

BLM LIBRARY  
88069875

PCT

UNITED STATES  
DEPARTMENT OF THE INTERIOR  
BUREAU OF MINES  
HELIUM ACTIVITY  
HELIUM RESEARCH CENTER  
INTERNAL REPORT

EXAMINATION AND RECALCULATION OF VIRIAL COEFFICIENTS OF HELIUM

FROM THE LOS ALAMOS SCIENTIFIC LABORATORY PVT DATA, OBTAINED BY KELLER

BY

B. J. Dalton

Robert E. Barieau

BRANCH                    FUNDAMENTAL RESEARCH  
PROJECT NO.              4335  
DATE                      December 1964

HD  
9660  
.H43  
M56  
no. 61

AMARILLO, TEXAS



#915076492

ID 88069875

Report No. 61

HD  
9660  
. H43  
M56  
no. 61

## HELIUM RESEARCH CENTER

## INTERNAL REPORT

Abstract	4
Introduction	5
EXAMINATION AND RECALCULATION OF VIRIAL COEFFICIENTS OF HELIUM FROM THE LOS ALAMOS SCIENTIFIC LABORATORY PVT DATA, OBTAINED BY KELLER	13
References	46

## TABLES

1. Original vapor pressure data obtained by Keller, uncorrected for temperature or gravity	7
2. Original vapor pressure data obtained by Keller, corrected to 0° C and standard gravity	10
3. Experimental PVT data for the isotherms of He <sup>4</sup> as originally reported by Keller	14
4. Details of $\Delta(PV/N)$ calculations to reduce experimental data to a true isotherm	20
5. Corrected values B. J. Dalton and Robert E. Barieau corrected pressures corresponding to the corrected $(PV/N)$ 's at the observed $(P/V)$ values	25
6. Values of $(PV/N)$ as corrected by the Helium Research Center along with the $(PV/N)$ 's as corrected by Keller (3)(a) Branch of Fundamental Research	30
7. Virial coefficients of He <sup>4</sup> as evaluated by the Helium Research Center for Project 4335 given in table 5 of this report	33
8. Values of $(PV/N)_{corr,obs.}$ December 1964 evaluated by the Helium Research Center from the data given in table 5	38

BUREAU OF LAND MANAGEMENT LIBRARY  
BLDG. 50,  
DENVER FEDERAL CENTER  
P.O. BOX 25047  
DENVER, COLORADO 80225



CONTENTS

	<u>Page</u>
9. Summary of the results obtained by the Helium Research Center from Keller's data . . . . .	62
10. Values of the second virial coefficient as calculated by the Helium Research Center and by Keller along with the values tabulated by Kilpatrick, Keller, and Hammel . . . . .	62
<b>Abstract . . . . .</b>	<b>4</b>
11. Thermodynamic properties of saturated helium . . . . .	42
Introduction . . . . .	5
work . . . . .	42
Recalculation of Keller's data . . . . .	13
References . . . . .	46

TABLES

1. Original vapor pressure data obtained by Keller, uncorrected for temperature or gravity . . . . .	7
2. Original vapor pressure data obtained by Keller, corrected to 0° C and standard gravity . . . . .	10
3. Experimental PVT data for the isotherms of He <sup>4</sup> as originally reported by Keller . . . . .	14
4. Details of $\Delta(PV/N)$ calculations to reduce experimental data to a true isotherm . . . . .	20
5. Corrected values of (PV/N) along with the corrected pressures corresponding to the corrected (PV/N)'s at the observed (N/V) values . . . . .	25
6. Values of (PV/N) as corrected by the Helium Research Center along with the (PV/N)'s as corrected by Keller (3)(4). . . . .	30
7. Virial coefficients of He <sup>4</sup> as evaluated by the Helium Research Center from the data given in table 5 of this report . . . . .	33
8. Values of (PV/N) <sub>corr.obs.</sub> minus (PV/N) <sub>corr.cal.</sub> as evaluated by the Helium Research Center from the data given in table 5 . . . . .	35



EXAMINATION AND RECALCULATION	<u>Page</u>
9. Summary of the results obtained by the Helium Research Center from Keller's data . . . . .	42
10. Values of the second virial coefficient as calculated by the Helium Research Center and by Keller along with the values tabulated by Kilpatrick, Keller, and Hammel . . . . .	44
11. Thermodynamic properties of saturated helium vapor as evaluated from the results of Keller's work . . . . .	45

#### ABSTRACT

The pressure-volume isotherms of  $\text{He}^4$ , published by the Los Alamos Scientific Laboratory, have been reevaluated using a least squares technique to evaluate the constants in the isothermal equations.

All of the original vapor pressure data, which Keller was kind enough to supply us, were corrected to read in mm Hg at 0° C and standard gravity.

The PV/N products were then represented in terms of a power series in  $\rho$  and in  $P$  for two- and three-constant equations and virial coefficients evaluated. It was concluded that the best representation of the isotherms of  $\text{He}^4$  is the linear expansion in  $\rho$ . This conclusion is based on statistical evidence which is given in this report.

- 
- <sup>1</sup>/ Research Chemist, Helium Research Center, Bureau of Mines, Amarillo, Texas.  
<sup>2</sup>/ Supervisory Research Chemist, Project Leader, Thermodynamics, Helium Research Center, Bureau of Mines, Amarillo, Texas.



EXAMINATION AND RECALCULATION  
OF VIRIAL COEFFICIENTS OF HELIUM  
FROM THE LOS ALAMOS SCIENTIFIC LABORATORY PVT DATA,  
OBTAINED BY KELLER

by

The long-range objective is the development of a single equation of state for helium that will allow properties to be calculated and will reproduce all of the data within the accuracy with which the data are known. A preliminary objective is to obtain the best values of second virial coefficients and to develop an equation that will reproduce all of the PV data on helium that appear in the literature.

ABSTRACT

The pressure-volume isotherms of  $\text{He}^4$ , published by the Los Alamos Scientific Laboratory, have been reevaluated using a least squares technique to evaluate the constants in the isothermal equations.

All of the original vapor pressure data, which Keller was kind enough to supply us, were corrected to read in mm Hg at 0° C and standard gravity.

The PV/N products were then represented in terms of a power series in  $\rho$  and in  $P$  for two- and three-constant equations and virial coefficients evaluated. It was concluded that the best representation of the isotherms of  $\text{He}^4$  is the linear expansion in  $\rho$ . This conclusion is based on statistical evidence which is given in this report.

1/ Research Chemist, Helium Research Center, Bureau of Mines, Amarillo, Texas.  
2/ Supervisory Research Chemist, Project Leader, Thermodynamics, Helium Research Center, Bureau of Mines, Amarillo, Texas.

determined. Keller's work can therefore be looked upon not only as the determination of the second virial coefficients of  $\text{He}^4$  but also as an independent determination of the vapor pressure of liquid helium as a

Work on manuscript completed December 1964.



## INTRODUCTION

The Helium Research Center is presently engaged in a critical examination of all of the PVT data on helium that appear in the literature. The long-range objective is the development of a single equation of state for helium that will allow all of the thermodynamic properties to be calculated and will reproduce all of the data within the accuracy with which the data are known. A preliminary objective is to obtain the best values of second virial coefficients and to develop an equation that will reproduce the best values as a function of temperature.

In this report we examined the pressure-volume isotherms of  $\text{He}^4$  of the Los Alamos Scientific Laboratory, obtained by William E. Keller (3).<sup>3/</sup>

---

3/ Underlined numbers in parentheses refer to items in the list of references at the end of this report.

This author reports a total of 64 points on the PVT surface distributed among five isotherms. Temperatures are from  $2^\circ$  to  $4^\circ$  K; pressures vary from around 10 mm to about 200 mm Hg.

Within his container, Keller had a  $\text{He}^4$  vapor pressure thermometer. His PV's, for each isotherm, can be extrapolated to zero density to obtain the thermodynamic temperature in terms of the thermodynamic temperature at room temperature, at which the number of moles of helium was determined. Keller's work can therefore be looked upon not only as the determination of the second virial coefficient of  $\text{He}^4$  but also as an independent determination of the vapor pressure of liquid helium as a



function of the absolute temperature. His work contributed to the realization that the  $\text{He}^4$  vapor pressure-temperature scale needed to be revised.

Unfortunately, Keller did not publish his original vapor pressures. However, he has been kind enough to supply us with his original observations of the measured vapor pressures, corrected by him for capillarity but uncorrected for temperature or gravity. These values, as received from Keller, are given in table 1.

For each pressure measurement is a given temperature, in degrees Celsius, of the mercury of the manometer; these temperatures are given in column 2 of table 1. Mr. Keller states that the value for the acceleration of gravity at Los Alamos is  $979.135 \text{ cm/sec}^2$ , ". . . as measured by the LASL standards laboratory about 100 yards from the location of the isotherm apparatus."<sup>6</sup>

We corrected Keller's vapor pressure data to mm of mercury at  $0^\circ \text{ C}$  using Beattie, et al.'s (1) equation for the coefficient of expansion of mercury, as recommended by Cook (2). We quote Cook:

In deciding on values to adopt for the expansion of mercury, the results of the absolute measurements must evidently be ignored because of the systematic errors with which they appear to be affected. Similarly, relative measurements in glass vessels are rejected since the expansion of the vessel cannot be determined sufficiently accurately, while high-temperature values deduced from the departures of mercury-in-glass thermometer scales from the International temperature scale are, in addition, subject to uncertainties in the pressure corrections. The only results which can be considered to be correct to within a few parts in a million of the volume are those of Harlow (see ref. 3) and of Beattie and others - These two series agree to within the probable standard deviation of their difference over the whole range from  $0$  to  $300^\circ \text{ C}$  but, pending further observations, it seems best to adopt Beattie's results as definitive since there is less doubt about the expansion of the silica vessels used.



TABLE 1. - Original vapor pressure data obtained by Keller, uncorrected for temperature or gravity

Exp. No.	$t$ °C	Vapor Pressure Thermometer, mm Hg	Bath Level Correction, mm Hg
A- 8- 1	32.5	587.84	2.15*
A- 8- 2	32.5	587.60	1.98*
A- 8- 3	32.6	586.80	1.60*
A- 9- 1	32.4	592.89	
A- 9- 2	32.4	593.13	
A- 9- 3	31.7	594.27	
A-11- 1	32.7	593.60	
A-11- 2	32.8	593.05	
A-11- 3	32.8	592.88	
A-12- 1	32.2	597.42	
A-12- 2	33.2	595.92	
A-12- 3	32.8	594.53	
B- 1- 1	27.8	284.80	
B- 1- 2	28.0	287.33	
B- 1- 3	27.9	289.06	
B- 2- 1	29.0	296.50	
B- 2- 2	29.0	295.94	
B- 2- 3	28.0	296.30	
B- 3- 1	32.6	296.96	
B- 4- 1	32.4	291.60	
B- 4- 2	33.0	292.62	
B- 4- 3	32.2	293.23	
B- 4- 4	32.6	293.88	
B- 5- 1	32.6	295.31	
B- 5- 2	32.4	295.99	
B- 5- 3	32.2	297.08	
C- 3- 1	32.6	145.55	
C- 3- 2	32.7	148.37	
C- 4- 1	32.4	147.90	
C- 4- 2	32.6	147.55	
C- 4- 3	33.0	147.92	
C- 4- 4	32.7	148.35	
C- 5- 1	32.2	149.44	
C- 5- 2	32.3	149.73	
C- 5- 3	32.5	150.10	
C- 5- 4	32.7	150.63	
C- 6- 1	32.0	148.88	
C- 6- 2	32.6	149.42	

\* Bath pressure used for these instead of vapor pressure thermometer.



Therefore, on the basis of Cook's review (2) of thermal expansion

TABLE 1. - Original vapor pressure data obtained by Keller, uncorrected for temperature or gravity (Cont.)

Exp. No.	$t_{Hg}^{\circ}$	Vapor Pressure Thermometer, mm Hg	Bath Level Correction, mm Hg
----------	------------------	--------------------------------------	---------------------------------

D- 2- 1	27.6	53.25	
D- 2- 2	27.8	53.31	
D- 2- 3	26.7	53.82	
D- 3- 1	32.2	53.26	
D- 3- 2	32.6	53.69	
D- 4- 1	32.3	52.45	
D- 5- 1	32.2	52.44	
D- 5- 2	32.4	53.12	
D- 6- 1	32.0	52.80	
D- 6- 2	32.2	53.60	
D- 9- 1	32.9	53.08	
D- 9- 2	32.7	53.72	
D- 10- 1	32.2	53.09	
D- 10- 2	32.5	53.63	
D- 10- 3	33.0	54.20	
D- 11- 1	32.4	51.74	
D- 11- 2	32.4	52.25	
E- 1- 1	32.8	35.70	
E- 2- 1	32.7	35.53	
E- 2- 2	32.4	35.59	
E- 3- 1	32.5	35.55	
E- 3- 2	33.6	35.61	
E- 4- 1	32.2	36.29	
E- 4- 2	32.3	36.39	
E- 5- 1	32.1	35.73	
E- 5- 2	32.4	35.88	

$$+ 28.625 \times 10^{-3} t^2 + 2.617 \times 10^{-6} t^3 \quad (3)$$

$$[0^\circ < t, {}^\circ C (Int) < 350^\circ]$$

where  $t$  is on the International temperature scale.

Table 2 gives values of the vapor pressure of helium as originally reported by Keller (see table 1), but corrected to  $0^\circ$  C and reduced to standard gravity. Column 1 gives the actual measured vapor pressures reported by Keller. Column 2 gives values of the temper-



Therefore, on the basis of Cook's review (2) of thermal expansion data for mercury, we accepted Beattie, et al.'s (1) results as being the most reliable values for the true and the mean coefficients of thermal dilation. We then proceeded to correct the pressure data for helium, table 1, to 0° C and  $g = 980.665 \text{ cm/sec}^2$ , by the following equation

$$(P_{v.p.})_{\text{corr.}} = (P_{v.p.})_{\text{obs.}} (\rho_t / \rho_{0^\circ})(g_L / g_S) \quad (1)$$

where  $(\rho_t / \rho_{0^\circ})$  is the ratio of the density of mercury at some temperature,  $t$ , to that at 0° C;  $g_L = 979.135 \text{ cm/sec}^2$ ;  $g_S = 980.665 \text{ cm/sec}^2$ ;  $(P_{v.p.})_{\text{obs.}}$  is the original vapor pressure of helium uncorrected for temperature or gravity, in mm Hg; and  $(P_{v.p.})_{\text{corr.}}$  is the vapor pressure of helium corrected to 0° C and reduced to standard gravity.

In equation (1),  $(\rho_t / \rho_{0^\circ})$  was calculated from Beattie, et al.'s equation (1):

$$(\rho_t / \rho_{0^\circ}) = \frac{1}{1 + \alpha t} \quad (2)$$

where  $\alpha$ , the mean coefficient of thermal expansion for mercury, is given (1) as

$$\begin{aligned} \alpha \times 10^8, (\text{°C})^{-1} &= 18144.01 + 70.16 \times 10^{-2} t \\ &\quad + 28.625 \times 10^{-4} t^2 + 2.617 \times 10^{-6} t^3 \end{aligned} \quad (3)$$

$$[0^\circ < t, \text{ °C (Int)} < 350^\circ]$$

where  $t$  is on the International temperature scale.

Table 2 gives values of the vapor pressure of helium as originally reported by Keller (see table 1), but corrected to 0° C and reduced to standard gravity. Column 1 gives the actual measured vapor pressures reported by Keller. Column 2 gives values of the tempera-



TABLE 2. - Original vapor pressure data for helium obtained by Keller, corrected to 0° C and standard gravity

$$(P_{v.p.})_{corr.} = (P_{v.p.})_{obs.} (\rho_t / \rho_{0^\circ}) (g_L / g_S)$$

$(P_{v.p.})_{obs.}$ mm Hg at 0° C	$t_{Hg}$ °C	$(P_{v.p.})_{corr.}$ mm Hg at 0° C	$T_{vap}(58)$ °K	Exp. No.
589.99	32.5	585.6113	3.9493	A- 8- 1
589.58	32.5	585.2044	3.9486	A- 8- 2
588.40	32.6	584.0226	3.9466	A- 8- 3
592.89	32.4	588.5005	3.9541	A- 9- 1
593.13	32.4	588.7387	3.9545	A- 9- 2
594.27	31.7	589.9450	3.9565	A- 9- 3
593.60	32.7	589.1732	3.9552	A-11- 1
593.05	32.8	588.6167	3.9543	A-11- 2
592.88	32.8	588.4480	3.9540	A-11- 3
597.42	32.2	593.0184	3.9616	A-12- 1
595.92	33.2	591.4224	3.9590	A-12- 2
594.53	32.8	590.0856	3.9567	A-12- 3
284.80	27.8	282.9269	3.3166	B- 1- 1
287.33	28.0	285.4299	3.3234	B- 1- 2
289.06	27.9	287.1536	3.3280	B- 1- 3
296.50	29.0	294.4859	3.3476	B- 2- 1
295.94	29.0	293.9297	3.3461	B- 2- 2
296.30	28.0	294.3406	3.3472	B- 2- 3
296.96	32.6	294.7508	3.3483	B- 3- 1
291.60	32.4	289.4411	3.3342	B- 4- 1
292.62	33.0	290.4220	3.3368	B- 4- 2
293.23	32.2	291.0696	3.3385	B- 4- 3
293.88	32.6	291.6937	3.3402	B- 4- 4
295.31	32.6	293.1130	3.3440	B- 5- 1
295.99	32.4	293.7986	3.3458	B- 5- 2
297.08	32.2	294.8912	3.3487	B- 5- 3



TABLE 2. - Original vapor pressure data for helium obtained by Keller, corrected to 0° C and standard gravity (Cont.)

$$(P_{v.p.})_{\text{corr.}} = (P_{v.p.})_{\text{obs.}} \left( \rho_t / \rho_{0^\circ} \right) \left( g_L / g_S \right)$$

$(P_{v.p.})_{\text{obs.}}$ mm Hg at 0° C	$t_{\text{Hg}}$ °C	$(P_{v.p.})_{\text{corr.}}$ mm Hg at 0° C	$T_{\text{vap}}(58)$ °K	Exp. No.
145.55	32.6	144.4672	2.8509	C- 3- 1
148.37	32.7	147.2635	2.8628	C- 3- 2
147.90	32.4	146.8050	2.8609	C- 4- 1
147.55	32.6	146.4523	2.8594	C- 4- 2
147.92	33.0	146.8089	2.8609	C- 4- 3
148.35	32.7	147.2437	2.8627	C- 4- 4
149.44	32.2	148.3390	2.8674	C- 5- 1
149.73	32.3	148.6241	2.8686	C- 5- 2
150.10	32.5	148.9860	2.8701	C- 5- 3
150.63	32.7	149.5067	2.8723	C- 5- 4
148.88	32.0	147.7884	2.8650	C- 6- 1
149.42	32.6	148.3084	2.8672	C- 6- 2
53.25	27.6	52.9017	2.3164	D- 2- 1
53.31	27.8	52.9594	2.3169	D- 2- 2
53.82	26.7	53.4767	2.3213	D- 2- 3
53.26	32.2	52.8676	2.3161	D- 3- 1
53.69	32.6	53.2906	2.3197	D- 3- 2
52.45	32.3	52.0626	2.3091	D- 4- 1
52.44	32.2	52.0536	2.3091	D- 5- 1
53.12	32.4	52.7267	2.3148	D- 5- 2
52.80	32.0	52.4129	2.3122	D- 6- 1
53.60	32.2	53.2051	2.3189	D- 6- 2
53.08	32.9	52.6823	2.3145	D- 9- 1
53.72	32.7	53.3194	2.3199	D- 9- 2
53.09	32.2	52.6988	2.3146	D- 10- 1
53.63	32.5	53.2320	2.3192	D- 10- 2
54.20	33.0	53.7929	2.3239	D- 10- 3
51.74	32.4	51.3569	2.3030	D- 11- 1
52.25	32.4	51.8632	2.3074	D- 11- 2



ture of the mercury of the manometer corresponding to a given

TABLE 2. - Original vapor pressure data for helium obtained by  
Keller, corrected to 0° C and standard gravity (Cont.)

$$(P_{v.p.})_{corr.} = (P_{v.p.})_{obs.} \left( \frac{\rho_t}{\rho_{0^\circ}} \right) \left( \frac{g_L}{g_S} \right)$$

From the data given in column 3 of table 2, we calculate the temper-

atures given in column 4 of table 2, using H. van Dijk, *Ned. Tijdschr. W.*

*Chem. en Phys.*, 1937, 1, 103, K. Tamm's (6) tables of density differences in which these

authors (6) say that linear interpolation is valid for all of their

$(P_{v.p.})_{obs.}$ mm Hg at 0° C	$t_{Hg}$ °C	$(P_{v.p.})_{corr.}$ mm Hg at 0° C	$T_{vap}(58)$ °K	Exp. No.
35.70	32.8	35.4331	2.1462	E- 1- 1
35.53	32.7	35.2650	2.1443	E- 2- 1
35.59	32.4	35.3265	2.1450	E- 2- 2
35.55	32.5	35.2862	2.1445	E- 3- 1
35.61	33.6	35.3387	2.1451	E- 3- 2
36.29	32.2	36.0226	2.1526	E- 4- 1
36.39	32.3	36.1212	2.1537	E- 4- 2
35.73	32.1	35.4674	2.1465	E- 5- 1
35.88	32.4	35.6144	2.1482	E- 5- 2

In table 3 we give the original PVT data, as reported by Keller, along with the vapor pressures from table 2. In column 5, we give values of  $(PV/N)_{obs.}$ , which is just column 2 divided by column 3. For a given isotherm these  $(PV/N)_{obs.}$ 's are not exactly at the same temperature as indicated by the vapor-pressure thermometer. They must therefore be corrected so that the data are truly isothermal. We make the correction at constant density. The correction is made in the following way. We assume the  $(PV/N)$  product is expressible as

$$\begin{aligned} (PV/N) &= RT \left[ 1 + \alpha(\theta/V) \right] \\ \left[ \frac{\partial(PV/N)/\partial\theta}{\partial V} \right]_{PV} &= R + R(\theta/V) \left( \frac{\partial(\theta/V)/\partial\theta}{\partial V} \right) \\ &= R \left[ 1 + \alpha(\theta) \left( \frac{\partial(\theta/V)/\partial\theta}{\partial V} \right) \right] \end{aligned}$$

Then the correction is

$$\begin{aligned} \delta(PV/N) &= RT \left[ 1 + \alpha(\theta) \left( \frac{\partial(\theta/V)/\partial\theta}{\partial V} \right) \right] \\ &= \frac{R/T}{\left( \frac{\partial\theta}{\partial T} \right)_{avg.}} \left[ 1 + \alpha(\theta) \left( \frac{\partial(\theta/V)/\partial\theta}{\partial V} \right) \right]. \end{aligned}$$



ture of the mercury of the manometer corresponding to a given  $(P_{v,p.})_{obs.}$  and column 3 gives values for the vapor pressure of helium, corrected to  $0^\circ C$  and  $g_S$ , calculated from equations (1), (2), and (3). From the data given in column 3 of table 2, we calculated the temperatures given in column 4 of table 2, using H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan's (6) tables of vapor pressures in which these authors (6) say that linear interpolation is valid for all of their tables and that the estimated uncertainty of the  $1958 He^4$  scale is about  $0.002^\circ$  for temperatures from  $1^\circ$  to  $4.5^\circ K$ .

We now proceed to recalculate Keller's data.

#### RECALCULATION OF KELLER'S DATA

In table 3 we give the original PVT data, as reported by Keller, along with the vapor pressures from table 2. In column 5, we give values of  $(PV/N)_{obs.}$ , which is just column 2 divided by column 3. For a given isotherm these  $(PV/N)_{obs.}$ 's are not exactly at the same temperature as indicated by the vapor-pressure thermometer. They must therefore be corrected so that the data are truly isothermal. We make the correction at constant density. The correction is made in the following way. We assume the  $(PV/N)$  product is expressible as

$$\begin{aligned} (PV/N) &= RT \left[ 1 + B(N/V) \right] \\ \left[ \frac{d(PV/N)/dT}{N/V} \right] &= R + R(N/V) \left( \frac{d(BT)/dT}{N/V} \right) \\ &= R \left[ 1 + (N/V) \left( \frac{d(BT)/dT}{N/V} \right) \right] \end{aligned}$$

Then the correction is

$$\begin{aligned} \Delta(PV/N) &= R\Delta T \left[ 1 + (N/V) \left( \frac{d(BT)/dT}{N/V} \right) \right] \\ &= \frac{R\Delta P}{(dP/dT)_{avg.}} \left[ 1 + N/V \left( \frac{d(BT)/dT}{N/V} \right) \right]. \end{aligned}$$



TABLE 3. - Experimental PVT data for the isotherms of He<sup>4</sup> as originally reported by Keller

Exp. No.	P mm Hg at 0°C	(N/V.) x 10 <sup>4</sup> mole/cc	(P <sub>v.p.</sub> ) <sub>corr.</sub> mm Hg at 0°C	(PV/N) <sub>obs.</sub> cc-mm/mole
$(P_{v.p.})_{avg.} = 588.5656 \text{ mm Hg at } 0^\circ \text{ C}$				
A- 8-1	202.40	8.8713	585.6113	228,151.5
A- 8-2	127.30	5.4105	585.2044	235,283.2
A- 8-3	80.65	3.3679	584.0226	239,466.7
A- 9-1	205.45	9.0060	588.5005	228,125.7
A- 9-2	135.16	5.7515	588.7387	234,999.6
A- 9-3	74.08	3.0817	589.9450	240,386.8
A-11-1	231.49 <sup>1/</sup>	10.2718	589.1732	225,364.6
A-11-2	166.58 <sup>1/</sup>	7.1878	588.6167	231,753.8
A-11-3	120.67	5.1171	588.4480	235,817.2
A-12-1	96.98	4.0649	593.0184	238,579.1
A-12-2	40.095	1.6462	591.4224	243,560.9
A-12-3	20.231	0.8252	590.0856	245,164.8

1/ The original published value for P is: P = 116.58 mm Hg. However, in a later publication (4), Keller points out that the P value for A-11-2 should be 166.58 mm Hg instead of 116.58 mm Hg.



TABLE 3. - Experimental PVT data for the isotherms of He<sup>4</sup> as originally reported by Keller (Cont.)

Exp. No.	P mm Hg at 0°C	(N/V) x 10 <sup>4</sup> mole/cc	(P <sub>v.p.</sub> ) <sub>corr.</sub> mm Hg at 0° C	(PV/N) <sub>obs.</sub> cc-mm/mole
$(P_{v.p.})_{avg.} = 291.2462 \text{ mm Hg at } 0^\circ \text{ C}$				
B- 1-1	163.01	8.6759	282.9269	187,888.3
B- 1-2	113.00	5.7961	285.4299	194,958.7
B- 1-3	36.676	1.8002	287.1536	203,732.9
B- 2-1	182.97	9.7495	294.4859	187,671.2
B- 2-2	133.89	6.9067	293.9297	193,855.2
B- 2-3	93.79	4.7326	294.3406	198,178.6
B- 3-1	64.23	3.1835	294.7508	201,759.1
B- 4-1	134.40	6.9601	289.4411	193,100.7
B- 4-2	98.98	5.0149	290.4220	197,371.8
B- 4-3	56.00	2.7703	291.0696	202,144.2
B- 4-4	24.422	1.1877	291.6937	205,624.3
B- 5-1	196.13	10.5701	293.1130	185,551.7
B- 5-2	153.56	8.0253	293.7986	191,344.9
B- 5-3	81.63	4.0860	294.8912	199,779.7



TABLE 3. - Experimental PVT data for the isotherms of He<sup>4</sup> as originally reported by Keller (Cont.)

Exp. No.	P mm Hg at 0°C	(N/V) x 10 <sup>4</sup> mole/cc	(P <sub>v.p.</sub> ) <sub>corr.</sub> mm Hg at 0°C	(PV/N) <sub>obs.</sub> cc-mm/mole
$(P_{v.p.})_{avg.} = 147.5494 \text{ mm Hg at } 0^\circ \text{ C}$				
C- 3-1	66.95	3.9594	144.4672	169,091.3
C- 3-2	25.923	1.4791	147.2635	175,262.0
C- 4-1	120.85	7.4690	146.8050	161,802.1
C- 4-2	81.55	4.8679	146.4523	167,526.0
C- 4-3	51.85	3.0197	146.8089	171,705.8
C- 4-4	16.844	0.9553	147.2437	176,321.6
C- 5-1	113.71	6.9623	148.3390	163,322.5
C- 5-2	72.72	4.2949	148.6241	169,317.1
C- 5-3	52.10	3.0250	148.9860	172,231.4
C- 5-4	14.080	0.7926	149.5067	177,012.4
C- 6-1	93.61	5.6311	147.7884	166,237.5
C- 6-2	39.109	2.2490	148.3084	173,895.1
D- 5-1	49.92	3.0096	52.6980	139,341.3
D- 5-2	39.590	2.4165	53.3320	139,339.8
D- 5-3	34.278	1.9936	53.7929	142,694.4
D- 5-4	51.05	3.0663	51.3569	130,813.1
D- 5-5	39.772	1.6751	51.8632	140,861.6

2/ The original published value for P is: 9 = 45.14 mm Hg. When we compared our (PV/N)<sub>corr.</sub> value with Keller's published (PV/N)<sub>corr.</sub> value, we found, for experiment D-5-1, the two values differed by 0.7%. This led us to believe that there must be an error in the published data for this experiment. In reply to a letter from us, Keller confirmed that there had been an error in transcription in the data for point D-5-1. We quote Keller: "... the P value for D-5-1 should be 45.31 mm Hg instead of 45.14. The N/V value for D-5-1 is correct as given. The pressure value is wrong due to a transcription error, 45.14 being the directly observed manometer height uncorrected for t and g. However the correct value of PV/N was used in the least squares treatment of PV/N vs N/V, ...".



TABLE 3. - Experimental PVT data for the isotherms of He<sup>4</sup> as originally reported by Keller (Cont.)

Exp. No.	P mm Hg at 0°C	(N/V) x 10 <sup>4</sup> mole/cc	(P <sub>v.p.</sub> ) <sub>corr.</sub> mm Hg at 0°C	(PV/N) <sub>obs.</sub> cc-mm/mole
$(P_{v.p.})_{avg.} = 52.7590 \text{ mm Hg at } 0^\circ \text{ C}$				
D- 2-1	40.346	2.9234	52.9017	138,010.5
D- 2-2	25.103	1.7845	52.9594	140,672.5
D- 2-3	12.905	0.9021	53.4767	143,055.1
D- 3-1	48.52	3.5557	52.8676	136,457.0
D- 3-2	26.510	1.8849	53.2906	140,644.1
D- 4-1	31.010	2.2310	52.0626	138,996.0
D- 5-1	43.81 <sup>2/</sup>	3.2104	52.0536	136,462.7
D- 5-2	15.684	1.1042	52.7267	142,039.5
D- 6-1	37.530	2.7069	52.4129	138,645.7
D- 6-2	20.574	1.4527	53.2051	141,625.9
D- 9-1	38.318	2.7686	52.6823	138,402.1
D- 9-2	16.887	1.1901	53.3194	141,895.6
D-10-1	49.62	3.6394	52.6988	136,341.2
D-10-2	33.560	2.4085	53.2320	139,339.8
D-10-3	14.278	1.0006	53.7929	142,694.4
D-11-1	41.65	3.0443	51.3569	136,813.1
D-11-2	20.772	1.4751	51.8632	140,817.6

2/ The original published value for P is:  $P = 44.14 \text{ mm Hg}$ . When we compared our  $(PV/N)_{corr.}$  value with Keller's published  $(PV/N)_{corr.}$  value,

we found, for experiment D-5-1, the two values differed by 0.7%. This led us to believe that there must be an error in the published data for this experiment. In reply to a letter from us, Keller confirmed that there had been an error in transcription in the data for point D-5-1. We quote Keller: "... the P value for D-5-1 should be 43.81 mm Hg instead of 44.14. The N/V value for D-5-1 is correct as given. The pressure value is wrong due to a transcription error, 44.14 being the directly observed meniscus height uncorrected for t and g. However the correct value of PV/N was used in the least squares treatment of PV/N vs N/V, ...".



For each isotherm we corrected each  $(PV/N)_{\text{obs.}}$  to the average value

of the pressure as given by the vapor pressure thermometer. We then used the calculated  $\bar{P}_{\text{v.p.}}$  values to calculate the corrected  $(PV/N)_{\text{corr.}}$ . The table as given

Exp. No.	P mm Hg at 0°C	$(N/V) \times 10^4$ mole/cc	$(P_{\text{v.p.}})_{\text{corr.}}$ mm Hg at 0°C	$(PV/N)_{\text{obs.}}$ cc-mm/mole
----------	----------------	-----------------------------	---	-----------------------------------

values of  $\bar{P}_{\text{v.p.}}$  avg. = 35.5417 mm Hg at 0°C

E- 1-1	19.138	1.4664	35.4331	130,510.1
E- 2-1	30.106	2.3463	35.2650	128,312.7
E- 2-2	14.989	1.1429	35.3265	131,148.8
E- 3-1	25.852	2.0024	35.2862	129,105.1
E- 3-2	12.406	0.9431	35.3387	131,544.9
E- 4-1	27.738	2.1448	36.0226	129,326.7
E- 4-2	10.718	0.8084	36.1212	132,582.9
E- 5-1	32.275	2.5216	35.4674	127,994.1
E- 5-2	21.604	1.6595	35.6144	130,183.8

not as originally published by Keller, but corrected to value (6) after indicated was necessary.

To represent the data in table 5, we evaluated the constants by means of least squares for the following four equations:

$$(PV/N)_{\text{corr.}} = a + b(N/V), \quad (6)$$

$$(PV/N)_{\text{corr.}} = a + b(N/V) + c(N/V)^2 \quad (7)$$

$$(PV/N)_{\text{corr.}} = a' + bP_{\text{corr.}} \quad (8)$$

$$(PV/N)_{\text{corr.}} = a' + bP_{\text{corr.}} + c'P_{\text{corr.}}^2 \quad (9)$$

We also evaluated the standard deviation for each constant evaluated. The constants evaluated along with their standard deviations are given in table 7.

In table 8, we give values of the difference between  $(PV/N)_{\text{corr.}}$  observed and the values calculated from our least squares treatment.



For each isotherm we corrected each  $(PV/N)_{\text{obs.}}$  to the average value of the pressure as given by the vapor pressure thermometer. We then used the calculated  $\Delta P$ 's and values of  $dP/dT$  from the  $T_{58}$  table as given by H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan (6). Values of  $d(BT)/dT$  were obtained from a first difference table of calculated values of BT versus T from the table of Kilpatrick, Keller, and Hammel (5). The details of the correction calculation are given in table 4.

In table 5, we give the corrected values of  $(PV/N)$  along with the corrected pressures corresponding to the corrected  $(PV/N)$ 's at the observed N/V values.

In table 6 we compare our corrected  $(PV/N)$  values with the values, not as originally published by Keller, but corrected as Keller (4) later indicated was necessary.

To represent the data in table 5, we evaluated the constants by means of least squares for the following four equations:

$$(PV/N)_{\text{corr.}} = A + b(N/V) \quad (4)$$

$$(PV/N)_{\text{corr.}} = A + b(N/V) + c(N/V)^2 \quad (5)$$

$$(PV/N)_{\text{corr.}} = A' + BP_{\text{corr.}} \quad (6)$$

$$(PV/N)_{\text{corr.}} = A' + BP_{\text{corr.}} + c' P_{\text{corr.}}^2 \quad (7)$$

We also evaluated the standard deviation for each constant evaluated. The constants evaluated along with their standard deviations are given in table 7.

In table 8, we give values of the difference between  $(PV/N)_{\text{corr.}}$  observed and the values calculated from our least squares treatment,



TABLE 4. - Details of  $\Delta(PV/N)$  calculations to reduce experimental data to a true isotherm (Cont.)

Exp. No.	$(P_{v.p.})_{corr.}$	$\Delta(P_{v.p.})$	$(dP/dT)_{avg.}$	$\Delta T \cdot 10^3$	$R\Delta T$	$\left[ 1 + \frac{N}{V} \left( \frac{d(BT)}{dT} \right) \right]$	$\Delta(PV/N)$
	mm Hg at 0° C	mm Hg at 0° C		°K	cc-mm/mole		cc-mm/mole

$$(P_{v.p.})_{avg.} = 588.5656 \text{ mm Hg at } 0^\circ \text{C}$$

$$T_{58} = 3.95420^\circ \text{ K}$$

$$(dP/dT)_{58} = 601.264$$

A- 8-1	585.6113	2.9543	600.2385	4.922	307.0	1.01881	312.8
A- 8-2	585.2044	3.3612	600.0950	5.601	349.3	1.01147	353.3
A- 8-3	584.0226	4.5430	599.6850	7.576	472.5	1.00714	475.9
A- 9-1	588.5005	0.0651	601.2430	0.108	6.7	1.01909	6.8
A- 9-2	588.7387	-0.1731	601.3270	-0.288	- 18.0	1.01219	- 18.2
A- 9-3	589.9450	-1.3794	601.7470	-2.292	-142.9	1.00653	-143.8
A-11-1	589.1732	-0.6076	601.4740	-1.010	- 63.0	1.02178	- 64.4
A-11-2	588.6167	-0.0511	601.2850	-0.085	- 5.3	1.01524	- 5.4
A-11-3	588.4480	-0.1176	601.2220	0.196	12.2	1.01085	12.3
A-12-1	593.0184	-4.4528	602.8180	-7.387	-460.7	1.00862	-464.7
A-12-2	591.4224	-2.8568	602.2720	-4.743	-295.8	1.00349	-296.8
A-12-3	590.0856	-1.5200	601.7890	-2.526	-157.5	1.00175	-157.8



TABLE 4. - Details of  $\Delta(PV/N)$  calculations to reduce experimental data to a true isotherm (Cont.)



TABLE 4. - Details of  $\Delta(PV/N)$  calculations to reduce experimental data to a true isotherm (Cont.)

Exp. No.	$(P_{v.p.})_{corr.}$ mm Hg at 0° C	$\Delta(P_{v.p.})$ mm Hg at 0° C	$(dP/dT)_{avg.}$	$\Delta T \cdot 10^3$ °K	$R\Delta T$ cc-mm/mole	$\left[ 1 + \frac{N}{V} \left( \frac{d(BT)}{dT} \right) \right]$	$\Delta(PV/N)$ cc-mm/mole
----------	---------------------------------------	-------------------------------------	------------------	-----------------------------	---------------------------	--	------------------------------

$$(P_{v.p.})_{avg.} = 147.5494 \text{ mm Hg at } 0^\circ \text{ C}$$

$$T_{58} = 2.86401^\circ \text{ K}$$

$$(dP/dT)_{58} = 236.043$$

C- 3-1	144.4672	3.0822	234.3385	13.153	820.3	1.00926	827.9
C- 3-2	147.2635	0.2859	235.8855	1.212	75.6	1.00346	75.9
C- 4-1	146.8050	0.7444	235.6385	3.159	197.0	1.01748	200.4
C- 4-2	146.4523	1.0971	235.4435	4.660	290.6	1.01139	293.9
C- 4-3	146.8089	0.7405	235.6385	3.143	196.0	1.00707	197.4
C- 4-4	147.2437	0.3057	235.8725	1.296	80.8	1.00224	81.0
C- 5-1	148.3390	-0.7896	236.4835	-3.339	-208.2	1.01629	-211.6
C- 5-2	148.6241	-1.0747	236.6395	-4.542	-283.3	1.01005	-286.1
C- 5-3	148.9860	-1.4366	236.8340	-6.066	-378.3	1.00708	-381.0
C- 5-4	149.5067	-1.9573	237.1090	-8.255	-514.8	1.00185	-515.8
C- 6-1	147.7884	-0.2390	236.1715	-1.012	-63.1	1.01318	-63.9
C- 6-2	148.3084	-0.7590	236.4575	-3.210	-200.2	1.00526	-201.3
D-10-1	51.0788	0.0002	116.5735	0.000	1.00000	1.00000	1.00000
D-10-2	51.2320	-0.4730	116.9895	-0.042	-252.1	1.00662	-253.8
D-10-3	51.7929	-1.0339	117.4015	-0.807	-549.2	1.00275	-550.7
D-11-1	51.3549	1.4021	115.5315	12.138	756.8	1.00837	763.1
D-11-2	51.8632	0.8736	115.9275	1.727	481.9	1.00406	483.9



TABLE 4. - Details of  $\Delta(PV/N)$  calculations to reduce experimental data to a true isotherm (Cont.)



TABLE 4. - Details of  $\Delta(PV/N)$  calculations to reduce experimental data to a true isotherm (Cont.)

Exp. No.	$(P_{v.p.})_{corr.}$ mm Hg at 0° C	$\Delta(P_{v.p.})$ mm Hg at 0° C	$(dP/dT)_{avg.}$	$\Delta T \cdot 10^3$ °K	RΔT cc-mm/mole	$\left[ 1 + \frac{N}{V} \left( \frac{d(BT)}{dT} \right) \right]$	$\Delta(PV/N)$ cc-mm/mole
E- 1-1	35.4331	0.1086	89.9850	1.207	75.3	1.00441	75.6
E- 2-1	35.2650	0.2767	89.8596	3.079	192.0	1.00706	193.4
E- 2-2	35.3265	0.2152	89.9058	2.394	149.3	1.00344	149.8
E- 3-1	35.2862	0.2555	89.8728	2.843	177.3	1.00603	178.4
E- 3-2	35.3387	0.2030	89.9124	2.258	140.8	1.00284	141.2
E- 4-1	36.0226	-0.4809	90.4048	-5.319	-331.7	1.00646	-333.8
E- 4-2	36.1212	-0.5795	90.4763	-6.405	-399.4	1.00243	-400.4
E- 5-1	35.4674	0.0743	90.0048	0.826	51.5	1.00759	51.9
E- 5-2	35.6144	-0.0727	90.1170	-0.807	- 50.3	1.00500	- 50.6



TABLE 5. - Corrected values of (PV/N) along with the corrected pressures corresponding to the corrected (PV/N)'s at the observed (N/V) values

P mm Hg at 0° C	(N/V) x 10 <sup>4</sup> mole/cc	(PV/N) <sub>obs.</sub> cc-mm/mole	Δ(PV/N) cc-mm/mole	(PV/N) <sub>corr., obs.</sub> cc-mm/mole	P <sub>corr. obs.</sub> mm Hg at 0° C
$(P_{v.p.})_{avg.} = 588.5656 \text{ mm Hg at } 0^\circ \text{ C}$					$T_{58} = 3.95420^\circ \text{ K}$
202.40	8.8713	228,151.5	312.8	228,464.3	202.678
127.30	5.4105	235,283.2	353.3	235,636.5	127.491
80.65	3.3679	239,466.7	475.9	239,942.6	80.810
205.45	9.0060	228,125.7	6.8	228,132.5	205.456
135.16	5.7515	234,999.6	- 18.2	234,981.4	135.150
74.08	3.0817	240,386.8	-143.8	240,243.0	74.036
231.49 <sup>1/</sup>	10.2718	225,364.6	- 64.4	225,300.2	231.424
166.58 <sup>1/</sup>	7.1878	231,753.8	- 5.4	231,748.4	166.576
120.67	5.1171	235,817.2	12.3	235,829.5	120.676
96.98	4.0649	238,579.1	-464.7	238,114.4	96.791
40.095	1.6462	243,560.9	-296.8	243,264.1	40.0461
20.231	0.8252	245,164.8	-157.8	245,007.0	20.2180

1/ See footnote 1 of table 3.



TABLE 5. - Corrected values of (PV/N) along with the corrected pressures corresponding to the corrected (PV/N)'s at the observed (N/V) values (Cont.)

P mm Hg at 0° C	(N/V) × 10 <sup>4</sup> mole/cc	(PV/N) <sub>obs.</sub> cc-mm/mole	△(PV/N) cc-mm/mole	(PV/N) <sub>corr. obs.</sub> cc-mm/mole	P <sub>corr. obs.</sub> mm Hg at 0° C
$(P_{v.p.})_{avg.} = 291.2462 \text{ mm Hg at } 0^\circ \text{ C}$					$T_{58} = 3.33904^\circ \text{ K}$
163.01	8.6759	187,888.3	1425.8	189,314.1	164.247
113.00	5.7961	194,958.7	987.6	195,946.3	113.572
36.676	1.8002	203,732.9	687.4	204,420.3	36.7997
182.97	9.7495	187,671.2	-549.1	187,122.1	182.435
133.89	6.9067	193,855.2	-452.3	193,402.9	133.578
93.79	4.7326	198,178.6	-518.8	197,659.8	93.544
64.23	3.1835	201,759.1	-585.3	201,173.8	64.044
134.40	6.9601	193,100.7	305.9	193,406.6	134.613
98.98	5.0149	197,371.8	138.9	197,510.7	99.050
56.00	2.7703	202,144.2	29.6	202,173.8	56.008
24.422	1.1877	205,624.3	-74.7	205,549.6	24.4131
196.13	10.5701	185,551.7	-317.5	185,234.2	195.794
153.56	8.0253	191,344.9	-431.4	190,913.5	153.214
81.63	4.0860	199,779.7	-609.9	199,169.8	81.381



TABLE 5. - Corrected values of (PV/N) along with the corrected pressures corresponding to the corrected (PV/N)'s at the observed (N/V) values (Cont.)

P mm Hg at 0° C	(N/V) × 10 <sup>4</sup> mole/cc	(PV/N) <sub>obs.</sub> cc-mm/mole	△(PV/N) cc-mm/mole	(PV/N) <sub>corr. obs.</sub> cc-mm/mole	P <sub>corr. obs.</sub> mm Hg at 0° C
$(P_{v.p.})_{avg.} = 147.5494 \text{ mm Hg at } 0^\circ \text{ C}$					$T_{58} = 2.86401^\circ \text{ K}$
66.95	3.9594	169,091.3	827.9	169,919.2	67.278
25.923	1.4791	175,262.0	75.9	175,337.9	25.9342
120.85	7.4690	161,802.1	200.4	162,002.5	121.000
81.55	4.8679	167,526.0	293.9	167,819.9	81.693
51.85	3.0197	171,705.8	197.4	171,903.2	51.910
16.844	0.9553	176,321.6	81.0	176,402.6	16.8517
113.71	6.9623	163,322.5	-211.6	163,110.9	113.563
72.72	4.2949	169,317.1	-286.1	169,031.0	72.597
52.10	3.0250	172,231.4	-381.0	171,850.4	51.985
14.030	0.7926	177,012.4	-515.8	176,496.6	13.9891
93.61	5.6311	166,237.5	-63.9	166,173.6	93.574
39.109	2.2490	173,895.1	-201.3	173,693.8	39.0637

See footnote 3 of table 3.



TABLE 5. - Corrected values of (PV/N) along with the corrected pressures corresponding to the corrected (PV/N)'s at the observed (N/V) values (Cont.)

P mm Hg at 0° C	(N/V) $\times 10^4$ mole/cc	(PV/N) <sub>obs.</sub> cc-mm/mole	$\Delta(PV/N)$ cc-mm/mole	(PV/N) <sub>corr. obs.</sub> cc-mm/mole	P <sub>corr. obs.</sub> mm Hg at 0° C
$(P_{v.p.})_{avg.} = 52.7590 \text{ mm Hg at } 0^\circ \text{ C}$					$T_{58} = 2.31513^\circ \text{ K}$
40.346	2.9234	138,010.5	- 76.8	137,933.7	40.3235
25.103	1.7845	140,672.5	-107.5	140,565.0	25.0838
12.905	0.9021	143,055.1	-382.9	142,672.2	12.8705
48.52	3.5557	136,457.0	- 58.7	136,398.3	48.499
26.510	1.8849	140,644.1	-284.8	140,359.3	26.4563
31.010	2.2310	138,996.0	376.4	139,372.4	31.0940
43.81 <sup>2/</sup>	3.2104	136,462.7	382.3	136,845.0	43.933
15.684	1.1042	142,039.5	17.4	142,056.9	15.6859
37.530	2.7069	138,645.7	186.9	138,832.6	37.5806
20.574	1.4527	141,625.9	-238.8	141,387.1	20.5393
38.318	2.7686	138,402.1	41.3	138,443.4	38.3294
16.887	1.1901	141,895.6	-299.6	141,596.0	16.8513
49.62	3.6394	136,341.2	32.5	136,373.7	49.632
33.560	2.4085	139,339.8	-253.8	139,086.0	33.4989
14.278	1.0006	142,694.4	-550.7	142,143.7	14.2229
41.65	3.0443	136,813.1	763.1	137,576.2	41.882
20.772	1.4751	140,817.6	483.9	141,301.5	20.8434

<sup>2/</sup> See footnote 2 of table 3.



TABLE 5. - Corrected values of (PV/N) along with the corrected pressures corresponding to the corrected (PV/N)'s at the observed (N/V) values (Cont.)

P mm Hg at 0° C	(N/V) × 10 <sup>4</sup> mole/cc	(PV/N) <sub>obs.</sub> cc-mm/mole	△(PV/N) cc-mm/mole	(PV/N) <sub>corr. obs.</sub> cc-mm/mole	P <sub>corr. obs.</sub> mm Hg at 0° C
$(P_{v.p.})_{avg.} = 52.7590 \text{ mm Hg at } 0^\circ \text{ C}$					$T_{58} = 2.31513^\circ \text{ K}$
40.346	2.9234	138,010.5	- 76.8	137,933.7	40.3235
25.103	1.7845	140,672.5	-107.5	140,565.0	25.0838
12.905	0.9021	143,055.1	-382.9	142,672.2	12.8705
48.52	3.5557	136,457.0	- 58.7	136,398.3	48.499
26.510	1.8849	140,644.1	-284.8	140,359.3	26.4563
31.010	2.2310	138,996.0	376.4	139,372.4	31.0940
43.81 <sup>2/</sup>	3.2104	136,462.7	382.3	136,845.0	43.933
15.684	1.1042	142,039.5	17.4	142,056.9	15.6859
37.530	2.7069	138,645.7	186.9	138,832.6	37.5806
20.574	1.4527	141,625.9	-238.8	141,387.1	20.5393
38.318	2.7686	138,402.1	41.3	138,443.4	38.3294
16.887	1.1901	141,895.6	-299.6	141,596.0	16.8513
49.62	3.6394	136,341.2	32.5	136,373.7	49.632
33.560	2.4085	139,339.8	-253.8	139,086.0	33.4989
14.278	1.0006	142,694.4	-550.7	142,143.7	14.2229
41.65	3.0443	136,813.1	763.1	137,576.2	41.882
20.772	1.4751	140,817.6	483.9	141,301.5	20.8434

<sup>2/</sup> See footnote 2 of table 3.



TABLE 5. - Corrected values of  $(PV/N)$  along with the corrected pressures corresponding to the corrected  $(PV/N)$ 's at the observed  $(N/V)$  values (Cont.)

P mm Hg at 0° C	$(N/V) \times 10^4$ mole/cc	$(PV/N)_{\text{obs.}}$ cc-mm/mole	$\Delta(PV/N)$ cc-mm/mole	$(PV/N)_{\text{corr. obs.}}$ cc-mm/mole	$P_{\text{corr. obs.}}$ mm Hg at 0° C
19.138	1.4664	130,510.1	75.6	130,585.7	19.1491
30.106	2.3463	128,312.7	193.4	128,506.1	30.1514
14.989	1.1429	131,148.8	149.8	131,298.6	15.0061
25.852	2.0024	129,105.1	178.4	129,283.5	25.8877
12.406	0.9431	131,544.9	141.2	131,686.1	12.4193
27.738	2.1448	129,326.7	-333.8	128,992.9	27.6664
10.718	0.8084	132,582.9	-400.4	132,182.5	10.6856
32.275	2.5216	127,994.1	51.9	128,046.0	32.2881
21.604	1.6595	130,183.8	- 50.6	130,133.2	21.5956

$$(P_{\text{v.p.}})_{\text{avg.}} = 35.5417 \text{ mm Hg at } 0^\circ \text{ C} \quad T_{58} = 2.14736^\circ \text{ K}$$

TABLE 5. - Corrected values of  $(PV/N)$  along with the corrected pressures corresponding to the corrected  $(PV/N)$ 's at the observed  $(N/V)$  values (Cont.)



TABLE 6. - Values of (PV/N) as corrected by the Helium Research Center along with the (PV/N)'s as corrected by Keller (3, 4)

Exp. No.	$(PV/N)_{corr. HRC}$ cc-mm/mole	$(PV/N)_{corr. Keller}$ cc-mm/mole	$\Delta^1/$ cc-mm/mole
		$(P_{v.p.})_{avg.} = 588.5656 \text{ mm Hg at } 0^\circ \text{ C}$	$T_{58} = 3.9542^\circ \text{ K}$
A- 8-1	228,464.3	228,464	+ 0.3
A- 8-2	235,636.5	235,658	-21.5
A- 8-3	239,942.6	239,965	-22.4
A- 9-1	228,132.5	228,187	-54.5
A- 9-2	234,981.4	235,001	-19.6
A- 9-3	240,243.0	240,203	+40.0
A-11-1	225,300.2	225,365	-64.8
A-11-2	231,748.4	231,753	- 4.6
A-11-3	235,829.5	235,879	-49.5
A-12-1	238,114.4	238,144	-29.6
A-12-2	243,264.1	243,316	-51.9
A-12-3	245,007.0	244,983	+24.0
		$(P_{v.p.})_{avg.} = 291.2462 \text{ mm Hg at } 0^\circ \text{ C}$	$T_{58} = 3.3390^\circ \text{ K}$
B- 1-1	189,314.1	189,337	-22.9
B- 1-2	195,946.3	195,965	-18.7
B- 1-3	204,420.3	204,487	-66.7
B- 2-1	187,122.1	187,228	-105.9
B- 2-2	193,402.9	193,352	+50.9
B- 2-3	197,659.8	197,490	+169.8
B- 3-1	201,173.8	201,197	-23.2
B- 4-1	193,406.6	193,405	+ 1.6
B- 4-2	197,510.7	197,558	-47.3
B- 4-3	202,173.8	202,204	-30.2
B- 4-4	205,549.6	205,569	-19.4
B- 5-1	185,234.2	185,299	-64.8
B- 5-2	190,913.5	190,967	-53.5
B- 5-3	199,169.8	199,152	+17.8

1/  $\Delta$  corresponds to the difference of  $(PV/N)_{corr. HRC}$  and  $(PV/N)_{corr. Keller}$



TABLE 6. - Values of (PV/N) as corrected by the Helium Research Center along with the (PV/N)'s as corrected by Keller (3, 4)

Exp. No.	$(PV/N)_{corr. HRC}$ cc-mm/mole	$(PV/N)_{corr. Keller}$ cc-mm/mole	$\Delta^1/$ cc-mm/mole
		$(P_{v.p.})_{avg.} = 588.5656 \text{ mm Hg at } 0^\circ \text{ C}$	$T_{58} = 3.9542^\circ \text{ K}$
A- 8-1	228,464.3	228,464	+ 0.3
A- 8-2	235,636.5	235,658	-21.5
A- 8-3	239,942.6	239,965	-22.4
A- 9-1	228,132.5	228,187	-54.5
A- 9-2	234,981.4	235,001	-19.6
A- 9-3	240,243.0	240,203	+40.0
A-11-1	225,300.2	225,365	-64.8
A-11-2	231,748.4	231,753	-4.6
A-11-3	235,829.5	235,879	-49.5
A-12-1	238,114.4	238,144	-29.6
A-12-2	243,264.1	243,316	-51.9
A-12-3	245,007.0	244,983	+24.0
		$(P_{v.p.})_{avg.} = 291.2462 \text{ mm Hg at } 0^\circ \text{ C}$	$T_{58} = 3.3390^\circ \text{ K}$
B- 1-1	189,314.1	189,337	-22.9
B- 1-2	195,946.3	195,965	-18.7
B- 1-3	204,420.3	204,487	-66.7
B- 2-1	187,122.1	187,228	-105.9
B- 2-2	193,402.9	193,352	+50.9
B- 2-3	197,659.8	197,490	+169.8
B- 3-1	201,173.8	201,197	-23.2
B- 4-1	193,406.6	193,405	+ 1.6
B- 4-2	197,510.7	197,558	-47.3
B- 4-3	202,173.8	202,204	-30.2
B- 4-4	205,549.6	205,569	-19.4
B- 5-1	185,234.2	185,299	-64.8
B- 5-2	190,913.5	190,967	-53.5
B- 5-3	199,169.8	199,152	+17.8

1/  $\Delta$  corresponds to the difference of  $(PV/N)_{corr. HRC}$  and  $(PV/N)_{corr. Keller}$



TABLE 6. - Values of (PV/N) as corrected by the Helium Research Center along with the (PV/N)'s as corrected by Keller (3, 4) (Cont.)

Exp. No.	$(PV/N)_{corr. HRC}$ cc-mm/mole	$(PV/N)_{corr. Keller}$ cc-mm/mole	$\Delta^1/$ cc-mm/mole
----------	------------------------------------	---------------------------------------	---------------------------

$$(P_{v.p.})_{avg.} = 147.5494 \text{ mm Hg at } 0^\circ \text{ C} \quad T_{58} = 2.8640^\circ \text{ K}$$

C- 3-1	169,919.2	169,592	+327.2
C- 3-2	175,337.9	175,007	+330.9
C- 4-1	162,002.5	161,676	+326.5
C- 4-2	167,819.9	167,465	+354.9
C- 4-3	171,903.2	171,581	+322.2
C- 4-4	176,402.6	176,068	+334.6
C- 5-1	163,110.9	162,756	+354.9
C- 5-2	169,031.0	168,628	+403.0
C- 5-3	171,850.4	171,483	+367.4
C- 5-4	176,496.6	176,136	+360.6
C- 6-1	166,173.6	165,796	+377.6
C- 6-2	173,693.8	173,329	+364.8

$$(P_{v.p.})_{avg.} = 52.7590 \text{ mm Hg at } 0^\circ \text{ C} \quad T_{58} = 2.3151^\circ \text{ K}$$

D- 2-1	137,933.7	137,947	- 13.3
D- 2-2	140,565.0	140,546	+ 19.0
D- 2-3	142,672.2	142,682	- 9.8
D- 3-1	136,398.3	136,394	+ 4.3
D- 3-2	140,359.3	140,397	- 37.7
D- 4-1	139,372.4	139,373	- 0.6
D- 5-1	136,845.0	136,900	- 55.0
D- 5-2	142,056.9	142,044	+ 12.9
D- 6-1	138,832.6	138,834	- 1.4
D- 6-2	141,387.1	141,377	+ 10.1
D- 9-1	138,443.4	138,464	- 20.6
D- 9-2	141,596.0	141,582	+ 14.0
D-10-1	136,373.7	136,405	- 31.3
D-10-2	139,086.0	139,092	- 6.0
D-10-3	142,143.7	142,200	- 56.3
D-11-1	137,576.2	137,559	+ 17.2
D-11-2	141,301.5	141,319	- 17.5

1/  $\Delta$  corresponds to the difference of  $(PV/N)_{corr. HRC}$  and  $(PV/N)_{corr. Keller}$ .



TABLE 6. - Values of (PV/N) as corrected by the Helium Research Center along with the (PV/N)'s as corrected by Keller (3, 4) (Cont.)

Exp. No.	$(PV/N)_{corr. HRC}$ cc-mm/mole	$(PV/N)_{corr. Keller}$ cc-mm/mole	$\Delta^1/$ cc-mm/mole
		$(P_{v.p.})_{avg.} = 35.5417 \text{ mm Hg at } 0^\circ \text{ C}$	$T_{58} = 2.1474^\circ \text{ K}$
E- 1-1	130,585.7	130,447	+138.7
E- 2-1	128,506.1	128,313	+193.1
E- 2-2	131,298.6	131,154	+144.6
E- 3-1	129,283.5	129,107	+176.5
E- 3-2	131,686.1	131,544	+142.1
E- 4-1	128,992.9	128,890	+102.9
E- 4-2	132,182.5	132,020	+162.5
E- 5-1	128,046.0	127,869	+177.0
E- 5-2	130,133.2	130,000	+133.2

1/  $\Delta$  corresponds to the difference of  $(PV/N)_{corr. HRC}$  and  $(PV/N)_{corr. Keller}$ .



TABLE 7.-Virial coefficients of He<sup>4</sup> as calculated by the Helium Research Center from the data given  
in table 5 of this report

Results using the equation:  $(PV/N)_{corr.} = A + b(N/V)$

<u>T<sub>58</sub>, °K</u>	<u>A, cc-mm/mole</u>	<u>-b·10<sup>-7</sup>, cc<sup>2</sup>-mm/mole<sup>2</sup></u>	<u>-(b/A)=-B, cc/mole</u>
3.9542	246,695.2 ± 98.9	2.069269 ± 0.016222	83.88 ± 0.63
3.3390	208,166.6 ± 107.8	2.156273 ± 0.016999	103.58 ± 0.77
2.8640	178,508.5 ± 66.1	2.200203 ± 0.015408	123.25 ± 0.82
2.3151	144,592.0 ± 125.1	2.283136 ± 0.052858	157.90 ± 3.53
2.1474	134,003.7 ± 54.7	2.349025 ± 0.030909	175.30 ± 2.24

Results using the equation:  $(PV/N)_{corr.} = A + b(N/V) + c(N/V)^2$

<u>T<sub>58</sub>, °K</u>	<u>A, cc-mm/mole</u>	<u>-b·10<sup>-7</sup>, cc<sup>2</sup>-mm/mole<sup>2</sup></u>	<u>-(b/A)=-B, cc/mole</u>	<u>-c·10<sup>-9</sup>, cc<sup>3</sup>-mm/mole<sup>3</sup></u>
3.9542	246,669.3 ± 177.0	2.056725 ± 0.071420	83.38 ± 2.84	0.111959 ± 0.618954
3.3390	208,010.3 ± 197.5	2.086124 ± 0.076035	100.29 ± 3.57	0.601382 ± 0.635188
2.8640	178,336.7 ± 93.0	2.081138 ± 0.053377	116.70 ± 2.94	1.476625 ± 0.642376
2.3151	144,331.3 ± 335.0	2.004482 ± 0.335941	138.88 ± 22.96	6.254702 ± 7.444764
2.1474	133,946.8 ± 184.9	2.270132 ± 0.245246	169.48 ± 18.08	2.387303 ± 7.353263



TABLE 7.-Virial coefficients of He<sup>4</sup> as calculated by the Helium Research Center from the data given in table 5 of this report (Cont'd.)

Results using the equation:  $(PV/N)_{corr.} = A' + BP_{corr.}$

<u>T<sub>58</sub>, °K</u>	<u>A', cc-mm/mole</u>	<u>-B, cc/mole</u>
3.9542	247,130.3 ± 154.9	92.52 ± 1.10
3.3390	208,812.8 ± 200.8	117.69 ± 1.66
2.8640	178,852.0 ± 139.4	136.75 ± 1.96
2.3151	144,750.9 ± 138.9	169.76 ± 4.25
2.1474	134,107.5 ± 60.5	186.06 ± 2.64

Results using the equation:  $(PV/N)_{corr.} = A' + BP_{corr.} + c' P_{corr.}^2$

<u>T<sub>58</sub>, °K</u>	<u>A', cc-mm/mole</u>	<u>-B, cc/mole</u>	<u>-c' · 10<sup>2</sup>, cc/mole, mm</u>
3.9542	246,642.8 ± 196.1	82.30 ± 3.44	4.003205 ± 1.308846
3.3390	207,925.7 ± 233.6	96.96 ± 4.73	9.425861 ± 2.099865
2.8640	178,285.9 ± 96.0	113.21 ± 3.33	17.821808 ± 2.452767
2.3151	144,295.6 ± 371.9	134.79 ± 26.92	56.943349 ± 43.306602
2.1474	133,936.6 ± 199.1	167.83 ± 20.37	42.679864 ± 47.301621



TABLE 8. - Values of  $(PV/N)_{corr. obs.}$  minus  $(PV/N)_{corr. cal.}$  as evaluated by the Helium Research Center from the data given in table 5

P Exp. No.	mm Hg at 0° C	$(N/V) \times 10^4$ mole/cc	$T_{vap.}(58)$ °K	$(PV/N)_{corr. obs.}$ cc-mm/mole	$\delta_1^{1/}$ cc-mm/mole	$\delta_2^{2/}$ cc-mm/mole	$\delta_3^{3/}$ cc-mm/mole	$\delta_4^{4/}$ cc-mm/mole
$T_{58} = 3.9542$ °K								
A- 8-1	202.40	8.8713	3.9493	228,464.3	126.19	128.91	85.02	146.09
A- 8-2	127.30	5.4105	3.9486	235,636.5	137.06	127.86	301.21	136.72
A- 8-3	80.65	3.3679	3.9466	239,942.6	216.47	212.82	288.56	211.78
A- 9-1	205.45	9.0060	3.9541	228,132.5	73.12	76.85	10.23	88.30
A- 9-2	135.16	5.7515	3.9545	234,981.4	187.58	178.37	354.69	192.47
A- 9-3	74.08	3.0817	3.9565	240,243.0	- 75.35	- 77.48	- 37.74	- 87.31
A-11-1	231.49	10.2718	3.9552	225,300.2	-139.90	-124.73	-419.62	-152.71
A-11-2	166.58	7.1878	3.9543	231,748.4	- 73.33	- 79.75	29.10	- 74.62
A-11-3	120.67	5.1171	3.9540	235,829.5	-277.06	-286.04	-136.29	-298.85
A-12-1	96.98	4.0649	3.9616	238,114.4	-169.45	-176.04	- 61.14	-187.59
A-12-2	40.095	1.6462	3.9590	243,264.1	- 24.69	- 16.41	-161.25	- 18.76
A-12-3	20.231	0.8252	3.9567	245,007.0	19.34	35.65	-252.77	44.48

1/  $\delta_1 = (PV/N)_{corr. obs.}$  minus  $(PV/N)_{corr. cal.}$  as evaluated from equation (4).  $\Sigma\delta_1^2 = 2.59189 \times 10^5$

2/  $\delta_2 = (PV/N)_{corr. obs.}$  minus  $(PV/N)_{corr. cal.}$  as evaluated from equation (5).  $\Sigma\delta_2^2 = 2.58250 \times 10^5$

3/  $\delta_3 = (PV/N)_{corr. obs.}$  minus  $(PV/N)_{corr. cal.}$  as evaluated from equation (6).  $\Sigma\delta_3^2 = 5.97689 \times 10^5$

4/  $\delta_4 = (PV/N)_{corr. obs.}$  minus  $(PV/N)_{corr. cal.}$  as evaluated from equation (7).  $\Sigma\delta_4^2 = 2.93067 \times 10^5$



TABLE 8. - Values of  $(PV/N)_{corr. obs.}$  minus  $(PV/N)_{corr. cal.}$  as evaluated by the Helium Research Center from the data given in table 5 (Cont.)

P Exp. No.	$(N/V) \times 10^4$ mm Hg at 0° C	$T_{vap.}(58)$ mole/cc	$(PV/N)_{corr. obs.}$ °K	$\delta_1^{1/}$ cc-mm/mole	$\delta_2^{2/}$ cc-mm/mole	$\delta_3^{3/}$ cc-mm/mole	$\delta_4^{4/}$ cc-mm/mole
$T_{58} = 3.3390$ °K							
B- 1-1	163.01	8.6759	3.3166	189,314.1	-144.90	-144.50	-168.57
B- 1-2	113.00	5.7961	3.3234	195,946.3	277.66	229.45	499.72
B- 1-3	36.676	1.8002	3.3280	204,420.3	135.41	184.96	- 61.56
B- 2-1	182.97	9.7495	3.3476	187,122.1	- 21.93	22.12	-220.04
B- 2-2	133.89	6.9067	3.3461	193,402.9	129.02	87.74	310.81
B- 2-3	93.79	4.7326	3.3472	197,659.8	-302.04	-342.99	-143.86
B- 3-1	64.23	3.1835	3.3483	201,173.8	-128.32	-134.35	-101.70
B- 4-1	134.40	6.9601	3.3342	193,406.6	247.86	207.29	436.32
B- 4-2	98.98	5.0149	3.3368	197,510.7	157.58	113.38	355.04
B- 4-3	56.00	2.7703	3.3385	202,173.8	- 19.29	- 11.13	- 47.45
B- 4-4	24.422	1.1877	3.3402	205,549.6	- 56.01	25.50	-390.03
B- 5-1	196.13	10.5701	3.3440	185,234.2	-140.39	- 53.63	-535.73
B- 5-2	153.56	8.0253	3.3458	190,913.5	51.63	32.32	132.36
B- 5-3	81.63	4.0860	3.3487	199,169.8	-186.28	-216.16	- 65.32

1/  $\delta_1 = (PV/N)_{corr. obs.}$  minus  $(PV/N)_{corr. cal.}$  as evaluated from equation (4).  $\Sigma\delta_1^2 = 3.88098 \times 10^5$

2/  $\delta_2 = (PV/N)_{corr. obs.}$  minus  $(PV/N)_{corr. cal.}$  as evaluated from equation (5).  $\Sigma\delta_2^2 = 3.58855 \times 10^5$

3/  $\delta_3 = (PV/N)_{corr. obs.}$  minus  $(PV/N)_{corr. cal.}$  as evaluated from equation (6).  $\Sigma\delta_3^2 = 12.37579 \times 10^5$

4/  $\delta_4 = (PV/N)_{corr. obs.}$  minus  $(PV/N)_{corr. cal.}$  as evaluated from equation (7).  $\Sigma\delta_4^2 = 4.37037 \times 10^5$



TABLE 8. - Values of  $(PV/N)_{\text{corr. obs.}}$  minus  $(PV/N)_{\text{corr. cal.}}$  as evaluated by the Helium Research Center from the data given in table 5 (Cont.)

P Exp. No.	$(N/V) \times 10^4$ mm Hg at 0° C	$T_{\text{vap.}}(58)$ mole/cc	$T$ °K	$(PV/N)_{\text{corr. obs.}}$ cc-mm/mole	$\delta_1^{1/}$ cc-mm/mole	$\delta_2^{2/}$ cc-mm/mole	$\delta_3^{3/}$ cc-mm/mole	$\delta_4^{4/}$ cc-mm/mole
$T_{58} = 2.8640$ °K								
C- 3-1	66.95	3.9594	2.8509	169,919.2	122.16	54.03	267.17	56.75
C- 3-2	25.923	1.4791	2.8628	175,337.9	83.69	111.70	32.27	107.95
C- 4-1	120.85	7.4690	2.8609	162,002.5	- 72.71	33.56	-303.27	24.73
C- 4-2	81.55	4.8679	2.8594	167,819.9	21.74	- 36.13	139.06	- 27.87
C- 4-3	51.85	3.0197	2.8609	171,903.2	38.63	- 14.45	149.66	- 25.56
C- 4-4	16.844	0.9553	2.8627	176,402.6	- 4.07	67.48	-145.02	75.14
C- 5-1	113.71	6.9623	2.8674	163,110.9	- 79.16	- 20.53	-211.85	- 19.73
C- 5-2	72.72	4.2949	2.8686	169,031.0	- 27.88	- 95.05	106.32	- 96.67
C- 5-3	52.10	3.0250	2.8701	171,850.4	- 2.51	- 55.75	107.11	- 68.48
C- 5-4	14.030	0.7926	2.8723	176,496.6	-268.05	-181.32	-442.47	-170.68
C- 6-1	93.61	5.6311	2.8650	166,173.6	54.63	24.21	117.44	42.04
C- 6-2	39.109	2.2490	2.8672	173,693.8	133.53	112.26	183.58	102.38

1/  $\delta_1 = (PV/N)_{\text{corr. obs.}}$  minus  $(PV/N)_{\text{corr. cal.}}$  as evaluated from equation (4).  $\Sigma \delta_1^2 = 1.28908 \times 10^5$

2/  $\delta_2 = (PV/N)_{\text{corr. obs.}}$  minus  $(PV/N)_{\text{corr. cal.}}$  as evaluated from equation (5).  $\Sigma \delta_2^2 = 0.81222 \times 10^5$

3/  $\delta_3 = (PV/N)_{\text{corr. obs.}}$  minus  $(PV/N)_{\text{corr. cal.}}$  as evaluated from equation (6).  $\Sigma \delta_3^2 = 5.38088 \times 10^5$

4/  $\delta_4 = (PV/N)_{\text{corr. obs.}}$  minus  $(PV/N)_{\text{corr. cal.}}$  as evaluated from equation (7).  $\Sigma \delta_4^2 = 0.78369 \times 10^5$

multisite and surface site (MVS) units with  $\sim 8$  sites

### 3.3.2. *Model selection*

Table 1 shows the relative model fit for each model type. The models were ranked by the relative decrease in the log-likelihood value.

The results show that the best-fitting model is the one with the highest number of parameters. This is because the model with the highest number of parameters is able to fit the data more precisely. The results also show that the model with the highest number of parameters is the one with the highest relative decrease in the log-likelihood value.

The results also show that the model with the highest number of parameters is the one with the highest relative decrease in the log-likelihood value.

The results also show that the model with the highest number of parameters is the one with the highest relative decrease in the log-likelihood value.

The results also show that the model with the highest number of parameters is the one with the highest relative decrease in the log-likelihood value.

The results also show that the model with the highest number of parameters is the one with the highest relative decrease in the log-likelihood value.

The results also show that the model with the highest number of parameters is the one with the highest relative decrease in the log-likelihood value.

The results also show that the model with the highest number of parameters is the one with the highest relative decrease in the log-likelihood value.

The results also show that the model with the highest number of parameters is the one with the highest relative decrease in the log-likelihood value.

The results also show that the model with the highest number of parameters is the one with the highest relative decrease in the log-likelihood value.

The results also show that the model with the highest number of parameters is the one with the highest relative decrease in the log-likelihood value.

The results also show that the model with the highest number of parameters is the one with the highest relative decrease in the log-likelihood value.

The results also show that the model with the highest number of parameters is the one with the highest relative decrease in the log-likelihood value.

The results also show that the model with the highest number of parameters is the one with the highest relative decrease in the log-likelihood value.

The results also show that the model with the highest number of parameters is the one with the highest relative decrease in the log-likelihood value.

The results also show that the model with the highest number of parameters is the one with the highest relative decrease in the log-likelihood value.

The results also show that the model with the highest number of parameters is the one with the highest relative decrease in the log-likelihood value.

The results also show that the model with the highest number of parameters is the one with the highest relative decrease in the log-likelihood value.

The results also show that the model with the highest number of parameters is the one with the highest relative decrease in the log-likelihood value.

TABLE 8. - Values of  $(PV/N)_{\text{corr. obs.}}$  minus  $(PV/N)_{\text{corr. cal.}}$  as evaluated by the Helium Research Center from the data given in table 5 (Cont.)

P Exp. No.	$(N/V) \times 10^4$ mm Hg at 0° C	$T_{\text{vap.}} (58)$ mole/cc	$(PV/N)_{\text{corr. obs.}}$ °K	$\delta_1^{1/}$ cc-mm/mole	$\delta_2^{2/}$ cc-mm/mole	$\delta_3^{3/}$ cc-mm/mole	$\delta_4^{4/}$ cc-mm/mole
$T_{58} = 2.3151$ °K							
D- 2-1	40.346	2.9234	2.3164	137,933.7	16.23	- 3.19	28.20
D- 2-2	25.103	1.7845	2.3169	140,565.0	47.27	9.84	72.38
D- 2-3	12.905	0.9021	2.3213	142,672.2	139.83	200.01	106.22
D- 3-1	48.52	3.5557	2.3161	136,398.3	- 75.54	- 14.92	-119.31
D- 3-2	26.510	1.8849	2.3197	140,359.3	70.80	28.43	99.68
D- 4-1	31.010	2.2310	2.3091	139,372.4	-125.91	-175.62	- 99.92
D- 5-1	43.81	3.2104	2.3091	136,845.0	-417.21	-406.50	-447.74
D- 5-2	15.684	1.1042	2.3148	142,056.9	- 14.05	15.17	- 31.13
D- 6-1	37.530	2.7069	2.3122	138,832.6	420.83	385.50	461.46
D- 6-2	20.574	1.4527	2.3189	141,387.1	111.82	99.67	123.00
D- 9-1	38.318	2.7686	2.3145	138,443.4	172.50	141.10	199.38
D- 9-2	16.887	1.1901	2.3199	141,596.0	-278.83	-261.22	-294.19
D-10-1	49.62	3.6394	2.3146	136,373.7	90.96	165.92	48.43
D-10-2	33.560	2.4085	2.3192	139,086.0	- 7.05	- 54.72	21.94
D-10-3	14.278	1.0006	2.3239	142,143.7	-163.78	-119.33	-192.69
D-11-1	41.65	3.0443	2.3030	137,576.2	- 65.24	- 73.22	- 64.73
D-11-2	20.772	1.4751	2.3074	141,301.5	77.37	63.07	89.02

1/  $\delta_1 = (PV/N)_{\text{corr. obs.}}$  minus  $(PV/N)_{\text{corr. cal.}}$  as evaluated from equation (4).  $\Sigma \delta_1^2 = 5.65378 \times 10^5$

2/  $\delta_2 = (PV/N)_{\text{corr. obs.}}$  minus  $(PV/N)_{\text{corr. cal.}}$  as evaluated from equation (5).  $\Sigma \delta_2^2 = 5.38241 \times 10^5$

3/  $\delta_3 = (PV/N)_{\text{corr. obs.}}$  minus  $(PV/N)_{\text{corr. cal.}}$  as evaluated from equation (6).  $\Sigma \delta_3^2 = 6.59356 \times 10^5$

4/  $\delta_4 = (PV/N)_{\text{corr. obs.}}$  minus  $(PV/N)_{\text{corr. cal.}}$  as evaluated from equation (7).  $\Sigma \delta_4^2 = 5.86879 \times 10^5$



TABLE 8. - Values of  $(PV/N)_{corr. obs.}$  minus  $(PV/N)_{corr. cal.}$  as evaluated by the Helium Research Center from the data given in table 5 (Cont.)

P Exp. No.	$(N/V) \times 10^4$ mm Hg at 0° C	$T_{vap. (58)}$ mole/cc	$T_{58} = 2.1474$ °K	$(PV/N)_{corr. obs.}$ cc-mm/mole	$\delta_1^{1/}$ cc-mm/mole	$\delta_2^{2/}$ cc-mm/mole	$\delta_3^{3/}$ cc-mm/mole	$\delta_4^{4/}$ cc-mm/mole
E- 1-1	19.138	1.4664	2.1462	130,585.7	26.63	19.20	41.01	19.53
E- 2-1	30.106	2.3463	2.1443	128,506.1	13.94	17.18	8.45	18.01
E- 2-2	14.989	1.1429	2.1450	131,298.6	- 20.38	- 22.44	- 16.92	- 23.30
E- 3-1	25.852	2.0024	2.1445	129,283.5	- 16.49	- 21.82	- 7.44	- 22.17
E- 3-2	12.406	0.9431	2.1451	131,686.1	- 102.22	- 98.46	- 110.71	- 100.23
E- 4-1	27.738	2.1448	2.1526	128,992.9	27.41	24.94	32.90	26.42
E- 4-2	10.718	0.8084	2.1537	132,182.5	77.77	86.52	63.12	88.09
E- 5-1	32.275	2.5216	2.1465	128,046.0	- 34.38	- 24.60	- 54.11	- 26.54
E- 5-2	21.604	1.6595	2.1482	130,133.2	27.73	19.47	43.69	20.19

1/  $\delta_1 = (PV/N)_{corr. obs.}$  minus  $(PV/N)_{corr. cal.}$  as evaluated from equation (4).  $\Sigma \delta_1^2 = 0.20789 \times 10^5$

2/  $\delta_2 = (PV/N)_{corr. obs.}$  minus  $(PV/N)_{corr. cal.}$  as evaluated from equation (5).  $\Sigma \delta_2^2 = 0.20430 \times 10^5$

3/  $\delta_3 = (PV/N)_{corr. obs.}$  minus  $(PV/N)_{corr. cal.}$  as evaluated from equation (6).  $\Sigma \delta_3^2 = 0.24255 \times 10^5$

4/  $\delta_4 = (PV/N)_{corr. obs.}$  minus  $(PV/N)_{corr. cal.}$  as evaluated from equation (7).  $\Sigma \delta_4^2 = 0.21357 \times 10^5$



along with the sum of the squares of the residuals. Columns 6, 7, 8, and 9 of table 8 give the values of  $(PV/N)_{corr.}$  observed minus  $(PV/N)_{corr.}$  calculated as evaluated by us using our least squares values for the constants of equations (4), (5), (6), and (7).

That the results of our least squares fit for the linear equation in density affords us a better representation of the data than a quadratic equation in  $N/V$ , we need only look at the values of our  $c$ 's evaluated from equation (5). We see that for equation (5), the value of the third virial for isotherms A, B, D, and E is less than the standard deviation in the third virial coefficient; also, we see that the value for the third virial at  $2.86401^\circ K$  is about twice the standard error in  $c$ . We interpret this to mean that the statistical significance of the third virial coefficient for isotherms A, B, D, and E is meaningless and that the statistical significance of  $c$  at  $2.86401^\circ K$  is essentially meaningless. Therefore, on the basis of the statistical significance of third virials evaluated by an equation such as equation (5), we conclude that the PV products are represented better by a linear equation in  $(N/V)$ , equation (4).

With regard to the results of our least squares fit for a quadratic equation in pressure, we see from the data given in column 9 of table 8 that the sum of the squares of the residuals, for each isotherm, are larger than the sum of the squares of the residuals evaluated from the data in column 7 of table 8. We also see that the value for  $c'$  for isotherm E is less than the standard error in  $c'$ ; and, the value for  $c'$  at  $2.31513^\circ K$  is of the same order of magnitude as its standard error. We interpret this to mean that the value of  $c'$  for isotherm D and iso-



therm E is not a statistically significant quantity. Therefore, on the basis of the fact that the  $\delta_4^2 > \delta_2^2$  and, also, on the fact that  $c'$  at  $2.31513^\circ$  K and at  $2.14736^\circ$  K is not statistically significant, we conclude that equation (5) is superior to equation (7). But we have already indicated that equation (4) is to be preferred to equation (5). Hence, equation (4) is to be preferred to equation (7).

Now for the equation

$$(PV/N)_{\text{corr.}} = A' + BP_{\text{corr.}} \quad (6)$$

we see from the data given in column 8 of table 8 that  $\delta_3^2$  is at least twice as large as  $\delta_1^2$  for the first three isotherms and that  $\delta_3^2$  is of the same order of magnitude as  $\delta_1^2$  for isotherms D and E. We interpret this to mean that since the sum of the squares of the residuals for equation (4) are smaller than those for equation (6), then equation (4) is to be preferred over equation (6).

We conclude, therefore, that the results of a least squares fit for the linear equation in N/V is the best representation of the pressure-volume isotherms of  $\text{He}^4$  in the temperature range  $2^\circ$  to  $4^\circ$  K. This is the same conclusion reached by Keller.

In table 9, we summarize the results obtained by us from Keller's data, along with the values of T and B published and corrected as indicated by him.

In calculating the thermodynamic temperatures given in columns 2 and 3 of table 9, it is necessary to divide A, as evaluated by least squares technique, by the gas constant R. The value of the absolute temperature is independent of any uncertainty in R, as the gas constant is used in calculating the number of moles of helium. It is thus only



TABLE 9.-Summary of the results obtained by the Helium Research Center from Keller's data

$(P_{v.p.})_{avg.}$	Temperature			B, cc/mole	
mm Hg at 0° C	HRC	Keller	58	HRC	Keller
588.5656	3.9558	3.9558	3.9542	- 83.88 ± 0.63	- 83.70 ± 0.64 <sup>1/</sup>
291.2462	3.3380	3.3378	3.3390	-103.58 ± 0.77	-103.4 ± 1.0 <sup>1/</sup>
147.5494	2.8624	2.8568	2.8640	-123.25 ± 0.82	-123.6 ± 0.9 <sup>1/</sup>
52.7590	2.3186	2.3186	2.3151	-157.9 ± 3.5	-157.7 ± 2.7 <sup>1/</sup>
35.5417	2.1488	2.1467	2.1474	-175.3 ± 2.2	-176.4 ± 2.7 <sup>1/</sup>

<sup>1/</sup> These deviations are standard deviations, which were evaluated by us from Keller's published values for the probable error in B: standard error = (probable error) ÷ 0.6745.

important to use the same value of R that was used in determining the number of moles. Keller did not publish the value of R used in his calculations; however, it was high enough to agree with our value of R.



important to use the same value of R that was used in determining the number of moles. Keller did not publish the value of R used in his calculations; however, he was kind enough to supply us with the value of R that he used. This value, as received from Keller, is:  $R = 62,363.09$  cc mm Hg at  $0^\circ C$  per  $^{\circ}K$  per mole. This value of R is based on  $0^\circ C = 273.16^\circ K$ .

In table 10, we compare values of B as calculated by us and Keller with the values tabulated by Kilpatrick, Keller, and Hammel (5).

In table 11, we give thermodynamic properties of saturated helium vapor calculated from the results of Keller's work. When  $(PV/N)$  is expressed as a power series in  $N/V$ , the expression for  $\ln f/P$  is given by

$$\ln f/P = (Z - 1) - \ln Z + \int_0^P (Z - 1) d\rho/\rho$$

where  $\rho$  is the molal density. With only the second virial included, this reduces to

$$\ln f/P = 2(Z - 1) - \ln Z.$$

We used the above expression in calculating the values of  $\ln f/P$  given in table 11.



TABLE 10. - Values of the second virial coefficient as calculated by the Helium Research Center and by Keller along with the values tabulated by Kilpatrick, Keller, and Hammel

$T_{\text{(isotherm)}}, {}^{\circ}\text{K}$	$-B, \text{ cc/mole}$		
	Kilpatrick	HRC	Keller
3.9558	82.88	83.88	83.70
3.3380	102.21	103.58	103.4
2.8624	122.94	123.25	123.6
2.3186	157.79	157.9	157.7
2.1488	172.37	175.3	176.4



TABLE 11. - Thermodynamic properties of saturated helium vapor as evaluated from the results of Keller's work

$T$ (isotherm) °K	$\rho_{\text{sat.}} \cdot 10^3$ mole/cc	$(P_{\text{v.p.}})_{\text{avg.}}$ mm Hg at 0 ° C	$Z$ (sat. vapor)
3.9558 ± 0.0016	3.298319 ± 0.008320	588.5656	0.723338 ± 0.002278
3.3380 ± 0.0017	1.697622 ± 0.001959	291.2462	0.824154 ± 0.001401
2.8624 ± 0.0011	0.9341167 ± 0.000547	147.5494	0.884866 ± 0.000809
2.3186 ± 0.0020	0.388159 ± 0.000223	52.7590	0.938709 ± 0.001420
2.1488 ± 0.0009	0.278861 ± 0.000085	35.5417	0.951117 ± 0.000643
$T$ (isotherm) °K	$-\ln f/P$	$\ln f$	$f/P$
3.9558 ± 0.0016	0.229444 ± 0.001407	6.148244 ± 0.001407	0.7949755
3.3380 ± 0.0017	0.158296 ± 0.001102	5.515873 ± 0.001102	0.8535971
2.8624 ± 0.0011	0.107950 ± 0.000704	4.886213 ± 0.000704	0.8976725
2.3186 ± 0.0020	0.059332 ± 0.001327	3.906402 ± 0.001327	0.9423936
2.1488 ± 0.0009	0.047648 ± 0.000610	3.523059 ± 0.000610	0.9534694

TABLE I. - Effect of temperature on the rate of self-dissolution

$\Delta H^\circ$ (cal/gm)	$T^\circ$ (degrees)	$K$
-1.14	25.188	1.0000
-1.14	25.200	0.9999
-1.14	25.212	0.9998
-1.14	25.225	0.9997
-1.14	25.237	0.9996
-1.14	25.250	0.9995
-1.14	25.262	0.9994
-1.14	25.275	0.9993
-1.14	25.287	0.9992
-1.14	25.300	0.9991
-1.14	25.312	0.9990
-1.14	25.325	0.9989
-1.14	25.337	0.9988
-1.14	25.350	0.9987
-1.14	25.362	0.9986
-1.14	25.375	0.9985
-1.14	25.387	0.9984
-1.14	25.400	0.9983
-1.14	25.412	0.9982
-1.14	25.425	0.9981
-1.14	25.437	0.9980
-1.14	25.450	0.9979
-1.14	25.462	0.9978
-1.14	25.475	0.9977
-1.14	25.487	0.9976
-1.14	25.500	0.9975
-1.14	25.512	0.9974
-1.14	25.525	0.9973
-1.14	25.537	0.9972
-1.14	25.550	0.9971
-1.14	25.562	0.9970
-1.14	25.575	0.9969
-1.14	25.587	0.9968
-1.14	25.600	0.9967
-1.14	25.612	0.9966
-1.14	25.625	0.9965
-1.14	25.637	0.9964
-1.14	25.650	0.9963
-1.14	25.662	0.9962
-1.14	25.675	0.9961
-1.14	25.687	0.9960
-1.14	25.700	0.9959
-1.14	25.712	0.9958
-1.14	25.725	0.9957
-1.14	25.737	0.9956
-1.14	25.750	0.9955
-1.14	25.762	0.9954
-1.14	25.775	0.9953
-1.14	25.787	0.9952
-1.14	25.800	0.9951
-1.14	25.812	0.9950
-1.14	25.825	0.9949
-1.14	25.837	0.9948
-1.14	25.850	0.9947
-1.14	25.862	0.9946
-1.14	25.875	0.9945
-1.14	25.887	0.9944
-1.14	25.900	0.9943
-1.14	25.912	0.9942
-1.14	25.925	0.9941
-1.14	25.937	0.9940
-1.14	25.950	0.9939
-1.14	25.962	0.9938
-1.14	25.975	0.9937
-1.14	25.987	0.9936
-1.14	25.999	0.9935
-1.14	26.012	0.9934
-1.14	26.025	0.9933
-1.14	26.037	0.9932
-1.14	26.050	0.9931
-1.14	26.062	0.9930
-1.14	26.075	0.9929
-1.14	26.087	0.9928
-1.14	26.100	0.9927
-1.14	26.112	0.9926
-1.14	26.125	0.9925
-1.14	26.137	0.9924
-1.14	26.150	0.9923
-1.14	26.162	0.9922
-1.14	26.175	0.9921
-1.14	26.187	0.9920
-1.14	26.200	0.9919
-1.14	26.212	0.9918
-1.14	26.225	0.9917
-1.14	26.237	0.9916
-1.14	26.250	0.9915
-1.14	26.262	0.9914
-1.14	26.275	0.9913
-1.14	26.287	0.9912
-1.14	26.300	0.9911
-1.14	26.312	0.9910
-1.14	26.325	0.9909
-1.14	26.337	0.9908
-1.14	26.350	0.9907
-1.14	26.362	0.9906
-1.14	26.375	0.9905
-1.14	26.387	0.9904
-1.14	26.400	0.9903
-1.14	26.412	0.9902
-1.14	26.425	0.9901
-1.14	26.437	0.9900
-1.14	26.450	0.9899
-1.14	26.462	0.9898
-1.14	26.475	0.9897
-1.14	26.487	0.9896
-1.14	26.500	0.9895
-1.14	26.512	0.9894
-1.14	26.525	0.9893
-1.14	26.537	0.9892
-1.14	26.550	0.9891
-1.14	26.562	0.9890
-1.14	26.575	0.9889
-1.14	26.587	0.9888
-1.14	26.600	0.9887
-1.14	26.612	0.9886
-1.14	26.625	0.9885
-1.14	26.637	0.9884
-1.14	26.650	0.9883
-1.14	26.662	0.9882
-1.14	26.675	0.9881
-1.14	26.687	0.9880
-1.14	26.700	0.9879
-1.14	26.712	0.9878
-1.14	26.725	0.9877
-1.14	26.737	0.9876
-1.14	26.750	0.9875
-1.14	26.762	0.9874
-1.14	26.775	0.9873
-1.14	26.787	0.9872
-1.14	26.800	0.9871
-1.14	26.812	0.9870
-1.14	26.825	0.9869
-1.14	26.837	0.9868
-1.14	26.850	0.9867
-1.14	26.862	0.9866
-1.14	26.875	0.9865
-1.14	26.887	0.9864
-1.14	26.900	0.9863
-1.14	26.912	0.9862
-1.14	26.925	0.9861
-1.14	26.937	0.9860
-1.14	26.950	0.9859
-1.14	26.962	0.9858
-1.14	26.975	0.9857
-1.14	26.987	0.9856
-1.14	27.000	0.9855
-1.14	27.012	0.9854
-1.14	27.025	0.9853
-1.14	27.037	0.9852
-1.14	27.050	0.9851
-1.14	27.062	0.9850
-1.14	27.075	0.9849
-1.14	27.087	0.9848
-1.14	27.100	0.9847
-1.14	27.112	0.9846
-1.14	27.125	0.9845
-1.14	27.137	0.9844
-1.14	27.150	0.9843
-1.14	27.162	0.9842
-1.14	27.175	0.9841
-1.14	27.187	0.9840
-1.14	27.200	0.9839
-1.14	27.212	0.9838
-1.14	27.225	0.9837
-1.14	27.237	0.9836
-1.14	27.250	0.9835
-1.14	27.262	0.9834
-1.14	27.275	0.9833
-1.14	27.287	0.9832
-1.14	27.300	0.9831
-1.14	27.312	0.9830
-1.14	27.325	0.9829
-1.14	27.337	0.9828
-1.14	27.350	0.9827
-1.14	27.362	0.9826
-1.14	27.375	0.9825
-1.14	27.387	0.9824
-1.14	27.400	0.9823
-1.14	27.412	0.9822
-1.14	27.425	0.9821
-1.14	27.437	0.9820
-1.14	27.450	0.9819
-1.14	27.462	0.9818
-1.14	27.475	0.9817
-1.14	27.487	0.9816
-1.14	27.500	0.9815
-1.14	27.512	0.9814
-1.14	27.525	0.9813
-1.14	27.537	0.9812
-1.14	27.550	0.9811
-1.14	27.562	0.9810
-1.14	27.575	0.9809
-1.14	27.587	0.9808
-1.14	27.600	0.9807
-1.14	27.612	0.9806
-1.14	27.625	0.9805
-1.14	27.637	0.9804
-1.14	27.650	0.9803
-1.14	27.662	0.9802
-1.14	27.675	0.9801
-1.14	27.687	0.9800
-1.14	27.700	0.9799
-1.14	27.712	0.9798
-1.14	27.725	0.9797
-1.14	27.737	0.9796
-1.14	27.750	0.9795
-1.14	27.762	0.9794
-1.14	27.775	0.9793
-1.14	27.787	0.9792
-1.14	27.800	0.9791
-1.14	27.812	0.9790
-1.14	27.825	0.9789
-1.14	27.837	0.9788
-1.14	27.850	0.9787
-1.14	27.862	0.9786
-1.14	27.875	0.9785
-1.14	27.887	0.9784
-1.14	27.900	0.9783
-1.14	27.912	0.9782
-1.14	27.925	0.9781
-1.14	27.937	0.9780
-1.14	27.950	0.9779
-1.14	27.962	0.9778
-1.14	27.975	0.9777
-1.14	27.987	0.9776
-1.14	28.000	0.9775
-1.14	28.012	0.9774
-1.14	28.025	0.9773
-1.14	28.037	0.9772
-1.14	28.050	0.9771
-1.14	28.062	0.9770
-1.14	28.075	0.9769
-1.14	28.087	0.9768
-1.14	28.100	0.9767
-1.14	28.112	0.9766
-1.14	28.125	0.9765
-1.14	28.137	0.9764
-1.14	28.150	0.9763
-1.14	28.162	0.9762
-1.14	28.175	0.9761
-1.14	28.187	0.9760
-1.14	28.200	0.9759
-1.14	28.212	0.9758
-1.14	28.225	0.9757
-1.14	28.237	0.9756
-1.14	28.250	0.9755
-1.14	28.262	0.9754
-1.14	28.275	0.9753
-1.14	28.287	0.9752
-1.14	28.300	0.9751
-1.14	28.312	0.9750
-1.14	28.325	0.9749
-1.14	28.337	0.9748
-1.14	28.350	0.9747
-1.14	28.362	0.9746
-1.14	28.375	0.9745
-1.14	28.387	0.9744
-1.14	28.400	0.9743
-1.14	28.412	0.9742
-1.14</		

## REFERENCES

1. Beattie, James A., B. E. Blaisdell, J. Kaye, H. T. Gerry, and C. A. Johnson. An Experimental Study of the Absolute Temperature Scale. VIII. The Thermal Expansion and Compressibility of Vitreous Silica and the Thermal Dilation of Mercury. Proceedings of the American Academy of Arts and Sciences, v. 74, 1941, pp. 371-388.
2. Cook, A. H. The Thermal Expansion of Mercury and Fused Silica Between 0 and 300° C. British Journal of Applied Physics, v. 7, 1956, pp. 285-293.
3. Keller, William E. Pressure-Volume Isotherms of He<sup>4</sup> Below 4.2° K. The Physical Review, v. 97, No. 1, January 1, 1955, pp. 1-8.
4. Keller, William E. Pressure-Volume Isotherms of He<sup>4</sup> Below 4.2° K. The Physical Review, v. 100, No. 6, December 15, 1955, p. 1790.
5. Kilpatrick, John E., William E. Keller, and Edward F. Hammel. Second Virial Coefficients of Helium from the Exp-Six Potential. The Physical Review, v. 97, No. 1, January 1, 1955, pp. 9-12.
6. van Dijk, H., M. Durieux, J. R. Clement, and J. K. Logan. The "1958 He<sup>4</sup> Scale of Temperatures." Part 2. Tables for the 1958 Temperature Scale. National Bureau of Standards Monograph No. 10, June 17, 1960, pp. 4-17.





