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Pressure-Volume Isotherms of He^4 below 4.2°K*

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A description is presented of a new apparatus for obtaining PV isotherms at very low temperatures, along with results of measurements on five isotherms at 3.961, 3.348, 2.862, 2.324, and 2.154°K for He^4 gas; the second virial coefficients, B, at these respective temperatures were found to be -83.70, -103.4, -123.6, -157.7, and -176.4 cc/mole. The reliability of previous data as well as of the several analytical treatments of the data is discussed, the conslusion being with respect to the latter that the He^4 isotherms below 4°K can be best represented by the equation $PV/N=RT(1+BN/V)$. When both the previous and the present data are analyzed in this way, a consistent set of values for B is obtained. From the values of RT measured here, corrections to the 1948 temperature scale are obtained in good agreement with modifications suggested by other authors.

I. INTRODUCTION

THE pressure-volume isotherms of He^4 were first determined at low temperatures by Kamerlingh Onnes and co-workers[1] in order to establish corrections to the helium gas thermometer. More recently the isotherms have been of interest primarily for the determination of the second virial coefficient, B, as a quantity useful in connection with the thermodynamic properties of the gas and one intimately associated with the intermolecular potential between two He particles. The demand for precise values of B below the normal boiling point has heretofore been satisfied by Keesom and collaborators[2–4] at Leyden.

It was the present author's original intention to construct an apparatus for the determination of B's for He^3 and to test the equipment by measuring one or two B values for He^4 using the generally accepted values as a guide. During the course of this work significant differences appeared between the present and previous data, an explanation for which was found to be an apparent error that was carried through all the Leyden work. It was therefore considered important to carry out a full-scale redetermination of the second virial coefficients at very low temperatures. We report in this communication a description of the apparatus in that it differs from that used at Leyden and the results of measurements with it on five isotherms of He^4 below 4.2°K.

II. APPARATUS AND EXPERIMENTAL PROCEDURE

In the introduction to their paper[4] Kistemaker and Keesom summarize the important difficulties encountered when one measures isotherms at very low temperature; briefly, these are: (1) uncertainty in determining pressures; (2) inability to maintain the bath at constant temperature for a time sufficiently long that equilibrium be established; and (3) uncertainty in determining the amount of gas in the noxious volumes or "dead" space. The apparatus employed for the present investigation was designed to avoid these difficulties in ways quite different from those used by Kistemaker and Keesom. Since, for the most part, we derived the gas-handling and cryogenic techniques from standard practices, in the following description we shall center our attention on the novel features of the apparatus.

A. Low-Temperature Cell

In order to avoid the difficulties and uncertainties often attendant to the measurement of the amounts of gas in the noxious volumes, the low-temperature cell

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[1] Complete references to the early low-temperature isotherm measurements are given in the monograph, *Helium*, W. H. Keesom (Elsevier Press, Amsterdam, Holland, 1942), pp. 31, 32, 143.

[2] W. H. Keesom and H. H. Kraak, Comm. Leiden, No. 234e (1935); Physica 2, 37 (1935).

[3] W. H. Keesom and W. K. Walstra, Comm. Leiden No. 260c (1940); Physica 7, 985 (1940).

[4] J. Kistemaker and W. H. Keesom, Comm. Leiden No. 269b (1946); Physica 12, 227 (1946).

was so designed as to eliminate the necessity for determining these amounts of gas while the gas remains in the connecting lines. The gas in the cell can be isolated from the gas in the connecting lines by a valve, as shown in Fig. 1. Hence measurements of pressure and temperature are made on a given number of moles of gas in the inner can with the valve open; the valve is then shut and the gas in the lines pumped away—to be discarded or sent to the volume-manometer (see below).

If one works above the λ point (2.19°K) of a liquid helium bath, great care must be exercised in order to determine the exact temperature of a gas held in a container immersed in the bath. In addition to the thermal gradient produced by the hydrostatic head of the liquid, transient gradients can arise from the combination of poor thermal conductivity of the liquid, heat leak from the warm portion of the apparatus, and inadequate stirring of the bath. To reduce the effects of these gradients the cell holding the gas [inner can (A), Fig. 1] is surrounded by an outer container (B) which can be evacuated. Furthermore, the temperature of the gas is measured with a helium vapor pressure thermometer (C), the lower end of which is surrounded by the experimental gas and the upper end vacuum jacketed. At the higher temperatures, where dP/dT is large, the thermometer serves as a very sensitive indicator for the attainment of equilibrium conditions in the cell. On the other hand, in order to reach equilibrium it is necessary to maintain the bath temperature essentially constant for periods of about one hour; to effect this control a Sommers-type[5] bath regulator is successfully employed with the heating element placed directly below the cell.

The inner and outer cans are coaxial cylinders of 0.794-mm-wall copper tubing, with respective inside dimensions of 2.311-cm diameter by 2.311-cm length and 3.175-cm diameter by 4.048-cm length. End plates are of 1.588-mm copper sheet except for the top of the inner can, which is copper 2.381 mm thick. All tubing connected to the cell is of thin-wall K-monel or inconel; the inside diameter of the vapor pressure thermometer tube is 1.422 mm. Solder connections to the inner can were made with helium gas flowing through it to avoid oxidation of the inner surfaces.

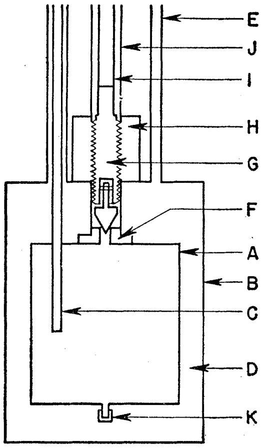

FIG. 1. Schematic diagram of low-temperature cell. A, inner can; B, outer can; C, vapor pressure thermometer; D, exchange gas or vacuum space; E, pumping tube; F, valve seat; G, valve stem; H, valve stem guide; I, valve stem extension; J, sample tube; K, seal of tube used during calibration.

Some of the details of the valve assembly are shown in Fig. 1. The valve seat (F) is copper and has an orifice 1.588 mm in diameter. A threaded cylinder of monel (H) (32 threads per inch) guides the stainless steel valve stem (G), while the tip of the stem possesses one degree of freedom so that it may find its own seat. Four slots 0.794 mm wide by 0.794 mm deep have been milled the length of the threaded portion of the stem to allow the passage of gas from the inner can to the anulus (inside diameter 3.175 mm; outside diameter 4.597 mm) formed by the extension of the valve stem (I) and the sample tube (J). The valve stem extension continues to the top of the cryostat and becomes accessible for operation by emerging from the sample space to the atmosphere through a double O-ring seal.

Calibration of the volume of the inner can was carried out only after the valve was opened and tightly closed many times in order to establish the final (or very nearly so) deformation of the seat. From the weight of air free distilled water the cell contained at 31.20°C, the cell volume at that temperature was determined to be 9.5907 cc with an average deviation of 0.0009 cc; from this value and with use of the formula for the thermal expansion of copper given by Keesom, van Agt, and Jansen[6] the volume of the cell at 20°K was calculated to be 9.4927 cc. It is assumed that no further volume changes take place on lowering the temperature to the liquid helium region.

B. Manometry

In the course of the experiment there are three sets of pressure measurements which must be made with high accuracy: that of the gas in the cell, in the vapor pressure thermometer, and in the volume-manometer. All of the manometers used for these determinations (with the exception of one arm of the volume-manometer—see below) are encased in a Lucite box, the air in which is vigorously circulated and accurately thermostated. Several Hg-in-glass thermometers resting in pools of mercury are placed at critical positions in the box. The manometers are viewed through a distortion-free section of plate glass with a 800-mm range Wild cathetometer, on which the scale reading may be safely estimated to 0.01 mm. An Invar standard meter-bar mounted adjacent to the manometers is used to calibrate the cathetometer scale, though invariably when the two are compared no correction need be applied to the latter within the precision of the measurements (±0.02 mm for full scale length).

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[5] H. S. Sommers, Jr., Rev. Sci. Instr. **25**, 793 (1954).

[6] Keesom, van Agt, and Jansen, Comm. Leiden, No. 182a (1926).

The manometers for measuring the cell pressure (for $P>40$ mm Hg) and the helium vapor pressure each have a bore of 20 mm in diameter and are filled with mercury. Capillary depression corrections are applied according to tables given by Blaisdell,[7] although for the wide tubes used, the correction is never greater than 0.01 mm and seldom that large. Thermometer pressures are corrected to read in mm Hg at 20°C to coincide with those on the 1948 temperature scale; others are corrected to 0°C. A correction for the acceleration of gravity at Los Alamos is applied to all pressure readings.

For cell pressures less than 40 mm Hg a 20-mm bore manometer filled with dibutyl sebacate is employed. Before the manometer was filled, the oil was boiled to rid it of volatile components and occluded air, and a sample was then taken for density determinations. The density of the oil was measured with a 20 cc pycnometer at close temperature intervals extending over the range in which pressure readings were to be made. Five measurements between 27 and 32°C showed the density-temperature relationship to be linear within 1 part in 100 000. It is interesting to note that a similar determination on the unboiled oil resulted in a curve exactly parallel to that for the boiled oil but with density values lower by 1 part in 1500 at the same temperature. With this oil manometer it is possible to read pressures to 0.002 mm Hg.

Figure 2 shows schematically the volume-manometer with which amounts of gas in the cell are determined. Gas is admitted to the glass bulbs through the tube on the left (inside diameter 1.0 mm) whereupon mercury is brought up to fiducial mark 4. A choice of which of the three volumes is to be used is made according to the arbitrary rule that the pressure to be measured be greater than about 150 mm Hg. Mercury from the reservoir is brought up approximately to the appropriate fiducial mark—1, 2, or 3; reproducible (±0.01 mm) final positioning of the meniscus is accomplished by remote manipulation of the motor-driven plunger with the experimenter monitoring the operation through the cathetometer telescope.

The three bulbs have nominal volumes of 200, 100, and 50 cc. Volumes 1–2 and 1–3 were calibrated by determining the weight of mercury contained between the fiducial marks; volumes 2–4 and 3–4 were obtained from P-V-T measurements with He gas, using 1–2 as a standard. From these measurements consistent values were obtained for the volumes to be used, i.e., 1–4, 2–4, and 3–4, as 363.23 ± 0.02 cc, 150.31 ± 0.02 cc, and 47.753 ± 0.016 cc, respectively (probable errors are given). All straight lengths of glass tubing, with the exception of the 1 mm capillary, are 10 mm inside diameter. The fiducial markers are centered in the tube and are attached to the tubing about 2 cm above the tip so that there is no distortion of the tubing where the menisci are to be read.

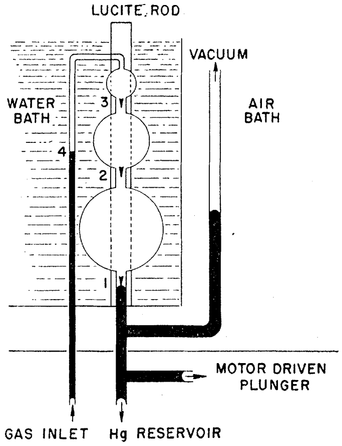

FIG. 2. Schematic arrangement of the volume-manometer.

A water bath surrounding the glass bulbs is thermostated to ±0.01°C and is maintained at a temperature no more than 1°C different from that of the air bath surrounding the other arm of the manometer. A Beckmann thermometer, direct reading to 0.01°C and calibrated against the $Na_2SO_4\cdot10H_2O$ transition temperature, is used to measure the water bath temperature. Optically, the water bath presents some problems, the most serious of which is a possible prism effect. To avoid this difficulty the plate glass window forming the side of the bath and through which the menisci are viewed is maintained perpendicular to the line of sight of the telescope. Frequent zero-pressure readings confirmed the absence of prism effects. Proper illumination of the menisci at the fiducial marks is accomplished by directing a beam of light down a 2-cm diameter rod of Lucite standing vertically in the water directly behind the marks (Fig. 2); horizontal cuts 1 cm wide at proper places on the rod scatter the vertical light beam and serve as excellent backgrounds for viewing the profiles of the menisci.

C. General Experimental Procedure

A typical experimental run begins, once the apparatus is cooled down to the approximate temperature of the run, with the filling of the cell and vapor pressure thermometer, helium exchange gas being in the space between the two cans. The helium gas used in the experiment is obtained from commercial tanks and is purified by passing through a charcoal trap at liquid air temperatures; any air picked up during gas-handling is removed from the experimental gas as it passes through a U-tube, partially immersed in the helium bath, before it enters the cell-filling line. After the cell is filled the U-tube is isolated from the experimental gas by closing a stopcock, the exchange gas is pumped away, and equilibrium is awaited.

Once equilibrium is obtained, the bath pressure, the vapor pressure thermometer, and the cell pressure are

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[7] B. E. Blaisdell, J. Math. Phys. 19, 217 (1940).

read. Immediately the cell valve is closed (in order to avoid a significant change in the volume of the system on closing the valve, during the wait for equilibrium the valve is kept open by 1/4 to 1/2 a turn). The gas in the lines is then pumped away and the valve opened for the next pressure measurements. Pressures are again read and the valve again closed. After the valve is closed this time—and succeeding times—the gas in the lines is pumped to the volume-manometer where we measure the decrement of the amount of gas corresponding to the drop of pressure in the cell. To test that all the gas has been removed from above the valve and to detect a possible leak through the valve, the pressure in the cell line is observed with the oil manometer. Excessive leak-up—greater than 1/5000 of the last cell pressure measured—is cause for discarding the run.

The cycle of measuring the cell pressure and the decrement of gas is continued until the lowest pressure and corresponding decrement is determined; then all of the gas remaining in the cell is pumped to the volume-manometer. By adding up all the decrements one may arrive at the amount of gas appropriate to the highest pressure, and so on. As few as one point and as many as four points on an isotherm were determined in a single run, this variation being an effort to determine the reproducibility of the experiment when we slightly change factors which should not affect the results.

III. RESULTS AND DISCUSSION

A. Data and Errors

Table I represents a collection of the data obtained for the five isotherms determined in the present investigation. In this table under the "Exp. No." column, A-9-1, for example, is to be interpreted as: isotherm A,

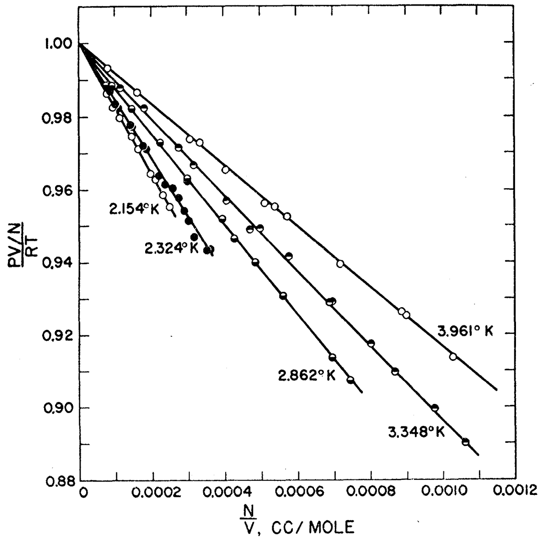

FIG. 3. Plot of $(PV/N)/RT$ *vs* N/V for He^4 gas below 4°K. Values of RT are taken from two-constant analysis.

TABLE I. Experimental data for the isotherms of He^4.

Exp. No.	P mm Hg	$(N/V)\times10^4$ cc/mole	$T_{\mathrm{vap}(48)}$ °K	$(PV/N)_{\mathrm{corr}}$ cc-mm/mole	δ_2
		$T_{48}=3.61$°K			
A-8-1	202.40	8.8713	3.956	228 713	− 90
A-8-2	127.30	5.4105	3.955	235 907	−135
A-8-3	80.65	3.3679	3.953	240 214	−227
A-9-1	205.45	9.0060	3.960	228 436	− 91
A-9-2	135.16	5.7515	3.961	235 250	−185
A-9-3	74.08	3.0817	3.963	240 452	126
A-11-1	231.49	10.2718	3.961	225 614	118
A-11-2	116.58	7.1878	3.961	232 002	98
A-11-3	120.67	5.1171	3.960	236 128	247
A-12-1	96.98	4.0649	3.968	238 393	155
A-12-2	40.095	1.6462	3.965	243 565	− 23
A-12-3	20.231	0.8252	3.963	245 232	− 6
		$T_{48}=3.348$°K			
B-1-1	163.01	8.6759	3.325	189 524	153
B-1-2	113.00	5.7961	3.332	196 152	−280
B-1-3	36.676	1.8002	3.336	204 674	−206
B-2-1	182.97	9.7495	3.355	187 415	− 48
B-2-2	133.89	6.9067	3.356	193 539	− 56
B-2-3	93.79·	4.7326	3.359	197 677	483
B-3-1	64.23	3.1835	3.357	201 384	109
B-4-1	134.40	6.9601	3.343	193 592	−224
B-4-2	98.98	5.0149	3.345	197 745	−196
B-4-3	56.00	2.7703	3.347	202 391	− 10
B-4-4	24.422	1.1877	3.349	205 756	30
B-5-1	196.13	10.5701	3.352	185 486	116
B-5-2	153.56	8.0253	3.354	191 154	− 78
B-5-3	81.63	4.0860	3.358	199 339	212
		$T_{48}=2.862$°K			
C-3-1	66.95	3.9594	2.854	169 717	−147
C-3-2	25.923	1.4791	2.866	175 132	−103
C-4-1	120.85	7.4690	2.864	161 801	− 44
C-4-2	81.55	4.8679	2.863	167 590	− 20
C-4-3	51.85	3.0197	2.864	171 706	− 68
C-4-4	16.844	0.9553	2.866	176 193	− 11
C-5-1	113.71	6.9623	2.871	162 881	79
C-5-2	72.72	4.2949	2.873	168 753	78
C-5-3	52.10	3.0250	2.874	171 608	19
C-5-4	14.030	0.7926	2.876	176 261	279
C-6-1	93.61	5.6311	2.869	165 921	− 31
C-6-2	39.109	2.2490	2.871	173 454	−119
		$T_{48}=2.324$°K			
D-2-1	40.346	2.9234	2.325	138 072	− 17
D-2-2	25.103	1.7845	2.326	140 671	− 19
D-2-3	12.905	0.9021	2.330	142 807	−144
D-3-1	48.52	3.5557	2.325	136 519	94
D-3-2	26.510	1.8849	2.328	140 522	− 99
D-4-1	31.010	2.2310	2.318	139 498	136
D-5-1	44.14	3.2104	2.317	137 025	376
D-5-2	15.684	1.1042	2.324	142 169	34
D-6-1	37.530	2.7069	2.321	138 959	−410
D-6-2	20.574	1.4527	2.328	141 502	− 94
D-9-1	38.318	2.7686	2.323	138 589	−181
D-9-2	16.887	1.1901	2.329	141 707	300
D-10-1	49.62	3.6394	2.323	136 530	−107
D-10-2	33.560	2.4085	2.328	139 217	12
D-10-3	14.278	1.0006	2.332	142 325	114
D-11-1	41.65	3.0443	2.312	137 684	95
D-11-2	20.772	1.4751	2.316	141 444	− 87
		$T_{48}=2.154$°K			
E-1-1	19.138	1.4664	2.155	130 509	− 38
E-2-1	30.106	2.3463	2.154	128 375	18
E-2-2	14.989	1.1429	2.154	131 216	19
E-3-1	25.852	2.0024	2.154	129 169	37
E-3-2	12.406	0.9431	2.154	131 606	101
E-4-1	27.738	2.1448	2.161	128 952	− 83
E-4-2	10.718	0.8084	2.163	132 082	− 57
E-5-1	32.275	2.5216	2.156	127 931	48
E-5-2	21.604	1.6595	2.157	130 062	− 47

run number 9, point number 1. Entries missing in the "run number" column indicate discarded or discontinued runs; for example, four early runs on isotherm A were discarded because the temperature was measured from the bath pressure with correction for the bath height above the cell and not from the more reliable vapor pressure thermometer—these four runs yielded a curve parallel to the accepted one, but displaced about 0.005° in temperature.

It will be observed that for the isotherms at the two highest temperatures, A and B, the largest pressures measured are, respectively, only 39 percent and 67 percent of the saturation pressures. Since the main object of the experiment is the determination of second virial coefficients, i.e.,

$$\left[\frac{d(PV/N)}{d(N/V)}\right]_{P=0} \quad \text{or} \quad \left[\frac{d(PV/N)}{dP}\right]_{P=0},$$

ranges limited in the above way are considered adequate; consequently we concentrate on the low pressure region. The lower limit of pressure is determined by the fact that thermomolecular pressure corrections are not accurately known for a tube with annular cross section; from the geometry of the tube and by analogy with the circular cross section corrections, a conservative estimate was made that no corrections within experimental error need be applied to pressures larger than 10 mm Hg. For isotherms C, D, and E, the measurements were carried up to a large fraction of the saturation pressure because of the limited pressure range before the onset of liquefaction. Even in the case of isotherm D where P/P_{sat} is the largest—93.6 percent—calculations based on the results of Bowers[8] indicate that the amount of gas adsorbed on the cell walls is far from significant.

Although one may represent the PV/N product for a gas in terms of a power series in either the pressure or the density, there is *a priori* no way to determine which of these offers the better description. Analytically, the coefficient of the linear term—the second virial coefficient, B—is the same for both representations; but, in practice, the same data usually produce different values of B from the two methods. We have therefore adopted the procedure of using that representation which exhibits the least curvature, for in this way the extrapolation of the slope from finite values of P or N/V to zero is less indefinite. We are able to demonstrate that for He^4 at low temperatures the expansion in N/V is to be preferred, and that in order to achieve the same accuracy in B's using the pressure expansion, one should obtain data at pressures an order of magnitude lower than our lowest pressures.

TABLE II. Calculations from the data.

Isotherm T_{48} °K	*A* 3.961	*B* 3.348	*C* 2.862	*D* 2.324	*E* 2.154
Results using two-constant equation					
1. $A=RT$, cc-mm/mole	246 942	208 341	178 285	144 720	133 934
2. p.e.[a] in A, °K	0.0010	0.0014	0.0008	0.0010	0.0007
3. $T_{48}-T_{\text{isotherm}}$	0.0012	0.0073	0.0032	0.0034	0.0063
4. B, cc/mole	−83.70	−103.4	−123.6	−157.7	−176.4
5. p.e.[a] in B, cc/mole	0.43	0.65	0.61	1.79	1.82
6. p.e.[b] of a measured point, %	0.04	0.07	0.05	0.09	0.03
7. N/V of saturated vapor, g/cc	0.01315	0.00671	0.00369	0.00155	0.00109
8. $\Sigma\delta_2^2/(n-2)=E_2$	24 536	45 608	14 495	36 129	4050
Results using three-constant equation					
9. A, cc-mm/mole	246 921	208 297	178 134	144 488	133 768
10. B, cc/mole	−83.31	−102.4	−117.8	−140.8	−159.3
11. C, cc²/mole²	−358	−823	−7282	−3855	−5231
12. $\Sigma\delta_3^2/(n-3)=E_3$	27 125	49 504	12 031	37 144	4167
13. $Q=E_2/E_3$	0.905	0.921	1.205	0.973	0.972

[a] The probable error (p.e.) is calculated according to equations given by R. T. Birge, Phys. Rev. **40**, 207 (1932).

[b] Calculated from the equation: p.e. $=0.6745[\Sigma\delta^2/(n-1)]^{\frac{1}{2}}$.

It follows then that, since all the points of an isotherm are not taken at exactly the same temperature (Table I, column 4; temperatures determined from the vapor pressure thermometer and the 1948 scale[9] are given) a correction to the raw PV/N product must be made in the following form:

$$\Delta\left(\frac{PV}{N}\right)=R\Delta T\left[1+\frac{N}{V}\left(B+T\frac{dB}{dT}\right)\right]. \qquad (1)$$

Since B is negative and dB/dT positive for the isotherms measured here, the term in inner parentheses is small so that in most cases $R\Delta T$ is the only significant term. Where the term $(B+TdB/dT)$ could not be neglected, values of B and dB/dT were taken from Table I of the paper[10] by Kilpatrick, Keller, Hammel, and Metropolis. Corrected PV/N products are given in column 5 of Table I.

Figure 3 shows the data graphically: the isotherms are reduced to the same ordinate by plotting $(PV/N)/RT$ *vs* N/V, for which RT was obtained from the linear fit to the data.

Perhaps the best picture of the precision of the measurements can be obtained from the probable error in the individual points and in the constants calculated from these points; these probable errors for fitting the data with a linear equation by the method of least squares are shown in lines 2, 5, and 6 of Table II. Column 6 of Table I shows the individual residuals (δ_2) for the linear equation. The rather wide scatter in the points for isotherm D is attributed to poor temperature control. For this isotherm most of the points were obtained with the bath regulator working inefficiently—it is believed that tape wrapped around the heater prevented free bubble formation; and in the region just above the λ point vigorous stirring of the bath is important. When the tape was removed, much better control resulted, though none of the points measured previous to this could be considered bad enough to

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[8] R. Bowers, Phil. Mag. **44**, 485 (1953).

[9] H. Van Dijk and D. Shoenberg, Nature **164**, 151 (1949).

[10] Kilpatrick, Keller, Hammel, and Metropolis, Phys. Rev. **94**, 1103 (1954).

discard. Indeed, it is felt that the large scatter of some other points such as B-2-3 and D-6-1, can also be attributed to nonequilibrium resulting from poor bath control. Evidence for this conclusion is found in the high precision in the measurements of the isotherm at 2.153°K. One would expect that because of the lower pressures and smaller amounts of gas involved, errors in P and N/V would be larger here than in the other isotherms; however, the temperature control was excellent, and below the λ point equilibrium was more rapidly established than above it.

B. Virial Coefficients

In the last section we mentioned only results derived from fitting the data with a two-constant equation, whereas previous authors[2–4] have analyzed their data in terms of three-constant equations, and, in one case, a four-constant equation. It is indeed obvious that if one has n sets of data the n sets will be better fitted the more constants are employed, this process reaching a limit in an n-constant polynomial exactly satisfied by all n-sets. However, the questions arise: What is the significance of these constants, and where does one stop this process? To answer these questions for our data, we proceed to justify the linear treatments.

For each isotherm, the data were fitted with two polynomials of the form

$$PV/N=a+b(N/V)+c(N/V)^2+\cdots, \quad a=A=RT;\quad b=aB;\quad c=aC;\quad \text{etc.,} \tag{2}$$

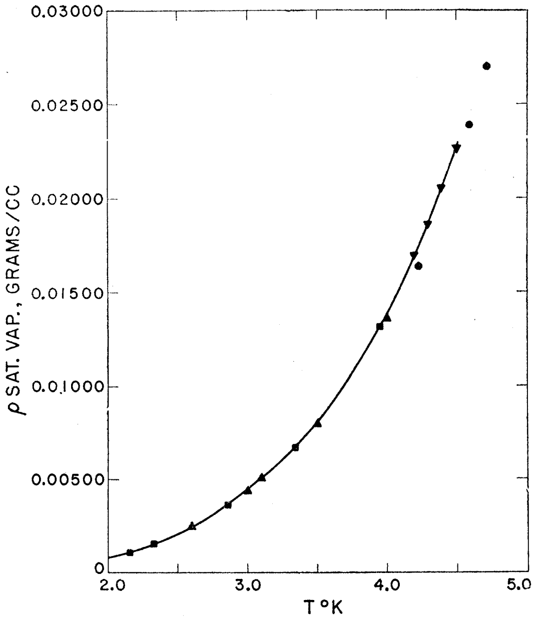

FIG. 4. Plot of the density of the saturated vapor of He^4 *vs* temperature. ● Mathias *et al.*; ▲ calculated from Keesom's accepted values of B and C; ▼ Berman *et al.*; ■ calculated from B's of the present work (two-constant equation).

in the first instance retaining only the first two terms and in the second only the first three terms. The constants obtained from these analyses are given on lines 1, 4, 9, 10, and 11 of Table II, from which it is seen that there is a significant difference in the B's obtained, especially for isotherms C, D, and E. One semiquantitative test which may be applied to effect a choice between the two analyses is to examine the quantity Q:

$$Q=E_k/E_{k'}=\left(\frac{\sum\delta_k^2}{n-k}\right)\Big/\left(\frac{\sum\delta_{k'}}{n-k'}\right),\quad k<k', \tag{3}$$

where $\sum\delta_k^2$ is the sum of the squares of the deviations of the n experimental points from the k-constant equation. Setting $k=2$ and $k'=3$, we obtain the values of E_2, E_3 and Q as given on lines 8, 12, and 13 of Table II. For isotherms A, B, D, and E we see that Q is less than unity, indicating that the addition of a third constant is not only superfluous, but may even cause the data to be misrepresented. The value of Q for isotherm C does not depart sufficiently from unity to warrant inclusion of the square term in the equation. An alternate statement of the above conclusion is that the addition of a square term does not significantly lower the probable error of a measured point since the curvature introduced is of the same order of magnitude as the scatter of the points. This can be seen to be so, qualitatively, by examining Fig. 3. Especially for the two end isotherms, A and E, it is difficult to imagine how any curve but a straight line could be drawn to represent the data.

That the results of the two-constant fit are consistent with thermodynamic data, we cite the values of the density of the saturated vapor of He^4 above 4.2°K recently calculated by Berman and Swenson[11] from latent heat measurements of Berman and Poulter.[12] Four of the values given in reference 11 are plotted in Fig. 4 along with those measured by Mathias, Crommelin, Onnes, and Swallow,[13] those calculated from Keesom's "adopted values" of the virial coefficients,[14] and those calculated from our B's determined with the linear equations (Table II, line 7). A curve passing through the points of Berman and Swenson joins nicely onto the section determined by points of the present investigation. Below about 2.5°K, the values of the vapor density are relatively insensitive to the exact value of B.

A more qualitative argument is one which requires the plot of B *vs* T to be smooth. Figure 5 shows such a plot for a variety of data: Keesom's B's re-evaluated (see below) using a linear and a quadratic fit, Kistemaker's B's re-evaluated, and the present values of B determined by two- and three-constant equations. It is

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[11] R. Berman and C. A. Swenson, Phys. Rev. **95**, 311 (1954).

[12] R. Berman and J. Poulter, Phil. Mag. **43**, 1047 (1952).

[13] Mathias, Crommelin, Onnes, and Swallow, Comm. Leiden, No. 172b (1926).

[14] See reference 1, p. 49.

TABLE III. Re-evaluation of data of Keesom and Walstra.

Isotherm °K[a]	4.245	3.721	3.105	2.610
Results using two-constant equation				
1. $A=RT$, cc-mm/mole	264 463	232 283	194 129	163 434
2. B, cc/mole	−74.45	−89.7	−114.6	−138.1
3. p.e. of a measured point, %	0.08	0.09	0.025	0.10
Results using three-constant equation				
4. A, cc-mm/mole	265 206	231 705	193 750	163 017
5. B, cc/mole	−78.25	−85.2	−108.3	−123.8
6. C, cc²/mole²	1013	−1747	−4361	−18 300
7. p.e. of a measured point, %	0.04	0.08	0.016	0.10
8. $Q=E_2/E_3$	4.454	0.991	1.808	0.981
Reported results of Keesom and Walstra				
9. A, cc-mm/mole	264 753[b]	232 095	193 660	162 809
10. B, cc/mole	−75.49	−87.9	−107	−118
11. C, cc²/mole²	−131	−779	−5280	−24 100

[a] These isotherms are labeled by the temperature given by Keesom and Walstra (reference 3).
[b] Keesom and Walstra give a value of D for this isotherm.

seen that when all the data are fitted to linear equations, B *vs* T is smoother than when fitted to quadratic equations, indicating that the former representation is to be preferred. The solid line in the figure represents a theoretical curve[15] calculated from potential constants which give the best fit to the low-temperature and high-temperature experimental second virial coefficients and high-temperature transport properties. Since the shape of the curve is not affected by a change in potential constants, it follows that its position could be adjusted by a fit of these constants to one experimental point. The nature of the agreement of this curve with all the "two-constant" B's is therefore extremely gratifying. On the other hand, whereas the present data and those of Keesom *et al.* yield a consistent set of B's calculated from two-constant equations, the values of C obtained from all the data by no means form a smooth pattern.

All of the above evidence taken together presents a compelling argument for terminating the virial expansion after the second term for the existing data on He^4 gas below 4°K. This does not preclude the possibility that in the future more accurate measurements will determine precise nonzero C's; but we strongly suspect that B's from these data will be closer to the values we select here than those given by the present quadratic expressions. It may appear anomalous that the third virial coefficient of the gas be unimportant over a considerable temperature range, but then there is no theory which at present can predict the behavior of C. Incidentally, C being zero or small for the density virial expansion implies that the third and possibly higher coefficients for the pressure expansion are of importance.

C. Data of Keesom *et al.*

We must now seek an explanation for the disagreement between the published virials of Keesom *et al.* and the ones determined in the present investigation. In their paper, Keesom and Walstra[3] state that the analysis of the data was carried out independent of the temperature and that the calculated values of A confirmed that they measured the temperature of the isotherms correctly. However, when we analyzed the isotherm data of Keesom and Walstra using the method of least squares, quite different results were obtained as shown in Table III. If, on the other hand, one treats the data with a quadratic least-squares analysis keeping A *fixed* by the temperature (i.e., treating RT as an experimental point), one arrives at the published values of B and C. From the arguments presented in the second paragraph of Sec. II-A of this paper and from the fact that the temperature scale used by Keesom is at present considered to be in error, the fixing of A in the above manner is highly susceptible to criticism. A dramatic effect in the change of B resulting from a change in temperature scale may be observed by comparing the

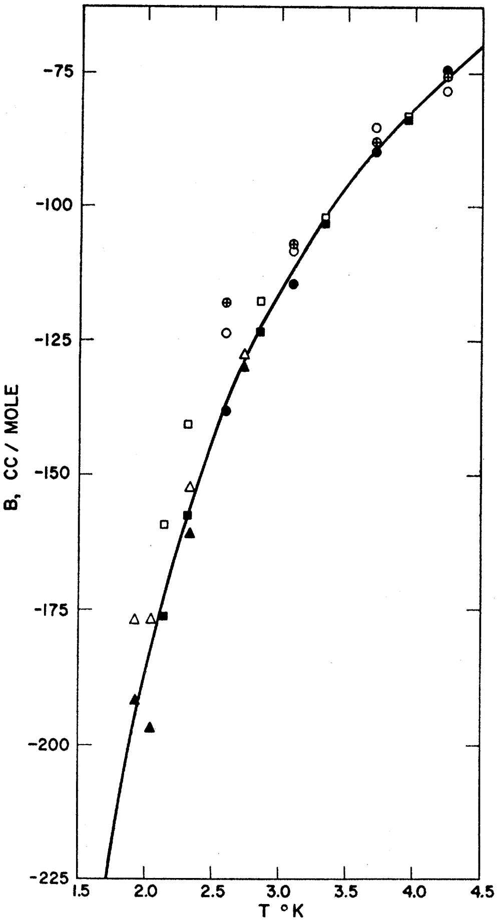

FIG. 5. Plot of B *vs* T. ⊕ Original values of Keesom and Walstra; ○ same data re-evaluated by three-constant equation; ● same data re-evaluated by two-constant equation. △ Original values of Kistemaker and Keesom; ▲ same data re-evaluated by two-constant equation. □ present data, three-constant equation; ■ same data, two-constant equation. Solid line represents theoretical curve.

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[15] Kilpatrick, Keller, and Hammel, following paper [Phys. Rev. 97, 9 (1955)].

isotherms of Keesom and Kraak[2] with those of Keesom and Walstra.[3]

A glance at line 8 of Table III discloses that perhaps the choice between a two-constant and a three-constant fit to the Dutch data is not quite so clear-cut as in the case discussed above. Indeed, the fact that for the isotherm at 4.245°K there are 18 experimental points and the probable error of a point is reduced by a factor of two when the data are fitted to an equation with three constants rather than two, suggests that the C for this isotherm possesses significance. On the other hand, for the 3.105°K isotherm one is inclined to discount the increased precision on adding a third constant since there are only five experimental points for this temperature. Also it is highly unreal to consider C important for this isotherm when the value of Q for isotherms on either side indicate negligible C's for these.

We have already observed that when our experimental data along with those of Keesom and Walstra are represented by two constant equations a remarkably consistent set of B's is obtained. This indicates that the resultant of the systematic errors in both investigations either is in the same direction and of nearly same magnitude, or, what is more probable, is quite small. Here too is seen an advantage of the density expansion over the pressure expansion, for the agreement in B's is achieved in spite of the fact that Keesom and Walstra's lowest pressures are correspondingly much higher than ours, *viz.:* on the 4.245°K isotherm the lowest pressure is 105 mm Hg; at 3.721°K, 96.8 mm; at 3.105°K, 61.8 mm; and at 2.610°K, 28.7 mm. For the pressure range of our measurements we again refer the reader to Table I.

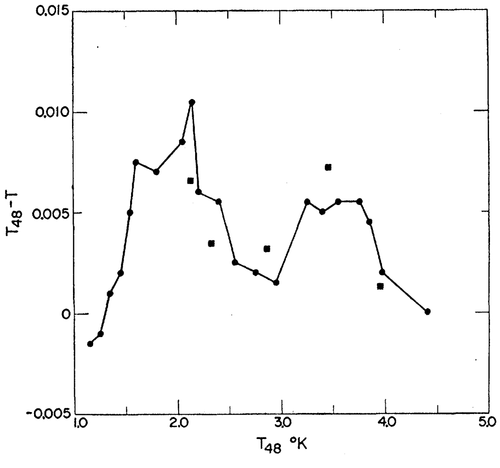

FIG. 6. Plot of deviations of the thermodynamic temperature from the 1948 scale *vs* T. ● Average values of Erickson and Roberts (Fig. 4, reference 17); ■ from isotherms of present work.

Accepting the conclusion that C is insignificant at least for the lowest three isotherms of Keesom and Walstra, the data of Kistemaker and Keesom[4] must be re-evaluated. Since the data for the isotherms below 2.7°K are not sufficiently precise to determine C's directly, the latter authors corrected their measured PV/N products using C's extrapolated from Keesom and Walstra's smoothed values of C above 2.7°K (these of course are erroneous even if the three-constant analysis were correct); the adjusted PV/N products were then used to determine B's. These and the B's that result if the corrections for C are not made are shown in Fig. 5.

D. The Temperature Scale

The type of measurements described here may serve to establish a thermodynamic temperature scale and at the same time to calibrate a convenient thermometric substance. Values of A divided by the gas constant R yield the absolute temperatures of the isotherms, which may be correlated with the vapor pressure of the liquid He in the thermometer. It has been suggested by Kistemaker[4,16] and more recently by Erickson and Roberts[17] from magnetic data that the 1948 temperature scale[9] is in error below 4.2°K. More weight is added to this conclusion by the present measurements, as shown on line 3 of Table II and in Fig. 6, where the deviations of the isotherm temperatures from the 1948 temperatures are compared with the average of all the magnetic data (reference 17, Fig. 4). The magnetic measurements are given relative to the chosen value for the temperature of the normal boiling point of He^4, whereas the isotherm data are independent of this value. However, Berman and Swenson[11] conclude that the accepted value of the boiling point is accurate to ±0.002°. It is seen from Fig. 6 that the agreement is within about 0.002° for the four highest isotherms and about 0.004° for the lowest; this is considered quite satisfactory, and is further confirmation of the above conclusion.

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[16] J. Kistemaker, Physica **12**, 272, 281 (1946).

[17] R. A. Erickson and L. D. Roberts, Phys. Rev. **93**, 957 (1954).