRYPTON

Temperature Range (^oK)	Mean Molal Volume (ml/gm mole)
- - -Solid- - -	
2.5 - 8	26.98 at 5° K
8 - 30	27.23 at 20° K
30 - 70	27.80 at 50° K
70 - 115.76	28.97 at 93° K
- - -Liquid- - -	
115.76 - 119.786	34.54 at 118° K

TABLE VI

MOLAL VOLUME OF SATURATED LIQUID KRYPTON

Temperature ^oK	Density gm/cm^3	Molal Volume ml/gm mole
116	2.441	34.33
118	2.426	34.54
120	2.412	34.74
122	2.397	34.96
124	2.382	35.18

and Fender and Halsey[14] reported values for the second virial coefficient of krypton over the range 270.3 to 109.95° K and 138.071 to 107.547° K, respectively. These data are shown in Figure 1. Fender and Halsey have concluded

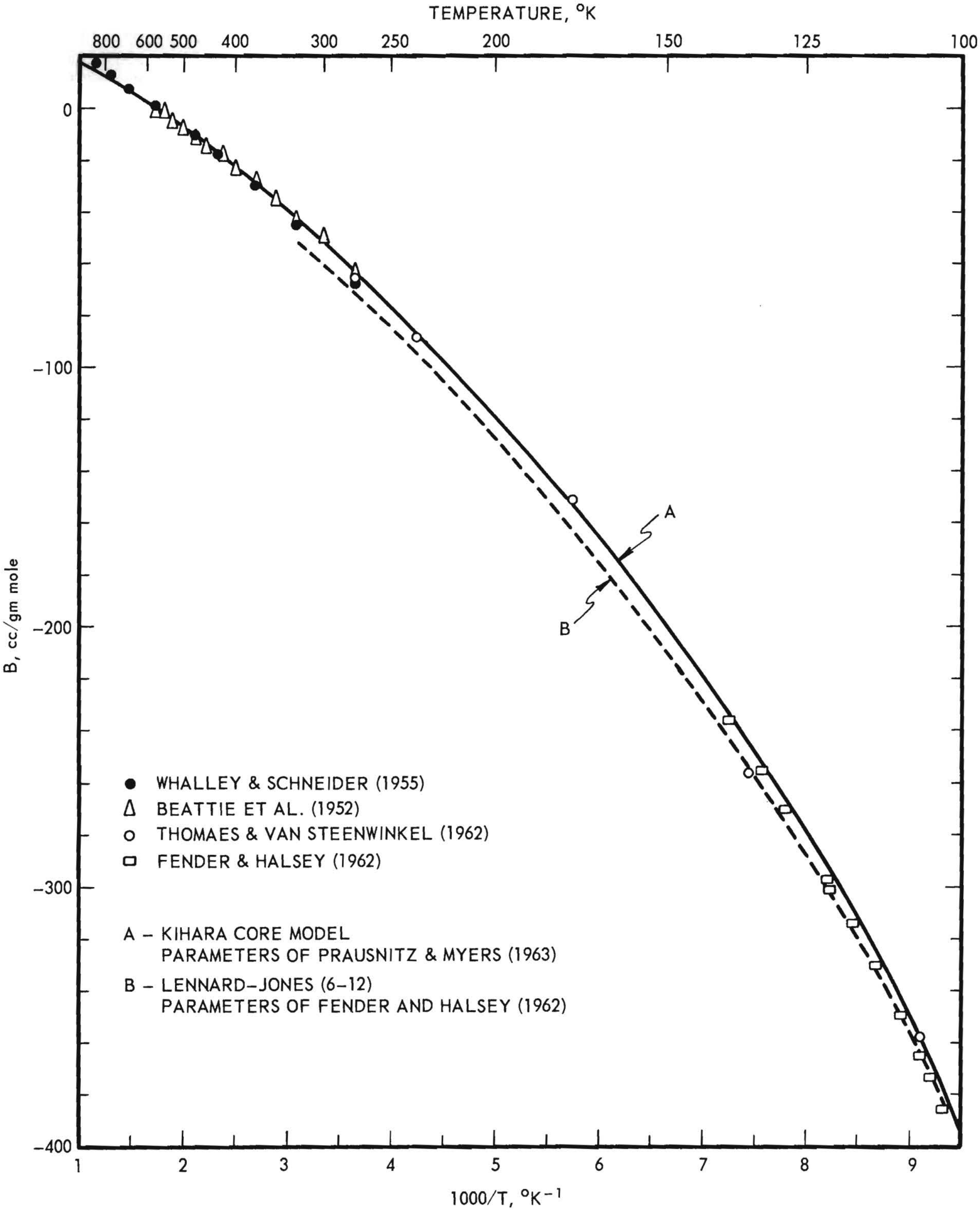

Figure 1. Second Virial Coefficient of Krypton.

that the Lennard-Jones 6-12 potential function fails to adequately describe both high and low temperature virial coefficient data with a single set of parameters. However, they did find that the parameters $\epsilon/k = 182.9^\circ$ K, $b_o = 58.42$ cc/gm mole ($\sigma = 3.591$ $\overset{o}{A}$) represented their own data reasonably well over the range 107.5 to 138° K.

Prausnitz and Myers[33] have used the second virial coefficient data of Beattie, et al[5] to obtain parameters for the Kihara core model. Their parameters are $U_o/k = 212.38^\circ$ K, $\rho_o = 3.483\ \overset{o}{A}$, $M_o = 2.639\ \overset{o}{A}$, $S_o = 0.5542(\overset{o}{A})^2$; and $V_o = 0.03879(\overset{o}{A})^3$. A comparison between values of the second virial coefficient computed using the parameters of Prausnitz and Myers and the experimental values of various investigators is shown in Figure 1. Also shown for comparison are values computed using the Lennard-Jones 6-12 parameters of Fender and Halsey.[14]

Examination of Figure 1 shows that the second virial coefficient of krypton computed using the parameters of Prausnitz and Myers is in good agreement with the experimental data over the entire temperature range. The Lennard-Jones 6-12 parameters of Fender and Halsey give a good representation of the experimental data at low temperatures but deviate at higher temperatures.

I. Vapor Pressure

The vapor pressure of krypton has been measured by Peters and Weil,[32] Keesom, et al,[20] Meihuizen and Crommelin,[24] Liang,[21] Freeman and Halsey,[17] Fisher and McMillan[16] and Beaumont, et al.[6] These data are summarized in Appendix C and discussed in Section IV B.

IV. CALCULATIONS

A. Introduction

The vapor pressure and heats of vaporization and sublimation of krypton have been computed by means of Equations (5) and (1) at one degree intervals from the normal boiling point, 119.786° K, to 12° K using a Burroughs 220 digital computer. These results are given in Table VII. The input data used are given in Table I, except that a triple point pressure was not required.

The thermodynamic properties of krypton at one atmosphere pressure in the ideal gas state were 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 krypton was used in Equation (12).

The input data selected depend heavily on the normal boiling point of Lovejoy[22] the triple point temperature and pressure of Lovejoy[22] and Beaumont, et al,[6] the heat of fusion and heat capacities of solid and liquid of Beaumont, et al,[6] and the second virial coefficient representation using the Kihara core model parameters of Prausnitz and Myers.[33]

The selection of a value for the heat of vaporization at the normal boiling point at first glance presented no problem since two independently determined values of Clusius, et al,[9] 2161.6 ± 3 cal/gm mole, and Beaumont, et al,[6] 2161.6 ± 1 cal/gm mole, were available. However, using the input data given in Table I together with Equation (8) it was evident that a value of $(\Delta H_v)_{nbp}$ as high as 2161 cal/gm mole was inconsistent with all the available experimental vapor pressure data, including the triple point pressure. The heat of vaporization was therefore decreased in steps of 2 cal/gm mole and the agreement between computed and experimental vapor pressure examined by a comparison such as that presented in Figure 2. A value of the heat of vaporization at the normal boiling point of 2154 cal/gm mole was finally selected as the best choice for this quantity (see also Section IV C).

B. Comparison of Computed and Experimental Vapor Pressures

The computed vapor pressures of krypton given in Table VII have been compared with the experimental vapor pressure data of Beaumont, et al,[6] Freeman and Halsey,[17] Keesom, et al,[20] Fisher and McMillan,[16] Liang,[21] and Michels, et al.[25] The measurements of Peters and Weil[32] and the single value reported by Liang[21] at 77.3° K appear to be greatly in error and have not been considered further.

All experimental vapor pressure data have been corrected where possible to the temperature scale used in this report. The experimental vapor pressure data used, together with the corrected temperatures, are given in Appendix C.

The comparison between the computed and experimental vapor pressures shown in Tables VII and XI was made by examining the temperature difference $(T_{calc}-T_{obs})$ as a function of temperature as shown in Figure 2. Here T_{obs} is the reported temperature (corrected where possible to an ice point of 273.15° K)

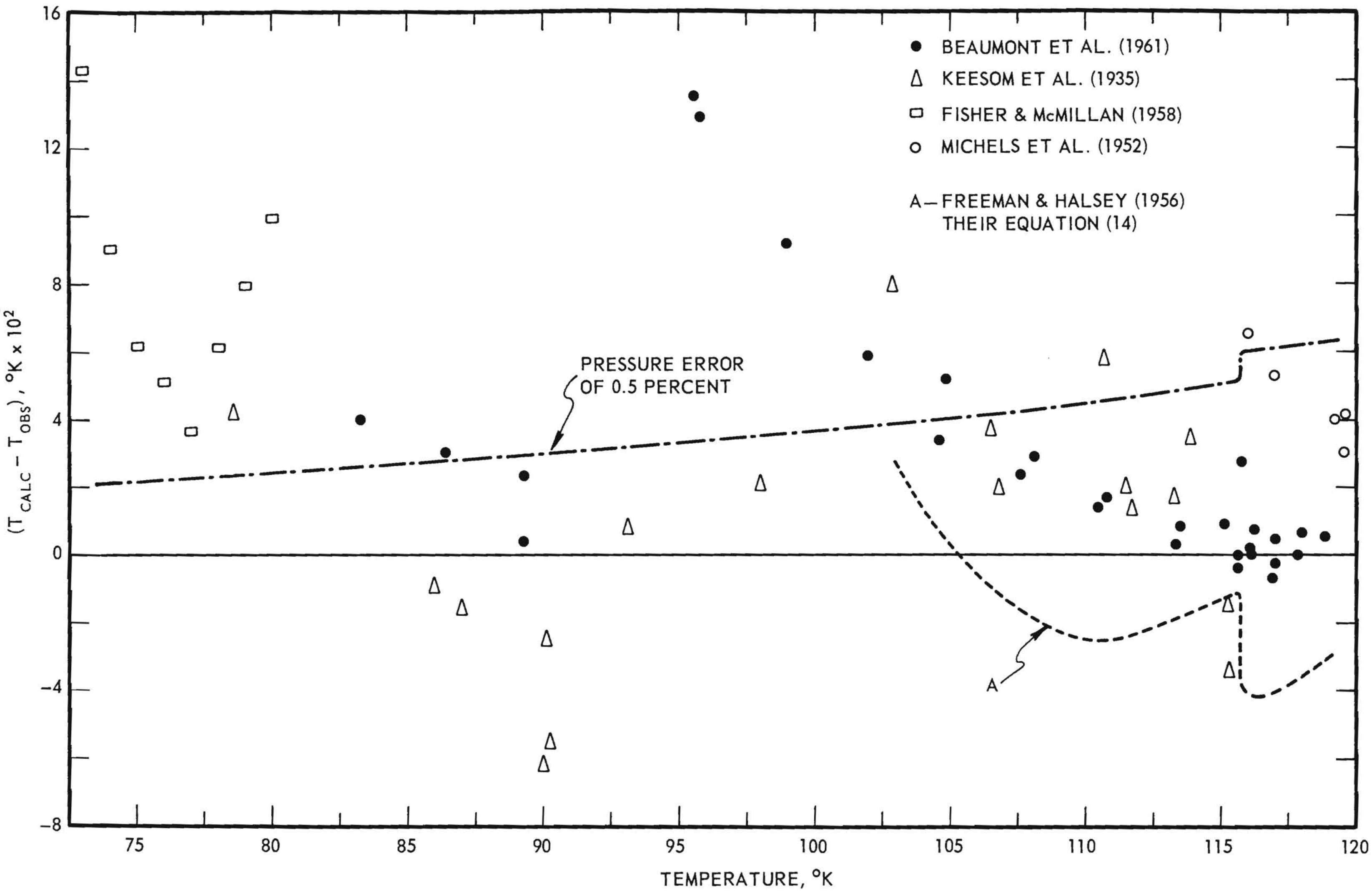

Figure 2. Comparison of Calculated and Experimental Vapor Pressure of Krypton.

TABLE VII

CALCULATED VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF KRYPTON

Temperature (^oK)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T ($^oK^{-1}$)	$Log_{10}P$	(dP/dT)/P ($^oK^{-1}$)
		- - -Liquid- - -			
119.786 (nbp)	7.6000 (2)[a]	2154.0	0.83482	2.88081	0.0782
119.0	7.1430 (2)	2159.5	0.84034	2.85388	0.0794
118.0	6.5927 (2)	2166.5	0.84746	2.81906	0.0809
117.0	6.0758 (2)	2173.4	0.85470	2.78360	0.0823
116.0	5.5909 (2)	2180.3	0.86207	2.74748	0.0839
115.76 (tp)	5.4792 (2)	2181.9	0.86386	2.73871	0.0843
		- - -Solid- - -			
115.76 (tp)	5.4792 (2)	2573.9	0.86386	2.73871	0.0985
115.0	5.0782 (2)	2577.8	0.86957	2.70571	0.1007
114.0	4.5871 (2)	2582.7	0.87719	2.66154	0.1024
113.0	4.1368 (2)	2587.4	0.88496	2.61667	0.1042
112.0	3.7237 (2)	2592.0	0.89286	2.57098	0.1061
111.0	3.3454 (2)	2596.3	0.90090	2.52445	0.1080
110.0	2.9998 (2)	2600.6	0.90909	2.47709	0.1100
109.0	2.6844 (2)	2604.6	0.91743	2.42885	0.1121
108.0	2.3971 (2)	2608.6	0.92593	2.37969	0.1142
107.0	2.1362 (2)	2612.4	0.93458	2.32964	0.1163
106.0	1.8994 (2)	2616.1	0.94340	2.27861	0.1186
105.0	1.6850 (2)	2619.7	0.95238	2.22661	0.1209
104.0	1.4914 (2)	2623.2	0.96154	2.17359	0.1232
103.0	1.3168 (2)	2626.6	0.97087	2.11952	0.1257
102.0	1.1597 (2)	2629.8	0.98039	2.06436	0.1282
101.0	1.0188 (2)	2633.0	0.99010	2.00810	0.1308
100.0	8.9266 (1)	2636.1	1.00000	1.95069	0.1335

Table VII (Continued)

TABLE VII (Continued)

CALCULATED VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF KRYPTON

Temperature (^{o}K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T (^{o}K^{-1})	Log$_{10}$P	(dP/dT)/P (^{o}K^{-1})
99.0	7.7999 (1)	2639.1	1.01010	1.89209	0.1363
98.0	6.7962 (1)	2642.0	1.02040	1.83226	0.1391
97.0	5.9044 (1)	2644.9	1.03092	1.77117	0.1421
96.0	5.1142 (1)	2647.6	1.04166	1.70878	0.1451
95.0	4.4162 (1)	2650.3	1.05263	1.64505	0.1483
94.0	3.8011 (1)	2653.0	1.06382	1.57991	0.1516
93.0	3.2610 (1)	2655.5	1.07526	1.51335	0.1549
92.0	2.7880 (1)	2658.0	1.08695	1.44530	0.1584
91.0	2.3752 (1)	2660.4	1.09890	1.37570	0.1620
90.0	2.0161 (1)	2662.8	1.11111	1.30452	0.1657
89.0	1.7049 (1)	2665.1	1.12359	1.23170	0.1696
88.0	1.4361 (1)	2667.4	1.13636	1.15718	0.1736
87.0	1.2047 (1)	2669.6	1.14942	1.08089	0.1777
86.0	1.0064 (1)	2671.7	1.16279	1.00278	0.1819
85.0	8.371	2673.9	1.17647	0.92278	0.1864
84.0	6.932	2675.9	1.19047	0.84083	0.1910
83.0	5.713	2678.0	1.20481	0.75686	0.1957
82.0	4.686	2679.9	1.21951	0.67078	0.2006
81.0	3.824	2681.9	1.2346	0.58251	0.2058
80.0	3.104	2683.8	1.2500	0.49199	0.2111
79.0	2.507	2685.7	1.2658	0.39911	0.2166
78.0	2.013	2687.6	1.2821	0.30379	0.2223
77.0	1.607	2689.4	1.2987	0.20593	0.2283
76.0	1.275	2691.2	1.3158	0.10544	0.2345
75.0	1.005	2693.0	1.3333	0.00222	0.2409
74.0	7.87 (-1)	2694.7	1.3514	-0.10388	0.2476

Table VII (Continued)

TABLE VII (Continued)

CALCULATED VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF KRYPTON

Temperature (°K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T (°K^{-1})	Log$_{10}$P	(dP/dT)/P (°K^{-1})
73.0	6.12 (-1)	2696.4	1.3699	-0.21295	0.2546
72.0	4.73 (-1)	2698.1	1.3889	-0.32511	0.2619
71.0	3.63 (-1)	2699.8	1.4085	-0.44050	0.2695
70.0	2.76 (-1)	2701.4	1.4286	-0.55925	0.2774
69.0	2.08 (-1)	2703.0	1.4493	-0.68152	0.2857
68.0	1.56 (-1)	2704.6	1.4706	-0.80747	0.2943
67.0	1.16 (-1)	2706.1	1.4925	-0.93724	0.3033
66.0	8.49 (-2)	2707.7	1.5152	-1.07102	0.3127
65.0	6.18 (-2)	2709.1	1.5385	-1.20900	0.3226
64.0	4.45 (-2)	2710.6	1.5625	-1.35136	0.3330
63.0	3.17 (-2)	2712.0	1.5873	-1.49832	0.3438
62.0	2.24 (-2)	2713.4	1.6129	-1.65010	0.3552
61.0	1.56 (-2)	2714.8	1.6393	-1.80693	0.3671
60.0	1.07 (-2)	2716.1	1.6667	-1.96907	0.3796
59.0	7.30 (-3)	2717.4	1.6949	-2.13679	0.3928
58.0	4.89 (-3)	2718.7	1.7241	-2.31037	0.4066
57.0	3.23 (-3)	2720.0	1.7544	-2.49013	0.4212
56.0	2.11 (-3)	2721.2	1.7857	-2.67639	0.4366
55.0	1.35 (-3)	2722.3	1.8182	-2.86951	0.4528
54.0	8.51 (-4)	2723.5	1.8519	-3.06987	0.4699
53.0	5.27 (-4)	2724.6	1.8868	-3.27788	0.4880
52.0	3.21 (-4)	2725.7	1.9231	-3.49397	0.5072
51.0	1.91 (-4)	2726.8	1.9608	-3.71863	0.5275
50.0	1.12 (-4)	2727.8	2.0000	-3.95236	0.5490
49.0	6.37 (-5)	2728.8	2.0408	-4.19572	0.5719
48.0	3.55 (-5)	2729.7	2.0833	-4.44932	0.5961

Table VII (Continued)

TABLE VII (Continued)

CALCULATED VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF KRYPTON

Temperature (^oK)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T ($^oK^{-1}$)	$Log_{10}P$	(dP/dT)/P ($^oK^{-1}$)
47.0	1.93 (-5)	2730.7	2.1277	-4.71379	0.6220
46.0	1.02 (-5)	2731.6	2.1739	-4.98986	0.6495
45.0	5.27 (-6)	2732.4	2.2222	-5.27829	0.6789
44.0	2.63 (-6)	2733.2	2.2727	-5.57992	0.7104
43.0	1.27 (-6)	2734.0	2.3256	-5.89567	0.7440
42.0	5.94 (-7)	2734.8	2.3810	-6.22656	0.7801
41.0	2.67 (-7)	2735.5	2.4390	-6.57367	0.8188
40.0	1.15 (-7)	2736.1	2.5000	-6.93823	0.8605
39.0	4.77 (-8)	2736.7	2.5641	-7.32158	0.9054
38.0	1.88 (-8)	2737.3	2.6316	-7.72519	0.9538
37.0	7.07 (-9)	2737.8	2.7027	-8.15070	1.0063
36.0	2.51 (-9)	2738.3	2.7778	-8.59993	1.0632
35.0	8.42 (-10)	2738.7	2.8571	-9.07490	1.1249
34.0	2.64 (-10)	2739.0	2.9412	-9.57788	1.1922
33.0	7.74 (-11)	2739.3	3.0303	-10.11141	1.2657
32.0	2.10 (-11)	2739.5	3.1250	-10.67834	1.3462
31.0	5.23 (-12)	2739.7	3.2258	-11.28188	1.4345
30.0	1.19 (-12)	2739.7	3.3333	-11.92568	1.5318
29.0	2.43 (-13)	2739.7	3.4483	-12.61388	1.6392
28.0	4.45 (-14)	2739.6	3.5714	-13.35123	1.7583
27.0	7.19 (-15)	2739.4	3.7037	-14.14315	1.8909
26.0	1.01 (-15)	2739.1	3.8462	-14.99590	2.0384
25.0	1.21 (-16)	2738.7	4.0000	-15.91676	2.2049
24.0	1.22 (-17)	2738.2	4.1667	-16.91418	2.3921
23.0	1.00 (-18)	2737.5	4.3478	-17.99811	2.6040
22.0	6.60 (-20)	2736.8	4.5455	-19.18028	2.8453

Table VII (Continued)

TABLE VII (Continued)

CALCULATED VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF KRYPTON

Temperature (^{o}K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T ($^{o}K^{-1}$)	$Log_{10}P$	(dP/dT)/P ($^{o}K^{-1}$)
21.0	3.35 (-21)	2735.9	4.7619	-20.47463	3.1217
20.0	1.26 (-22)	2734.8	5.0000	-21.89791	3.4404
19.0	3.39 (-24)	2733.6	5.2632	-23.47035	3.8103
18.0	6.07 (-26)	2732.2	5.5556	-25.21666	4.2433
17.0	6.80 (-28)	2730.5	5.8824	-27.16734	4.7544
16.0	4.36 (-30)	2728.7	6.2500	-29.36047	5.3636
15.0	1.43 (-32)	2726.7	6.6667	-31.84425	6.0980
14.0	2.09 (-35)	2724.4	7.1429	-34.68057	6.9944
13.0	1.12 (-38)	2721.8	7.6923	-37.95033	8.1042
12.0	1.73 (-42)	2718.9	8.3333	-41.76124	9.5013

[a] Numbers in parentheses indicate powers of 10 by which pressure entry is to be multiplied.

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 VII).*

Examination of Figure 2 shows that the vapor pressure data of Beaumont, et al[6] agree very well with the computed vapor pressures from the normal boiling point to the triple point of krypton. The computed triple point pressure of 547.919 mm Hg agrees reasonably well with the value of 548.7 ± 0.1 mm Hg reported by Beaumont, et al at the same temperature (115.76° K). The data of Michels, et al[25] show a deviation which is consistent with the lower normal boiling point temperature reported by them.

Examination of Figure 2 shows the wide disagreement between the vapor pressure data reported by different investigators for solid krypton. Fisher and McMillan[16] have commented on a possible error in their measurements due to the presence of a trace of nitrogen and estimate that their measured vapor pressures may be as much as 5 per cent too high at 75° K, the error becoming greater at lower temperatures. The presence of such an error at 75° K would account for the observed (T_{calc}-T_{obs}). Below 73° K the vapor pressures found by Fisher and McMillan appear to be much too large. It is interesting to note that these investigators made use of a thermodynamic relation similar

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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.[28] 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.

to Equation (5) except that it is based on the heat of sublimation at 0° K. Their theoretical relation also predicted vapor pressures below 73° K which were smaller than the observed vapor pressures.

The vapor pressure data of Keesom, et al[20] agree (except for two points) within ± 0.05° of the computed values. The vapor pressure data of Beaumont et al[6] agree fairly well with the computed values near the triple point and 85° K, though marked disagreement is to be noted near 95° K.

Freeman and Halsey[18] have expressed their vapor pressure data for solid krypton over the range 87.2° to 121.0° K by two equations of the form,

$$\log P(\mathrm{mm}) = A - B/T. \tag{13}$$

Their data are shown as a dotted curve in Figure 2. The temperatures have been corrected slightly (see Appendix C). Their triple point temperature, 115.6° K and triple point pressure 538.1 mm Hg, both appear to be too low.

C. Effect of Variation of Input Parameters on Computed Vapor Pressures

1. Variation of Heat of Vaporization at the Normal Boiling Point

As mentioned in Sections III E and IV B, a value of 2154 cal/gm mole for the heat of vaporization at the normal boiling point appeared to give the best overall agreement between the experimental and computed vapor pressures when the other input data given in Table I were used in these computations. This value is about 7 cal/gm mole smaller than the experimental value of 2161 cal/gm mole.[6, 9] A further decrease in heat of vaporization decreases the quantity (T_{calc}-T_{obs}) by an amount which depends upon the temperature. It is evident that such a decrease in $(\Delta H_v)_{nbp}$ would result in a somewhat improved fit with the data of Beaumont, et al[6] and Keesom, et al[20] in the range 115 to 95° K but would produce poorer agreement for those data near 85° K.

The effect of variation of $(\Delta H_v)_{nbp}$ on the computed vapor pressure keeping all other input data from Table I constant, is shown in Table VIII.

2. Variation of Second Virial Coefficient

Vapor pressures were also computed using the Lennard-Jones 6-12 parameters $e/k = 182.9^\circ$ K, $b_o = 58.42$ cc/gm mole (i.e., $\sigma = 3.591$ Å) of Fender and Halsey[14] instead of the Kihara core model and parameters of Prausnitz and Myers.[33] All other input data were the same as those used to compute Table VII. The effect of this change on the computed vapor pressure, heat of vaporization and sublimation and the amount by which $(T_{calc}-T_{obs})$ is decreased by this change is shown in Table IX for selected temperatures.

D. Comparison of Computed and Experimental Heats of Vaporization and Sublimation

The only experimental measurement of the heat of vaporization of krypton below the normal boiling point is that of Beaumont, et al[6] who reported a value of 2179.2 ± 0.9 cal/gm mole at 116.85° K. Interpolation in Table VII gave a value of 2172.4 cal/gm mole at this temperature.

Beaumont, et al have computed a value of 2666 ± 7 cal/gm mole for the heat of sublimation of krypton at 0° K. Using the heats of sublimation at 12° K given in Table VIII, the heat capacity of solid krypton from Table IV and assuming C_p^o of 2.5 R for krypton in the gas state one obtains the heats of sublimation at 0° K given in Table VIII.

TABLE VIII

EFFECT OF VARIATION OF HEAT OF VAPORIZATION ON COMPUTED VAPOR PRESSURE AND HEAT OF SUBLIMATION OF KRYPTON

$(\Delta H_v)_{nbp}$ = (cal/gm mole)	2150	2154	2158
Temperature (^{o}K)		Vapor Pressure (mm Hg)	
119.786(nbp)	760	760	760
115.76(tp)	548.248	547.919	547.589
100	89.565	89.266	88.967
80	3.131	3.104	3.079
60	1.092(-2)[a]	1.074(-2)	1.056(-2
40	1.192(-7)	1.153(-7)	1.115(-7
20	1.376(-22)	1.265(-22)	1.163(-2
12	2.015(-42)	1.733(-42)	1.490(-4
		Heat of Sublimation (cal/gm mole)	
12	2714.94	2718.94	2722.94
0	2662.72	2666.72	2670.72

---

[a] Numbers in parentheses indicate powers of 10 by which pressure entry is to be multiplied; thus 1.092(-2) = 0.01092.

TABLE IX

COMPARISON OF VAPOR PRESSURES AND HEATS OF VAPORIZATION AND SUBLIMATION OF KRYPTON COMPUTED USING DIFFERENT SECOND VIRIAL COEFFICIENT RELATIONS

	Kihara Core Model of Prausnitz and Myers[33] (Table VII)		Lennard-Jones 6-12 Paramaters of Fender and Halsey[14]		
Temperature (°K)	Vapor Pressure (mm Hg)	ΔH_V (cal/gm mole)	Vapor Pressure (mm Hg)	ΔH_V (cal/gm mole)	Change in (T_{calc}-T_{obs}) (°K)
		- - -Liquid- - -			
119.786(nbp)	760	2154	760	2154	0
118	659.265	2166.52	659.244	2166.47	0.000
116	559.093	2180.29	559.065	2180.20	0.001
115.76(tp)	547.919	2181.93	547.891	2181.83	0.000
		- - -Solid- - -			
115.76(tp)	547.919	2573.93	547.891	2573.83	0.000
100	89.266	2636.10	89.301	2635.45	-0.003
90	20.161	2662.80	20.181	2661.95	-0.006
80	3.104	2683.82	3.110	2682.89	-0.008
70	0.276	2701.40	0.277	2700.44	-0.009
60	1.074(-2)[a]	2716.12	1.078(-2)	2715.15	-0.010
50	1.116(-4)	2727.78	1.122(-4)	2726.81	-0.010
40	1.153(-7)	2736.12	1.162(-7)	2735.15	-0.009
30	1.187(-12)	2739.73	1.201(-12)	2738.77	-0.008
20	1.265(-22)	2734.79	1.291(-22)	2733.83	-0.006
12	1.733(-42)	2718.94	1.797(-42)	2717.98	-0.004
0		2666.72		2665.76	

[a] Numbers in parentheses indicate powers of 10 by which pressure entry is to be multiplied; thus 1.073(-2) = 0.01073.

E. Comparison of the Calorimetric and Statistical Entropy of Ideal Gas

The thermal data used to compute the vapor pressure and heats of vaporization and sublimation given in Table VII were used to compute the calorimetric entropy of the ideal gas at the normal boiling point (119.786° K), assuming the entropy of the solid to be zero at 0° K. The results of the calculation are shown in Table X.

V. CONCLUSIONS

Thermodynamic relations have been used to compute the vapor pressure and heats of vaporization and sublimation of krypton at one degree intervals from 119.786° K (the normal boiling point) to 12° K. The results are presented in Table VII. These calculations are based on the "best" available experimental thermal and second virial coefficient data. In obtaining the results given in Table VII, corrections for gas imperfection were made using a theoretical representation of the second virial coefficient based on the Kihara core model with parameters given by Prausnitz and Myers.[33]

The effect on the computed results of varying separately the heat of vaporization at the normal boiling point and the use of a simple Lennard-Jones 6-12 intermolecular potential function due to Fender and Halsey[14] to represent the second virial coefficient was studied.

In order to obtain reasonably good agreement between the experimental and computed vapor pressures it was found necessary to use a value of the heat of vaporization at the normal boiling point of 2154 cal/gm mole, a value approximately 7 cal/gm mole smaller than the best experimental value.

It was found that the vapor pressures computed using the Lennard-Jones 6-12 parameters of Fender and Halsey to represent the second virial coefficient

TABLE X

COMPARISON OF CALORIMETRIC AND STATISTICAL ENTROPY OF KRYPTON AS IDEAL GAS AT 119.786° K AND 1 ATM.

Temperature Range (°K)	Entropy Change (cal/gm mole °K)	Comments
0-2.5	0.006	Debye T^3 - law, Table IV
2.5-8	0.275	Integration c_s'/T using appropriate polynomial in Table IV
8-30	3.845	Same
30-70	4.931	Same
70-115.76	3.665	Same
115.76 (tp)	3.386	Fusion, 392/115.76
115.76-119.786	0.362	Integration, $c_s' = 10.567$
119.786 (nbp)	17.982	Vaporization, 2154/119.786
119.786	0.124	Correction for nonideality using Eq. (3), Prausnitz and Myers[33] parameters, Kihara core model.

$(S^o_{cal}) = 34.576$

$(S^o_{stat}) = 34.662$ Calculated from Eq. (12)

differed only slightly from those in Table VII, being only about two per cent higher at 20° K ($P \sim 10^{-22}$ mm Hg).

The input data used to compute the results given in Table VII were used to compute the calorimetric entropy of the ideal gas at the normal boiling point from the third law. The resulting value, 34.576 cal/gm mole °K, agrees very well with the value of 34.662 cal/gm mole °K calculated from statistical mechanics.

The computed vapor pressures given in Table VII are believed to represent the vapor pressure of krypton as a function of temperature below 119.786° K very nearly within the uncertainty of the experimental data. The computed values are especially recommended for use below 75° K where experimental data are scanty or lacking.

VI. ACKNOWLEDGEMENT

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VIII. APPENDICES

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 = velocity of light = 2.99702×10^{10} cm/sec.

c_s' = molal heat capacity of saturated condensed phase.

h = Planck's constant = 6.62377×10^{-27} erg-sec/molecule.

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

(ΔH_{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 through T_1.

$(H^o - H^o_o)''_T$ = enthalpy function for ideal gas at T.

k = Boltzmann constant = 1.38038×10^{-16} erg/°K-molecule.

M = molecular weight.

M_o, S_o, V_o = parameters of Kihara core model.

N_o = Avogadro's Number = 6.02380×10^{23} molecules/gm mole.

P = pressure.

P_1 = pressure of a known point on the vapor pressure curve.

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).

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

---

* The physical constants used were those of Rossini et al[35] adjusted to an ice point of 273.150° K.

$(S^{o})''_{T}$ = entropy of ideal gas at $P = 1$ atm and T.

T = temperature on the thermodynamic scale with an assigned ice point of 273.15° K.

T_1 = temperature of a known point on the vapor pressure curve.

T_o = ice point on thermodynamic scale.

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

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

U_o = minimum potential energy between molecules.

V = molal volume of gas

v'_s = molal volume of saturated condensed phase.

δ = defined by Equation (2) and Equation (4).

ϵ = defined by Equation (6) and Equation (7).

ρ_o = shortest distance between molecular cores at minimum potential energy.

σ = separation of molecular centers at zero potential energy.

Superscripts

$'$ = condensed phase

$''$ = gas phase

$*$ = refers to temperature scale of individual investigator.

Subscripts

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

Temperatures reported by a given investigator were converted to a consistent thermodynamic scale based on an ice point, T_o, of 273.150° K where possible. The best value for the normal boiling point of oxygen has been taken to be 90.168° K, the value selected by van Dijk.[37,39] This temperature agrees closely with the value of 90.170° K given more recently by Barber.[4] The various methods used for making these corrections are given below. The final corrected temperature in ° K used in this paper is represented by T, the temperature reported by the investigator is represented by T^*.

1. Methods Involving Only Ice Point Ratios

$$T = T^* (T_o/T_o^*) \qquad (14)$$

$$T = T^* (273.15/273.144) \qquad (15)$$

$$T = T^* (273.15/273.16) \qquad (16)$$

2. Method Involving International Temperature Scale

When both an ice point and oxygen (normal boiling) point were given (e.g., the International Temperature Scale) the correction procedure used above the oxygen point was a linear one based on the following:

$$T = T^* -(90.180-90.168)\left(\frac{273.15-T^*}{273.15-90.18}\right) \qquad (17)$$

3. Method Involving a Known Oxygen Point

For temperatures below the oxygen point the relation used was:

$$T = T^* (90.168/90.180) \qquad (18)$$

C. Experimental Vapor Pressure Data for Krypton

The experimental vapor pressure data presented in Figure 2 are collected in Table XI. The corrected observed temperature, T_{obs}, of Figure 2 is given in Column 2 of Table XI. The vapor pressure data listed for Freeman and Halsey[17] were computed from parameters given for Equation (13) by these investigators, i.e., A = 6.9861, B = 4919 for the range 115.6 to 121.0° K; and A = 7.7447, B = 579.6 for the range 87.2 to 115.6° K.

TABLE XI

EXPERIMENTAL VAPOR PRESSURES FOR KRYPTON

Reported Temperature (^oK)	Method of Temperature Correction[a]	Corrected Temperature (^oK)	Reported Vapor Pressure (mm Hg)	$(T_{Calc}-T_{Obs}) \times 10^2$ (^oK)
Beaumont, Chihara and Morrison[6]				
		- - -Liquid- - -		
118.923	Equations (17) and (18)	118.913	709.70	0.6
117.937		117.927	655.73	0.7
117.880		117.870	652.39	0.1
117.045		117.035	609.57	0.5
117.024		117.014	608.15	-0.2
116.845		116.835	598.98	-0.7
116.240		116.230	570.33	0.8
116.129		116.119	564.68	0.0
116.045		116.035	560.82	0.2
		- - -Solid- - -		
115.776(tp)		115.760	548.70 ± 0.10	1.4
115.758		115.748	548.75	2.8
115.661		115.651	542.04	0.1
115.626		115.616	539.91	-0.4
115.112		115.102	513.49	0.9
113.447		113.437	433.27	0.9
113.228		113.218	423.30	0.3
110.836		110.826	328.86	1.6
110.495		110.484	316.81	1.4
108.125		108.114	243.66	2.9
107.651		107.640	230.65	2.3
104.906		104.895	167.42	5.2

(Table XI (Continued))

TABLE XI (Continued)

EXPERIMENTAL VAPOR PRESSURES FOR KRYPTON

Reported Temperature (°K)	Method of Temperature Correction[a]	Corrected Temperature (°K)	Reported Vapor Pressure (mm Hg)	$(T_{Calc} - T_{Obs}) \times 10^2$ (°K)
104.691		104.680	162.76	3.4
101.984		101.973	116.44	5.8
98.959		98.948	78.42	9.2
95.831		95.819	50.76	12.9
92.603		92.591	31.25	13.5
89.273		89.261	17.89	2.4
89.266		89.254	17.81	0.4
86.319		86.307	10.70	3.0
83.282		83.271	6.07	4.0
Michels, Wassenaar and Zwietering[25]				
119.624	None		752.86	4.1
119.609			751.34	3.0
119.272			732.18	4.0
117.033			611.88	5.3
115.979			561.18	6.5
Keesom, Mazur and Meihuizen[20]				
115.94	Equation (15)	115.942	549.00	-16.3
115.32		115.322	522.74	- 3.4
115.29		115.292	522.18	- 1.5
113.84		113.842	452.96	3.5
112.28		112.282	384.36	1.7
111.73		111.732	362.46	1.4
111.51		111.512	354.26	2.0
110.54		110.542	320.34	5.8
106.804		106.806	209.32	2.0

(Table XI (Continued))

TABLE XI (Continued)

EXPERIMENTAL VAPOR PRESSURES FOR KRYPTON

Reported Temperature (^oK)	Method of Temperature Correction[a]	Corrected Temperature (^oK)	Reported Vapor Pressure (mm Hg)	$(T_{Calc}-T_{Obs}) \times 10^2$ (^oK)
106.52		106.522	202.89	3.7
102.854		102.856	130.62	8.0
98.04		98.042	68.56	2.1
93.145		93.147	33.40	0.8
90.215		90.217	20.71	- 5.5
90.165		90.167	20.64	- 2.5
90.06		90.062	20.16	- 6.2
86.95		86.952	11.91	- 1.6
86.00		86.002	10.05	- 1.0
82.913		82.915	5.49	-11.7
78.66		78.662	2.35	4.2
Freeman and Halsey[17]				
		- - -Liquid- - -		
119.00	Equation (17)	118.990	712.02	- 3.0
118.00		117.990	656.86	- 3.5
117.00		116.990	605.10	- 3.9
116.00		115.990	556.65	- 4.2
		- - -Solid- - -		
115.60[b]	Equations (17) and (18)	115.590	538.10[b]	- 1.1
114.00		113.990	457.60	- 1.3
112.00		111.989	371.28	- 1.7
110.00		109.989	298.96	- 2.0
108.00		107.989	238.80	- 2.2
106.00		105.989	189.14	- 2.5
104.00		103.989	148.46	- 2.6
102.00		101.989	115.44	- 2.5

(Table XI (Continued))

TABLE XI (Continued)

EXPERIMENTAL VAPOR PRESSURES FOR KRYPTON

Reported Temperature (°K)	Method of Temperature Correction[a]	Corrected Temperature (°K)	Reported Vapor Pressure (mm Hg)	$(T_{Calc}-T_{Obs}) \times 10^2$ (°K)
100.00		99.989	88.858	- 2.3
98.00		97.989	67.672	- 1.9
96.00		95.988	50.957	- 1.3
94.00		93.988	37.909	- 0.6
92.00		91.988	27.842	0.3
90.00		89.988	20.170	1.5
88.00		87.988	14.399	2.7
Fisher and McMillan[16]				
80	None		3.17	9.9
79			2.55	7.9
78			2.04	6.1
77			1.62	3.6
76			1.29	5.1
75			1.020	6.1
74			0.805	9.0
73			0.635	14.3
72			0.498	19.7
71			0.386	23.2
70			0.298	27.9
69			0.229	33.5
68			0.174	37.8
67			0.132	44.2
66			0.1005	54.4
65			0.0765	66.8
64			0.0577	78.8
63			0.0428	88.1

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[a] See Appendix B for method of temperature correction

[b] All values computed from Equation (13) with values of A and B given by Freeman and Halsey.

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CALCULATION OF THE VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF LIQUIDS AND SOLIDS BELOW ONE ATMOSPHERE PRESSURE. VII ETHANE

by

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

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GEORGIA INSTITUTE OF TECHNOLOGY
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ABSTRACT

Thermodynamic relations have been used to compute the vapor pressure and heats of vaporization and sublimation of ethane at one degree intervals from 184.52° K (the normal boiling point) to 20° K. The results are presented in Table VIII. These calculations made use of the "best" available experimental data for the normal boiling point and triple point temperatures, the heat of vaporization at the normal boiling point and heat of fusion at the triple point, heat capacity and density of the saturated condensed phases, and a representation of the second virial coefficient as a function of temperature based on the Kihara core model. The necessary thermodynamic properties of the ideal gas phase were computed from statistical mechanical relations using an internal rotation barrier of 2875 cal/gm mole.

Comparison of the computed vapor pressures with the available experimental data strongly suggest that only the vapor pressure data of Loomis and Walters[21] and the smoothed data of the American Petroleum Institute Research Project 44[1] (which are based at least in part on the data of Loomis and Walters) are reasonably consistent with the thermodynamic data used to compute the vapor pressures. By variation of the internal rotation barrier height and the theoretical representation of the second virial coefficient computed vapor pressures which agree somewhat better with the data of Loomis and Walters than those given in Table VIII were obtained. However, in view of the uncertainty in the temperature scale of Loomis and Walters and the thermal input data (including the second virial coefficient) it is believed that the vapor pressures and heats of vaporization and sublimation given in Table VIII represent these properties of ethane as satisfactorily as they are known at this time.

No comparison of the computed heats of vaporization and sublimation with experimental values was possible, since no measured values of these quantities appear to have been made.

The thermodynamic functions $(H^o-H^o_o)$, S^o and $C_p{}^o$ of ethane in the ideal gas state at one atmosphere pressure have been computed at 10° K intervals from 20 to 300° K using an internal rotation barrier of 2875 cal/gm mole. They are given in Table XI.

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Figure 2. Comparison of Calculated and Experimental Vapor Pressure of Ethane 31

I. INTRODUCTION

In a previous report[48] 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 thermodynamic relations are similar in principle to relations used by other investigators.[11,12,27,28,41,45] These relations have been used to compute the vapor pressures and heats of vaporization and sublimation of parahydrogen,[30] oxygen,[31] ethylene,[48] argon,[49] methane,[5] nitrogen,[51] fluorine,[51] carbon monoxide,[32] carbon dioxide[32] and krypton[52] from approximately the normal boiling point to or below 20° K. In the case of parahydrogen the calculations were made to 1° K.

The present report is concerned with the application to ethane of the thermodynamic relations previously developed.[48,52] The thermodynamic data used for the computations were : (1) the heat capacity and volume of the saturated condensed phase as a function of temperature over the range of interest; (2) the heat of vaporization at a known temperature and pressure (e.g., the normal boiling point); (3) the triple point temperature and the heat of fusion; (4) the thermodynamic functions of the ideal gas calculated from statistical mechanics; (5) an equation of state for the gas phase. These thermodynamic data have been used to compute the vapor pressure and heats of vaporization and sublimation of ethane from its normal boiling point (184.52° K) to 20° K, where its vapor pressure is computed to be 1.04 x 10^{-45} mm Hg. The computed results have been compared with the available experimental vapor pressure. In addition, a comparison has been made between the "third law" entropy calculated from calorimetric data and the entropy calculated using statistical mechanics. No experimental values of the heats of vaporization or sublimation were available for comparison with the computed values. The temperature scales used by different investigators have been converted where possible to a thermodynamic scale with an ice point of 273.15° K.

The thermodynamic relations used are presented in Section II. The experimental data for ethane are reviewed in Section III and the values selected for the various physical quantities needed in the calculations are given. The calculations of vapor pressure and heats of vaporization and sublimation are presented in Section IV, together with a discussion of the agreement between the computed and experimental vapor pressures. Conclusions and recommendations regarding the use of the computed results are given in Section V.

II. THERMODYNAMIC RELATIONS

A. 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[48]

$$\begin{aligned}\ln P \;=\; & \ln P_1 - (\Delta H_v)_{T_1}(T_1 - T)/RTT_1 + \left[(H^o - H^o_o)''_{T_1} - (H^o - H^o_o)''_T\right]/RT \\ & - \left[(S^o)''_{T_1} - (S^o)''_T\right]/R - \left(\int_T^{T_1} c_s' \, dT\right)/RT - \left(\sum_T^{T_1} (\Delta H_{tr})'\right)/RT \\ & + \left(\int_T^{T_1} c_s' \, dT/T\right)/R + \left(\sum_T^{T_1} (\Delta H_{tr})'/T_{tr}\right)/R + \delta_1(T_1 - T)/T \\ & - \epsilon_1 + \epsilon - \left(\int_P^{P_1} v_s' \, dP\right)/RT \end{aligned} \qquad (1)$$

In this equation* the quantities δ and ϵ are given by the relations

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

$$\epsilon = [H^o(T) - H(P,T)]''/RT - [S^o(P,T) - S(P,T)]''/R \qquad (3)$$

The quantities δ_1 and ϵ_1, are the values of δ and ϵ at the known point (P_1,T_1). The prime (') and double prime (") symbols refer to the condensed and vapor phases, respectively. The evaluation of δ and ϵ requires an equation of state for the vapor. If a virial form of the equation of state is used, namely,

$$PV = RT(1 + \frac{B}{V}) \qquad (4)$$

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* All symbols are defined in Appendix A.

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

$$\delta = (B - T\frac{dB}{dT})/V \tag{5}$$

$$\epsilon = \ln(PV/RT) - 2B/V \tag{6}$$

Equation (1), which may also be considered to be an integration of the Clapeyron equation, can be solved if appropriate data are available: thermal data for the condensed phase; $(\Delta H_v)_{T_1}$ at (P_1,T_1); an equation of state for the real gas; and the requisite molecular structure data for the ideal gas. Solution of Equation (1) requires iteration since the last two terms are pressure dependent.

B. Variation of Heat of Vaporization and Sublimation with Temperature

By performing an enthalpy cycle between a point (P,T) and a known point (P_1,T_1) on the vapor pressure curve of a pure substance it can be shown[48] that the heat of vaporization or sublimation at the temperature T can be computed from Equation (7).

$$(\Delta H_v)_T = (\Delta H_v)_{T_1} + \int_T^{T_1} c_s' \, dT + \sum_T^{T_1} (\Delta H_{tr})'$$
$$- [(H^o - H_o^o)''_{T_1} - (H^o - H_o^o)''_T] - RT_1\delta_1 + RT\delta + \int_P^{P_1} v_s' \, dP \tag{7}$$

For temperatures below the triple point, $(\Delta H_v)_T$ in Equation (7) is the heat of sublimation rather than the heat of vaporization. The evaluation of the last two terms of Equation (7) 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 (7).

III. EXPERIMENTAL DATA FOR ETHANE

A. Introduction

The calculation of the vapor pressures from Equation (1) and heats of vaporization and sublimation from Equation (7) from 184.52° K (the normal boiling point) to 20° K required the following data: molecular weight, the temperatures of the normal boiling point and triple point; the heat of vaporization at the normal boiling point and heat of fusion at the triple point; the heat capacity and molal volume of the saturated condensed phase; and the second virial coefficient of the gas. (The contribution of higher virial coefficients was assumed to be negligible at pressures below one atmosphere.) 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.

From a survey of the literature a selection was made of the "best" values of these thermal and related data for ethane. These selected values are summarized in Table I. The reasons for making these selections are given below. The temperatures of all transition points and vapor pressure data have been corrected where possible to a thermodynamic temperature scale having an assigned triple point of ice of 273.16° K (ice point of 273.15° K). A further discussion of this scale and the methods of temperature correction used are given in Appendix B. No temperature corrections have been applied to heat capacity and molal volume of the condensed phase or second virial coefficient data since such corrections are believed to be smaller than the experimental error of these data. All calculations have been made on the basis of the defined calorie (1 defined calorie = 4.1840 ab. joules = 4.1833 int. joules).

No corrections have been applied to energy quantities to bring them to this uniform base.

TABLE I

SELECTED PHYSICAL PROPERTIES OF ETHANE

Property	Selected Value	Table No. or Section
Molecular Weight	30.070	Ref. 5
Normal boiling point (nbp)	184.52° K	II
Triple point (tp)	89.89° K	III
Heat of vaporization (nbp)	3517 cal/gm mole °K	D
Heat of fusion (tp)	683.4 cal/gm mole °K	D
Heat capacity of condensed phases	Polynomial expressions for different temperature intervals	IV
Mean Molal Volumes of Condensed Phases	Solid: 43.4 cc/gm mole at 89.89° K Liquid: 53.5 cc/gm mole at 172° K	F
Second Virial Coefficient	Adjusted parameters, Kihara Core Model	VI(Curve C)
Molecular Constants		VII

B. Normal Boiling Point

The normal boiling point temperature of ethane reported by a number of investigators is given in Table II. The measurements of Loomis and Walters[21] and Porter[36] appear to have been done with great care. The same platinum resistance thermometer,[22] calibrated in °C using fixed points based on the

Centigrade temperature scale of Henning and Heuse,[15] was employed in both researches. They reported their results in °K but failed to state the ice point used. For this reason no correction has been applied to their reported temperature data. Rossini, et al[1] (their Table 23-2 (1.101)-m issued April 30, 1960) have selected a value of -88.63° C (Int. 1948) for the normal boiling point for inclusion in the extensive compilation carried out by them at the National Bureau of Standards under the American Petroleum Research Project No. 44. As a basis for this choice they cited unpublished work carried out at the National Bureau of Standards by Cragoe, in addition to the work of Witt and Kemp[47] and Loomis and Walters.[21] Rossini, et al[1] also cited the work of Wiebe, et al.[46] However, it appears to the writers that the value given by Wiebe, et al may not be independent of the measurements of Loomis and Walters[21] and Porter.[36] The value of 184.1 ± 0.1° K reported by Witt and Kemp[47] was stated by them to be a "rough measurement." The values of the normal boiling point reported by Maass and McIntosh[23] and Maass and Wright[24] appear to be of lesser accuracy.

The value of the normal boiling point of Rossini, et al has been arbitrarily selected as the best choice of this somewhat uncertain datum.

C. Triple Point Temperature

The triple point temperature of ethane reported by Wiebe, et al,[46] Witt and Kemp,[47] and Clusius,[6] is shown in Table III. There appears to be considerable uncertainty in this quantity. The value found by Wiebe, et al is considered to be low because of impurities present in their ethane, as shown by the considerable pre-melting observed by them. The higher melting point, 89.87° K, and smaller pre-melting effects found by Witt and Kemp suggest that their sample was purer than that of Wiebe, et al. However, the still higher value of 90.35° K reported by Clusius and Weigand[6] suggests, as was pointed out by them, that the ethane used by Witt and Kemp may have contained appreciable impurity. The melting point found by Witt and Kemp has been selected as the "best value" of the triple point because of the selection of their heat capacity and heat of fusion data for use in the calculations made in the present paper.

No measurement of the triple point pressure has been reported.

TABLE II

NORMAL BOILING POINT OF ETHANE

Reported Temp. °K	Method of Temperature Correction[a]	Corrected Temp. (To = 273.15°) °K	Investigator	Year
-88.5° C	Eq. (23)	184.65	Maass and McIntosh[23]	1914
-88.3° C	Eq. (23)	184.85	Maass and Wright[24]	1921
184.46_7	None	184.46_7	Loomis and Walters[21]	1926
184.48	None	184.48	Porter[36]	1926
184.1 ± 0.1	Eq. (25)	184.13	Witt and Kemp[47]	1937
-88.63	Eq. (23)	184.52	API Project 44[1]	1960
Selected Value		184.52		

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[a] See Appendix B for method of temperature correction.

TABLE III

TRIPLE POINT TEMPERATURE OF ETHANE

Reported Temperature °K	Method of Temperature Correction	Corrected Temp. (To = 273.15°) °K	Investigator	Year
89.52	None	89.52	Wiebe, et al[46]	1930
89.87	Eq. (25)	89.89	Witt and Kemp[47]	1937
90.35	None	90.35	Clusius and Weigand[6]	1940
Selected Value		89.89		

D. Heats of Vaporization and Fusion

The only direct measurement of the heat of vaporization of ethane is that of Witt and Kemp[47] who reported a value of 3514 ± 3.5 cal/gm mole at the normal boiling point of 184.1 ± 0.1° K. This is based on a molecular weight of ethane of 30.0462. Conversion to the currently accepted value of 30.070 results in the selected value of 3517 ± 3.5 cal/gm mole given in Table I, in agreement with the value given by Rossini, et al[1] (Table 23-2 (1.101)-m).

The heat of fusion of ethane has been measured by Wiebe, et al[46] and Witt and Kemp[47] who reported values of 667.5 ± 3 and 682.9 ± 0.7 cal/gm mole, respectively. The measurement of Wiebe, et al appears to be too low because of extensive pre-melting, indicating the presence of impurities. The value of Witt and Kemp, corrected for change in molecular weight to 683.4 ± 0.7 cal/gm mole, has been selected for use in the present calculations. This choice is also consistent with the use of the data of Witt and Kemp for the heat capacity of solid ethane in the calculations made in this paper. The value given by Witt and Kemp was corrected by them for some pre-melting.

E. Heat Capacity of Saturated Liquid and Solid Ethane

1. Heat Capacity of Saturated Liquid

The heat capacity of liquid ethane has been measured from the triple point to the normal boiling point by Wiebe, et al[46] and Witt and Kemp.[47] These data are in good agreement. The data of Eucken and Hauck[9] show large deviations (10-20%) from these measurements. The data of Wiebe, et al and Witt and Kemp have been fitted by a least squares procedure to an equation of the form

$$c_s' = A_o + A_1T + A_2T^2 + A_3T^3 \qquad (8)$$

The coefficients obtained are given in Table IV.

2. Heat Capacity of Saturated Solid

The heat capacity of solid ethane has been measured by Wiebe, et al[46] over the range 67.46 to 75.67° K and by Witt and Kemp[47] over the range 15.53 to 86.73° K. In the overlap region the heat capacity data of Wiebe, et al are 2 to 5 per cent larger than those of Witt and Kemp. Witt and Kemp also give a table of smoothed values that are smaller than their experimental values near the melting point because of pre-melting. Their computed heat of fusion is apparently based on these lower smoothed values. Since their heat of fusion has been used in the vapor pressure calculations made in the present paper, their smoothed values (their Table II) were fitted to Equation (8), a value of 14.25 cal/gm mole °K being assigned to c_s' at 89.89° K to guide the fitted curve. The coefficients obtained are given in Table IV.

TABLE IV

COEFFICIENTS OF HEAT CAPACITY POLYNOMIALS FOR SOLID AND LIQUID ETHANE

Coefficient	Liquid	Solid		
A_0	1.3756481(+1)	-0.26681378	-7.5526443	-0.50509717
A_1	5.9011254(-2)	0.16205380	0.45816262	-7.0191655(-3
A_2	-4.6413692(-4)		3.0157202(-3)	6.5416471(-3
A_3	1.3741601(-6)			-5.8193713(-5
Temperature range used in fit, °K	91.59° to 190.00°	50° to 89.89°	35° to 50°	15° to 40°
Temperature range used in vapor pressure calculations, °K	89.89° to 184.52°	50° to 89.89°	35° to 50°	15° to 35°

F. Molal Volumes of Saturated Solid and Liquid Ethane

The molal volume of solid ethane has been measured by Heuse,[17] Stewart and LaRock[42] and Mark and Pohland[25] who found values (in cc/gm mole) of 39.9 at 20° K, 42.2 at 77° K, and 43.4 at the melting point, respectively. Clusius and Weigand[6] computed a value of 5.11 cc/gm mole for the difference between the volumes of saturated solid and liquid ethane at the triple point from the slope of the melting curve and the heat of fusion.

Rossini, et al[1] (Table 1d, dated Oct. 31, 1952) have presented the density of liquid ethane as a function of temperature based on available density data. These data converted to cc/gm mole are given in Table V.

TABLE V

MOLAL VOLUME OF LIQUID ETHANE

Temperature °C	Molal Volume cc/gm mole	Temperature °C	Molal Volume cc/gm mole
-180	46.05	-130	50.35
-170	46.84	-120	51.35
-160	47.65	-110	52.41
-150	48.50	-100	53.57
-140	49.41	-90	54.85

In computing the integrals involving v_s' in Equations (1) and (7) v_s' was taken to be constant since the contribution of these integrals is very small. For the solid range the value of v_s' used was 43.4 cc/gm mole, the molal volume at the triple point. For the liquid, the value of v_s' used was 53.5 cc/gm mole which corresponds to a vapor pressure of about 380 mm.

G. Second Virial Coefficient

The second virial coefficient of ethane has been measured by Eucken and Parts[10] (192 to 273° K) and Lambert, et al[20] (20 to 80° C). Michels, et al[26] have measured the P-V-T relations for ethane over the range 0 to 150° C and presented the second and higher virial coefficients derived from their isotherms.

Beattie, et al[2] have measured the P-V-T relations for ethane over the range 25 to 250° C and have expressed their results in the form of the Beattie-Bridgeman equation of state from which the second virial coefficient may be computed.

These several results for the second virial coefficient of ethane are presented in Figure 1. The values of Michels, et al shown in Figure 1 are those obtained by them from their low pressure data (Amagat density, $d_A < 50$).

Also shown in Figure 1 are three curves which have been computed using the Kihara core model. The parameters used are shown in Table VI. Prausnitz and Myers[37] have used the second virial coefficient data of Michels, et al[26] and the empirical correlation of Pitzer and Curl[34] to obtain optimum parameters for this model assuming that the ethane core is a triangular prism. The second virial coefficient computed using these parameters is shown in Figure 1 as Curve A. More recently Prausnitz and Myers[38] have used the data of Michels, et al[26] alone to obtain a second set of parameters based on a spherical core. The second virial coefficient computed using these parameters is shown as Curve B. Curves A and B, while agreeing quite well with the data of Michels, et al in the range 0° to 150° C, do not agree with the measurements of Eucken and Parts[10] at low temperatures. It may be that these latter data are in error. However, the present authors have empirically adjusted the parameter U_o/k for the Prausnitz-Myers triangular prism core model to obtain the improved fit shown in Figure 1 as Curve C. This representation of the second virial coefficient of ethane has been used in the calculations presented in this paper.

The Lennard-Jones 6-12 parameters ($e/k = 243^\circ$ K, $b_o = 78$ cc/gm mole) given

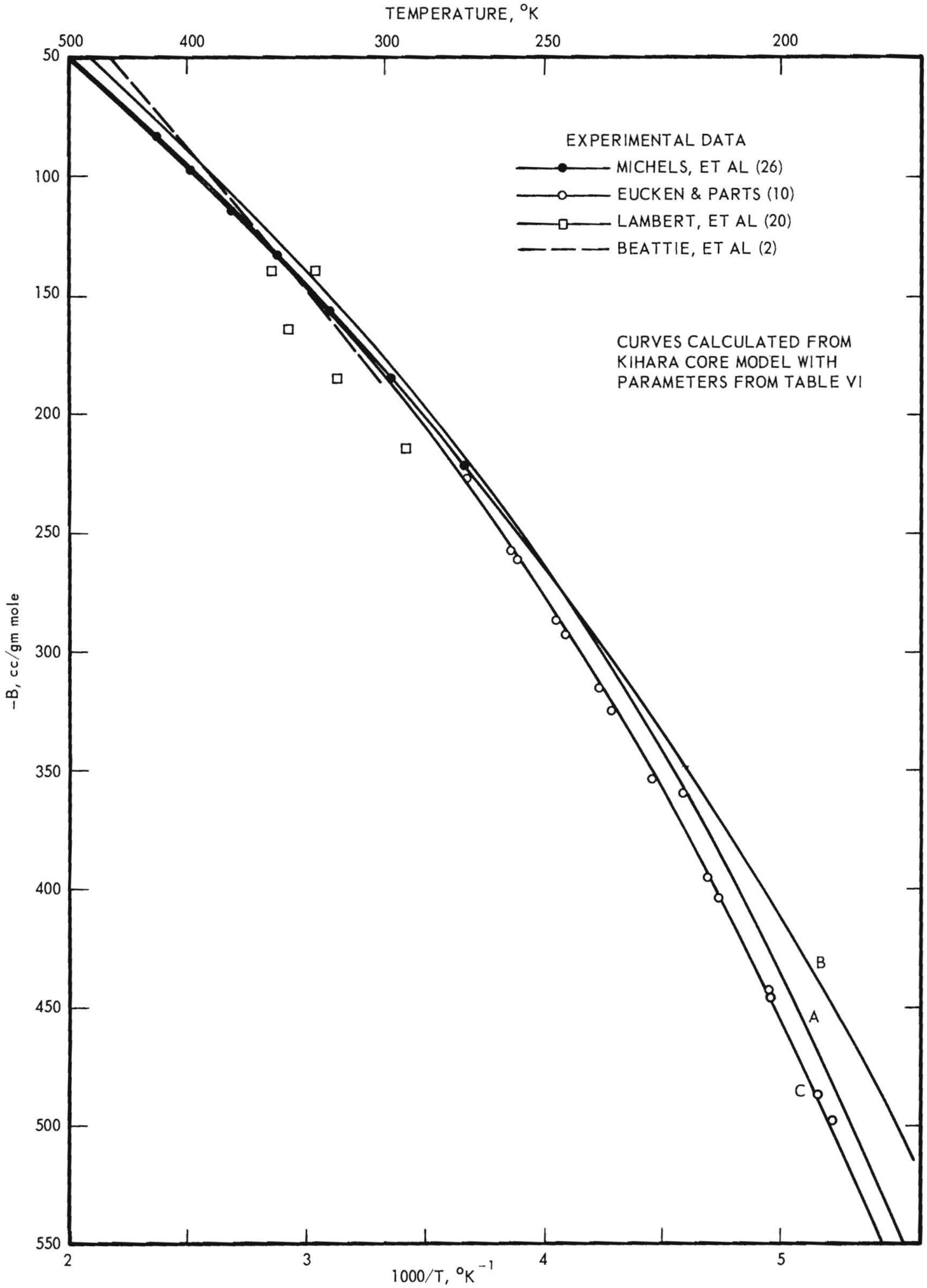

Figure 1. Second Virial Coefficient of Ethane.

by Hirschfelder, et al[18] gave much less negative values of the second virial coefficient at low temperatures than the data of Eucken and Parts and Curves A, B, and C.

TABLE VI

PARAMETERS USED TO COMPUTE SECOND VIRIAL COEFFICIENT FROM KIHARA CORE MODEL

Parameter	Units	Curve A	Curve B	Curve C
Core		Triangular prism[37]	Sphere[38]	Triangular prism
U_o/k	°K	444.00	346.7	453.00
ρ_o	Å	2.840	3.668	2.840
M_o	Å	10.17	6.572	10.17
S_o	$(\text{Å})^2$	5.770	3.437	5.770
V_o	$(\text{Å})^3$	0.6530	0.5992	0.6530

H. Thermodynamic Functions of the Ideal Gas

The computation of the vapor pressure and heats of vaporization and sublimation by means of Equations (1) and (7) requires a knowledge of the thermodynamic functions of ethane as an ideal gas at one atmosphere pressure. Strictly speaking, it suffices to know C_p^o as a function of temperature over the temperature range of the proposed calculations. The existence of internal rotation in the ethane molecule makes the exact calculation of the thermodynamic functions difficult.

The approach used here, in general, parallels that used by Halford[13] and Pitzer and Gwinn.[35] A rotator harmonic-oscillator model was used, the partition function for internal hindered rotation and external rotation being treated as separable. The molecular parameters of ethane used in the calculations are given in Table VII. Nuclear spin and isotopic effects have been ignored. In addition to computing $(H^o-H_o^o)$ and S^o as needed for use in Equations (1) and (7), the quantities $(H^o-H_o^o)$, S^o and C_p^o have been computed from 20 to 300° K at intervals of 10° K. These latter quantities are given in Appendix C, Table XI, where additional information regarding these calculations is presented.

The total partition function, Q, represented by the product

$$Q = Q_t \cdot Q_v \cdot Q_{XR} \cdot Q_{IR} \tag{9}$$

gave the following separate contributions to the thermodynamic properties

$$K^o = K_t^o + K_v^o + K_{XR}^o + K_{IR}^o \tag{10}$$

where

K^o = S^o, $(H^o-H_o^o)$ or C_p^o

K_t^o = classical translational contribution

K_v^o = vibrational contribution

K_{XR}^o = external rotational contribution

K_{IR}^o = internal rotational contribution

The translation contributions were computed using the relations

$$S_t^o = R\left[\frac{5}{2}\ \ln T + \frac{3}{2} \ln M - 1.164862\right] \tag{11}$$

TABLE VII

MOLECULAR PARAMETERS OF ETHANE

A. Fundamental Frequencies[14]

Frequency, i	Symmetry (for D_{3d})	w, cm^{-1}	Degeneracy
1	A_{1g}	2915	1
2	A_{1g}	1400	1
3	A_{1g}	993	1
4[a]	A_{1u}	(275)	(1)
5	A_{2u}	2915	1
6	A_{2u}	1379.2	1
7	E_u	2995.5	2
8	E_u	1472.2	2
9	E_u	821.52	2
10	E_g	2955	2
11	E_g	1460	2
12	E_g	1190	2

B. External Rotational Constants[19,39]

$A_o = 2.578\ cm^{-1}$

$B_o = 0.66310\ cm^{-1}$

C. Internal Rotation Barrier

$V_o = 2875$ cal/gm mole

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[a] The frequency, w_4, is the CH_3-CH_3 torsional frequency which is taken into account by the internal rotation contribution.

$$(H^o - H^o_o)_t = \frac{5}{2} RT \tag{12}$$

$$(C_p{}^o)_t = \frac{5}{2} R \tag{13}$$

The molecular weight of ethane was taken to be 30.070.[5]

The vibrational contributions were computed using the relations

$$S^o_v = R \sum_i p_i \left[x_i/(e^{x_i} - 1) - \ln (1 - e^{-x_i}) \right] \tag{14}$$

$$(H^o - H^o_o)_v = RT \sum_i p_i \; x_i/(e^{x_i} - 1) \tag{15}$$

$$(C^o_p)_v = R \sum_i p_i \left[x_i{}^2 \; e^{x_i}/(e^{x_i} - 1)^2 \right] \tag{16}$$

where

x_i = $hwc_i/(kT)$

w_i = fundamental vibrational wave number (in cm^{-1})

p_i = degeneracy of the i-th vibration.

The fundamental frequencies of Hansen and Dennison,[14] given in Table VII, were used in all calculations.

The contributions of external rotation to the thermodynamic functions were computed using the relations

$$S^o_{XR} = R(\ln Q_{XR} - \frac{Q'_{XR}}{Q_{XR} T} - \ln s) \tag{17}$$

$$(H^o - H^o_o)_{XR} = - R \frac{Q'_{XR}}{Q_{XR}} \tag{18}$$

$$(C^o_p)_{XR} = \frac{R}{T^2} \left[\frac{Q''_{XR}}{Q_{XR}} - (\frac{Q'_{XR}}{Q_{XR}})^2 \right] \tag{19}$$

where s = external rotational symmetry number (= 6 for ethane)

$$Q'_{XR} = \frac{dQ_{XR}}{d\Theta} ; \quad Q''_{XR} = \frac{dQ'_{XR}}{d\Theta} ; \quad \Theta = 1/T \tag{20}$$

The relation for the external rotational partition function of a symmetrical top, given by Herzberg[16] was used.

$$Q_{XR} = e \frac{c_2 B_o}{4T} \left(\frac{\pi}{B_o^2 A_o}\right)^{1/2} \left(\frac{T}{c_2}\right)^{3/2} \left[1 + \frac{1}{12}\left(1 - \frac{B_o}{A_o}\right)\left(\frac{c_2 B_o}{T}\right) + \frac{7}{480}\left(1 - \frac{B_o}{A_o}\right)^2 \left(\frac{c_2 B_o}{T}\right)^2 + \ldots\right] \tag{21}$$

where

c_2 = hc/k = second radiation constant

A_o = $h/8\pi^2 c I_A$

B_o = $h/8\pi^2 c I_B$

I_A = moment of inertia about C-C bond of ethane

I_B = one of the two equal moments of inertia; i.e., the moment of inertia perpendicular to the C-C bond.

The rotational constants $B_o = 0.66310\ \text{cm}^{-1}$, given by Lafferty and Plyler,[19] and $A_o = 2.578\ \text{cm}^{-1}$, given by Romanko, et al[39] were used.

The contribution of hindered internal rotation to the thermodynamic functions was computed using expressions of the form given in Equations (17), (18), and (19), except that no symmetry number was used. The partition function Q_{IR} was given by the relation

$$Q_{IR} = \sum_{n=o}^{n} e^{-E_u/kT} \tag{22}$$

The partition function and its derivatives, Q'_{IR} and Q''_{IR}, were evaluated for the first forty energy levels for hindered rotation in ethane. These energy levels were evaluated using the approach outlined by Halford[13] for values of V_o, the internal rotation barrier, of 2750, 2875 and 3000 cal/gm mole. These values of V_o were selected following the suggestion of Pitzer.[33] The contributions to the thermodynamic function computed using the energy levels so derived agreed with values obtained using the Pitzer and Gwinn[35] tables for computing such internal rotation contributions. These calculations are discussed in greater detail in Appendix C.

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

A. Introduction

The vapor pressure and heats of vaporization and sublimation of ethane have been computed at one degree intervals from the normal boiling point (184.52° K) to 20° K by means of Equations (1) and (7), using a Burroughs 220 digital computer. The results are given in Table VIII. The input data used are given in Tables I and VII.

B. Comparison of Computed and Experimental Vapor Pressures

The computed vapor pressures of ethane given in Table VIII have been compared in Figure 2 with the experimental data of Burrell and Robertson[3,4] (113.4 - 183.8° K), Maass and McIntosh[23] (165 - 185° K), Maass and Wright[24] (172 - 185° K Loomis and Walters[21] (136 - 187° K), Tickner and Lossing[43] (83 - 131° K) and the smoothed vapor pressure data of the American Petroleum Institute[1] (130 - 184° K) The measurements of Delaplace[8] (83 - 105° K) deviate very greatly from the computed results and are therefore not shown. The vapor pressure data reported by these various investigators have been corrected where possible to the temperature scale used in this report. The experimental vapor pressure data used, together with the corrected temperatures, are given in Appendix D.

The comparison shown in Figure 2 between the experimental vapor pressures and the computed vapor pressures given in Table VIII was made by examining the temperature difference ($T_{calc}-T_{obs}$) as a function of temperature. Here 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

TABLE VIII

CALCULATED VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF ETHANE

Temperature (°K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T (°K^{-1})	Log$_{10}$P	(dP/dT)/P (°K^{-1})
		- - -Liquid- - -			
184.52(nbp)	7.6000(2)[a]	3517.0	0.54195	2.88081	0.0542
184	7.3880(2)	3522.0	0.54348	2.86853	0.0545
183	6.9935(2)	3531.5	0.54645	2.84469	0.0552
182	6.6156(2)	3541.0	0.54945	2.82057	0.0558
181	6.2539(2)	3550.4	0.55249	2.79615	0.0565
180	5.9078(2)	3559.8	0.55556	2.77143	0.0572
179	5.5770(2)	3569.1	0.55866	2.74640	0.0579
178	5.2610(2)	3578.3	0.56180	2.72107	0.0587
177	4.9592(2)	3587.5	0.56497	2.69541	0.0594
176	4.6713(2)	3596.6	0.56818	2.66944	0.0601
175	4.3968(2)	3605.6	0.57143	2.64313	0.0609
174	4.1351(2)	3614.6	0.57471	2.61649	0.0617
173	3.8860(2)	3623.6	0.57803	2.58951	0.0625
172	3.6490(2)	3632.4	0.58140	2.56218	0.0633
171	3.4236(2)	3641.3	0.58480	2.53449	0.0641
170	3.2095(2)	3650.1	0.58824	2.50644	0.0650
169	3.0062(2)	3658.8	0.59172	2.47801	0.0658
168	2.8133(2)	3667.5	0.59524	2.44921	0.0667
167	2.6305(2)	3676.1	0.59880	2.42003	0.0676
166	2.4573(2)	3684.7	0.60241	2.39046	0.0685
165	2.2934(2)	3693.3	0.60606	2.36048	0.0694

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[a] Numbers in parentheses indicate powers of 10 by which pressure entry is to be multiplied.

(continued)

TABLE VIII (continued)

CALCULATED VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF ETHANE

Temperature (^{o}K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T (^{o}K^{-1})	Log$_{10}$P	(dP/dT)/P (^{o}K^{-1})
164	2.1384(2)	3701.8	0.60976	2.33010	0.0704
163	1.9920(2)	3710.3	0.61350	2.29930	0.0714
162	1.8538(2)	3718.7	0.61728	2.26807	0.0723
161	1.7235(2)	3727.1	0.62112	2.23641	0.0734
160	1.6007(2)	3735.5	0.62500	2.20430	0.0744
159	1.4851(2)	3743.8	0.62893	2.17175	0.0754
158	1.3763(2)	3752.1	0.63291	2.13873	0.0765
157	1.2742(2)	3760.3	0.63694	2.10524	0.0776
156	1.1783(2)	3768.5	0.64103	2.07127	0.0787
155	1.0884(2)	3776.7	0.64516	2.03680	0.0799
154	1.0042(2)	3784.9	0.64935	2.00184	0.0810
153	9.2547(1)	3793.0	0.65360	1.96636	0.0822
152	8.5184(1)	3801.1	0.65790	1.93036	0.0835
151	7.8311(1)	3809.2	0.66225	1.89382	0.0847
150	7.1902(1)	3817.3	0.66667	1.85674	0.0860
149	6.5932(1)	3825.3	0.67114	1.81909	0.0873
148	6.0378(1)	3833.3	0.67568	1.78088	0.0886
147	5.5218(1)	3841.3	0.68027	1.74208	0.0900
146	5.0430(1)	3849.3	0.68493	1.70269	0.0914
145	4.5992(1)	3857.2	0.68966	1.66268	0.0928
144	4.1885(1)	3865.1	0.69444	1.62205	0.0942
143	3.8088(1)	3873.0	0.69930	1.58079	0.0957
142	3.4583(1)	3880.9	0.70423	1.53887	0.0972
141	3.1353(1)	3888.8	0.70922	1.49628	0.0988
140	2.8380(1)	3896.7	0.71429	1.45301	0.1004

(continued)

TABLE VIII (continued)

CALCULATED VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF ETHANE

Temperature (°K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T (°K^{-1})	Log$_{10}$P	(dP/dT)/P (°K^{-1})
139	2.5647(1)	3904.5	0.71942	1.40904	0.1020
138	2.3140(1)	3912.4	0.72464	1.36436	0.1037
137	2.0842(1)	3920.2	0.72993	1.31894	0.1054
136	1.8740(1)	3928.0	0.73529	1.27278	0.1071
135	1.6821(1)	3935.8	0.74074	1.22585	0.1089
134	1.5071(1)	3943.6	0.74627	1.17814	0.1107
133	1.3478(1)	3951.4	0.75188	1.12962	0.1126
132	1.2030(1)	3959.2	0.75758	1.08028	0.1145
131	1.0717(1)	3966.9	0.76336	1.03009	0.1165
130	9.529	3974.7	0.76923	0.97905	0.1185
129	8.455	3982.5	0.77519	0.92711	0.1206
128	7.486	3990.2	0.78125	0.87427	0.1227
127	6.615	3998.0	0.78740	0.82050	0.1248
126	5.832	4005.7	0.79365	0.76578	0.1271
125	5.130	4013.5	0.80000	0.71009	0.1293
124	4.502	4021.2	0.80645	0.65338	0.1317
123	3.941	4029.0	0.81301	0.59566	0.1341
122	3.443	4036.7	0.81967	0.53688	0.1365
121	2.999	4044.5	0.82645	0.47701	0.1391
120	2.606	4052.2	0.83333	0.41604	0.1416
119	2.259	4060.0	0.84034	0.35393	0.1443
118	1.953	4067.7	0.84746	0.29065	0.1470
117	1.683	4075.4	0.85470	0.22616	0.1498
116	1.447	4083.2	0.86207	0.16045	0.1527
115	1.240	4091.0	0.86957	0.09347	0.1557

(continued)

TABLE VIII (continued)

CALCULATED VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF ETHANE

Temperature (°K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T ($°K^{-1}$)	$Log_{10}P$	(dP/dT)/P ($°K^{-1}$)
114	1.060	4098.7	0.87719	0.02518	0.1587
113	9.03(-1)	4106.5	0.88496	-0.04444	0.1618
112	7.67(-1)	4114.2	0.89286	-0.11543	0.1650
111	6.49(-1)	4122.0	0.90090	-0.18784	0.1683
110	5.47(-1)	4129.8	0.90909	-0.26170	0.1717
109	4.60(-1)	4137.6	0.91743	-0.33706	0.1752
108	3.86(-1)	4145.3	0.92593	-0.41396	0.1788
107	3.22(-1)	4153.1	0.93458	-0.49244	0.1825
106	2.68(-1)	4160.9	0.94340	-0.57255	0.1863
105	2.22(-1)	4168.7	0.95238	-0.65433	0.1902
104	1.83(-1)	4176.5	0.96154	-0.73784	0.1943
103	1.50(-1)	4.184.3	0.97087	-0.82314	0.1984
102	1.23(-1)	4192.1	0.98039	-0.91026	0.2027
101	1.00(-1)	4200.0	0.99010	-0.99928	0.2071
100	8.12(-2)	4207.8	1.00000	-1.09025	0.2117
99	6.56(-2)	4215.6	1.01010	-1.18322	0.2164
98	5.27(-2)	4223.5	1.02040	-1.27827	0.2212
97	4.21(-2)	4231.3	1.03092	-1.37546	0.2263
96	3.35(-2)	4239.2	1.04166	-1.47486	0.2314
95	2.65(-2)	4247.0	1.05263	-1.57654	0.2368
94	2.09(-2)	4254.9	1.06382	-1.68057	0.2423
93	1.63(-2)	4262.7	1.07526	-1.78704	0.2480
92	1.27(-2)	4270.6	1.08695	-1.89603	0.2539
91	9.83(-3)	4278.5	1.09890	-2.00761	0.2599
90	7.55(-3)	4286.4	1.11111	-2.12188	0.2662
89.89(tp)	7.33(-3)	4287.3	1.11247	-2.13462	0.2669

(continued)

TABLE VIII (continued)

CALCULATED VAPOR PRESSURE AND HEATS OF

VAPORIZATION AND SUBLIMATION OF ETHANE

Temperature (°K)	Pressure, P (mm Hg)	Heat of Sublimation (cal/gm mole)	100/T (°K^{-1})	Log$_{10}$P	(dP/dT)/P (°K^{-1})
		- - -Solid- - -			
89.89 (tp)	7.33(-3)	4970.7	1.11247	-2.13462	0.3097
89	5.55(-3)	4975.8	1.12359	-2.25553	0.3161
88	4.03(-3)	4981.5	1.13636	-2.39445	0.3236
87	2.91(-3)	4987.0	1.14942	-2.53672	0.3315
86	2.08(-3)	4992.4	1.16279	-2.68247	0.3396
85	1.47(-3)	4997.6	1.17647	-2.83180	0.3480
84	1.04(-3)	5002.7	1.19047	-2.98484	0.3567
83	7.22(-4)	5007.6	1.20481	-3.14173	0.3657
82	4.98(-4)	5012.4	1.21951	-3.30260	0.3751
81	3.41(-4)	5017.1	1.23456	-3.46760	0.3847
80	2.31(-4)	5021.5	1.25000	-3.63688	0.3948
79	1.55(-4)	5025.9	1.26582	-3.81060	0.4052
78	1.03(-4)	5030.1	1.28205	-3.98892	0.4160
77	6.73(-5)	5034.1	1.29870	-4.17202	0.4272
76	4.36(-5)	5038.0	1.31578	-4.36009	0.4389
75	2.80(-5)	5041.7	1.33333	-4.55332	0.4510
74	1.77(-5)	5045.3	1.35135	-4.75191	0.4636
73	1.11(-5)	5048.8	1.36986	-4.95610	0.4767
72	6.82(-6)	5052.1	1.38888	-5.16609	0.4903
71	4.15(-6)	5055.2	1.40845	-5.38213	0.5046
70	2.49(-6)	5058.2	1.42857	-5.60448	0.5194

(continued)

TABLE VIII (continued)

CALCULATED VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF ETHANE

Temperature (^{o}K)	Pressure, P (mm Hg)	Heat of Sublimation (cal/gm mole)	100/T (^{o}K^{-1})	Log$_{10}$P	(dP/dT)/P (^{o}K^{-1})
69	1.47(-6)	5061.0	1.44927	-5.83341	0.5349
68	8.53(-7)	5063.7	1.47058	-6.06920	0.5510
67	4.87(-7)	5066.3	1.49253	-6.31216	0.5679
66	2.74(-7)	5068.6	1.51515	-6.56260	0.5855
65	1.51(-7)	5070.9	1.53846	-6.82086	0.6039
64	8.18(-8)	5073.0	1.56250	-7.08731	0.6232
63	4.34(-8)	5074.9	1.58730	-7.36232	0.6434
62	2.26(-8)	5076.7	1.61290	-7.64631	0.6645
61	1.15(-8)	5078.3	1.63934	-7.93971	0.6867
60	5.72(-9)	5079.8	1.66666	-8.24298	0.7100
59	2.78(-9)	5081.1	1.69491	-8.55662	0.7345
58	1.31(-9)	5082.3	1.72413	-8.88115	0.7602
57	6.07(-10)	5083.3	1.75438	-9.21715	0.7873
56	2.72(-10)	5084.1	1.78571	-9.56520	0.8158
55	1.19(-10)	5084.9	1.81818	-9.92597	0.8458
54	5.01(-11)	5085.4	1.85185	-10.30015	0.8775
53	2.05(-11)	5085.8	1.88679	-10.68848	0.9110
52	8.10(-12)	5086.0	1.92307	-11.09177	0.9464
51	3.08(-12)	5086.1	1.96078	-11.51089	0.9839
50	1.13(-12)	5086.0	2.00000	-11.94678	1.0237
49	3.98(-13)	5085.8	2.04081	-12.40044	1.0658
48	1.34(-13)	5085.4	2.08333	-12.87298	1.1106
47	4.31(-14)	5084.8	2.12765	-13.36557	1.1583
46	1.32(-14)	5084.1	2.17391	-13.87952	1.2090
45	3.84(-15)	5083.1	2.22222	-14.41622	1.2631

(continued)

TABLE VIII (concluded)

CALCULATED VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF ETHANE

Temperature (°K)	Pressure, P (mm Hg)	Heat of Sublimation (cal/gm mole)	100/T (°K^{-1})	Log$_{10}$P	(dP/dT)/P (°K^{-1})
44	1.05(-15)	5082.0	2.27272	-14.97720	1.3209
43	2.73(-16)	5080.7	2.32558	-15.56414	1.3827
42	6.62(-17)	5079.2	2.38095	-16.17885	1.4489
41	1.50(-17)	5077.6	2.43902	-16.82336	1.5199
40	3.16(-18)	5075.7	2.50000	-17.49984	1.5963
39	6.16(-19)	5073.5	2.56410	-18.21074	1.6785
38	1.10(-19)	5071.2	2.63157	-18.95872	1.7672
37	1.79(-20)	5068.6	2.70270	-19.74676	1.8630
36	2.64(-21)	5065.8	2.77777	-20.57813	1.9669
35	3.50(-22)	5062.8	2.85714	-21.45651	2.0796
34	4.11(-23)	5059.5	2.94117	-22.38597	2.2023
33	4.26(-24)	5055.9	3.03030	-23.37109	2.3362
32	3.83(-25)	5052.2	3.12500	-24.41703	2.4826
31	2.95(-26)	5048.2	3.22580	-25.52959	2.6433
30	1.93(-27)	5043.9	3.33333	-26.71536	2.8201
29	1.04(-28)	5039.5	3.44827	-27.98180	3.0153
28	4.60(-30)	5034.8	3.57142	-29.33748	3.2315
27	1.61(-31)	5029.9	3.70370	-30.79219	3.4719
26	4.39(-33)	5024.7	3.84615	-32.35723	3.7403
25	9.00(-35)	5019.4	4.00000	-34.04572	4.0412
24	1.34(-36)	5013.8	4.16666	-35.87293	4.3801
23	1.39(-38)	5008.1	4.34782	-37.85678	4.7638
22	9.58(-41)	5002.1	4.54545	-40.01845	5.2006
21	4.14(-43)	4996.0	4.76190	-42.38312	5.7006
20	1.04(-45)	4989.6	5.00000	-44.98100	6.2769

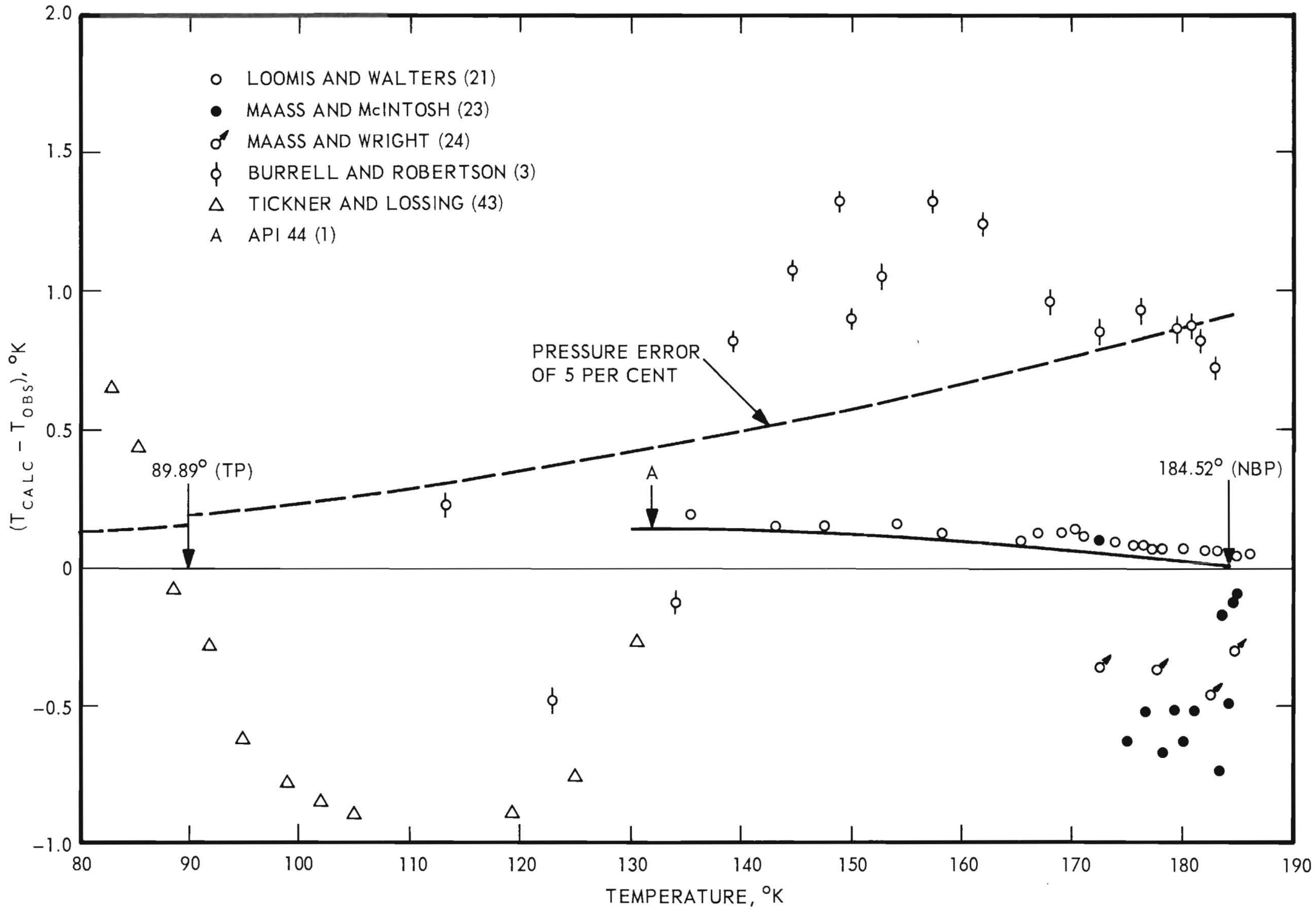

Figure 2. Comparison of Calculated and Experimental Vapor Pressure of Ethane.

in the computed vapor pressure table (Table VIII).*

Examination of Figure 2 shows that only the vapor pressure data of Loomis and Walters[21] and the smoothed API data[1] agree reasonably well with the computed results. The small scatter in the data of Loomis and Walters is an indication of the precision of these measurements. The agreement between the smoothed API vapor pressure data and the measurements of Loomis and Walters is not surprising since the API values are based at least in part on the data of Loomis and Walters. The slightly better agreement of the computed vapor pressures with the API data arises primarily from the fact that the computed values make use of the API normal boiling point (184.52° K).

C. Effect of Variation of Input Parameters on Computed Vapor Pressure and Heats of Vaporization and Sublimation

The possibility exists that the second virial coefficient data of Eucken and Parts are somewhat in error, and hence that the theoretical expression chosen for computing this quantity at low temperatures is in error. Vapor pressure and heats of vaporization and sublimation were therefore recomputed using the same input data as were used to compute Table VIII except that the spherical Kihara core model recommended by Prausnitz and Myers[38] (parameters corresponding to Curve B, Table VI) were used instead of the parameters

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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.[29] 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.

corresponding to Curve C. The results of these calculations are compared in Table IX. Comparison of the vapor pressure computed using this spherical core model for the second virial coefficient agree somewhat better with the experimental data of Loomis and Walters[22] than do the vapor pressures (Table VIII) computed using a virial coefficient based on the data of Eucken and Parts. However, in view of the uncertainty of the temperature scale of Loomis and Walters and the thermal input data (including the second virial coefficient) it is believed that the vapor pressures and heats of vaporization and sublimation given in Table VIII represent these properties of ethane as satisfactorily as they are known at this time.

D. Comparison of Calorimetric and Statistical Entropy of Ideal Gas

The thermal data used to compute the vapor pressure and heats of vaporization and sublimation given in Table VIII were used to compute the calorimetric entropy of the ideal gas at the normal boiling point (184.52° K) assuming the entropy of the solid to be zero at 0° K. The results of the calculation are shown in Table X. The agreement shown between the value of the entropy derived from the thermal data and the statistical entropy is certainly within the probable error of both values.

The statistical entropy was computed at 180° K for three values of barrier height, V_o = 2750, 2875, 3000 cal/gm mole; the corresponding values of entropy found were S^o = 49.354, 49.315 and 49.279 e.u., respectively. Thus the entropy is not very sensitive to the choice of barrier height over this range of V_o.

The correction for non-ideality using the adjusted triangular prism and spherical core models was 0.182 (Curve C, Fig. 1) and 0.138 (Curve B, Fig. 1) respectively. This difference is well within the probable experimental error of the calorimetric entropy.

TABLE IX

COMPARISON OF VAPOR PRESSURE AND HEATS OF
VAPORIZATION AND SUBLIMATION OF ETHANE COMPUTED USING
DIFFERENT SECOND VIRIAL COEFFICIENT PARAMETERS

	Kihara Core Model Curve C, Table VI		Kihara Core Model Curve B, Table VI	
Temperature (°K)	Vapor Pressure (mm Hg)	Heat of Vaporization (cal/gm mole)	Vapor Pressure (mm Hg)	Heat of Vaporization (cal/gm mole)
		- - -Liquid- - -		
184.52	760.000	3517.00	760.000	3517.00
180	590.783	3559.78	591.459	3558.43
170	320.949	3650.06	322.144	3646.13
160	160.067	3735.45	161.091	3729.51
150	71.902	3817.27	72.560	3809.83
140	28.380	3896.68	28.722	3888.21
130	9.529	3974.71	9.673	3965.59
120	2.606	4052.20	2.655	4042.73
110	5.474(-1)	4129.77	5.597(-1)	4120.13
100	8.124(-2)	4207.79	8.343(-2)	4198.08
90	7.553(-3)	4286.38	7.800(-3)	4276.66
89.89	7.335(-3)	4287.25	7.575(-3)	4277.53
		- - -Solid- - -		
89.89	7.335(-3)	4970.65[a]	7.575(-3)	4960.93[a]
80	2.307(-4)	5021.53	2.399(-4)	5011.81
70	2.486(-6)	5058.19	2.607(-6)	5048.46
60	5.715(-9)	5079.78	6.064(-9)	5070.06
50	1.130(-12)	5086.03	1.219(-12)	5076.31
40	3.163(-18)	5075.65	3.496(-18)	5065.92
30	1.926(-27)	5043.93	2.217(-27)	5034.21
20	1.044(-45)	4989.61	1.305(-45)	4979.88

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[a] Heat of sublimation

TABLE X

COMPARISON OF CALORIMETRIC AND STATISTICAL ENTROPY OF ETHANE AS IDEAL GAS AT 184.52° K AND 1 ATMOSPHERE

Temperature Range (°K)	Entropy Change (cal/gm mole °K)	Comments
0 - 15	0.224	Θ(Debye) = 167°, six deg. freedom
15 - 35	1.936	
35 - 50	2.256	
50 - 89.89	6.308	
89.89 (tp)	7.603	Fusion, 683.4/89.89
89.89 - 184.52	11.996	
184.52 (nbp)	19.060	Vaporization, 3517/184.52
184.52	0.182	Correction for non-ideality (Curve C, Table VI)
$(S^o)_{cal}$	49.565	
$(S^o)_{stat}$	49.559	(V_o = 2875 cal/gm mole)

V. CONCLUSIONS

Thermodynamic relations have been used to compute the vapor pressure and heats of vaporization and sublimation of ethane at one degree intervals from 184.52° K (the normal boiling point) to 20° K. Comparison of the computed vapor pressures with the available experimental data strongly suggest that only the vapor pressure data of Loomis and Walters[21] and the smoothed data of the American Petroleum Institute Research Project[1] (which are based at least in part on the data of Loomis and Walters) are reasonably consistent with the thermodynamic data used to compute the vapor pressures. By variation of (1) the internal rotation barrier height and (2) the theoretical representation of the second virial coefficient, computed vapor pressures which agree somewhat better with the data of Loomis and Walters than those given in Table VIII were obtained. However, in view of the uncertainty in (1) the temperature scale of Loomis and Walters and (2) the thermal input data (including the second virial coefficient) it is believed that the vapor pressures and heats of vaporization and sublimation given in Table VIII represent these properties of ethane as accurately as they are known at this time.

VI. ACKNOWLEDGEMENT

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VIII. APPENDICES

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 = velocity of light = 2.99702×10^{10} cm/sec.

c_2 = hc/k

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

h = Planck's constant = 6.62377×10^{-27} erg-sec/molecule.

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

(ΔH_{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 through T_1

$H(P,T)$ = enthalpy of gas at P and T

$H^o(T)$ = enthalpy of ideal gas at T.

$(H^o - H^o_o)''_T$ = enthalpy function for ideal gas at T.

k = Boltzmann constant = 1.38038×10^{-16} erg/°K-molecule.

M = molecular weight = 30.070 for ethane

M_o, S_o, V_o = parameters of Kihara core model.

N_o = Avogadro's Number = 6.02380×10^{23} molecules/gm mole.

P = pressure.

P_1 = pressure of a known point on the vapor pressure curve.

p_i = degeneracy of quantum level. See Eq. (14)-(16).

---

*The physical constants used were those of Rossini et al[40] adjusted to an ice point of 273.15° K.

Q = molecular partition function. See Eqs. (9)-(22).

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 = symmetry number (6 for ethane).

$S(P,T)$ = entropy of gas at P and T

$S^{o}(P,T)''$ = entropy of the ideal gas at P and T.

$(S^{o})''_{T}$ = entropy of ideal gas at P = 1 atm and T.

T = temperature on the thermodynamic scale with an assigned ice point of 273.15° K.

T_1 = temperature of a known point on the vapor pressure curve.

T_{tr} = temperature of a condensed phase transition.

T_o = ice point on thermodynamic scale.

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.

δ = defined by Eqs. (2) and (5).

ϵ = defined by Eqs. (3) and (6).

Superscripts

$'$ = condensed phase

$''$ = vapor phase

Subscripts

i = quantum level. See Eq. (14)-(16).

IR = internal rotation

s = saturated condensed phase

v = vibration

XR = external rotation

B. Conversion of Temperature Scales

Temperatures reported by a given investigator have been converted to a consistent thermodynamic scale based on an ice-point, T_o, of 273.15° K where possible. In view of the fact that the uncertainty between the International Practical Temperature Scale and the absolute thermodynamic scale may be as much as 0.04° in the range between -182.97 and 0° C,[44] no attempt was made to correct the IPTS to the absolute Kelvin scale.

The various methods used for making these corrections are given below. The final corrected temperature in °K used in this paper is represented by T, the temperature reported by the investigator is represented by T^*.

1. Conversion of Celsuis to Kelvin Scale

Conversion to the thermodynamic scale was made using the relation

$$T = t^* + 273.15 \tag{23}$$

2. Conversion Involving Ice-Point Ratio

When the Kelvin scale, T^*, used by an investigator was based on a stated ice-point, T_o^*, conversion to the temperature scale used in this paper was made by the relation

$$T = T^* \frac{273.15}{T_o^*} \tag{24}$$

$$T = T^* \frac{273.15}{273.10} \tag{25}$$

C. Calculation of Thermodynamic Functions of Ethane

The first forty energy levels for hindered rotation in ethane were evaluated using the approach outlined by Halford.[13] Two sets of energy levels were computed corresponding to the parameter $\sigma = 0$ and $\sigma = -3/2$ in the notation of Halford. The two sets of energy levels corresponding to $\sigma = 0$ and $\sigma = -3/2$ were computed using a value of $A_o = 2.578$ cm^{-1} and V_o = 2750, 2875 and 3000 cal/gm mole.[33] These energy levels actually correspond to the limiting values of energy bands. Their numerical values depend upon the value of the height of the potential barrier, V_o , and the rotational constant, A_o , corresponding to the moment of inertia of the symmetrical top molecule about the C-C axis. The contribution of these two sets of energy levels to the thermodynamic properties was computed by evaluating the internal rotation partition function Q_{IR}, Equation (22), and the corresponding derivatives Q'_{IR} and Q''_{IR}, corresponding to Equation (22), and substituting the sums so obtained in equations similar to Equations (17), (18) and (19). The "best values" of S^o_{IR} , $(H^o-H^o_o)_{IR}$ and $(C^o_p)_{IR}$ were obtained by averaging the results obtained for the two limiting cases. It was found that the energy levels corresponding to V_o = 2875 cal/gm mole gave the best agreement between experimental and computed values of C^o_p as a function of temperature and between the calorimetric and computed values of S^o at the normal boiling point. This finding is in agreement with Pitzer's selection[33] of this value for V_o.

In Table XI are given the contribution of internal rotation to the thermodynamic functions for ethane based on these energy levels as well as the total values of the functions, including translation, external rotation, and vibration, based on the data of Table VII. In no instance did values of $(S^o)_{IR}$, $(H^o-H^o_o)_{IR}$ and $(C^o_p)_{IR}$ computed for $\sigma = 0$ and $\sigma = -3/2$ differ by as much as 0.001 from the value tabulated in Table XI.

D. Experimental Vapor Pressure Data for Ethane

The experimental vapor pressure data presented in Figure 2 are collected in Table XII. The corrected observed temperature, T_{obs}, of Figure 2 is given in Column 3 of Table XII. The temperature T_{calc} is the temperature found by interpolation in Table VIII corresponding to the reported experimental vapor pressure.

The smoothed experimental values given in the API Research Project 44 tabulation were computed using an Antoine equation

$$\log P(\text{mm}) = A-B/(C+t) \tag{26}$$

where $A = 6.80266$, $B = 656.40$, $C = 256.00$

TABLE XI

IDEAL GAS THERMODYNAMIC FUNCTIONS OF ETHANE

	Internal Rotation (V_o = 2875)			Total		
Temp. (^oK)	$(H^o-H^o_o)_{IR}$ cal/gm mole	$(S^o)_{IR}$ cal/gm mole ^oK	$(C^o_p)_{IR}$ cal/gm mole ^oK	$(H^o-H^o_o)$ cal/gm mole	S^o cal/gm mole ^oK	C^o_p cal/gm mole ^oK
20	0.009	0.000	0.000	158.36	30.993	7.949
40	0.043	0.001	0.009	317.37	36.504	7.958
60	0.984	0.019	0.109	477.29	39.744	8.058
80	5.292	0.079	0.337	640.58	42.092	8.286
100	14.782	0.184	0.614	809.09	43.970	8.567
120	29.784	0.320	0.882	983.31	45.558	8.854
140	49.857	0.474	1.120	1163.25	46.944	9.141
160	74.341	0.637	1.323	1349.05	48.184	9.443
180	102.581	0.803	1.496	1541.17	49.315	9.774
200	133.976	0.969	1.639	1740.29	50.364	10.145
220	167.980	1.131	1.757	1947.25	51.350	10.559
240	204.102	1.288	1.851	2162.94	52.288	11.017
260	241.896	1.439	1.925	2388.21	53.189	11.517
280	280.966	1.584	1.979	2623.84	54.062	12.052
300	320.962	1.722	2.018	2870.47	54.913	12.616

TABLE XII

EXPERIMENTAL VAPOR PRESSURES FOR ETHANE

Reported Temperature	Method of Temperature Correction[a]	Corrected Temperature T_o = 273.15 T_{obs} (°K)	Reported Vapor Pressure mm Hg	$(T_{calc}-T_{obs})$ x 10 (°K)
Burrell and Robertson[3,4]				
(°K)				
183.8[b]	none		760	72
182.2			700	81.7
180.8			650	88.5
179.4			600	87.1
176.2			500	93.8
172.6			400	86.4
168.0			300	96.9
161.8			200	125.6
157.8			150	133.3
152.9			100	104.8
149.9			77	90.1
149.0			74	133.5
144.6			49	108.6
139.4			29	81.6
134.1			15	-14.2
123.6			4	-49.0

---

[a] See Appendix B for method of temperature correction.

[b] Temperatures measured with pentane thermometer to 0.1 to 0.2°, T_o = 273.10° K

(continued)

TABLE XII

EXPERIMENTAL VAPOR PRESSURES FOR ETHANE

Reported Temperature	Method of Temperature Correction	Corrected Temperature $T_o = 273.15$ T_{obs} (^oK)	Reported Vapor Pressure mm Hg	$(T_{calc}-T_{obs}) \times 10^2$ (^oK)
Burrell and Robertson[3,4] (continued)				
(^oK)				
118.5			3	250.2
115.4			2	276.3
113.4			1	23.6
Maass and McIntosh[23]				
(^oC)				
-88.4[c]	Eq.(23)	184.75	765	-10.9
-88.5		184.65	760	-13.0
-88.6		184.55	754	-17.6
-89.3		183.85	713	-49.9
-89.9		183.25	681	-73.0
-91.5		181.65	630	-52.0
-93.0		180.15	575	-62.1
-94.0		179.15	546	-51.5
-95.0		178.15	510	-67.8
-97.1		176.05	454	-52.2
-98.2		174.95	422	-62.0
-100.4		172.75	385	10.1

---

[c] Hydrogen gas thermometer. Temperature constant to 0.1°.

(continued)

TABLE XII

EXPERIMENTAL VAPOR PRESSURES FOR ETHANE

Reported Temperature	Method of Temperature Correction	Corrected Temperature $T_o = 273.15$ T_{obs} (^oK)	Reported Vapor Pressure mm Hg	$(T_{calc}-T_{obs}) \times 10^2$ (^oK)
Maass and McIntosh[23] (continued)				
(^oC)				
-102.4		170.75	354	77.3
-107.9		165.25	288	310.2
Maass and Wright[24]				
(^oC)				
-88.3[d]	Eq. (23)	184.85	760	-33.0
-88.4		184.75	753	-40.0
-90.6		182.55	664.5	-47.0
-95.5		177.65	504.0	-37.8
-100.8		172.35	364.5	-36.7
Loomis and Walters[21]				
(^oK)				
187.302[e]	None		883.0	3.0
186.609			874.6	54.1
185.914			820.8	3.7
185.137			787.8	4.8
184.539			763.0	5.4
183.778			732.2	5.8
182.463			681.2	6.2

---

[d] Platinum resistance thermometer. Maximum temperature error of 0.2°.

[e] Platinum resistance thermometer. No ice point given; temperature held constant to 0.01°. Third decimal place uncertain.

(continued)

TABLE XII

EXPERIMENTAL VAPOR PRESSURE FOR ETHANE

Reported Temperature	Method of Temperature Correction	Corrected Temperature $T_o = 273.15$ T_{obs} (^oK)	Reported Vapor Pressure mm Hg	$(T_{calc}-T_{obs}) \times 10^2$ (^oK)
Loomis and Walters[21] (continued)				
(^oK)				
181.506			645.9	6.7
179.750			584.9	7.5
178.621			548.0	7.7
177.623			517.1	8.4
175.708			461.5	9.1
174.062			417.8	10.5
170.602			336.7	13.9
171.700			360.5	10.9
169.175			306.5	12.0
135.736			18.62	20.4
143.267			39.67	15.9
147.324			57.68	16.2
154.546			106.4	17.0
158.385			143.3	14.4
162.629			195.5	10.9
165.529			240.2	14.0
167.836			280.7	13.1

(continued)

TABLE XII

EXPERIMENTAL VAPOR PRESSURE FOR ETHANE

Reported Temperature	Method of Temperature Correction	Corrected Temperature $T = 273.15$ T_{obs} (^{o}K)	Reported Vapor Pressure mm Hg	$(T_{calc}-T_{obs}) \times 10^2$ (^{o}K)
Delaplace[8] (^{o}C)				
-190	Eq. (23)	83	4 (-4)[f]	>200 for all points
-188		85	7.5(-4)	
-186		87	1.5(-3)	
-184		89	2.3(-3)	
-183		90	2.78(-3)	
-182		91	3.6(-3)	
-181		92	4.28(-3)	
-180		93	5.10(-3)	
-179		94	6 (-3)	
-178		95	7.20(-3)	
-177		96	8.63(-3)	
-176		97	1.88(-2)	
-175		98	1.28(-2)	
-174		99	1.65(-2)	
-173		100	2.32(-2)	
-172		101	3.3(-2)	
-171		102	4.8(-2)	
-170		103	6.4(-2)	

---

[f] No pressure units are given in Ref. 8. The units are presumed to be baryes since these are used by Delaplace in other papers.[7]

(continued)

TABLE XII

EXPERIMENTAL VAPOR PRESSURES FOR ETHANE

Reported Temperature	Method of Temperature Correction	Corrected Temperature $T_o = 273.15$ T_{obs} (^oK)	Reported Vapor Pressure mm Hg	$(T_{calc}-T_{obs}) \times 10^2$ (^oK)
Delaplace[8] (continued)				
(^oC)				
-169		104	7.9(-2)	>200 for all points
-168		105	10.4(-2)	
Tickner and Lossing[43]				
(^oC)				
-142.5[g]	Eq.(23)	130.65	10	-24.2
-147.6		125.55	5	-74.7
-154.1		119.05	2	-88.7
-158.5		114.65	1	-102.0
-162.6		110.55	0.5	-107.0
-167.8		105.35	0.2	-88.7
-171.3		101.85	0.1	-85.8
-174.6		98.55	0.05	-78.6
-178.7		94.45	0.02	-62.4
-181.8		92.07	0.01	-28.3
-184.4		88.75	0.005	- 8.0
-187.7		85.45	0.002	43.8
-189.9		83.25	0.001	65.2

---

[g] Temperatures accurate to ± 0.3° C.

(continued)

TABLE XII

EXPERIMENTAL VAPOR PRESSURES FOR ETHANE

Reported Temperature	Method of Temperature Correction	Corrected Temperature $T_o = 273.15$ T_{obs} (°K)	Reported Vapor Pressure mm Hg	$(T_{calc}-T_{obs}) \times 10^2$ (°K)
American Petroleum Institute Research Project 44[1] Table 20k (Part 1), Page 1 December 31, 1952.				
(°C)				
-88.63[h]	Eq. (23)	184.52	760[i]	0.0
-88.88		184.27	750	0.6
-89.12		184.03	740	0.0
-89.37		183.78	730	0.1
-89.63		183.52	720	0.9
-89.88		183.27	710	0.4
-90.14		183.01	700	0.7
-92.90		180.25	600	2.1
-96.05		177.10	500	3.8
-99.74		173.41	400	5.4
-104.25		168.90	300	6.9
-106.98		166.17	250	8.2
-110.19		162.96	200	9.6
-114.12		159.03	150	10.3
-119.33		153.82	100	12.8
-122.03		151.12	80	13.2
-125.36		147.79	60	13.9
-127.39		145.76	50	14.6
-129.78		143.37	40	14.4
-132.74		140.41	30	14.5
-136.69		136.46	20	15.0
-142.88		130.27	10	13.8

---

[h] International Temperature Scale (Int. 1948).

[i] Computed from Antoine equation.

TECHNICAL REPORT NO. 3

PROJECT NO. A-764

THE SYSTEM HELIUM-ARGON FROM 65° TO 140° K UP TO PRESSURES OF 120 ATM. CORRELATION OF AVAILABLE PHASE EQUILIBRIUM DATA

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GEORGIA INSTITUTE OF TECHNOLOGY
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ABSTRACT

The available phase equilibrium data for the helium-argon system have been examined critically and a correlation of the gas and condensed phase compositions presented from 65° to 140° K at pressures up to 120 atmospheres. No data are available for the solubility of helium in solid argon, but the locus of the three-phase line suggests that the condensed solid phase is very nearly pure argon. The results of the correlations are presented in tabular form at 5° K and 5 atm intervals with the compositions of the equilibrium gas and liquid phases expressed in terms of mole fractions. In addition, K(=y/x) factors are given for both argon and helium as a function of temperature and pressure. The estimated maximum uncertainty of the gas phase composition in terms of the argon concentration is believed to vary as follows: ± 4 per cent from 65° to 110° K, ± 7 per cent from 110° to 125° K and ± 10 per cent at 140° K. The estimated maximum uncertainty of the liquid phase composition expressed in terms of helium concentration is believed to be ± 2 per cent up to 110° K and ± 5 per cent from 110° to 140° K.

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I. INTRODUCTION

The purpose of this work was to examine the available phase equilibrium data for the helium-argon system and to prepare a correlation of these data over as wide a temperature and pressure range as practical.

The experimental data available (see Section III and Appendix B) consisted of measurements by Mullins[23,24] of gas-solid and gas-liquid equilibrium data (68° to 108° K, pressure up to 120 atm) and measurements of the three-phase line (84.4° to 86.3° K, pressure up to 120 atm); the dew-point and bubble-point measurements of McCain[20] (100° to 150° K, up to 70 atm); and the limited solubility measurements for helium in liquid argon (84.1° to 87.5° K, up to 1.2 atm pressure) of Karasz.[11,12]

The liquid phase composition data were correlated by empirically fitting the data by a least squares method described in Appendix D. Two analytical expressions were developed. One was used to represent the data from the locus of the three-phase line to 110° K up to 120 atm pressure; the second covered the range 110° to 140° K up to 70 atm pressure.

Two different correlations were also developed to represent the gas phase compositions. They are further discussed in Section IV and Appendices D and E. One of the correlations which extended from 65° to 110° K up to 120 atm, was obtained by empirically fitting the gas composition data of Mullins by the least squares method described in Appendix D. From 110° to 140° K the gas phase compositions were calculated from a thermodynamic relation. This relation is believed to provide a better representation of the gas phase compositions than that which would have been obtained from a least squares fit to the scattered dew-point data of McCain.

These four correlations have been used to compute the equilibrium gas and liquid phase compositions given in Table III at 5° K and 5 atm intervals over the range 65° to 140° K. The smoothed values so obtained have been used to compute the K(= y/x) factors shown in Figures 3 and 4.

II. THERMODYNAMIC RELATIONS

A. General

The thermodynamic relations used to correlate the phase equilibrium data for the helium-argon system are taken from relations given by Kirk[14,15,16] and Mullins.[23] A useful parameter for expressing the gas phase composition is the enhancement factor. This parameter was first extensively used by Dokoupil, et al[8] and is defined by Equation (1).*

$$\Phi = \frac{Py_1}{p_{01}} \tag{1}$$

If the partial pressure, Py_1, is set equal to p_{01}, then the enhancement factor is equal to unity. The enhancement factor provides a convenient means of representing experimental data for the gas phase since it does not require a knowledge of the composition of the condensed phase. For the helium-argon system the enhancement factor is not very sensitive to temperature and pressure and is easily presented in graphical form.

A relation which has been rather widely used to correlate the solubility of gases in liquids is the Henry's law constant relation. The Henry's law constant is usually defined at constant temperature as

$$H^o = \left[\lim_{x_2 \to 0} \left(\frac{f_2}{x_2} \right) \right] \tag{2}$$

A more convenient form of Henry's law constant which is used in the present paper is defined by Equation (3).

$$H = \frac{P - p_{01}}{x_2} \tag{3}$$

---

[*] All symbols are defined in Appendix A.

This permits the use of H as a correlating parameter without a knowledge of the composition or fugacity of the gas phase.

As a convenience in certain types of calculations, the gas-liquid and gas-solid compositions can also be presented as K factors defined in the usual way, where

$$K_i = \frac{y_i}{x_i} \tag{4}$$

B. Enhancement Factor

The enhancement factor defined by Equation (1) can be calculated from an equation of state for the gas phase, a knowledge of the activity coefficient of component 1 (the condensable component) in the condensed phase, the composition of the condensed phase and the compressibility of the pure condensed argon. Equation (5) is an exact thermodynamic relation which can be used to calculate the enhancement factor.[23]

$$\ln \Phi = Z_{01} - 1 - \ln Z_{01} + \frac{1}{RT}\int_{P_{01}}^{P} v_1 dP + \frac{1}{RT}\int_{V_{01}}^{\infty} (P - \frac{RT}{V_1})\, dV_1 + \ln Z_m$$

$$- \frac{1}{RT}\int_{V_m}^{\infty} \left[\left(\frac{\partial P}{\partial n_1} \right)_{V,T,n_2} - \frac{RT}{V_m} \right] dV_m + \ln \gamma_1 x_1 \tag{5}$$

The activity coefficient, γ_1, in Equation (5) is referred to pure condensed argon at T and P as the standard state. A similar equation has been derived by Dokoupil, et al[8] for the assumption of a pure condensed phase, in which case the term $\ln \gamma_1 x_1$ is absent. Beattie and Stockmayer[3] have also given a similar equation in which the composition of the condensed phase is considered, but the independent variable is pressure rather than volume.

In order to evaluate Φ from Equation (5), an equation of state for the gas mixture and pure argon gas must be assumed. Here use has been made of the virial equation of state truncated after the third virial coefficient.

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} \tag{6}$$

For the gas mixture the second and third virial coefficients are given by

$$B_m = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \tag{7}$$

$$C_m = y_1^3 C_{111} + 3y_1^2 y_2 C_{112} + 3y_1 y_2^2 C_{122} + y_2^3 C_{222} \tag{8}$$

If the molal volume of pure condensed argon is represented as a function of pressure by the relation

$$v_1 = A_1 + A_2(P-p_{01}) + A_3(P-p_{01})^2 \tag{9}$$

then Equation (5) can be integrated to give

$$\begin{aligned} \ln \Phi = {} & \frac{1}{RT}\left[A_1(P-p_{01}) + \frac{A_2}{2}(P-p_{01})^2 + \frac{A_3}{3}(P-p_{01})^3\right] \\ & + 2\,B_{11}/V_{01} + 3C_{111}/2V_{01}^2 - \ln Z_{01} + \ln Z_m + \ln \gamma_1 x_1 \\ & - 2(y_1 B_{11} + y_2 B_{12})/V_m - 3(y_1^2 C_{111} + 2y_1 y_2 C_{112} + y_2^2 C_{122})/2V_m^2 \end{aligned} \tag{10}$$

At this point it is useful to make several general observations about the solution of Equation (10) for the helium-argon system over the temperature range 65° to 140° K. The solubility of helium in liquid argon is quite small, the maximum solubility being less than 3 mole per cent at pressures up to 70 atmospheres at 140° K. At these low concentrations of helium, the activity coefficient of argon in the liquid phase is probably very nearly unity. The three-phase line indicates that in the solid-gas region the solid is pure argon. At low concentrations of argon in the gas phase the properties of the gas phase will be very nearly represented by Equation (6) with only an approximate representation of the third virial coefficient. Solution of Equation (10) must be accomplished iteratively since y_1 appears both in Φ and also in the calculation of V_m from Equation (6).

III. EXPERIMENTAL DATA

A. General

Two types of experimental data were used to prepare the correlations developed for the helium-argon system. The primary data are the phase equilibrium data for the helium-argon system itself. These data consist of gas compositions in equilibrium with either a solid or liquid phase, liquid compositions, and the locus of the three-phase line. This category includes equivalent data such as dew- and bubble-point measurements on binary mixtures. The secondary data consist of data for the pure components and homogeneous binary gas mixtures which are used here to develop certain correlations based on the general thermodynamic relations considered in Chapter II. The primary data presented represent all of the available data. The choice made of the secondary data used does not necessarily represent a "best" set of data, though the values selected are believed to be completely adequate for their intended purpose.

B. Phase Equilibrium Data for the Helium-Argon System

The available experimental phase equilibrium data for the helium-argon system are the dew-point and bubble-point measurements of McCain[20] (99.74° to 150.62° K, $P \leqq 70$ atm); the solid-gas and liquid-gas measurements of Mullins[23,24] (68.04° to 108.04° K, $P \leqq 120$ atm) made using a single-pass, flow apparatus described by Kirk;[15,16] measurements of the three-phase locus by Mullins[23,24] (84.44° to 86.33° K, $P \leqq 120$ atm); and the measurements of the solubility of helium in liquid argon (84.05° to 87.53° K, $P \leqq 1.2$ atm) of Karasz.[11,12] All of these measurements, with the exception of those of

Karasz, were made in the Low Temperature Laboratory of the Georgia Institute of Technology.

The measurements of McCain[20] were made by injecting a helium-argon mixture of known composition into a glass equilibrium cell maintained at constant temperature, and observing the pressure at which the dew- or bubble-point occurred. Dew points were measured for six mixtures of helium-argon ranging in composition from 1.042 to 84.84 mole per cent helium. Bubble points were measured for six mixtures which contained from 0.746 to 2.656 mole per cent helium. The maximum pressure at which the measurements were made was 70 atmospheres. Temperatures ranged from 99.74° to 150.62° K. A tabulation of the data of McCain[20] is given in Table IV and V of Appendix B. The accuracy of the measurements, expressed in terms of the minor component, varied considerably with temperature. McCain[20] claimed the accuracy of the bubble points above 110° K to be ± 2 per cent of the helium concentration. Below 110° K he stated that the uncertainty increased to about ± 5 per cent with the point at 99.92° K being perhaps 20 per cent in error.

The accuracy of the dew points, expressed in terms of the composition of the minor component, was thought by McCain to vary with temperature as follows:[20]

1. ± 2 per cent of the concentration of the minor component (helium) at temperatures between 135° K and 145° K.

2. ± 5 per cent of the concentration of the minor component (argon or helium) at temperatures between 125° K and 130° K.

3. ± 10 per cent of the concentration of the minor component (argon) at temperatures between 110° K and 120° K.

4. ± 15 per cent of the concentration of the minor component (argon) at 105° K.

The increased error at low temperatures was attributed by him to the difficulty of observing a dew point at low concentrations of argon without changing the gas composition considerably. An analysis of McCain's data in Chapter IV indicates that the bubble-point data may be nearly as good as he claims, but that the dew-point measurements are not.

The recently completed phase equilibrium measurements of Mullins[23,24] consisted of eight isotherms between 68.07° and 108.02° K at pressures to 120 atmospheres. Gas phase compositions for the gas-solid equilibrium were determined at 68.07°, 74.05°, 77.90°, and 80.06° K. Gas and liquid phase compositions were determined at 86.02°, 91.98°, 97.51°, and 108.02° K. The temperature and pressure of each phase equilibrium point were measured with an accuracy of ± 0.03° K and ± 1/2 per cent of the reported pressure. The data for the gas and liquid phase compositions are given in Tables VI and VII of Appendix B. The gas phase compositions are believed to be accurate to ± 3 per cent of the concentration of the minor component, argon. The data for the solubility of helium in liquid argon are believed to be accurate to ± 2 per cent.

In addition to these measurements of gas and liquid phase compositions, the locus of the three-phase line up to 120 atmospheres has been determined by Mullins[23] (84.44° - 86.33° K) with an accuracy of ± 0.05° K and ± 1/2 per cent of the reported pressure. These data were fitted by Mullins[23] by the method of least squares to obtain Equation (11).

$$T = 83.796 + 0.0208365P + 2.267 \times 10^{-5}P^2 - 1.726 \times 10^{-7}P^3 \tag{11}$$

In fitting Equation (11), the selected value of the triple point temperature of argon (83.80° K),[28] corrected to the NBS 1955 scale (83.81° K), was used in addition to the points listed in Table I. The experimental data for the three-phase line are compared in Table I with the results calculated from Equation (11) in the column headed $T_{calc}-T_{obs}$.

TABLE I

THREE-PHASE LINE. HELIUM-ARGON

Pressure atm	Observed Temp °K	$T_{calc}-T_{obs}$ °K
120.00	86.33	-0.006
80.30	85.54	-0.014
114.30	86.21	+0.006
100.10	85.93	+0.006
60.00	85.08	+0.011
30.00	84.44	-0.003

C. Activity Coefficient of Liquid Argon Along Three-Phase Line

Mullins[23] has calculated the activity coefficient of liquid argon in solution with helium along the three-phase line assuming the solid phase to be pure argon. His results are given below in Table II. These results were based on his own measurements of the solubility of helium in argon, the locus of the three-phase line, Equation (11), and the melting curve of pure argon determined by Clusius and Weigand.[5] The activity coefficient is referred to pure liquid argon at T and P. Since the activity coefficient is very nearly unity, the solution may be considered to be ideal over this range.

TABLE II

ACTIVITY COEFFICIENT OF LIQUID ARGON ALONG THE THREE-PHASE LINE OF THE HELIUM-ARGON SYSTEM

Pressure atm	Temperature $^{\circ}K$	Liquid Composition Mole Per Cent Helium	Activity Coefficient of Argon
20	84.22	0.130	0.9997
40	84.65	0.265	0.9996
60	85.09	0.399	0.9997
80	85.52	0.534	0.9998
100	85.93	0.667	0.9996
120	86.32	0.799	0.9991

D. Selection of Other Data Used in Correlations of Liquid and Gas Compositions

The additional data used to compute the enhancement factors from Equations (1) and (10) and to correlate the Henry's law constant defined by Equation (3) consisted of the vapor pressure of argon, the molal volume of pure liquid and solid argon as a function of temperature and pressure, and the parameters required to represent the virial coefficients of argon and helium-argon gas mixtures. A discussion of the various values selected is given in Appendix C.

IV. CORRELATION OF PHASE EQUILIBRIUM DATA

A. General

Four correlation functions were developed to represent the available phase equilibrium data for the helium-argon system. The correlations of the experimental gas phase and liquid phase equilibrium data were carried out separately, the enhancement factor, Φ , defined by Equation (1), serving as the correlating variable for the gas phase and the Henry's law constant, defined by Equation (3), serving as the correlating variable for the liquid phase.

The development of these four correlating functions is discussed in greater detail below and in Appendices D and E. They have been used to compute the smoothed phase composition data given in Table III and the K factors given in Figures 3 and 4, for the range 65° to 140° K.

B. Liquid Phase Correlations

Two correlating functions of the form

$$\log H = L(P-p_{01}, 1/T) \tag{12}$$

were developed by means of a least squares surface fit to the available experimental liquid phase data using a modification of the orthogonal function representation of Bain.[1] Each of these analytical expressions represented log H as a power series in the two independent variables 1/T and $(P-p_{01})$. These expressions were obtained by a least squares surface fit using orthogonal functions as described in Appendices D and E.

Mullins[23] has fitted his liquid phase data (Table VII) by means of such a least squares technique to obtain the analytical correlating function used to represent the liquid phase data for this system over the range 83.81° to 110° K. The orthogonal coefficients, weighting factors and normalizing constants for this correlating function are given in Table XII, Appendix E. This representation was found to represent his data for log H with an average deviation of 0.0016 (0.37 per cent in x_2); the deviation of individual data points is given in Table VII. The liquid phase composition computed from the least squares fit and constants of Table XII are compared with the experimental data of Karasz (84.05 to 87.53° K) in Table VIII. No reason could be found for the large disagreement between the data of Karasz and the data of Mullins on which this correlation is based. The data of Karasz were therefore not considered further.

A similar analytical correlating function was fitted to the liquid phase composition data (86.00° to 108.04° K)(Table VII) of Mullins[23] (weighted twice) and the bubble-point data (109.46° to 149.60° K)(Table IV) of McCain[20] (weighted once). The bubble-point of McCain at 99.92° K was discarded because it appeared to be greatly in error. This arbitrary weighting of the data was made because of the higher accuracy of Mullins data in the range 100° to 108° K and the smaller number of his experimental points. The orthogonal coefficients, weighting factors and normalizing constants of this correlation are given in Table XIII, Appendix E. This correlating function was found to represent the data of Mullins expressed as log H with an average deviation of 0.0068 (1.6 per cent in x_2) and the data of McCain with an average deviation of 0.018 (4.2 per cent in x_2). The deviation of McCain's individual data points from this correlation is shown in Table IV.

C. Gas Phase Correlations

Two analytical expressions were used to represent the gas phase compositions. Between 65° and 110° K a function of the form

$$\log \Phi = G(P-p_{01}, 1/T) \qquad (13)$$

was used. In the range 110° to 140° K Equation (10) was used as the correlating function.

From 65° through 110° K the values of y_1 reported in Table III were calculated from a least squares surface fit to the gas phase composition data (68.04 to 108.04° K)(Table VI) of Mullins.[23] The least squares fit was of the same general type as that used for the liquid composition correlation as described in Appendices D and E. The orthogonal coefficients, weighting factor and normalizing constants are given in Table XIV of Appendix E. The average deviation of $(\log \Phi)/(P-p_{01})$ from the experimental data is 0.000053, corresponding to an average deviation of 0.83 per cent in y_1. The deviation for individual data points is given in Table VI.

The values of Φ computed from this least squares fit are compared in Figure 1 with the experimental data of Mullins[23] at 68.07° and 108.02° K. Also shown in Figure 1 are values of the enhancement factor computed from Equation (10). In computing Φ from Equation (10) the activity coefficient was assumed to be unity and the x_1 computed from the liquid phase correlation (Table XII) at the experimental temperature and pressure. For the solid range the solid was assumed to be pure argon. The other physical data used are given in Appendix C. These calculations made use of an adjusted value of $(U_0/k)_{12} = 29.8°$ K to compute the second virial interaction coefficient B_{12}.

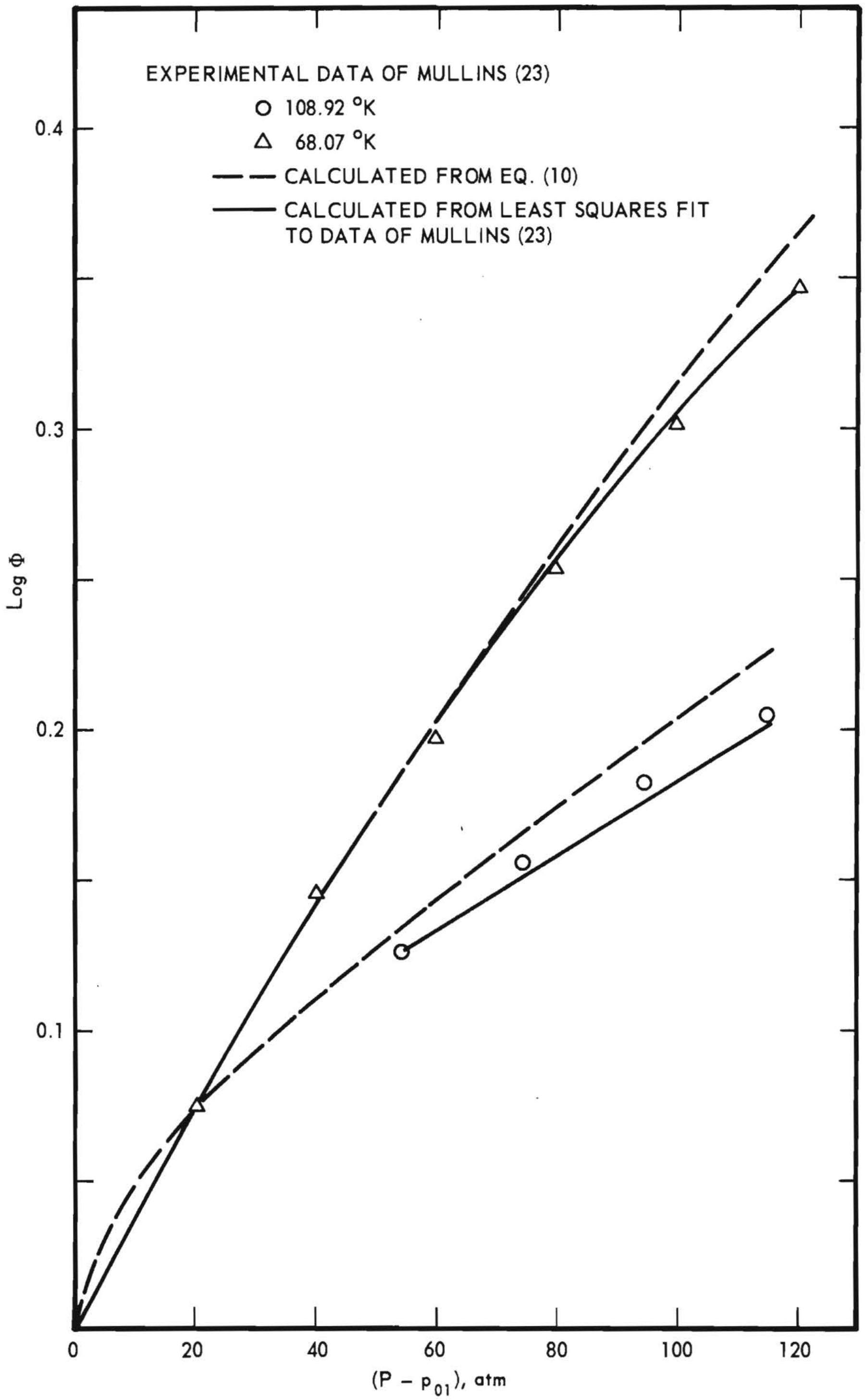

Figure 1. Comparison of Calculated Enhancement Factors with Data of Mullins at 68.07° and 108.02° K.

Values of Φ computed from Equation (10) in the manner just described showed very good agreement with the experimental values of Φ determined by Mullins over the range 68° to 108° K up to pressures of 120 atm. The maximum deviation, which occurred at 108° K, was 3 per cent at 70 atm and 4.5 per cent at 120 atm, the computed values of Φ being too large. This good agreement suggested the possible use of Equation (10) as a correlating device for the temperature range above 110° K.

Since the dew-point data of McCain were measured at constant gas phase composition, Equation (10) was used to compute a table of values of Φ at even temperatures and pressures over the range 100° to 140° K and pressures to 70 atm. Interpolation* in this table gave enhancement factors at constant composition as a function of temperature. These lines of constant composition are compared with the experimental dew-point data of McCain[20] in Figure 2. This figure clearly shows the discrepancies existing in the data of McCain, especially below 110° K. The relatively good agreement of the experimental values of Φ obtained by McCain at higher temperatures (125° to 140° K) and by Mullins below 108° K with those computed from Equation (10) provided the basis for the use of Equation (10) as a correlating device in the range 110° to 140° K. The smoothed values of y_1 given in Table III were computed in this manner using the same parameters (see Appendix C) as those used to compute Φ in the liquid range below 108° K except that x_1 was computed from the liquid correlation given in Table XIII. The activity coefficient was assumed to be unity. It should be pointed out that at sufficiently large values of y_1 Equation (10) fails to converge at high pressures.

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* Aikens[22] iterative method of interpolation was employed with log Φ as the independent variable and the pressure as the dependent variable.

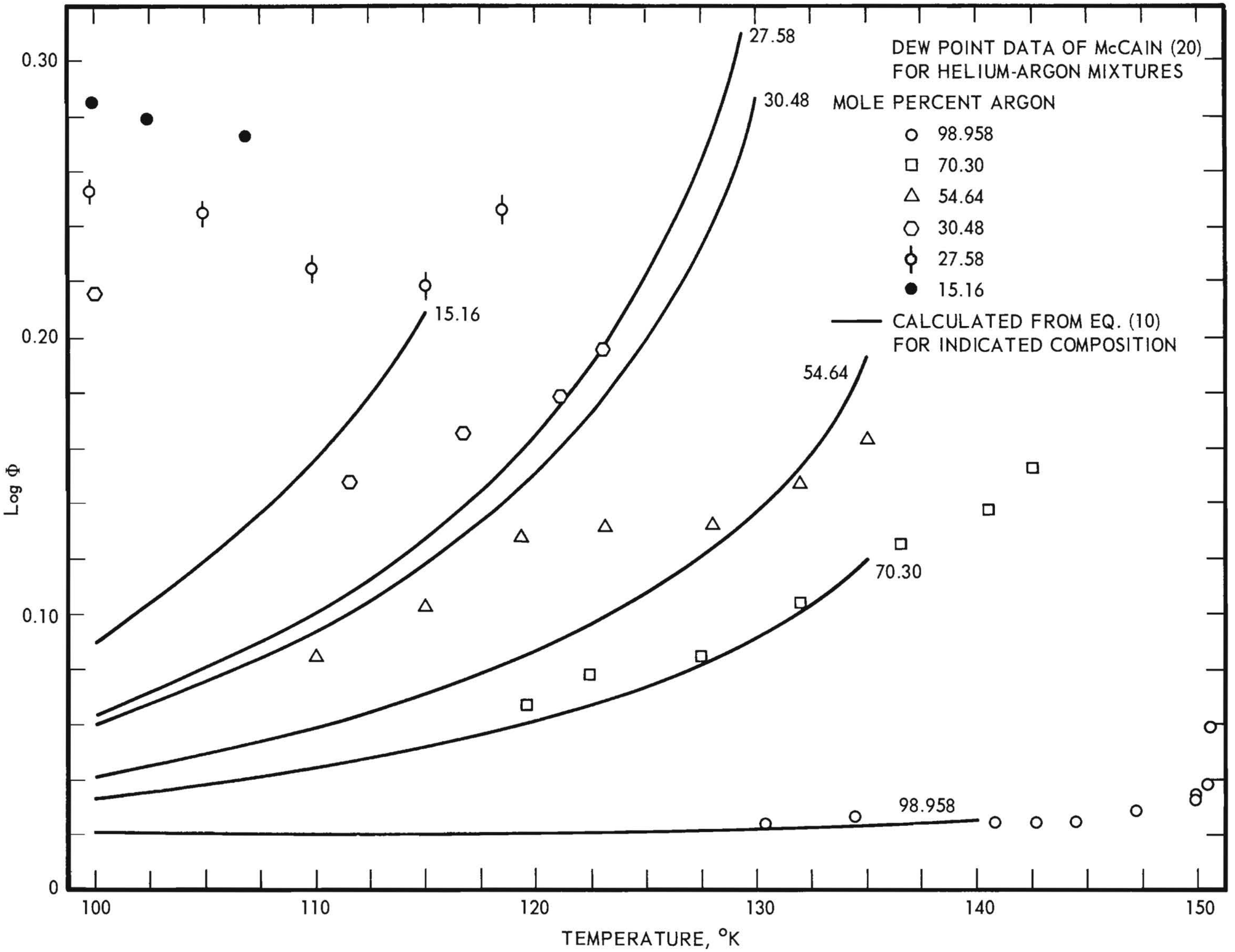

Figure 2. Comparison of Calculated Enhancement Factors with Dew-Point Data of McCain.

D. Smoothed Equilibrium Gas and Liquid Phase Compositions for the Helium-Argon System

The four correlating functions described in Sections B and C were used to compute the equilibrium gas and liquid phase compositions given in Table III at 5° K and 5 atm intervals over the range 65° through 140° K. These smoothed values were used to obtain the K(= y/x) factors shown in Figures 3 and 4. Below 115° the maximum pressure of 120 atm corresponds to the maximum pressure of the experimental data of Mullins. Above 110° the maximum pressure of 70 atm corresponds to the maximum pressure of the dew-point and bubble-point data of McCain. The correlations were not extended above 140° K because of the limited experimental data available.

The estimated maximum uncertainty of the gas phase composition in terms of argon concentration is believed to vary as follows: ± 4 per cent from 65° to 110° K, ± 7 per cent from 110° to 125° K and ± 10 per cent at 140° K. The estimated maximum uncertainty of the liquid phase compositions expressed in terms of helium concentration is believed to be ± 2 per cent up to 110° K and ± 5 per cent from 110° to 140° K. The number of significant figures of the composition given in Table III are greater than is warranted by these estimated errors. This greater number has been included to permit more accurate interpolation.

TABLE III

SMOOTHED EQUILIBRIUM GAS AND LIQUID PHASE COMPOSITIONS FOR THE HELIUM-ARGON SYSTEM

- - -Solid-Gas Region- - -

T, °K	65	70	75	80
Vapor Pressure p_{01}, atm	0.02488	0.07149	0.1780	0.3949
Pressure atm	Mole Per Cent Argon $100y_1$			
5	0.524	1.492	3.70	8.18
10	0.275	0.778	1.919	4.24
15	0.1924	0.539	1.325	2.92
20	0.1512	0.420	1.028	2.26
25	0.1265	0.349	0.849	1.862
30	0.1102	0.301	0.730	1.596
35	0.0987	0.267	0.644	1.405
40	0.0901	0.242	0.580	1.262
45	0.0835	0.222	0.531	1.150
50	0.0783	0.207	0.491	1.061
55	0.0741	0.1942	0.459	0.988
60	0.0707	0.1837	0.432	0.928
65	0.0678	0.1750	0.410	0.876
70	0.0654	0.1675	0.390	0.833
75	0.0633	0.1611	0.374	0.796
80	0.0615	0.1555	0.359	0.763

(continued)

TABLE III (Continued)

SMOOTHED EQUILIBRIUM GAS AND LIQUID PHASE COMPOSITIONS FOR THE HELIUM-ARGON SYSTEM

- - -Solid-Gas Region- - -

T, °K	65	70	75	80
Vapor Pressure p_{01}, atm	0.02488	0.07149	0.1780	0.3949
Pressure atm	Mole Per Cent Argon $100y_1$			
85	0.0599	0.1506	0.347	0.734
90	0.0584	0.1462	0.336	0.709
95	0.0571	0.1422	0.326	0.687
100	0.0559	0.1385	0.316	0.667
105	0.0547	0.1351	0.308	0.648
110	0.0535	0.1318	0.300	0.632
115	0.0523	0.1286	0.293	0.616
120	0.0510	0.1255	0.286	0.601

- - -Liquid-Gas Region- - -

T, °K	85		90		95	
Vapor Pressure p_{01}, atm	0.7784		1.325		2.115	
	Mole Per Cent Argon (1) or Helium (2)					
Pressure P, atm	$100y_1$	$100x_2$	$100y_1$	$100x_2$	$100y_1$	$100x_2$
5	16.07	0.0304	27.3	0.0351	43.3	0.0358
10	8.32	0.0660	14.1	0.0822	22.5	0.0973
15	5.73	0.1012	9.73	0.1288	15.50	0.1578
20	4.43	0.1359	7.52	0.1746	11.99	0.218
25	3.65	0.1701	6.19	0.220	9.86	0.276

(continued)

TABLE III (Continued)

SMOOTHED EQUILIBRIUM GAS AND LIQUID PHASE COMPOSITIONS FOR THE HELIUM-ARGON SYSTEM

		- - -Liquid-Gas Region- - -				
T, °K	85		90		95	
Vapor Pressure p_{01}, atm	0.7784		1.325		2.115	
Pressure	Mole Per Cent Argon (1) or Helium (2)					
P, atm	$100y_1$	$100x_2$	$100y_1$	$100x_2$	$100y_1$	$100x_2$
30	3.12	0.204	5.30	0.264	8.44	0.334
35	2.74	0.237	4.65	0.308	7.41	0.392
40	2.46	0.270	4.17	0.352	6.63	0.448
45	2.24	0.302	3.79	0.395	6.02	0.504
50	2.06	0.334	3.48	0.437	5.53	0.558
55	1.915	0.366	3.23	0.479	5.12	0.612
60	1.794	-Solid-Gas-	3.02	0.520	4.79	0.666
65	1.692		2.84	0.560	4.50	0.718
70	1.604		2.69	0.600	4.25	0.770
75	1.529		2.56	0.640	4.04	0.821
80	1.464		2.45	0.679	3.86	0.872
85	1.407		2.35	0.717	3.70	0.921
90	1.356		2.26	0.755	3.55	0.970
95	1.312		2.18	0.793	3.43	1.019
100	1.272		2.12	0.830	3.31	1.066
105	1.236		2.05	0.866	3.21	1.114
110	1.203		2.00	0.902	3.12	1.160
115	1.173		1.95	0.938	3.04	1.206
120	1.145		1.90	0.973	2.97	1.251

(continued)

TABLE III (Continued)

SMOOTHED EQUILIBRIUM GAS AND LIQUID PHASE
COMPOSITIONS FOR THE HELIUM-ARGON SYSTEM

- - -Liquid-Gas Region- - -

T, ^{o}K	100		105		110	
Vapor Pressure p_{01}, atm	3.213		4.682		6.588	
Pressure atm	$100y_1$	$100x_2$	$100y_1$	$100x_2$	$100y_1$	$100x_2$
5	65.2	0.0284	93.9	0.0064		
10	33.9	0.1073	49.0	0.1061	67.9	0.0847
15	23.4	0.1849	33.9	0.204	47.1	0.207
20	18.14	0.261	26.3	0.301	36.6	0.328
25	14.94	0.337	21.7	0.396	30.2	0.447
30	12.78	0.411	18.55	0.490	25.9	0.564
35	11.22	0.484	16.30	0.582	22.8	0.679
40	10.04	0.556	14.58	0.673	20.4	0.792
45	9.12	0.627	13.23	0.763	18.52	0.904
50	8.37	0.698	12.14	0.851	16.99	1.014
55	7.75	0.767	11.23	0.938	15.71	1.122
60	7.23	0.835	10.47	1.024	14.64	1.229
65	6.79	0.902	9.82	1.109	13.71	1.334
70	6.41	0.968	9.26	1.192	12.92	1.438
75	6.08	1.033	8.78	1.274	12.23	1.539
80	5.79	1.097	8.35	1.355	11.62	1.640
85	5.54	1.161	7.98	1.434	11.08	1.739
90	5.32	1.223	7.65	1.513	10.60	1.836
95	5.12	1.285	7.35	1.590	10.18	1.932
100	4.95	1.345	7.09	1.666	9.80	2.03
105	4.79	1.405	6.86	1.742	9.46	2.12
110	4.65	1.464	6.65	1.816	9.16	2.21
115	4.53	1.523	6.46	1.889	8.88	2.30
120	4.41	1.580	6.29	1.961	8.64	2.39

(continued)

TABLE III (Continued)

SMOOTHED EQUILIBRIUM GAS AND LIQUID PHASE COMPOSITIONS FOR THE HELIUM-ARGON SYSTEM

- - -Liquid-Gas Region- - -

T, $^{\circ}$K	115		120		125	
Vapor Pressure p_{01}, atm	9.000		11.989		15.632	
Pressure atm	$100y_1$	$100x_2$	$100y_1$	$100x_2$	$100y_1$	$100x_2$
10	91.8	0.0324				
15	65.4	0.1906	84.0	0.1231		
20	51.2	0.343	66.8	0.319	83.5	0.226
25	42.4	0.489	55.7	0.506	70.7	0.470
30	36.3	0.631	48.1	0.685	61.5	0.700
35	31.9	0.768	42.4	0.857	54.7	0.919
40	28.6	0.901	38.1	1.022	49.4	1.126
45	26.0	1.031	34.7	1.180	45.2	1.324
50	23.9	1.157	32.0	1.334	41.8	1.514
55	22.2	1.281	29.7	1.484	38.9	1.697
60	20.7	1.402	27.8	1.629	36.5	1.873
65	19.47	1.521	26.2	1.771	34.5	2.04
70	18.42	1.639	24.8	1.911	32.7	2.21
T, $^{\circ}$K	130		135		140	
Vapor Pressure p_{01}, atm	20.009		25.207		31.321	
Pressure atm	$100y_1$	$100x_2$	$100y_1$	$100x_2$	$100y_1$	$100x_2$
20						
25	86.2	0.327				
30	76.0	0.633	90.2	0.401		
35	68.2	0.918	82.2	0.788	95.0	0.397
40	62.1	1.187	75.7	1.147	89.2	0.896

(concluded)

TABLE III (Concluded)

SMOOTHED EQUILIBRIUM GAS AND LIQUID PHASE COMPOSITIONS FOR THE HELIUM-ARGON SYSTEM

		- - -Liquid-Gas Region- - -				
T, ^{o}K		130		135		140
Vapor Pressure p_{01}, atm		20.009		25.207		31.321
Pressure atm	$100y_1$	$100x_2$	$100y_1$	$100x_2$	$100y_1$	$100x_2$
45	57.2	1.440	70.4	1.480		
50	53.1	1.679	66.0	1.790		
55	49.7	1.906	62.3	2.08		
60	46.9	2.12	59.2	2.36		
65	44.4	2.33	56.5	2.62		
70	42.3	2.53	54.2	2.86		

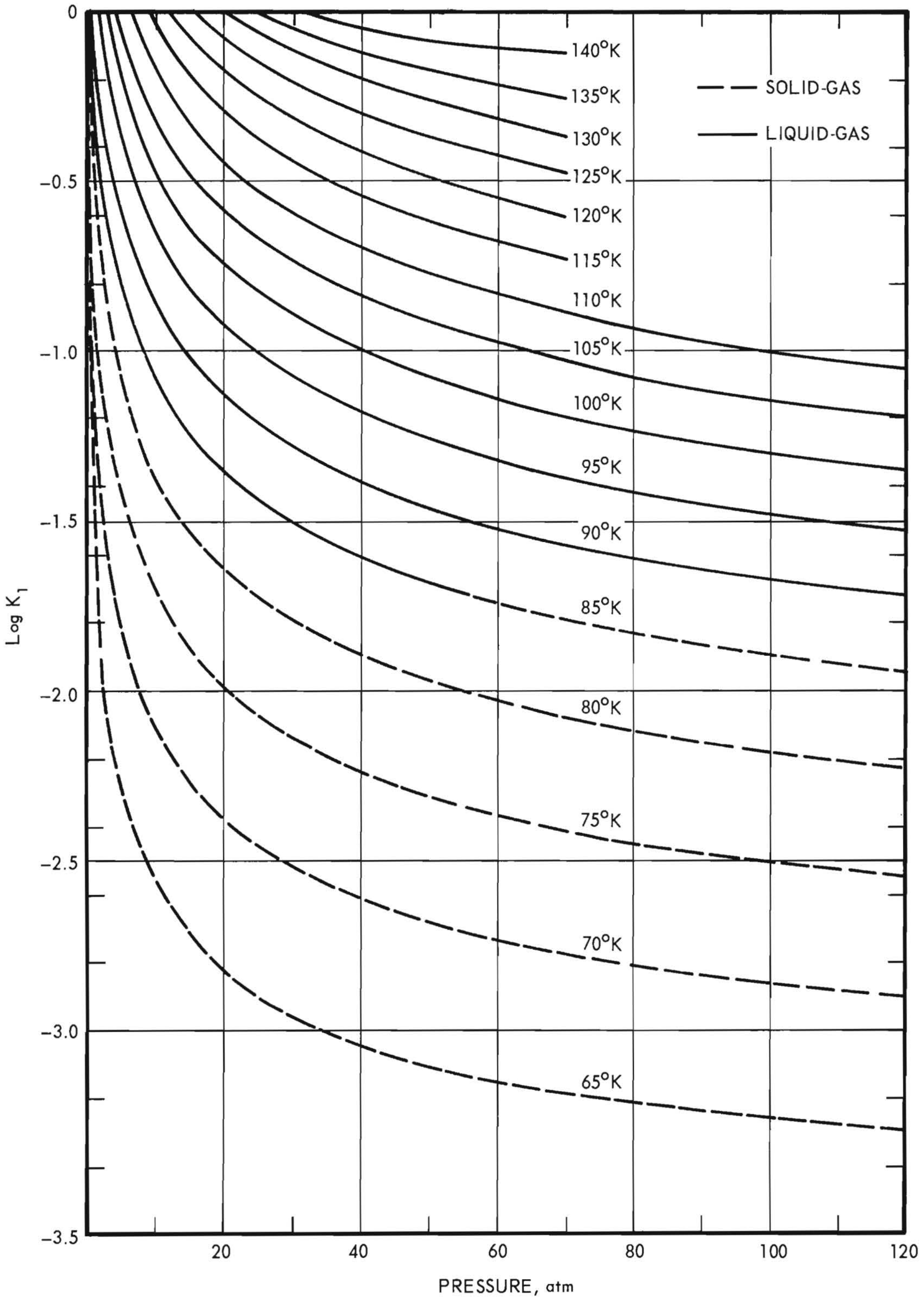

Figure 3. K Factor Chart for Argon.

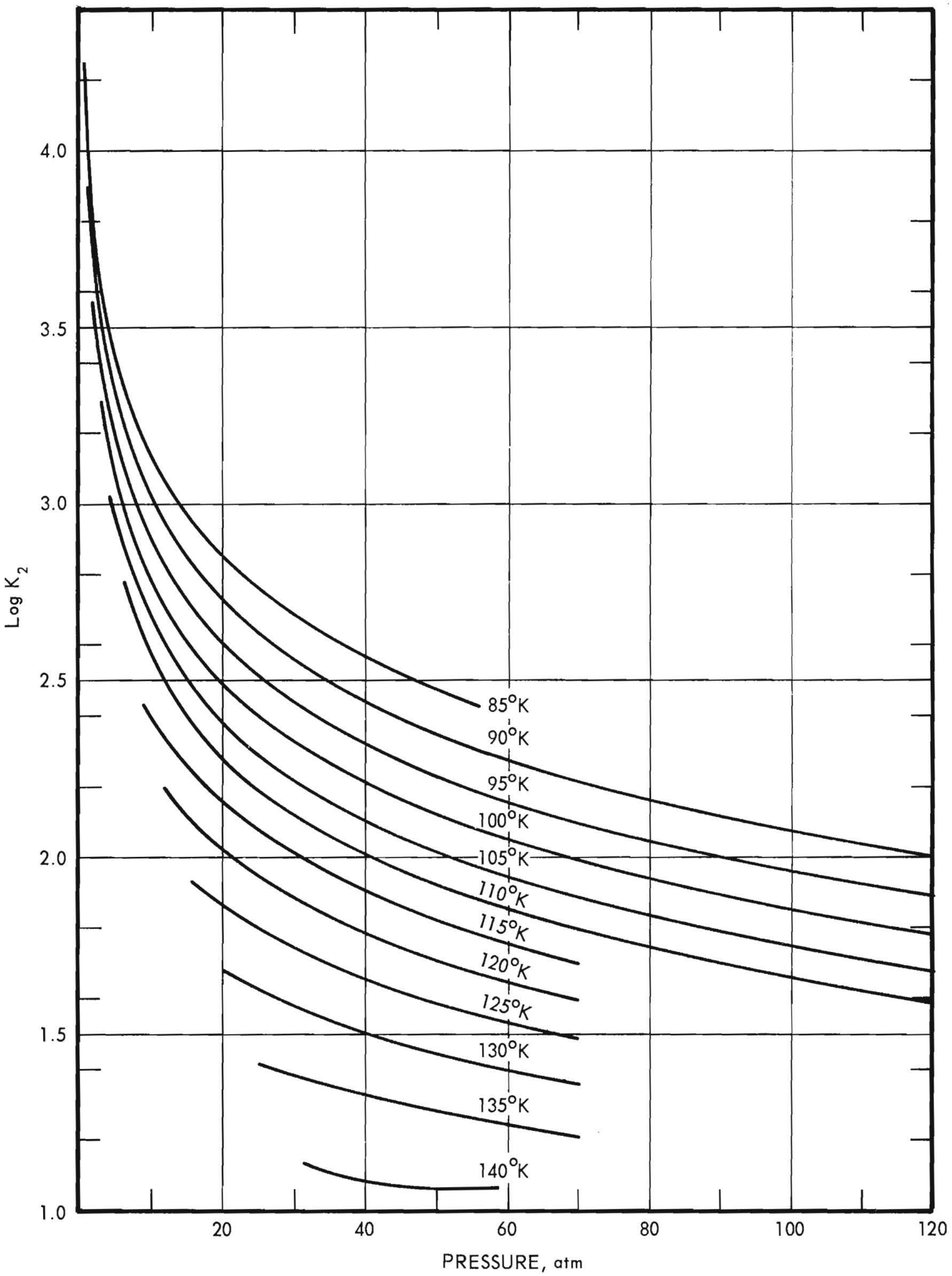

Figure 4. K Factor Chart for Helium.

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VII. APPENDICES

A. Nomenclature and Physical Constants

A_1, A_2, A_3 = constants in Equation (9).

b_o = parameter in Lennard-Jones (6-12) intermolecular potential function = $2\pi\sigma^3/3$.

B = second virial coefficient.

C = third virial coefficient.

C_j = weighting factor in least squares surface fit.

e = minimum potential energy between molecules in Lennard-Jones intermolecular potential function.

F_1, F_2, F_3 = functions in the Kihara core model for the second virial coefficient defined by Equation (22).

f_2 = fugacity of component 2 in gas mixture.

g = maximum power of x or y in orthogonal function.

H^o = a Henry's law constant defined by Equation (2).

H = a Henry's law constant defined by Equation (3).

h = Planck constant = 6.62377×10^{-27} erg sec/molecule.

K_i = y_i/x_i.

k = Boltzmann constant = 1.38038×10^{-16} erg/^{o}K molecule.

M = mass of atom.

M_o, S_o, V_o = parameters of Kihara core model related to core size and shape.

N_o = Avogadro's Number = 6.02380×10^{23} molecules/gm mole.

n = number of gram moles.

P = pressure.

p_{01} = vapor pressure of saturated argon at T.

p = maximum power of x in orthogonal function.

q = maximum power of y in orthogonal function.

A. Nomenclature and Physical Constants (concluded)

R = gas constant = 0.0820574 liter atm/gm mole °K.

T = temperature in degrees Kelvin. Ice Point = 273.15° K.

U = potential energy between molecules.

U_o = minimum potential energy between molecules for Kihara core model.

v_l = molal volume of condensed argon.

x,y,z = variables in general least squares surface fit.

x_i = mole fraction component i in the condensed phase.

y_i = mole fraction component i in the gas phase.

Z = compressibility factor. $Z = PV/RT$; also used as (U_o/kT) in F_1, F_2, and F_3.

α_{ij} = coefficients in orthogonal functions.

Λ^* = quantum mechanical parameter defined by Equation (25).

μ = reduced mass. Defined by Equation (31).

ρ = shortest distance between molecular cores for Kihara core model.

ρ_o = shortest distance between molecular cores at minimum potential energy for Kihara core model.

σ = separation of molecular centers at zero potential energy in Lennard-Jones intermolecular potential function.

Φ = enhancement factor. Defined by Equation (1).

ψ_j = function in set of orthogonal functions in least squares surface fit.

Subscripts

1 = component 1 = argon.

2 = component 2 = helium.

m = mixture of argon and helium.

max = maximum value of variable in data set.

B. Experimental Phase Equilibrium Data

In Tables IV through VIII are given the experimental data for the gas phase compositions (Mullins[23,24] and McCain[20]) and liquid phase compositions (Mullins,[23,24] McCain[20] and Karasz[11,12]) for the helium-argon system. These data are compared with the smoothed values computed from the final correlation given in Table III. The comparison of the experimental data is made in terms of the enhancement factor defined by Equation (1) and the Henry's law constant defined by Equation (3). This is equivalent to presuming that the reported temperature and pressure are correct and that the error is in the reported composition.

TABLE IV

EXPERIMENTAL BUBBLE-POINT DETERMINATIONS OF McCAIN[20]

Temperature ^{o}K	Pressure atm	Mole Per Cent Helium $100x_2$	H_{obs} $(P-p_{01})/x_2$	Per Cent Deviation[a] $100(H_{calc}-H_{obs})/H_{calc}$
140.37	54.2	2.050	1066	-2.37
145.85	54.8	2.050	777	5.70
136.26	55.3	2.050	1343	-4.01
130.77	58.4	2.050	1801	-1.96
123.24	66.6	2.050	2622	2.63
126.17	62.9	2.050	2275	0.69
143.67	42.8	0.746	794	-7.20
145.84	45.3	0.746	708	-4.73
147.69	47.4	0.746	641	3.05
139.00	37.9	0.746	1009	-4.69
143.60	42.6	0.746	796	-5.31
99.92	43.5	0.746	668	19.11[b]
109.46	36.7	0.746	4354	6.59
128.10	31.9	0.746	1768	-3.45
145.65	61.0	2.656	832	2.58
139.22	62.7	2.656	1209	-0.86
138.53	63.9	2.656	1264	-2.68
143.19	60.8	2.656	959	1.63
140.46	62.1	2.656	1127	-0.78
149.60	60.4	2.656	648	16.44
137.35	66.0	2.656	1361	-5.20
145.89	59.6	2.353	810	-3.64
140.27	60.0	2.353	1121	-7.35
148.79	59.0	2.353	673	9.15

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[a] H_{calc} calculated from least squares surface fit; constants from Table XIII.

[b] This point excluded in fitting and also in computing average deviation.

(continued)

TABLE IV (concluded)

EXPERIMENTAL BUBBLE-POINT DETERMINATIONS OF McCAIN[20]

Temperature ^{o}K	Pressure atm	Mole Per Cent Helium $100x_2$	H_{obs} $(P-p_{01})/x_2$	Per Cent Deviation $100(H_{calc}-H_{obs})/H_c$
135.06	62.6	2.353	1496	-6.05
129.92	68.1	2.353	1965	-4.18
135.10	47.9	1.632	1358	-1.89
139.91	48.7	1.632	1048	-2.33
139.78	48.6	1.632	1055	-2.07
124.99	51.3	1.632	2284	4.29
129.98	48.9	1.632	1777	0.33
115.33	68.4	1.632	3659	0.84
120.62	55.7	1.632	2828	6.20
143.86	51.5	1.632	851	-6.32
148.95	53.3	1.460	628	8.33
143.14	48.4	1.460	864	-0.85
137.92	46.1	1.460	1149	-3.99
110.86	69.2	1.460	4388	2.86
119.70	49.8	1.460	2885	9.76
130.15	45.1	1.460	1724	0.88

TABLE V

EXPERIMENTAL DEW POINT DETERMINATIONS OF McCAIN[20]

Temperature °K	Pressure atm	Mole Per Cent Helium $100y_2$	Φ_{obs} (Py_1/p_{01})	Per Cent Deviation[a] $100(\Phi_{calc}-\Phi_{obs})/\Phi_{calc}$
130.47	20.9	1.042	1.010	-2.5
134.50	25.3	1.042	1.015	-1.4
140.82	33.1	1.042	1.010	-[b]
142.47	35.5	1.042	1.012	-
144.53	38.6	1.042	1.012	-
147.45	43.7	1.042	1.020	-
150.04	48.9	1.042	1.033	-
150.48	50.2	1.042	1.043	-
149.96	48.5	1.042	1.028	-
150.62	52.9	1.042	1.094	-
110.00	14.0	45.36	1.161	-5.4
114.99	19.9	45.36	1.208	-6.3
119.31	27.1	45.36	1.283	-8.5
123.14	33.6	45.36	1.293	-6.6
128.06	43.3	45.36	1.298	-2.1
131.87	53.6	45.36	1.340	-0.6
135.01	64.2	45.36	1.391	-4.0
119.60	18.6	29.70	1.114	-1.3
122.42	22.2	29.70	1.141	-3.9
127.44	29.2	29.70	1.161	-2.6
131.96	37.9	29.70	1.214	-2.6
136.54	48.9	29.70	1.273	-
140.61	59.9	29.70	1.310	-
142.53	67.3	29.70	1.359	-

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[a] Φ_{calc} interpolated from Table III.

[b] Outside range of calculated values in Table III.

TABLE V (concluded)

EXPERIMENTAL DEW POINT DETERMINATIONS OF McCAIN[20]

Temperature ^{o}K	Pressure atm	Mole Per Cent Helium $100y_2$	Φ_{obs} (Py_1/p_{01})	Per Cent Deviation $100(\Phi_{calc}-\Phi_{obs})/\Phi_{calc}$
111.54	32.0	69.52	1.340	-9.6
116.65	45.5	69.52	1.398	-7.2
121.21	60.6	69.52	1.442	-3.1
123.18	70.0	69.52	1.499	-2.8
99.89	16.4	69.52	1.569	-39.2
106.83	62.9	84.84	1.790	-29.8
102.35	46.2	84.84	1.817	-41.0
99.88	38.7	84.84	1.843	-47.7
115.06	51.8	72.42	1.581	-18.3
118.49	67.3	72.42	1.684	-17.9
109.91	38.1	72.42	1.604	-27.8
104.94	28.4	72.42	1.680	-40.2
99.74	19.5	72.42	1.708	-49.2

TABLE VI

EXPERIMENTAL EQUILIBRIUM GAS PHASE COMPOSITIONS OF MULLINS[23,24]

Temperature ^{o}K	Pressure atm	Mole Per Cent Argon $100y_1$	Φ_{obs} (Py_1/p_{01})	Per Cent Deviation[a] $100(\Phi_{calc}-\Phi_{obs})/\Phi_{calc}$
80.03	120.48	0.589	1.788	-2.3
80.08	101.16	0.659	1.668	-1.6
80.01	80.90	0.752	1.539	-0.8
80.06	60.68	0.916	1.395	-1.3
80.07	41.57	1.220	1.271	-1.3
80.10	20.53	2.234	1.144	-0.3
73.96	115.88	0.2516	1.960	1.7
74.02	101.02	0.2706	1.818	0.4
74.16	81.50	0.3200	1.693	2.9
74.03	61.43	0.3665	1.495	1.0
73.91	41.16	0.476	1.329	0.6
73.90	19.96	0.855	1.159	1.1
74.02	120.34	0.2460	1.969	0.7
68.04	120.27	0.0891	2.225	0.3
68.10	100.07	0.0976	2.002	-1.5
68.07	79.73	0.1089	1.792	-1.1
68.08	60.00	0.1276	1.576	-1.1
68.07	40.07	0.1691	1.398	0.9
68.08	20.22	0.2849	1.186	-0.3
77.90	80.00	0.562	1.570	-0.0
77.90	60.14	0.680	1.430	0.3
91.99	80.20	2.947	1.471	0.0
91.99	60.30	3.616	1.357	-0.6
92.00	40.14	5.04	1.257	0.0
91.95	19.92	9.16	1.140	0.5
91.96	119.80	2.252	1.684	-1.2

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[a] Φ_{calc} computed from least squares fit using constants from Table XIV.

(continued)

TABLE VI (concluded)

EXPERIMENTAL EQUILIBRIUM GAS PHASE COMPOSITIONS OF MULLINS[23, 24]

Temperature ^{o}K	Pressure atm	Mole Per Cent Argon $100y_1$	Φ_{obs} (Py_1/p_{01})	Per Cent Deviation $100(\Phi_{calc}-\Phi_{obs})/\Phi_{cal}$
91.98	100.27	2.535	1.584	-0.1
97.50	120.07	3.583	1.641	-1.5
97.50	100.07	4.03	1.538	-1.0
97.51	80.00	4.70	1.432	-1.3
97.51	60.25	5.88	1.349	-0.4
97.51	40.04	8.21	1.252	-0.0
97.52	20.02	14.78	1.127	-0.4
97.50	60.20	5.84	1.342	-0.9
86.02	80.14	1.649	1.517	1.2
86.02	60.30	2.011	1.392	0.8
86.03	39.52	2.805	1.271	0.9
86.02	19.95	4.98	1.141	0.3
86.02	120.07	1.274	1.756	0.0
86.01	120.23	1.276	1.762	0.3
86.00	100.38	1.427	1.648	1.2
86.00	120.00	1.295	1.788	1.9
86.02	120.00	1.273	1.754	-0.0
108.01	120.00	7.71	1.602	0.8
108.01	100.07	8.77	1.520	1.4
108.04	80.00	10.34	1.430	0.9
108.04	60.00	12.90	1.338	0.1

TABLE VII

EXPERIMENTAL LIQUID PHASE COMPOSITIONS OF MULLINS[23,24]

Temperature °K	Pressure atm	Mole Per Cent Helium $100x_2$	$H_{obs} \times 10^{-2}$ $(P-p_{01})/x_2$	Per Cent Deviation[a] $100(H_{calc}-H_{obs})/H_{calc}$
91.99	80.20	0.756	104.0	0.4
92.00	60.41	0.580	101.4	0.2
92.00	40.14	0.387	99.6	-0.8
91.96	19.92	0.192	95.4	0.9
91.97	119.80	1.071	110.4	-0.4
91.96	100.27	0.917	107.6	-0.3
97.51	120.07	1.406	83.5	-0.3
97.50	100.07	1.212	80.4	0.9
97.50	80.00	0.985	78.6	0.5
97.52	60.20	0.756	76.2	0.7
97.51	40.14	0.499	75.2	-0.8
97.52	20.02	0.240	72.5	-0.0
97.51	60.20	0.748	77.0	-0.3
86.02	80.14	0.550	144.1	0.1
86.02	60.27	0.418	142.1	-1.0
86.03	39.52	0.283	136.6	0.2
86.00	19.97	0.143	133.6	0.0
86.01	19.97	0.143	133.6	-0.0
86.01	100.41	0.675	147.5	0.4
108.02	120.07	2.216	51.6	-0.0
108.03	100.07	1.879	50.2	-0.1
108.03	80.00	1.523	48.7	-0.1
108.04	60.00	1.145	47.3	-0.2

---

[a] H_{calc} calculated from least squares fit using constants from Table XII.

TABLE VIII

EXPERIMENTAL LIQUID PHASE COMPOSITIONS OF KARASZ[a]

Temperature °K	$P-p_{01}$ atm	Mole Fraction Helium $x_2 \cdot 10^5$	$H_{obs} \times 10^{-3}$ $(P-p_{01})x_2$	Per Cent Deviati $100(H_{calc}-H_{obs})/H_{c}$
84.05	0.13459	2.22	6.05	58.5
84.05	0.13603	2.20	6.18	57.6
84.54	0.07525	1.35	5.58	60.6
84.54	0.15013	2.69	5.58	60.6
85.20	0.13716	2.67	5.13	62.4
85.41	0.03866	1.268	3.05	77.4
85.41	0.08447	2.616	3.22	76.1
85.41	0.12808	4.399	2.91	78.4
85.41	0.17533	5.660	3.09	77.1
86.11	0.07663	1.65	4.63	64.2
86.11	0.14818	3.20	4.63	64.2
86.11	0.21199	4.58	4.66	64.0
86.45	0.13920	2.82	4.95	61.0
86.89	0.03267	0.77	4.24	65.8
86.89	0.10018	2.27	4.41	64.4
86.89	0.16579	3.59	4.61	62.8
87.53	0.14022	3.36	4.17	65.1
87.53	0.13896	3.33	4.17	65.1

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[a] The units and nomenclature of Karasz[11] have been changed to correspond with this work.

[b] H_{calc} calculated from least squares fit using constants from Table XII.

C. Selection of Physical Data Used in Correlation of Liquid and Gas Phase Compositions

1. General

The computation of Φ and H from Equations (1) and (3) required, in addition to experimental phase equilibrium values for x, y, P, and T, data for the vapor pressure of argon as a function of temperature.

The computation of Φ from Equation (10) required, in addition to the vapor pressure of argon, (1) the molal volume of liquid and solid argon as a function of temperature and pressure; (2) the second and third virial coefficients of argon and the second and third interaction virial coefficients of the helium-argon gas mixture as a function of temperature; (3) the composition of the condensed phase and the activity coefficient of argon in the condensed phase. The selection of these data is described in the following sections.

2. Vapor Pressure of Argon

The vapor pressure of argon below 88° K has been calculated by Ziegler, et al[28] and compared with the available experimental data. These calculated results have been fitted by Mullins to two equations applicable from 65° to 88° K.

The calculated data of Ziegler, et al[28] were adjusted slightly by the ratio of the oxygen point used by Mullins (90.18° K), and the oxygen point used by Ziegler, et al (90.168° K).

For

$T \leq 83.81^{\circ}$ K

$$\log p_{01}(\mathrm{atm}) = 5.9057813 - \frac{740.68409}{T} + \frac{35110.773}{T^2} - \frac{1661065.3}{T^3} + \frac{28979491.0}{T^4} \tag{14}$$

For

$83.81 \leq T \leq 88.0^{\circ}$ K

$$\log p_{01}(\mathrm{atm}) = 3.7109859 - \frac{298.12324}{T} - \frac{2257.2649}{T^2} \tag{15}$$

Above 88° K the vapor pressure of argon was represented by an equation reporte by Michels, et al.[21]

$$\log p_{01}(\mathrm{atm}) = -\frac{550.8211}{T} - 8.7849395 \log (T) + 0.0174713(T) + 21.83790 \tag{16}$$

3. Molal Volume of Condensed Argon

a. Liquid Argon. The density of liquid argon as a function of temperature and pressure has been determined by van Itterbeek and Verbeke[26] from 86.6° K to 90.5° K and by van Itterbeek, et al[27] from 90° to 148° K. These values are in good agreement with the saturated densities reported by Mathias, et al[19] from 90° to 148° K. The earlier density values of Baly and Donnan[2] from 84.5° to 89° K are about 0.7 per cent higher than those of van Itterbeek and Verbeke.[26] The data of van Itterbeek and Verbeke[26] and van Itterbeek, et al[27] have been fitted from 86.6° to 130.85° K and pressures to 150 atmospheres by Mullins[23] using the least squares surface fit as describe in Appendix D in which the variables were:

$$x = (P-p_{01})/(P-p_{01})_{max} \tag{17}$$

$$y = T/T_{max} \tag{18}$$

$$z = v_1/(v_1)_{max} \tag{19}$$

The data from 130.85° to 146.63° K and pressures up to 160 atmospheres have been fitted here using the same method. The data were fitted up to 130° K with an average deviation of 0.074 cc/gm mole. Above 130° K the average deviation was 0.145 cc/gm mole. From the least square surface fits, the value of the coefficients A_1, A_2, and A_3 in Equation (9) were determined for each temperature at which the calculation of the enhancement factors were made. The values of these coefficients are given in Table IX.

b. <u>Solid Argon</u>. For the calculation of the enhancement factor from Equation (10) the molal volume of solid argon was assumed to be incompressible. The value of the molal volumes used in the calculations are given in Table X. These values are the same ones used by Mullins[23] and are based on the values given by Dobbs, et al,[7] Clusius and Weigand,[5] and Henshaw.[9]

4. Virial Coefficients of Argon and Helium

a. <u>General</u>. The calculation of Φ from Equation (10) requires that the second and third virial and virial interaction coefficients be known as a function of temperature. The approach used in the present paper has been to compute the second virial and second virial interaction coefficients for helium

TABLE IX

COEFFICIENTS OF EQUATION (9) USED TO REPRESENT THE MOLAL VOLUME OF LIQUID ARGON

Temperature $^{\circ}K$	$A_1 \cdot 10^2$ liters/gm mole	$A_2 \cdot 10^5$ liters/gm mole atm	$A_3 \cdot 10^8$ liters/gm mole atm^2
85	2.8376544	-0.74713828	2.7431250
90	2.9066305	-0.97441015	2.7430468
95	2.9822848	-1.2016921	2.7431250
100	3.0646175	-1.4289687	2.7431250
105	3.1536285	-1.6562476	2.7431250
110	3.2493169	-1.8835218	2.7431250
115	3.3516860	-2.1108132	2.7431250
120	3.4607303	-2.3380687	2.7431250
125	3.5764544	-2.5653500	2.7431250
130	3.6988576	-2.7926257	2.7430468
135	3.9536852	-6.0946968	18.879609
140	4.1755423	-7.1804382	18.879609
145	4.4011321	-8.2661687	18.879531

TABLE X

MOLAL VOLUME OF SOLID ARGON

T $^{\circ}K$	Molal Volume cc/gm mole
65	23.82
70	24.01
75	24.21
80	24.42

and argon using a Kihara core model[13] and to compute the third virial and third virial interaction coefficients using the Lennard-Jones (6-12) potential function following the method described by Hirschfelder, et al.[10] The parameters used in these calculations are given in Table XI.

<u>b. Second Virial Coefficients</u>. Kihara[13] has derived general expressions for the second virial coefficient of gases assuming an impenetrable core for the gas molecule rather than the point center model used in the Lennard-Jones model. This core may be any convex shaped model and is normally determined from the geometry of the molecule. The potential energy is written as a function of the shortest distance between molecular cores, which for the (6-12) intermolecular potential function is

$$U = U_o\left[\left(\frac{\rho_o}{\rho}\right)^{12} - 2\left(\frac{\rho_o}{\rho}\right)^{6}\right] \tag{20}$$

The second virial coefficient is then written as

$$\frac{B}{N_o} = \frac{2\pi}{3}\rho_o^3 F_3 + M_o\rho_o^2 F_2 + \left(S_o + \frac{M_o^2}{4\pi}\right)\rho_o F_1 + \left(V_o + \frac{M_o S_o}{4\pi}\right) \tag{21}$$

The functions F_1, F_2 and F_3 are functions of $Z(Z = U_o/kT)$ and may be obtained from tabulated results* or calculated from Equation (22).

$$F_s = -\frac{s}{12}\sum_{t=0}^{\infty}\left[\frac{2^t}{t!}\Gamma\left(\frac{6t-s}{12}\right)\right]Z^{(6t+s)/12} \tag{22}$$

The parameters M_o, S_o and V_o can be calculated directly from the size and shape of the core.

Prausnitz and Myers[25] have obtained parameters for the Kihara core model for a number of gases. The parameters reported by them for helium and argon

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*The functions have been tabulated by Connolly and Kandalic[6] with Z as the argument from 0.01 to 7.0 in steps of 0.01.

are given in Table XI. They included a correction for the quantum effects on the second virial coefficient of helium and other gases which exhibit quantum effects at the temperatures of the experimental data. The second virial coefficient for these gases is expressed as

$$B = B_{\mathrm{Kihara}} + B_{\mathrm{quantum}} \tag{23}$$

The correction for the quantum effects due to translation only can be written as a series expansion in Λ^*, which is valid for helium above about 40° K.

$$B_{\mathrm{quantum}} = \frac{2}{3} \pi N_o \sigma^3 \left[\Lambda^{*2} B_I^* + \Lambda^{*4} B_{II}^* + \ldots - \Lambda^{*3} B_o^* \right] \tag{24}$$

$$\Lambda^* = \frac{h}{\sigma \sqrt{M U_o}} \tag{25}$$

Equations (24) and (25) are for the Lennard-Jones (6-12) potential function and are strictly valid only for a vanishing core. The relation between σ and ρ_o, which is exact for the spherical cores used here is

$$\sigma = 2^{-1/6} \rho_o + \frac{M_o}{2\pi} \tag{26}$$

The coefficients B_I^*, B_{II}^* and B_o^* arefunctions of (1/Z) and are tabulated by Hirschfelder, et al.[10] Presumably, this was the source used by Prausnitz and Myers[25] for the fit of the parameters of helium. Unfortunately, there is an error in these tables which has been discussed by Kirk,[15] who gives corrected and extended tables. These corrected tables have been used here, though the difference is slight.

TABLE XI

PARAMETERS USED FOR CALCULATING THE VIRIAL COEFFICIENTS OF ARGON AND HELIUM

	Kihara Core Model					Lennard-Jones (6-12)	
	U_o/k	ρ_o	M_o	S_o	V_o	e/k	b_o
Substance	°K	Å	Å	Å^2	Å^3	°K	cc/gm mole
Argon	146.10	3.328	2.199	0.3848	0.02245	119.3	50.91
Helium	9.927	2.921	0	0	0	7.022	23.16

c. Second Virial Interaction Coefficient. In order to calculate the second virial interaction coefficient, B_{ij}, Prausnitz and Myers[25] rewrite Equation (21).

$$\frac{B_{ij}}{N_o} = \frac{2\pi}{3}\rho_{oij}^3 F_3 + \frac{M_{oi} + M_{oj}}{2}\rho_{oij}^2 F_2 + \left(\frac{S_{oi} + S_{oj}}{2} + \frac{M_{oi}M_{oj}}{4\pi}\right)\rho_{oij} F_1$$

$$+ \frac{V_{oi} + V_{oj}}{2} + \frac{M_{oi}S_{oj} + M_{oj}S_{oi}}{8\pi} \tag{27}$$

where

$$\rho_{oij} = \frac{(\rho_{oi} + \rho_{oj})}{2} \tag{28}$$

$$U_{oij} = \sqrt{U_{oi}U_{oj}} \tag{29}$$

For the calculation of the translational quantum correction

$$\Lambda^*_{ij} = \frac{h}{\sigma_{ij}\sqrt{2\mu_{ij}U_{oij}}} \tag{30}$$

where

$$\frac{1}{\mu_{ij}} = \left(\frac{1}{M_i} + \frac{1}{M_j}\right) \tag{31}$$

and

$$\sigma_{ij} = 2^{-1/6}\ \rho_{oij} + \frac{M_{oi} + M_{oj}}{4\pi} \tag{32}$$

Values of B_{12} computed from Equations (27)-(32) using the parameters of Prausnitz and Myers given in Table XI are shown as Curve A in Figure 5.

Mullins[23] has used his phase equilibrium data, together with Equation (10) and the parameters of Table XI for the second virial coefficient of pure helium and argon, to compute "experimental" values for B_{12}.

For each temperature, the value of B_{12} was computed at each experimental pressure. The limiting value of B_{12} at $P-p_{01} = 0$ was determined graphically. These limiting values of B_{12} are shown in Figure 5 compared with the one low temperature value of B_{12} at 90° K determined by Knobler, et al[17] as corrected by Prausnitz and Myers.[25] This value of B_{12} was determined by observing the pressure change on mixing helium and argon and a knowledge of the second virial coefficients of helium and argon. Prausnitz and Myers corrected the value of B_{12} reported by Knobler, et al[17] from +6.6 to + 0.4 cc/gm mole using the second virial coefficients of pure argon and helium calculated from the Kihara core model.

The disagreement between the "experimental" values of B_{12} and the B_{12} calculated from Equations (27)-(32) suggested that an empirical adjustment of $(U_o/k)_{12}$ might provide a means of improving the representation of B_{12} as a function of temperature. Curve B in Figure 3 was calculated in the same way as Curve A except that the value of 38.08° K given by Equation (29) was

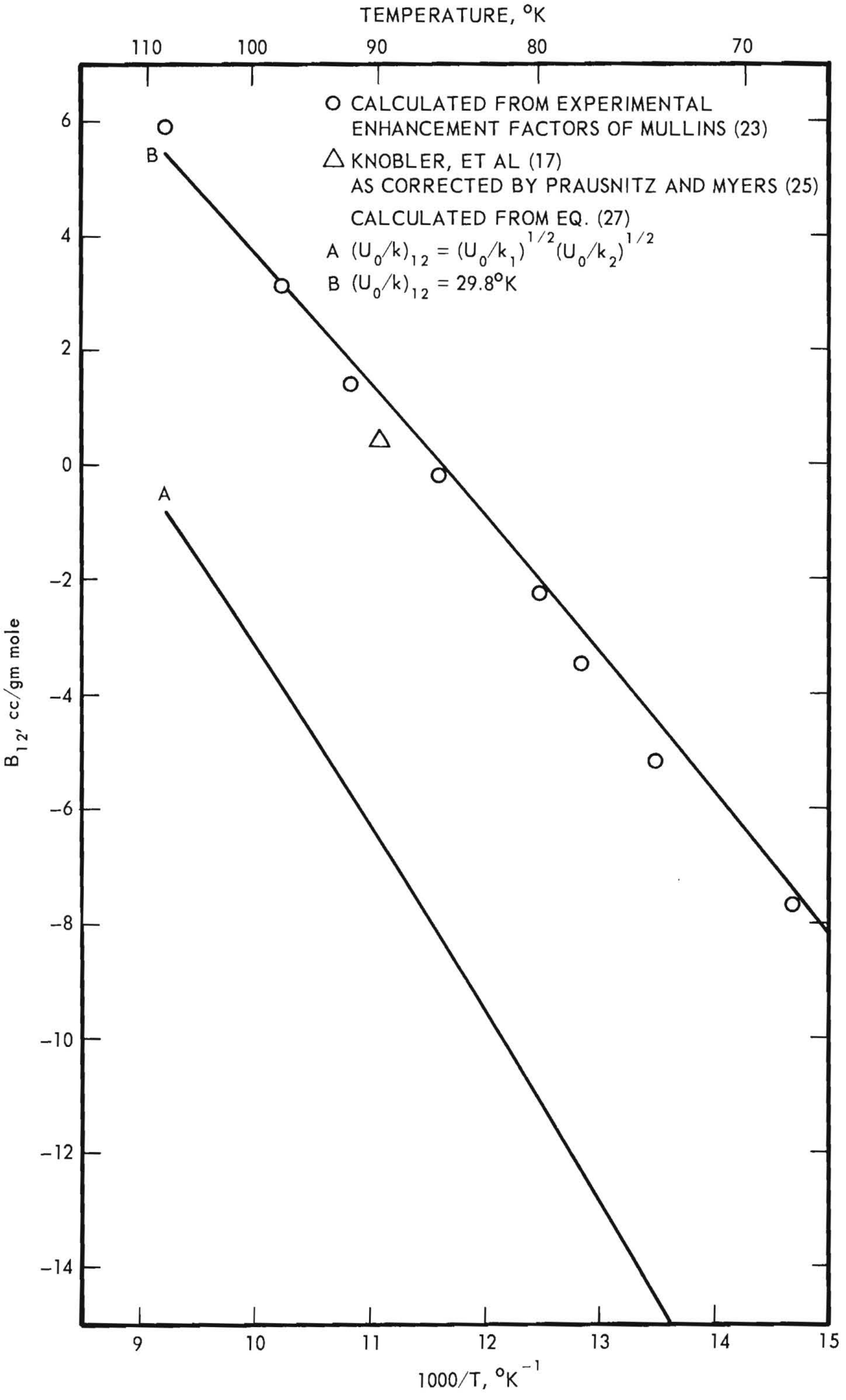

Figure 5. Second Virial Interaction Coefficient of Helium-Argon.

arbitrarily adjusted to a value of 29.8° K. This arbitrary adjustment is in the direction one would expect. Prausnitz and Myers remark that the geometric average can be shown to give too large a value for $(U_o/k)_{12}$ in molecules with greatly different values of (U_o/k).

In all calculations involving Equation (10) B_{12} was computed using Equations (27)-(32) and the parameters of Table XI except that the adjusted value of $(U_o/k)_{12}$ was taken to be 29.8° K.

d. Third Virial Coefficients. The third virial coefficients were calculated from the Lennard-Jones (6-12) potential function using the method described by Hirschfelder, et al.[10] No quantum corrections were made for the third virial coefficient. The parameters for the Lennard-Jones (6-12) potentia function were taken from Levelt[18] and McCain[20] for argon and helium respectivel Values of the parameters used for computing the third virial and third virial interaction coefficients in Equation (10) are given in Table XI.

5. Activity Coefficient of Argon in the Liquid Phase

Measurements of Mullins[23] (See Table II) along the three-phase line suggest that the activity coefficient of argon in the liquid phase is very nearly unity in the temperature range 84.22° to 86.32° K even up to pressures of 120 atm where the concentration of helium in the liquid phase is 0.799 mole per cent. In all calculations of the enhancement factor from Equation (10) the activity coefficient has been arbitrarily set equal to unity. This assumption appears to be reasonable since the concentration of helium in the liquid phase never exceeds 3 mole per cent in the temperature and pressure region covered by the computations.

D. Least Square Surface Fit Using Orthogonal Functions*

Several times in the course of this investigation a method of fitting data on a thermodynamic surface was needed in order to obtain or compare values at other points on the surface. Since, in general, the data are not at evenly spaced intervals, and are not smoothed data, no simple interpolation scheme was suitable. The method used here is a modification of the method described by Bain,[1] who fitted P-V-T data for steam by a least squares approach in which the compressibility was represented by a double finite series in density and inverse temperature.

Bain's method was slightly modified to permit a truncation of one independent variable. The method is then as follows. A set of (M + 1) functions $\{\psi_k(x,y)\}$ are said to be orthogonal over a data set consisting of N data points (x_i, y_i, z_i) if the following equation is satisfied.

$$\sum_{i=1}^{N} \psi_j(x_i,y_i)\psi_k(x_i,y_i) = 0 \quad (j \neq k) \tag{33}$$

Given a set of functions, orthogonal with respect to a particular data set, the value of the dependent variable z, can be represented as

$$z = \sum_{j=0}^{M} C_j \psi_j(x,y) \tag{34}$$

The C_j are weighting factors which are determined by the criteria used to fit z_i. In this case they were found by requiring that the sum of the squares of the residuals,

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* The description appearing here was taken from the thesis of Mullins[23] with only the equation and reference numbers changed.

$$\sum_{i=1}^{N} R_i^{\ 2} = \sum_{i=1}^{N} \left[z_i - \sum_{j=0}^{M} C_j \psi_j \ (x_i, y_i) \right]^2 \tag{35}$$

be minimized. Equating the partial derivatives with respect to each of the weighting factors, C_j, equal to zero, results in the following solution for each C_j.

$$C_j = \sum_{i=1}^{N} z_i \psi_j (x_i, y_i) / \sum_{i=1}^{N} \psi_j (x_i, y_i) \psi_j (x_i, y_i); \ j=0,\ 1,\ 2,\ \ldots,\ M \tag{36}$$

The set $\{\psi_j\}$ may be generated in a number of ways. The method used here is described as follows. Let p and q be the maximum powers of x and y, respectively, occurring in the set $\{\psi_j\}$. Further, let $p \geq q$. The set $\{\psi_j\}$ contains terms $x^m y^n$ such that $0 \leq m \leq p$ and $0 \leq n \leq q$. Let $\{g\}$ be a subset of $\{\psi_j\}$ such that $\{g\}$ consists of all the ψ_j's containing terms with a maximum power (m+n) of g. The orthogonal functions are then generated in the following manner

$$\begin{array}{lll}
g = 0 & \psi_0 & = 1.0 \\
g = 1 & \psi_1 & = x - \alpha_{0,1}\psi_0 \\
 & \psi_2 & = y - \alpha_{0,2}\psi_0 - \alpha_{1,2}\psi_1 \\
g = 2 & \psi_3 & = x^2 - \alpha_{0,3}\psi_0 - \alpha_{1,3}\psi_1 - \alpha_{2,3}\psi_2 \\
 & \psi_4 & = xy - \alpha_{0,4}\psi_0 - \alpha_{1,4}\psi_1 - \alpha_{2,4}\psi_2 - \alpha_{3,4}\psi_3 \\
 & \psi_5 & = y^2 - \alpha_{0,5}\psi_0 - \alpha_{1,5}\psi_1 - \alpha_{2,5}\psi_2 - \alpha_{3,5}\psi_3 - \alpha_{4,5}\psi_4 \\
 & & \vdots \\
g = q & \psi_r & = x^q - \alpha_{0,r}\psi_0 - \ldots \alpha_{r-1,r}\psi_{r-1} \qquad ; \ r = g(g+1)/2 \\
 & \psi_{r+1} & = x^{q-1}y^1 - \alpha_{0,r+1}\psi_0 - \ldots \alpha_{r,r+1}\psi_r \qquad 0 \leqq g \leqq q \\
 & & \vdots
\end{array}$$

$$\psi_{r+g} = y^q - \alpha_{0,r+g}\psi_0 - \dots \alpha_{r+g-1,r+g}\psi_{r+g-1}$$

$$\vdots$$

$$> q \quad \psi_r = x^g - \alpha_{0,r}\psi_0 - \dots \alpha_{r-1,r}\psi_{r-1} \; ; \; r = (q+1)(2g-q)/2$$

$$\psi_{r+1} = x^{g-1}y^1 - \alpha_{0,r+1}\psi_0 - \dots \alpha_{r,r+1}\psi_r \quad q \leqq g \leqq p$$

$$\vdots$$

$$\psi_{r+q} = x^{g-q}y^q - \alpha_{0,r+q}\psi_0 - \dots \alpha_{r+q-1,r+q}\psi_{r+q-1}$$

The orthogonal coefficients, α_{ij} , are determined from the requirement of rthogonality. The coefficients for the first group, $g = 1$, are given below.

$$\alpha_{0,1} = \frac{\Sigma\, x_i\, \psi_0}{\Sigma\, \psi_0\, \psi_0}$$

$$\alpha_{0,2} = \frac{\Sigma\, y_i\, \psi_0}{\Sigma\, \psi_0\, \psi_0} \qquad \alpha_{1,2} = \frac{\Sigma\, y_i \psi_1(x_i)}{\Sigma\, \psi_1(x_i)\psi_1(x_i)} \tag{37}$$

The advantages of using a fitting scheme as described above are several. In general, less error due to loss of significant figures is incurred than is normally the case for schemes which require matrix inversion. Another advantage is that the power of the fitting function can be increased without recalculating any of the previously calculated C_j and α_{ij}. One disadvantage may occur if it is necessary to convert the coefficients and weighting factors of the orthogonal functions to the coefficients of the power series. Not only can this be quite involved, but a loss of accuracy may result.

E. Correlation of Liquid and Gas Phase Equilibrium Data

1. Liquid Phase Correlations

The experimental liquid phase equilibrium data were expressed in terms of the Henry's law constant defined by Equation (3) and fitted to analytical expressions in the form of a power series in the two independent variables $(P-p_{01})$ and $1/T$, using the least squares method described in Appendix D.

The analytical function fitted for the range 83.81° to 110° K made use of the experimental data of Mullins[23,24] for the liquid phase. The values of the dependent variable z and the two independent variables x and y used in this fit are given below

$$x = (P-p_{01})/(P-p_{01})_{max} \tag{38}$$

$$y = (1/T)/(1/T)_{max} \tag{39}$$

$$z = [\log(H)-2]\,/\,[\log(H)-2]_{max} \tag{40}$$

Values of the orthogonal coefficients, the weighting factors, and the normalizing constants reported by Mullins[23] are given in Table XII. The equation whic was selected to represent the least squares fit was one which was truncated wit $p = 2$ and $q = 2$, i.e., the maximum power of x and y respectively.

A similar analytical function was fitted to the experimental liquid phase composition data (86.00° to 108.04° K) (Table VII) of Mullins[23] (weighted twice and the bubble-point data (109.46° to 149.6° K)(Table IV) of McCain[20] (weighted once). The values of the dependent variable z, and the two independent variables x and y are given below.

TABLE XII

COEFFICIENTS, WEIGHTING FACTORS AND NORMALIZING CONSTANTS FOR LEAST SQUARE FIT OF HENRY'S LAW CONSTANT FOR HELIUM IN ARGON. SELECTED LIQUID PHASE DATA OF MULLINS

Coefficients, α_{ij}

j	1	2	3	4	5
	0.56115578	0.91160368	0.38939987	0.50595465	0.83578360
		-0.75125434(-1)	0.11233292(+1)	0.87582371	-0.13541417
			0.11073534	0.59610957	0.18037185(+1)
				-0.93705141(-1)	-0.39941218(-2)
					-0.14065213

Weighting Factors, C_j

j	0	1	2
	0.90105686	-0.47653714(-1)	0.10587829(+1)
j	3	4	5
	0.19665421(-2)	0.42012667(-1)	-0.45548984

Normalizing Constants

$(P-p_{01})_{max}$ = 0.118196645(+3); $(1/T)_{max}$ = 0.11627906(-1)

$[Log(H)-2]_{max}$ = 0.21686921(+1)

$$x = (1/T)/(1/T)_{max} \qquad (41$$

$$y = (P-p_{01})/(P-p_{01})_{max} \qquad (42$$

$$z = [\log(H)-2] / [\log(H)-2]_{max} \qquad (43$$

In this representation the independent variables were reversed. The fit was one which was truncated at $p = 3$, $q = 2$ (maximum power of x and y respectively. The values of the orthogonal coefficients, the weighting factors and the normal zing constants are given in Table XIII.

TABLE XIII

COEFFICIENTS, WEIGHTING FACTORS AND NORMALIZING CONSTANTS FOR LEAST SQUARES FIT OF HENRY'S LAW CONSTANT FOR HELIUM IN ARGON. COMBINED LIQUID PHASE DATA OF McCAIN AND MULLINS

Coefficients, α_{ij}

j	1	2	3	4
0	0.78589472	0.40563154	0.64015505	0.34114468
1		0.99275276	0.15718265(+1)	0.11128888(+1)
2			-0.30519739(-1)	0.85400522
3				0.14171184(+1)

j	5	6	7	8
0	0.24059811	0.53849872	0.29317083	0.20926314
1	0.89585084	0.18857668(+1)	0.11648950(+1)	0.88329634
2	0.10446846(+1)	-0.73518652(-1)	0.73124915	0.90547127
3	0.18443491(+1)	0.23884330(+1)	0.26445612(+1)	0.27281684(+1)
4	0.79667458	-0.32770603(-1)	0.16500554(+1)	0.14655201(+1)
5		-0.64329597(-2)	-0.32637632(-1)	0.82284982
6			0.11268652(+1)	0.13807143(+1)
7				0.22499337(+1)

Weighting Factors, C_j

j	0	1	2	3
	0.72416415	0.13935428(+1)	0.83014327(-1)	-0.16076656(+1)

j	4	5	6	7
	-0.37961793	-0.80264824(-1)	0.56923238(+1)	0.21615633(+1)

j	8
	0.41078823

(continued)

TABLE XIII (concluded)

COEFFICIENTS, WEIGHTING FACTORS AND NORMALIZING CONSTANTS FOR LEAST SQUARES FIT OF HENRY'S LAW CONSTANT FOR HELIUM IN ARGON. COMBINED LIQUID PHASE DATA OF McCAIN AND MULLINS

Normalizing Constants

$(1/T)_{max}$ = 0.11627906(-1); $(P-p_{01})_{max}$ = 0.11819645(+3)

$[\log(H)-2]_{max}$ = 0.21686921(+1)

2. Gas Phase Correlations

From 65° to 110° K the values of y_1 reported in Table III were calculated from the least squares surface fit to the gas phase composition data Table VI) of Mullins.[23] The least squares fit developed by Mullins[23] was of he same general type as that used for the liquid composition correlation and escribed in Appendix D. The variables used were

$$x = (P-p_{01})/(P-p_{01})_{max} \tag{44}$$

$$y = (1/T)/(1/T)_{max} \tag{45}$$

$$z = [\log(\Phi)/(P-p_{01})] \,/\, [\log(\Phi)/(P-p_{01})]_{max} \tag{46}$$

he orthogonal coefficients, the weighting factors and the normalizing constants re given in Table XIV. The best fit was obtained for $p = 3$, $q = 3$. The average deviation of $\log(\Phi)/(P-p_{01})$ from the experimental data was 0.000053 corresonding to an average deviation of 0.83 per cent in y_1.

Over the range 115° to 140° K and up to 70 atm, Equation (10) was used as he correlating function to compute Φ, and hence y_1, as a function of temperaure and pressure. This approach was dictated partly because of the difficulty f fitting the scattered dew-point data of McCain[20] and partly because of the arge uncertainty in these data near 110° K. Furthermore, the values of Φ comuted from Equation (10) were shown to agree very well with the experimental ata of Mullins in the temperature range below 108° K, the maximum error in Φ eing 3 per cent at 70 atm and 4.5 per cent at 120 atm, both at 108° K.

TABLE XIV

COEFFICIENTS, WEIGHTING FACTORS AND NORMALIZING CONSTANTS
FOR LEAST SQUARE FIT OF THE ENHANCEMENT FACTOR OF ARGON
IN HELIUM. SELECTED GAS-PHASE DATA OF MULLINS

Coefficients, α_{ij}

i j	1	2	3	4	5
0	.62045127	.81365544	.46394791	.50405238	.67409965
1		-.98887927(-2)	.11964232(+1)	.81468159	-.17177829(
2			.44024294(-1)	.61382117	.16436560(
3				-.64197867(-2)	-.21832444(
4					-.48056356(
5					
6					
7					
8					

j	6	7	8	9
0	.38236014	.37709004	.41688902	.56831476
1	.12142656(+1)	.97702080	.67392190	-.22941423(-1)
2	.81112722(-1)	.48380258	.10054272(+1)	.20507637(+1)
3	.17389383(+1)	.80948843	-.25258523(-1)	-.51449988(-1)
4	.22558742(-1)	.11871133(+1)	.16366201(+1)	-.11378367
5	-.71075817(-1)	.11787410	.64950233	.24490852(+1)
6		.45448357(-1)	-.29169182(-1)	.33321332(-2)
7			-.52040109(-1)	-.19854891(-1)
8				.61305645(-2)

(continued)

TABLE XIV (concluded)

COEFFICIENTS, WEIGHTING FACTORS AND NORMALIZING CONSTANTS FOR LEAST SQUARE FIT OF THE ENHANCEMENT FACTOR OF ARGON IN HELIUM. SELECTED GAS-PHASE DATA OF MULLINS

Weighting Factors, C_j

j	0	1	2	3	4
	.68073551	-.29441770	.80019809	.24266136	.22585073
	5	6	7	8	9
	.262944435(+1)	-.30757094	-.14714614(+1)	-.29673696(+1)	.68741501(+1)

Normalizing Constants

$(P-p_{01})_{max}$ = .12022184(+3) $(1/T)_{max}$ = .14697236(-1) $(\frac{\log \Phi}{P-p_{01}})_{max}$ = .36727528(-2)

FINAL REPORT

PROJECT NO. A-764

CORRELATION OF VAPOR PRESSURES OF PURE SUBSTANCES AND PHASE EQUILIBRIA AT LOW TEMPERATURES

W. T. ZIEGLER

Contract No. CST-1154
National Standard Reference Data Program
National Bureau of Standards
U. S. Department of Commerce
Washington, D. C.

March 22, 1965

Georgia Institute of Technology
Engineering Experiment Station
Atlanta, Georgia

This contract extended from January 1, 1964 through December 31, 1964. Because of certain unavoidable delays resulting from moving into a new building, printing of the last two technical reports was delayed until February, 1965.

The stated objectives of this contract were (1) the computation of the vapor pressures of several pure substances from thermodynamic relations using thermodynamic data existing in the published literature and (2) the correlation of the phase equilibria of the helium-argon systems. The results of these studies have been presented in three technical reports as follows:

Technical Report No. 1

Calculation of the Vapor Pressures and Heats of Vaporization and Sublimation of Liquids and Solids Below One Atmosphere Pressure VI. Krypton. W. T. Ziegler, D. W. Yarbrough and J. C. Mullins (dated July 15, 1964).

Technical Report No. 2

Calculation of the Vapor Pressure and Heats of Vaporization and Sublimation of Liquids and Solids Below One Atmosphere Pressure. VII. Ethane. W. T. Ziegler, B. S. Kirk, J. C. Mullins and A. R. Berquist (dated December 31, 1964).

Technical Report No. 3

The System-Helium-Argon from 65° to 140° K up to Pressures of 120 Atm. Correlation of Available Phase Equilibrium Data. J. C. Mullins and W. T. Ziegler (dated January 10, 1965).

Twenty copies of each of these reports were transmitted to the sponsor. In addition, 300 copies each of Technical Reports 1 and 2 were prepared for the Cryogenic Data Center, National Bureau of Standards, Boulder, Colorado, by separate arrangement with this group. (Mr. V. J. Johnson).

In addition, the literature on acetylene and xenon were examined. The data found for acetylene were insufficient to permit the desired vapor pressure computations to be made. Sufficient data were found to permit making vapor pressure calculations for xenon. However, insufficient time and funds were available to complete a report on this substance. It is intended that further work will be done on xenon and a report issued under the sponsorship of the Engineering Experiment Station with appropriate acknowledgement of the support of the National Bureau of Standards under this contract.

The undersigned wish to express their appreciation for the sponsor's support of the work carried out under this contract.

Respectfully submitted:

W. T. Ziegler
Project Director

Approved:

Dr. F. Bellinger, Chief
Chemical Sciences and Materials Division

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TECHNICAL REPORT NO. 3

PROJECT NOS. A-764 and E-115

CALCULATION OF THE VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF LIQUIDS AND SOLIDS BELOW ONE ATMOSPHERE PRESSURE. VIII. XENON

by

W. T. Ziegler, J. C. Mullins, and A. R. Berquist

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National Bureau of Standards
U. S. Department of Commerce
Washington, D. C.

1966

April 29, 1966

Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
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TECHNICAL REPORT NO. 3

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CALCULATION OF THE VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF LIQUIDS AND SOLIDS BELOW ONE ATMOSPHERE PRESSURE. VIII. XENON

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April 29, 1966

ABSTRACT

The "best" available experimental thermal data, together with suitable thermodynamic relations, have been used to compute the vapor pressure and heats of vaporization and sublimation of xenon at one degree intervals from 165.02 (the normal boiling point) to 20°K ($p = 1.05 \times 10^{-34}$ mm Hg). The computed vapor pressures have been compared with the available experimental vapor pressure data. The computed triple point pressure, 612.45 mm Hg, is in excellent agreement with the best experimental value (612.5 mm Hg.). It is believed that the computed values represent the experimental data within the present limits of uncertainty of the measurements and the temperature scales used by the different investigators. The computed values are especially recommended for use in the temperature range below the triple point (161.37°K) where experimental data are scanty or lacking. The computed values are compared with the independently computed values of Grütter and Shorrock[13].

The heat of sublimation of xenon at 0°K has been computed to be 3798 cal/gm mole. The calorimetric entropy of the ideal gas has been re-computed to be 37.708 cal/gm mole °K.

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I. INTRODUCTION

In a previous report[40] thermodynamic relations were presented for the calculation of the vapor pressure and heats of vaporization and sublimation of liquids and solids. These thermodynamic relations are similar in principle to relations developed or used by other investigators[11,12,9,36,37,23,24]. These relations have been used to compute the vapor pressures and heats of vaporization and sublimation of parahydrogen[26], oxygen[27], ehtylene[40], argon[41], methane[42], nitrogen[43], fluorine[43], carbon monoxide[28], carbon dioxide[28], krypton[44], and ethane[45] from approximately their normal boiling point to or below 20°K. In the case of parahydrogen the calculations were made to 1°K.

The present report is concerned with the application to xenon of the thermodynamic relations previously developed. The thermodynamic data needed for the computations are: (1) the heat capacity and volume of the saturated condensed phase as a function of temperature over the range of interest; (2) the heat of fusion and one heat of vaporization or sublimation at a known temperature and pressure (e.g., the normal boiling point); (3) the triple point temperature; (4) the heat capacity of the gas phase or thermodynamic functions of the ideal gas calculated from statistical mechanics; (5) an equation of state for the gas phase. These thermodynamic data have been used to compute the vapor pressure and heats of vaporization and sublimation of xenon from its normal boiling point (165.02°K) to 20°K, where its vapor pressure is computed to be 1.05×10^{-34} mm Hg. The computed results have been compared with the available experimental vapor pressure and heats of vaporization and sublimation. In addition, a comparison has been made between the "third law" entropy calculated from calorimetric data and the entropy calculated using statistical mechanics.

Naturally occurring xenon consists of a mixture of nine isotopes. The calculations made in this paper have taken this fact into account only in that an average molecular weight has been used.

Because of the uncertainty of the relation between the International Practical Temperatures Scale and the thermodynamic temperature scale, no corrections have been made to any of the reported temperatures except to convert $^{\circ}C$ to $^{\circ}K$ using an ice point of $273.15^{\circ}K$.

The thermodynamic relations used are presented in Section II. The experimental data for xenon are reviewed in Section III and the best values selected for the various physical quantities needed in the calculations are given. The calculations of vapor pressure and heats of vaporization and sublimation are presented in Section IV, together with a discussion of the agreement between the computed and experimental data. Conclusions and recommendations regarding the use of the computed results are given in Section V.

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[40] that the heat of vaporization or sublimation at the temperature T 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 δ is given by the relation,

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

and δ_1 is the value of δ at the point (P_1,T_1). The prime (') and double prime (") symbols refer to the condensed and vapor phases, respectively. 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,

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

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

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

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

---

[*] All symbols are defined in Appendix A.

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[40]

$$\begin{aligned}\ln P = {} & \ln P_1 - (\Delta H_v)_{T_1} (T_1 - T)/RTT_1 + \left[(H^o - H^o_o)''_{T_1} - (H^o - H^o_o)''_T\right]/RT \\ & - \left[(S^o)''_{T_1} - (S^o)''_T\right]/R - \left(\int_T^{T_1} c_s' \, dT\right)/RT - \left(\sum_T^{T_1} (\Delta H_{tr})'\right)/RT \\ & + \left(\int_T^{T_1} c_s' \, dT/T\right)/R + \left(\sum_T^{T_1} (\Delta H_{tr})'/T_{tr}\right)/R + \delta_1 (T_1 - T)/T \\ & - \epsilon_1 + \epsilon - \left(\int_P^{P_1} v_s' \, dP\right)/RT \qquad (5)\end{aligned}$$

where

$$\epsilon = \left[H^o(T) - H(P,T)\right]''/RT - \left[S^o(P,T) - S(P,T)\right]''/R \qquad (6)$$

and ϵ_1 is the value of ϵ at (P_1, T_1). If the virial form of the equation of state is assumed, i.e., Equation (3), then ϵ becomes,

$$\epsilon = \ln (PV/RT) - 2B/V \qquad (7)$$

Equation (5), which may be considered to be an integration of the Clapeyron equation, can be solved if appropriate data are available: thermal data for the condensed phase; $(\Delta H_v)_{T_1}$ at (P_1,T_1); an equation of state for the real gas; and the requisite molecular structure data for the ideal gas. Solution of Equation (5) requires iteration since the last two terms are pressure dependent.

Equation (5) can be rearranged as follows:

$$\begin{aligned}(\Delta H_v)_{T_1} = \Big\{ & RT \ln P_1/P + \left[(H^\circ - H^\circ_0)''_{T_1} - (H^\circ - H^\circ_0)''_T\right] \\ & - \int_T^{T_1} c_s' \, dT - \sum_T^{T_1} (\Delta H_{tr})' - T\left[(S^\circ)''_{T_1} - (S^\circ)''_T\right] \\ & + T\int_T^{T_1} c_s' \, dT/T + T \sum_T^{T_1} (\Delta H_{tr})'/T_{tr} \\ & + R(T_1 - T)\delta_1 - RT\epsilon_1 + RT\epsilon - \int_P^{P_1} v_s' \, dP \Big\} T_1/(T_1 - T) \qquad (8)\end{aligned}$$

Equation (8) may 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. It may also 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. Neither of these uses of Equation (8) requires an iterative procedure in the calculations.

III. EXPERIMENTAL DATA FOR XENON

A. Introduction

The calculation of the vapor pressure of xenon from Equation (5) and heats of vaporization and sublimation from Equation (1) from the normal boiling point (165.02°K) to 20°K made use of the following data: molecular weight; the temperature of the normal boiling point and triple point; the heat of vaporization at the normal boiling point; the heat capacity and molal volume of the saturated condensed phase; and the second virial coefficient of the gas. The contribution of higher virial coefficients was assumed to be negligible at pressures below one atmosphere.

From a survey of the literature a selection was made of the "best" values of these thermal and related data of xenon. These selected values are summarized in Table I.

TABLE I

SELECTED PHYSICAL PROPERTIES OF XENON

Property	Selected Value	Table No. or Section
Molecular weight	131.30	Section B
Normal boiling point (nbp)	165.02°K	II
Triple point (tp)	161.37°K	III
Triple point pressure	612.5 mm Hg	III
Heat of vaporization (nbp)	3020 ± 3 cal/gm mole	Section E
Heat of fusion	552.9 ± 1 cal/gm mole	Section E
Heat capacity of ideal gas	5/2R	
Heat capacity of saturated condensed phases	polynomicals for different temperature intervals	IV
Mean molal volumes of condensed phases		Section G
Second virial coefficient		Section H

B. Molecular Weight

Naturally occurring xenon consists of a mixture of isotopes in the following proportions[7]:

Isotope Mass Number	Abundance Percent
124	0.096
126	0.090
128	1.919
129	26.44
130	4.08
131	21.18
132	26.89
134	10.44
136	8.87
Avg. atomic weight[3]	131.30

The presence of these different isotopes will be expected to have some effect on the equilibrium vapor pressure of naturally occurring xenon. These effects have not been taken into account in the present vapor pressure computations except insofar as the use of the average molecular weight of 131.30 provides some compensation.

C. Normal Boiling Point

The normal boiling point (P = 1 atm) of xenon as reported by a number of investigators is given in Table II. The "best" value of the normal boiling point was taken to be 165.02°K, the average of the values reported by Michels and Wassenaar[21], Freeman and Halsey[10] and Lovejoy[19]. The values of Freeman and Halsey and Lovejoy are on the International Practical Kelvin Scale.

D. Triple Point Temperature and Pressure

The triple point temperature of xenon reported by a number of investigators is presented in Table III. The "best" value of the triple point

TABLE II

NORMAL BOILING POINT OF XENON

Reported Temperature °K	Assigned Temperature (T_o = 273.15°) °K	Investigator	Year
164.36		Peters & Weil[31]	1930
(-107.1°C)	166.05	Allen & Moore[1]	1931
(-108.05°C)	165.10	Heuse & Otto[15]	1932
165.13	165.13	Clusius & Riccoboni[5]	1938
(-108.12°C)	165.03	Michels & Wassenaar[21]	1950
165.00	165.00	Freeman & Halsey[10]	1956
165.0435	165.0435	Lovejoy[19]	1963
Selected Value	165.02		

TABLE III

TRIPLE POINT TEMPERATURE AND PRESSURE OF XENON

Reported Temperature °K	Assigned Temperature (T_o = 273.15°) °K	Reported Pressure mm Hg	Investigator	Year
(-112.0°C)		615.5	Peters & Weil[31]	1930
(-111.5°C)	161.65	600 ± 20	Allen & Moore[1]	1931
(-111.88°C)	161.27	606.2	Heuse & Otto[15]	1932
161.3	161.3	611 ± 1.5	Clusius & Riccoboni[5]	1938
161.36	161.36		Clusius & Weigand[6]	1940
161.36	161.36	612.2 ± 0.2	Clusius[4]	1941
160.56	160.56	575.6	Freeman & Halsey[10]	1956
161.38	161.38	612.5 ± 1	Heastie & Lefebure[14]	1960
161.362	161.362	612.5	Michels & Prins[20]	1962
161.3806	161.3806		Lovejoy[19]	1963
Selected Value	161.37	612.5		

temperature has been selected as 161.37°K, based on the work of Heastie and Lefebure[14], Michels and Prins[20], and Lovejoy[19]. This value agrees well with the triple point temperatures reported by Clusius[4,6].

Values of the triple point pressure of xenon are also tabulated in Table III. The "best" value has been taken as 612.5 mm Hg, based on the work of Heastie and Lefebure[14] and Michels and Prins[20]. This value is in good agreement with values reported by Clusius[5,6].

E. Heats of Vaporization and Fusion

1. Heat of Vaporization

The only direct measurement of the heat of vaporization of xenon found in the literature was that of Clusius and Riccoboni[5], who reported a value of 3020 ± 3 cal/gm mole at the normal boiling point.

2. Heat of Fusion

Clusius and Riccoboni[5] have reported the heat of fusion of xenon to be 548.5 cal/gm mole. This value has been re-calculated to be 552.9 cal/gm mole, using the pre-melting data given by these authors (their Table 4) and the heat capacity of solid xenon obtained from the equations developed in Section F.

F. Heat Capacity of Saturated Liquid and Solid Xenon

1. Heat Capacity of Saturated Liquid

The heat capacity of saturated liquid xenon has been measured by Clusius and Riccoboni[5], from the triple point to slightly above the normal boiling point. A constant value of 10.683 cal/gm mole °K was chosen as representative of the data over this temperature range.

2. Heat Capacity of Saturated Solid

Clusius and Riccoboni[5] have measured the heat capacity of solid xenon from 10.41 to 156.9°K. These data have been fitted by a least squares technique by two equations of the form

$$C_s/_T = A_1 + A_2T + A_3T^2 + A_4T^3 \tag{9}$$

over the ranges 10.41 - 13.36°K and 13.36 - 53.80°K. Over the range 42.02 - 150.7°K an equation of the form

$$C_s = A_o + A_1T + A_2T^2 + A_3T^3 + A_4T^4 \tag{10}$$

was used. The coefficients of the several polynominals found are given in Table IV, together with the temperature range over which these equations were used in the actual vapor pressure calculations. For the range 0 to 10.41°K, the heat capacity of the solid was assumed to follow the Debye theory, the Debye theta (θ_D) being determined from the heat capacity derived from the least squares fit. The value so determined at 10.41°K was 2.089 cal/gm mole °K in close agreement with the value of 2.07 cal/gm mole °K found experimentally by Clusius and Riccoboni. The heat capacity value of 2.089 gave a θ_D of 53.7°K. No correction was applied for the difference (C_p - C_v). The value reported for θ_D by Clusius and Riccoboni is 55°K.

G. Molal Volumes of Saturated Liquid and Solid Xenon

1. Molal Volume of Saturated Liquid

The density of saturated liquid xenon has been measured by Patterson, et al[30], over the range -66.8 to 16°C. Cook[7] has extrapolated these data

TABLE IV

COEFFICIENTS OF HEAT CAPACITY POLYNOMIALS FOR LIQUID AND SOLID XENON

Coefficient (Eq. 9 or 10)	Liquid	Solid		
A_o	10.683	3.2135810	0	0
A_1	0	1.1141582(-1)[a]	2.2634820(-1)	-5.7575960(-2)
A_2	0	-1.6114266(-3)	6.5122400(-4)	4.0088959(-2)
A_3	0	1.1121431(-5)	-1.1809317(-4)	-1.4670832(-3)
A_4	0	-2.6091077(-8)	1.2437651(-6)	0
Temperature range used in L.S. fit (°K)		42.02 to 150.7	13.23 to 53.80	10.41 to 13.36
Temperature range used in vapor pressure calculations (°K)	161.37 to 165.02	48 to 161.37	13.36 to 48	

[a] Number in parentheses indicates power of 10 by which entry is to be multiplied.

to obtain a density of 3.084 gm/cc. at the triple point. This value (42.6 cc/gm mole) has been used in the vapor pressure calculations made for the range 161.37 to 165.02°K.

2. Molal Volume of Saturated Solid

The density of solid xenon has been measured by x-ray diffraction techniques by Eatwell and Smith[8] (20 to 120°K) and Sears and Klug[35] (5.5 to 75°K). The density of solid xenon has been obtained by Packard and Swenson[29] (0 to 160°K) by extrapolation of P-V-T data to "zero pressure." These data are in good agreement with one another. The following mean molal volumes were used to carry out the vapor pressure calculations made in the present paper. The values chosen correspond approximately to the mean vapor pressure of the temperature interval.

Temperature Range °K	Molal Volume Used cc/gm mole
10.41 to 13.36	34.7 (value at 12°K)
13.36 to 48	34.9 (value at 31°K)
48 to 161.37	38.3 (value at 152°K)

H. Second Virial Coefficient

The second virial coefficient of xenon has been determined from P-V-T measurements by Beattie, Barriault and Brierly[2] (16.65 to 300°C), Michels, Wassenaar and Louwerse[22] (0 to 150°C) and Whalley, Lupien and Schneider[38] (0 to 700°C). No measurements of the second virial coefficient of xenon appear to have been made below 0°C.

These investigators have used this second virial coefficient data to obtain the following parameters for the Lennard-Jones 6-12 intermolecular potential function

e/k (°K)	σ (Å)	Temp. Range (°K)	Reference
224.5	4.064	300 - 573	2
212.7	4.22	273 - 423	22
225.3	4.07	273 - 973	39

Prausnitz and Myers[33] have used the experimental second virial coefficient data mentioned above for the range 273 to 873°K to determine the parameters of the Kihara potential function assuming a spherical core. Their values of these constants are $M_o = 3.142$ Å; $S_o = 0.7854$ $(\text{Å})^2$; $V_o = 0.06545$ $(\text{Å})^3$; $\rho_o = 3.874$ Å; $U_o/k = 281.80$°K. The second virial coefficient of xenon computed using the Kihara potential function with these parameters is in good agreement with the second virial coefficient data reported by Beattie, et al[2] and Michels, et al[22]. The computed values disagree somewhat with the second virial coefficient values reported by Whalley, Lupien and Schneider[38], but are in agreement with a later set of values reported by Whalley and Schneider[39], presumably calculated from the experimental data of Whalley, et al[38].

In the absence of any experimental second virial coefficient data for xenon below 0°C, the Kihara potential parameters developed by Prausnitz and Myers[33] were used to compute the second virial coefficient of xenon below the normal boiling point for use in the vapor pressure calculations. The method of computation used is outlined in the paper by Prausnitz and Myers.

I. Vapor Pressure

The vapor pressure of xenon has been measured by Peters and Weil[31] (95.2 to 164°K), Allen and Moore[1] (-117.2 to -107.0°C), Heuse and Otto[15] (-112 to -107°C), Michels and Wassenaar[21] (-110 to 16°C), Heastie and Lefebure[14] (125.26 to 161.38°K), Liang[18] (77.3°K), Freeman and Halsey[10] (110 to 160.56°K), and Podgurski and Davis[32] (70 to 90°K).

These data are summarized in Appendix B and are discussed in Section IV, B.

IV. CALCULATIONS

A. Introduction

The vapor pressure and heats of vaporization and sublimation of xenon have been computed by means of Equations (5) and (1) at one degree intervals from the normal boiling point, 165.02°K, to 20°K, using a Burroughs 220 digital computer. These results are given in Table V. The input data used are given in Table I, except that a triple point pressure was not required.

The thermodynamic properties of xenon at one atmosphere pressure in the ideal gas state were calculated assuming the atom to be in its ground electronic state. The enthalpy is given by,

$$(H^\circ - H^\circ_0)'' = \frac{5}{2} RT \tag{11}$$

and the entropy by,

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

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

B. Comparison of Computed and Experimental Vapor Pressures

The computed vapor pressures of xenon given in Table V have been compared in Figure 1 with the experimental vapor pressure data (see Appendix B) of Michels and Wassenaar[21], Heuse and Otto[15], Heastie and Lefebure[14], Liang[18], Freeman and Halsey[10], and Podgurski and Davis[32]. The data of Peters and Weil[31] and Allen and Moore[1], were not plotted since the data of these investigators showed such large deviations from the computed values and from what are believed to be the better experimental values.

The comparison between the computed and experimental vapor pressures shown in Figure 1 and Table VIII (Appendix B) was made by examining the temperature difference ($T_{calc} - T_{obs}$) as a function of temperature. Here T_{obs} is the 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 table (Table V).*

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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[25]. 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.

TABLE V

CALCULATED VAPOR PRESSURE AND HEATS OF VAPORIZATION AND SUBLIMATION OF XENON

Temperature (^{o}K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T ($^{o}K^{-1}$)	$\text{Log}_{10}P$	(dP/dT)/P ($^{o}K^{-1}$)
		- - - Liquid - - -			
165.02(nbp)	7.6000(2)[a]	3020.0	0.60599	2.88081	0.0577
165	7.5912(2)	3020.1	0.60606	2.88031	0.0577
164	7.1626(2)	3027.2	0.60976	2.85507	0.0585
163	6.7529(2)	3034.3	0.61350	2.82949	0.0592
162	6.3617(2)	3041.3	0.61728	2.80357	0.0600
161.37(tp)	6.1245(2)	3045.7	0.61969	2.78707	0.0605
		- - - Solid - - -			
161.37(tp)	6.1245(2)	3598.6	0.61969	2.78707	0.0715
161	5.9641(2)	3600.3	0.62112	2.77554	0.0718
160	5.5480(2)	3605.1	0.62500	2.74413	0.0727
159	5.1563(2)	3609.7	0.62893	2.71234	0.0736
158	4.7879(2)	3614.3	0.63291	2.68014	0.0745
157	4.4416(2)	3618.7	0.63694	2.64754	0.0755
156	4.1165(2)	3623.1	0.64103	2.61453	0.0765
155	3.8115(2)	3627.4	0.64516	2.58109	0.0774
154	3.5255(2)	3631.6	0.64935	2.54722	0.0784
153	3.2577(2)	3635.7	0.65359	2.51291	0.0795
152	3.0071(2)	3639.8	0.65789	2.47815	0.0805

TABLE V (Continued)

Temperature (^oK)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T ($^oK^{-1}$)	$Log_{10}P$	(dP/dT)/P ($^oK^{-1}$)
		- - - Solid - - - (Continued)			
151	2.7728(2)	3643.7	0.66225	2.44292	0.0816
150	2.5540(2)	3647.6	0.66667	2.40722	0.0827
149	2.3498(2)	3651.4	0.67114	2.37103	0.0838
148	2.1595(2)	3655.2	0.67568	2.33435	0.0850
147	1.9823(2)	3658.9	0.68027	2.29717	0.0862
146	1.8175(2)	3662.5	0.68493	2.25947	0.0874
145	1.6643(2)	3666.0	0.68966	2.22124	0.0886
144	1.5222(2)	3669.5	0.69444	2.18247	0.0899
143	1.3904(2)	3672.9	0.69930	2.14314	0.0911
142	1.2684(2)	3676.3	0.70423	2.10326	0.0925
141	1.1556(2)	3679.6	0.70922	2.06279	0.0938
140	1.0513(2)	3682.8	0.71429	2.02173	0.0952
139	9.5515(1)	3686.0	0.71942	1.98007	0.0966
138	8.6654(1)	3689.1	0.72464	1.93779	0.0980
137	7.8501(1)	3692.2	0.72993	1.89488	0.0995
136	7.1010(1)	3695.2	0.73529	1.85132	0.1010
135	6.4135(1)	3698.2	0.74074	1.80709	0.1026
134	5.7835(1)	3701.1	0.74627	1.76219	0.1041
133	5.2071(1)	3704.0	0.75188	1.71660	0.1057
132	4.6805(1)	3706.8	0.75758	1.67029	0.1074
131	4.2001(1)	3709.5	0.76336	1.62326	0.1091
130	3.7625(1)	3712.3	0.76923	1.57548	0.1108
129	3.3646(1)	3715.0	0.77519	1.52694	0.1126
128	3.0034(1)	3717.6	0.78125	1.47761	0.1144
127	2.6760(1)	3720.2	0.78740	1.42749	0.1163

TABLE V (Continued)

Temperature (^{o}K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T (^{o}K^{-1})	Log$_{10}$P	(dP/dT)P (^{o}K^{-1})
- - - Solid - - - (Continued)					
126	2.3799(1)	3722.7	0.79365	1.37655	0.1182
125	2.1124(1)	3725.3	0.80000	1.32477	0.1202
124	1.8713(1)	3727.7	0.80645	1.27213	0.1222
123	1.6543(1)	3730.2	0.81301	1.21861	0.1242
122	1.4594(1)	3732.6	0.81967	1.16418	0.1263
121	1.2848(1)	3734.9	0.82645	1.10883	0.1285
120	1.1286(1)	3737.3	0.83333	1.05253	0.1307
119	9.891	3739.6	0.84034	0.99525	0.1330
118	8.649	3741.8	0.84746	0.93697	0.1353
117	7.545	3744.1	0.85470	0.87767	0.1377
116	6.566	3746.3	0.86207	0.81732	0.1402
115	5.700	3748.4	0.86957	0.75588	0.1427
114	4.936	3750.6	0.87719	0.69334	0.1453
113	4.262	3752.7	0.88496	0.62966	0.1479
112	3.671	3754.8	0.89286	0.56480	0.1506
111	3.153	3756.8	0.90090	0.49875	0.1534
110	2.701	3758.9	0.90909	0.43146	0.1563
109	2.306	3760.9	0.91743	0.36291	0.1593
108	1.964	3762.9	0.92593	0.29305	0.1623
107	1.667	3764.8	0.93458	0.22185	0.1655
106	1.410	3766.8	0.94340	0.14928	0.1687
105	1.189	3768.7	0.95238	0.07528	0.1720
104	1.000	3770.6	0.96154	-0.00017	0.1754
103	8.37(-1)	3772.4	0.97087	-0.07713	0.1789
102	6.99(-1)	3774.3	0.98039	-0.15563	0.1825

TABLE V (Continued)

Temperature (^oK)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T ($^oK^{-1}$)	$Log_{10}P$	(dP/dT)P ($^oK^{-1}$)
		- - - Solid - - - (Continued)			
101	5.81(-1)	3776.1	0.99010	-0.23572	0.1862
100	4.81(-1)	3777.9	1.00000	-0.31746	0.1901
99	3.97(-1)	3779.7	1.01010	-0.40088	0.1940
98	3.27(-1)	3781.5	1.02040	-0.48604	0.1981
97	2.67(-1)	3783.2	1.03092	-0.57300	0.2023
96	2.18(-1)	3784.9	1.04166	-0.66182	0.2066
95	1.77(-1)	3786.6	1.05263	-0.75254	0.2111
94	1.43(-1)	3788.3	1.06382	-0.84523	0.2157
93	1.15(-1)	3790.0	1.07526	-0.93996	0.2205
92	9.19(-2)	3791.7	1.08695	-1.03679	0.2254
91	7.31(-2)	3793.3	1.09890	-1.13579	0.2305
90	5.79(-2)	3794.9	1.11111	-1.23703	0.2357
89	4.56(-2)	3796.5	1.12359	-1.34059	0.2411
88	3.58(-2)	3798.1	1.13636	-1.44655	0.2468
87	2.79(-2)	3799.7	1.14942	-1.55499	0.2526
86	2.16(-2)	3801.3	1.16279	-1.66600	0.2586
85	1.66(-2)	3802.8	1.17647	-1.77967	0.2648
84	1.27(-2)	3804.4	1.19047	-1.89609	0.2713
83	9.65(-3)	3805.9	1.20481	-2.01536	0.2780
82	7.28(-3)	3807.4	1.21951	-2.13759	0.2849
81	5.46(-3)	3808.9	1.2346	-2.26289	0.2921
80	4.06(-3)	3810.4	1.2500	-2.39137	0.2995
79	3.00(-3)	3811.8	1.2658	-2.52315	0.3073
78	2.20(-3)	3813.3	1.2821	-2.65837	0.3153
77	1.60(-3)	3814.7	1.2987	-2.79715	0.3237

TABLE V (Continued)

Temperature (^{o}K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T (^{o}K^{-1})	Log$_{10}$P	(dP/dT)/P (^{o}K^{-1})
		- - - Solid - - - (Continued)			
76	1.15(-3)	3816.1	1.3158	-2.93963	0.3324
75	8.20(-4)	3817.6	1.3333	-3.08597	0.3415
74	5.80(-4)	3818.9	1.3514	-3.23632	0.3509
73	4.07(-4)	3820.3	1.3699	-3.39085	0.3607
72	2.82(-4)	3821.7	1.3889	-3.54972	0.3709
71	1.94(-4)	3823.1	1.4085	-3.71313	0.3816
70	1.31(-4)	3824.4	1.4286	-3.88126	0.3927
69	8.82(-5)	3825.7	1.4493	-4.05433	0.4043
68	5.85(-5)	3827.0	1.4706	-4.23256	0.4164
67	3.84(-5)	3828.4	1.4925	-4.41616	0.4291
66	2.48(-5)	3829.6	1.5152	-4.60539	0.4424
65	1.58(-5)	3830.9	1.5385	-4.80051	0.4562
64	9.96(-6)	3832.2	1.5625	-5.00180	0.4707
63	6.17(-6)	3833.4	1.5873	-5.20954	0.4860
62	3.77(-6)	3834.7	1.6129	-5.42405	0.5019
61	2.26(-6)	3835.9	1.6393	-5.64567	0.5187
60	1.33(-6)	3837.1	1.6667	-5.87475	0.5363
59	7.73(-7)	3838.3	1.6949	-6.11166	0.5548
58	4.40(-7)	3839.4	1.7241	-6.35682	0.5743
57	2.45(-7)	3840.6	1.7544	-6.61066	0.5948
56	1.34(-7)	3841.7	1.7857	-6.87364	0.6164
55	7.14(-8)	3842.8	1.8182	-7.14627	0.6392
54	3.72(-8)	3843.9	1.8519	-7.42908	0.6635
53	1.89(-8)	3845.0	1.8868	-7.72264	0.6887
52	9.38(-9)	3846.1	1.9231	-8.02757	0.7157

TABLE V (Continued)

Temperature ($^{\circ}$K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T ($^{\circ}$K^{-1})	$\mathrm{Log}_{10}P$	(dP/dT)/P ($^{\circ}$K^{-1})
- - - Solid - - - (Continued)					
51	4.52(-9)	3847.1	1.9608	-8.34456	0.7442
50	2.12(-9)	3848.2	2.0000	-8.67430	0.7745
49	9.60(-10)	3849.2	2.0408	-9.01760	0.8067
48	4.21(-10)	3850.1	2.0833	-9.37530	0.8408
47	1.79(-10)	3851.1	2.1277	-9.74831	0.8772
46	7.28(-11)	3852.0	2.1739	-10.13763	0.9160
45	2.86(-11)	3852.9	2.2222	-10.54435	0.9574
44	1.07(-11)	3853.7	2.2727	-10.96965	1.0016
43	3.85(-12)	3854.6	2.3256	-11.41483	1.0490
42	1.31(-12)	3855.4	2.3810	-11.88131	1.0998
41	4.26(-13)	3856.2	2.4390	-12.37065	1.1543
40	1.30(-13)	3857.0	2.5000	-12.88456	1.2130
39	3.76(-14)	3857.7	2.5641	-13.42493	1.2762
38	1.01(-14)	3858.4	2.6316	-13.99385	1.3445
37	2.55(-15)	3859.1	2.7027	-14.59362	1.4184
36	5.93(-16)	3859.7	2.7778	-15.22683	1.4986
35	1.27(-16)	3860.3	2.8571	-15.89632	1.5857
34	2.48(-17)	3860.8	2.9412	-16.60529	1.6805
33	4.39(-18)	3861.3	3.0303	-17.35733	1.7842
32	6.97(-19)	3861.7	3.1250	-18.15646	1.8976
31	9.83(-20)	3862.0	3.2258	-19.00724	2.0222
30	1.22(-20)	3862.3	3.3333	-19.91480	2.1594
29	1.30(-21)	3862.5	3.4483	-20.88501	2.3110
28	1.19(-22)	3862.6	3.5714	-21.92456	2.4791
27	9.10(-24)	3862.6	3.7037	-23.04113	2.6662

TABLE V (Continued)

Temperature (^{o}K)	Pressure, P (mm Hg)	Heat of Vaporization (cal/gm mole)	100/T ($^{o}K^{-1}$)	Log$_{10}$9	(dP/dT)/P ($^{o}K^{-1}$)
		- - - Solid - - - (Continued)			
26	5.71(-25)	3862.5	3.8462	-24.24357	2.8751
25	2.87(-26)	3862.3	4.0000	-25.54216	3.1096
24	1.12(-27)	3861.9	4.1667	-26.94886	3.3738
23	3.33(-29)	3861.5	4.3478	-28.47774	3.6732
22	7.15(-31)	3860.9	4.5455	-30.14539	4.0141
21	1.07(-32)	3860.2	4.7619	-31.97156	4.4047
20	1.05(-34)	3859.4	5.0000	-33.97994	4.8551

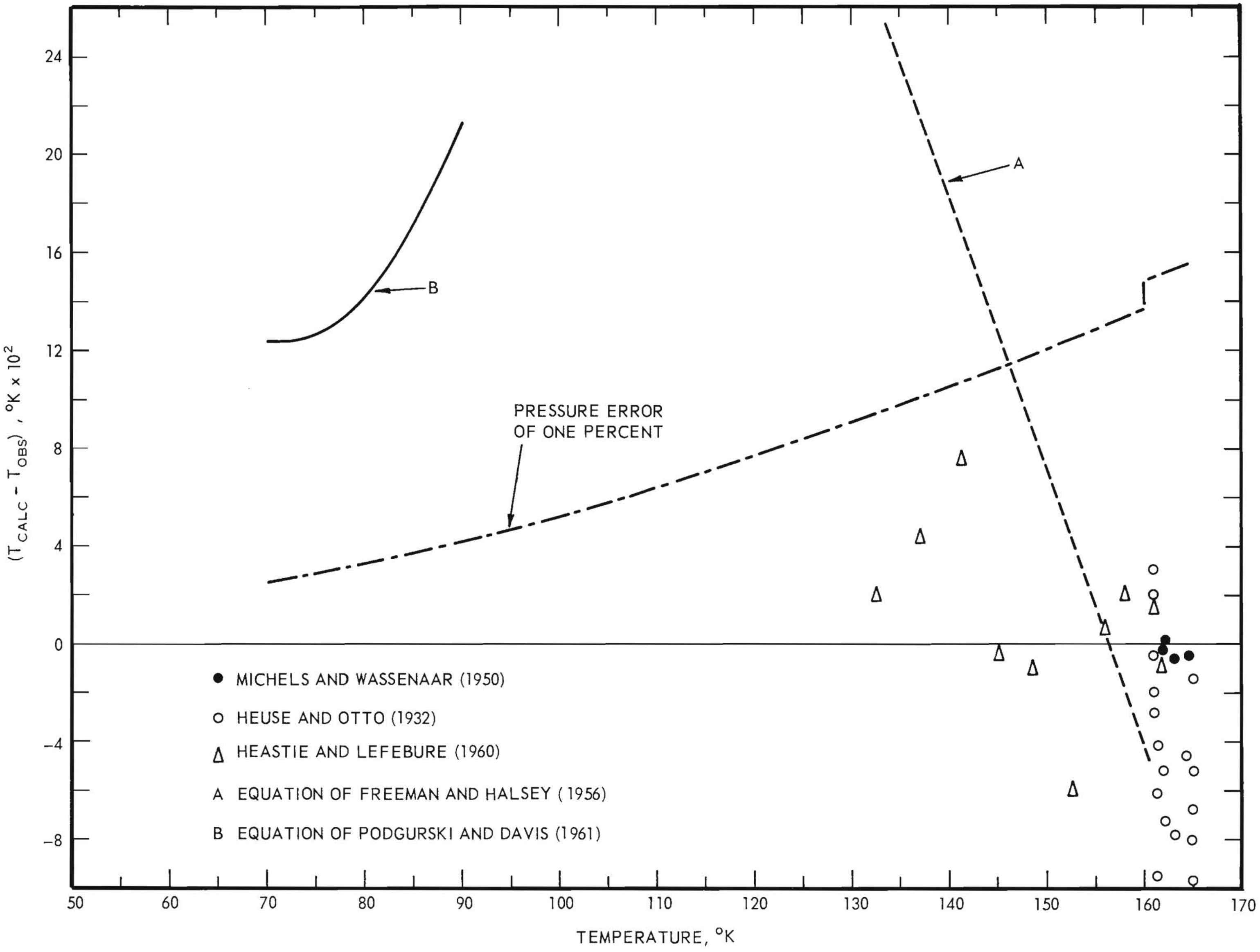

Figure 1. Comparison of Calculated and Experimental Vapor Pressure of Xenon.

The vapor pressures computed for liquid xenon in the range below the normal boiling point are in good agreement with the data of Michels and Wassenaar[21]. Furthermore, the computed triple point pressure of 612.45 mm Hg is in excellent agreement with the value of 612.5 mm Hg reported by Heastie and Lefebure[14] and Michels and Prins[20]. The equation of Freeman and Halsey[10] and the experimental data of Heuse and Otto[15] show considerably larger disagreement.

In the solid range, the computed values agree reasonably well with the scattered data of Heastie and Lefebure[14]. The equations used by Freeman and Halsey[10] to represent their experimental data for the vapor pressure of solid xenon in the range 110° to 160.56°K is seen (Figure 1) to disagree with the computed values and with the experimental data of Heastie and Lefebure[14]. The vapor pressure data of Podgurski and Davis[32] (70 to 90°K) are about 4 percent larger than the computed values. This difference is about twice the maximum uncertainty (± 2 percent) ascribed by Podgurski and Davis to their pressure measurements.

After the calculations presented in the present paper were computed (November 1964), a similar calculation of the vapor pressure of xenon was published by Grütter and Shorrock[13]. The calculations of these investigators were also based on the thermal data of Clusius and Riccoboni[5]. Use was made of the somewhat smaller heat of fusion (548.5 cal/mole) of Clusius and Riccoboni; corrections for gas imperfection were made using the Berthelot equation of state in reduced form. The vapor pressures computed by Grütter and Storrock and those of the present work are compared in Table VI.

TABLE VI

COMPARISON OF COMPUTED VAPOR PRESSURES

Temperature (°K)	Computed Vapor Pressure mm Hg This Work	 Grütter & Shorrock[13]
70	1.31 (-4)	1.39 (-4)
80	4.06 (-3)	4.24 (-3)
90	5.79 (-2)	5.99 (-2)
100	4.81 (-1)	4.95 (-1)
110	2.70	2.76
120	1.13 (1)	1.15 (1)
130	3.76 (1)	3.82 (1)
140	1.05 (2)	1.06 (2)
150	2.55 (2)	2.58 (2)
160	5.54 (2)	5.62 (2)

It is difficult to determine the relative probable accuracy of these two calculations. The excellent agreement between the computed and experimental triple point pressure obtained in the present work suggests that the second virial coefficient computed from the Kihara core model may be a good representation of this quantity. At the normal boiling point the second virial coefficient obtained from the Kihara core model is -395 cc/mole compared to a value of -505 cc/mole computed from the reduced Berthelot equation of state used by Grütter and Shorrock[13]. Other differences, such as the exact method used to carry out the necessary integration of the heat capacity data, the choice of the heat of fusion and triple point temperature probably accounts for the remaining difference.

C. Comparison of Computed and Experimental Heats of Vaporization and Sublimation

No experimental data could be found for the heat of vaporization of xenon, other than the value of the normal boiling point reported by Clusius and Riccoboni[5] (and used in these calculations). No direct measurements of the heat of sublimation appear to have been made.

The heat of sublimation of xenon at 0°K has been computed from the value at 20°K given in Table V, using the polynomials for the heat capacity of solid xenon given in Table IV for the range 20 to 10.41°K. The enthalpy change below 10.41°K was computed using the Debye theory with $\theta_D = 53.7$°K. The resulting value of $\Delta H_o = 3798$ cal/gm mole at 0°K may be compared with the value of 3778 cal/gm mole given by Kane[16] (see also Cook[7]). A value of 3780 cal/gm mole has been reported by Grütter and Shorrock[13]. The higher value of 3798 cal/gm mole found in the present work is, of course, consistent with the lower vapor pressures found relative to the computed vapor pressures of Grütter and Shorrock.

D. Comparison of the Calorimetric and Statistical Entropy of Ideal Gas

The thermal data used to compute the vapor pressure and heats of vaporization and sublimation given in Table V were used to compute the calorimetric entropy of the ideal gas at the normal boiling point (165.02°K) and one atm. pressure, assuming the entropy of the solid to be zero at 0°K. The results of the calculation are shown in Table VII.*

Clusius and Riccoboni[5] have reported a value of 37.66 ± 0.1 e.u. for the calorimetric entropy. However, their reported values for the entropy

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* The recent measurements of the heat capacity of xenon reported by Fenichel and Serin, Phys. Rev. 142, 490 (1966), for the range 1 to 24°K, suggest the entropy of xenon at 10°K is 0.05 e.u. smaller than is shown in this table. Above 15°K the heat capacity values reported by Fenichel and Serin are 3 percent higher than those of Clusius and Riccoboni.

TABLE VII

COMPARISON OF CALORIMETRIC AND STATISTICAL ENTROPY OF XENON AS IDEAL GAS AT 165.02°K AND 1 ATM

Temperature Range (°K)	Entropy Change (cal/gm mole °K)	Comments
0-10	0.828	Debye $\theta_D = 53.7^\circ K$
10-161.37 (tp)	14.798	Integration of C_s'/T using appropriate polynomial in Table IV
161.37	3.426	Fusion, 552.9/161.37
161.37 - 165.02 (nbp)	0.239	Integration, $C_s' = 10.683$
165.02	18.301	Vaporization, 3020/165.02
165.02	0.116	Correction for non-ideality using Eq. (3), Prausnitz and Myers[33] parameters, Kihara core model

$(S^o_{cal}) = 37.708$

$(S^o_{stat}) = 37.592$

increments from 10°K to the triple point, 161.3°K (ΔS = 14.14 e.u.) and from the triple point to the normal boiling point, 165.13°K (ΔS = 0.904 e.u.) appear to be grossly in error. The values obtained by us for these increments were 14.798 e.u., and 0.239 e.u. respectively. Kelley[17] using the thermal data of Clusius and Riccoboni[5] found (S^{o}_{cal}) = 37.72 ± 0.3 e.u. Kelley found for the above mentioned intervals ΔS of 14.82 e.u. and 0.25 e.u. respectively.

V. CONCLUSIONS

Thermodynamic relations have been used to compute the vapor pressure and heats of vaporization and sublimation of xenon at one degree intervals from 165.02°K (the normal boiling point) to 20°K. The normal boiling point and triple point temperatures used are essentially on the International Practical Kelvin Scale. The results are presented in Table V. These calculations are based on the "best" available experimental thermal data. In the absence of second virial coefficient data below 0°C, correction for gas imperfection below the normal boiling point was made using a theoretical representation of the second virial coefficient based on the Kihara core model with parameters given by Prausnitz and Myers[33].

The input data used to compute the vapor pressures given in Table V were used to compute the calorimetric entropy of the ideal gas at 165.02°K (nbp) from the third law. The resulting value, 37.708 cal/gm mole °K, is in good agreement with the value of 37.592 cal/gm mole °K calculated from statistical thermodynamics.

The computed vapor pressures given in Table V were compared with the available experimental data. The computed triple point pressure, 612.45 mm Hg, is in excellent agreement with the best experimental value (612.5 mm Hg). It is believed that the computed values represent the experimental data within the present limits of uncertainty of the measurements and the temperature scales used by the investigators. The computed values are especially recommended for use in the temperature range below the triple point (161.37°K), where experimental data are scanty or lacking. The computed values are compared with the independently computed values of Grütter and Shorrock[13].

The heat of sublimation of xenon at 0°K was found to be 3798 cal/gm mole.

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VIII. APPENDICES

A. Nomenclature and Physical Constants*

B = second virial coefficient of gas.

c = velocity of light = 2.99702×10^{10} cm/sec.

c_s' = molal heat capacity of saturated condensed phase.

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

h = Planck's constant = 6.62377×10^{-27} erg-sec/molecule.

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

(ΔH_{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 through T_1.

$(H^o - H^o_o)''_T$ = enthalpy function for ideal gas at T.

k = Boltzmann constant = 1.38038×10^{-16} erg/°K-molecule.

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* The physical constants used were those of Rossini et al[34] adjusted to an ice point of 273.150°K.

M = molecular weight.

M_o, S_o, V_o = parameters of Kihara core model.

N_o = Avogadro's Number = 6.02380×10^{23} molecules/gm mole.

P = pressure.

P_1 = pressure of a known point on the vapor pressure curve.

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).

$S^{o}(P,T)''$ = entropy of the ideal gas at P and T.

$(S^{o})''_{T}$ = entropy of ideal gas at P = 1 atm and T.

T = temperature on the thermodynamic scale with an assigned ice point of 273.15°K.

T_1 = temperature of a known point on the vapor pressure curve.

T_o = ice point on thermodynamic scale.

U_o = minimum potential energy between molecules (Kihara core model).

V = molal volume of gas.

v'_s = molal volume of saturated condensed phase.

δ = defined by Equation (2) and Equation (4).

ϵ = defined by Equation (6) and Equation (7).

ρ_o = shortest distance between molecular cores at minimum potential energy (Kihara core model).

Superscripts

' = condensed phase.

" = gas phase.

Subscripts

s = saturated vapor or condensed state.

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

B. Experimental Vapor Pressure Data for Xenon

The experimental vapor pressure data presented in Figure 1 are collected in Table VIII. The vapor pressure data of Freeman and Halsey[10] and Podgurski and Davis[32] were computed from equations presented by these investigators since no tabular data were given by them. Also given in Table VIII is the difference between the observed temperature and the temperature calculated for the reported vapor pressure (see Section IV B).

Table VIII

EXPERIMENTAL VAPOR PRESSURES OF XENON

Reported Temperature ($^\circ$K)	Reported Pressure (mm Hg)	$(T_{calc} - T_{obs}) \times 10^2$ ($^\circ$K)
Michels & Wassenaar[21]		
	- - - Liquid - - -	
161.698	624.758	0.13
162.328	648.789	-0.03
162.331	648.896	-0.05
163.529	696.532	-0.47
163.531	696.677	-0.32
163.993	715.852	-0.26
164.426	734.084	-0.45
164.427	734.145	-0.41
164.705	746.145	-0.29
164.953	756.808	-0.58
Heuse & Otto[15]		
	- - - Liquid - - -	
164.91	751.7	-8.0
164.92	753.4	-5.1
165.01	755.3	-9.7
162.02	635.0	-5.1
162.20	641.0	-7.4
163.22	681.0	-7.8
164.80	747.5	-6.7
164.81	750.2	-1.4
164.85	749.1	-8.0
163.97	713.2	-4.3
162.12	639.0	-4.6
161.61	619.1	-6.1
164.86	749.0	-9.2
162.40	649.7	-4.9

Reported Temperature (°K)	Reported Pressure (mm Hg)	$(T_{calc} - T_{obs}) \times 10^2$ (°K)
	- - - Solid - - -	
161.29	606.2	-6.3
161.22	605.3	-1.4
161.23	605.6	-1.7
160.81	589.1	1.9
160.61	581.2	3.1
161.01	596.3	-1.2
161.18	603.4	-1.8
161.19	603.4	-2.8
161.15	602.7	-0.4
161.25	605.4	-4.2
161.23	606.1	-0.5
161.28	606.4	-4.9
161.34	607.0	-9.5
Heastie & Lefebure[14]		
	- - - Solid - - -	
125.26	22.9	41.5
132.56	49.8	2.0
137.11	79.7	4.3
141.01	116.5	7.7
145.33	171.3	-0.4
148.50	225.1	-1.0
152.39	308.8	-6.0
156.14	416.3	0.7
158.10	483.1	2.0
160.42	572.7	1.8
161.38 (tp)	612.5 (tp)	-0.9
Liang[18]		
77.3	1.93×10^{-3}	29.3

Reported Temperature ($^{\circ}$K)	Reported Pressure (mm Hg)	$(T_{calc} - T_{obs}) \times 10^2$ ($^{\circ}$K)
Freeman & Halsey[10]		
	- - - Liquid - - -	
161	592.1[a]	-10.0
161.37	606.3	-14.1
162	631.0	-13.6
163	671.9	- 8.4
164	715.0	- 3.1
165	760.2	2.4

[a] These pressures calculated from equation

$$\log P(\text{mm}) = 7.2488 - 720.7/T$$

	- - - Solid - - -	
110	2.969[b]	60.9
114	5.339	54.3
118	9.227	48.0
122	15.39	41.9
126	24.83	36.1
130	38.92	30.6
134	59.38	25.4
138	88.41	20.5
142	128.72	15.9
146	183.57	11.4
150	256.90	7.1
154	353.3	2.7
158	478.2	-1.7
160	553.0	-4.5

[b] These pressures calculated from equation

$$\log P(\text{mm}) = 7.7371 - 799.1/T$$

Podgurski & Davis[32]		
	- - - Solid - - -	
70.00	1.38×10^{-4}[c]	12.4
72.00	2.95×10^{-4}	12.2
74.00	6.06×10^{-4}	12.3

Reported Temperature (°K)	Reported Pressure (mm Hg)	$(T_{calc} - T_{obs}) \times 10^2$ (°K)
76.00	1.20×10^{-3}	13.1
78.00	2.29×10^{-3}	13.3
80.00	4.24×10^{-3}	14.4
82.00	7.61×10^{-3}	15.4
84.00	1.33×10^{-2}	17.0
86.00	2.26×10^{-2}	17.9
88.00	3.75×10^{-2}	19.2
90.00	6.09×10^{-2}	21.2

[c] These pressures calculated from equation

$$\log P(\text{mm}) = 8.044 - 833.33/T$$

Allen & Moore[1]

154.05	454	*[d]
155.95	465	*
156.95	482	*
156.95	491	*
157.85	501	76.0
158.75	525	49.0
158.75	525	49.0
159.65	544	8.0
159.75	560	37.8
159.95	583	73.4
160.15	586	60.5
160.25	588	55.3
160.45	590	40.0
160.55	594	39.0
160.95	571	-55.0
160.95	600	13.4
161.15	581	-51.3
161.15	604	2.6
161.45	581	-81.3
161.55	585	-81.3
162.45	602	*
161.45	618	6.9

Reported Temperature (^{o}K)	Reported Pressure (mm Hg)	$(T_{calc} - T_{obs}) \times 10^2$ (^{o}K)
163.95	723	21.0
164.15	717	-13.2
164.15	756	-22.1
165.55	750	-75.9
165.95	755	*
166.05	760	*
166.15	760	*

[d] the asterisk* implies differences greater than one degree.

Peters & Weil[31]

	- - - Liquid - - -	
161.15 (tp)	615.5	30.2
161.35	622.4	28.7
161.65	630.0	18.8
163.95	741.0	63.3
	- - - Solid - - -	
95.15	0.3	*
103.65	1.0	35.2
108.55	2.0	-43.7
111.15	3.0	-47.4
114.15	4.3	*
116.15	6.0	-79.0
120.85	10.0	*
129.95	32.5	*
133.15	45.7	*
134.15	53.0	-98.3
135.15	60.0	-79.6
141.45	110.7	-90.1
142.15	124.8	-32.5
143.15	132.2	-70.1
143.35	140.5	-23.5
145.15	166.5	-14.5
146.15	185.0	5.3
149.15	227.5	-53.5
151.15	275.0	-25.1
155.05	373.5	-31.1
155.65	390.5	-33.6
155.85	398.0	-29.0
156.15	407.0	-30.0
156.25	415.5	-12.8
156.85	449.0	29.4
158.25	476.0	-32.8