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Compressibility of Gases at High Temperatures. II. The Second Virial Coefficient of Helium in the Temperature Range 0°C to 600°C

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The second virial coefficient of helium was measured in the temperature range 0° to 600°C by an expansion procedure previously described. Within our limits of error, estimated to be approximately 0.5 percent at 0° and approximately 1 percent at 600°, the results (expressed in Amagat units of volume) are given by: $10^3 B_T = 0.5485 - 0.1315 \times 10^{-3} T + (3.754/T)$ where T is in °K. A comparison with existing data is given.

INTRODUCTION

IN a recent paper¹ methods for measuring the compressibility of gases at high temperatures were described. These were based on an expansion method due to Burnett² and eliminate the necessity of making volume measurements directly. The pressure of the gas in a pipet maintained at constant temperature is measured, the gas is then expanded into a second pipet at the same temperature, and the pressure is re-measured. If P_m and P_{m+1} are the respective pressures before and after expansion, it can easily be shown that:

$$P_m/P_{m+1} = N + (N-1)(B_T/A_T)P_m, \quad (1)$$

where N is the ratio of the sum of the two gas-pipet volumes to the volume of the first pipet, and A_T and B_T are the first and second virial coefficients, respectively, at temperature T .

Equation (1) supposes that the isotherm can be expressed by the simple linear relation:

$$PV/n = A_T + B_TP, \quad (2)$$

where n is the mole number. The helium isotherms are accurately represented by Eq. (2) at temperatures above 0°C and at pressures at least up to 100 atmospheres. In the present work, expansion measurements were made for helium at pressures from approximately 75 or 80 atmos. down to about 6 atmos. Several such series of expansions were carried out at 100-degree intervals in the range from 0°C to 600°C. At each temperature a least-squares plot was made of the pressure

ratios P_m/P_{m+1} against P_m , the pressures before expansion. From the slope and intercept of this plot, the second virial coefficient was evaluated in accordance with Eq. (1). Typical plots of this kind for a series of expansions at 0°C and at 600°C are reproduced in reference 1 (hereafter referred to as *I*).

The first virial coefficients are given by:

$$A_T = A_0 T/T_0, \quad (3)$$

where A_0 is the corresponding coefficient at 0°C. The latter was evaluated from a pressure ratio-pressure plot at 0°C and the additional relation

$$A_0 + B_0 = 1, \quad (4)$$

which follows from the definition of Amagat units.

For the measurements at 600°C a few runs were also carried through, with the first pipet at 600°C and the second pipet at 0°C, in order to test the feasibility of applying this method at even higher temperatures where the first pipet could be heated in a furnace. In this case, in place of Eq. (1) we obtain

$$\begin{aligned} P_m/P_{m+1} + (B_0/A_0)(P_m - P_{m+1}) \\ - (M-1)(B_T/A_T)^2 P_m P_{m+1} \\ = M + (M-1)(B_T/A_T)(P_m + P_{m+1}), \end{aligned} \quad (5)$$

where $(M-1) = (A_TV_0/A_0V_T) = (T/T_0)(N-1)$ and $N = (V_T + V_0/V_T)$, V_T being the volume of the first pipet which is at temperature T , and V_0 the volume of the second pipet held at 0°. The third term on the left is small and can be evaluated by an iteration process.

¹ W. G. Schneider, Can. J. Research 27, 339-353 (1949).

² E. S. Burnett, J. App. Mech. 3, A137-A140 (1936).

RESULTS

The results of the measurements are summarized in Table I, where values of the first and second virial coefficients are shown at each temperature, both in terms of Amagat units of volume and in terms of cm^3/mole . For the case of 600° the mean value of the second virial coefficient measured with both pipets at 600° , and that obtained with one pipet at 600° , and the second at 0° , are shown separately and are in excellent agreement. In the sixth column of Table I are shown, for each temperature, the number of runs which were averaged to give the final result shown, each run consisting of about six expansions.

A number of measurements of the second virial coefficient of helium have been reported. These measurements have recently been summarized by Keesom.³ Two sets of data cover a fairly wide temperature range, the measurements of Keesom and co-workers at Leiden extending from -259° to 100°C , and those of Holborn and Otto⁴ from -258° to 400°C . The discrepancy between these two sets of data, amounting at 0°C to approximately 5 percent, is considerably larger than the estimated limits of error in the measurements. Table II shows a comparison of the two sets of data with the present measurements. Included also are some measurements by Wiebe, Gaddy, and Heins⁵ and by Michels and Wouters.⁶ Figure 1 is a graphical comparison. At 0°C and 100°C all the measurements are in fair agreement except those of the Leiden workers. It is difficult to account for this discrepancy. However, it is interesting to note that the Leiden measurements were carried out with a multiple mercury column as the pressure-measuring instrument, whereas in all the other measurements a free piston gauge was employed.

The present measurements agree with those of Holborn and Otto to about 0.2 percent at 0° , 100° , and 200° . At

300° and 400° our values are approximately 3 percent higher.

A smooth curve drawn through our values from 0° to 600° can be fitted within our limits of error by the equation:

$$10^3 B_T = 0.5485 - 0.1315 \times 10^{-3} T + (3.754/T). \quad (6)$$

From 200° to 600° the second virial coefficient appears to fall off linearly with temperature.

TREATMENT OF DATA

Before a pressure ratio-pressure plot is made, a number of corrections have to be applied to the pressures measured by the free piston gauge. These include corrections for:

- variation in barometric pressure;
- air buoyancy of the weights and the scale pan of the piston gauge;
- variation in the temperature of the piston;
- a small hydrostatic pressure due to the oil in the line connecting the piston gauge to the mercury U-tube serving as a null indicator.
- lack of uniformity of temperature due to a small dead space or unheated space in the capillaries connecting the gas pipets to the expansion valve and mercury U-tube, the latter being outside the thermostat.

The barometric reading is corrected in the usual manner to give the atmospheric pressure.

The steel weights used with the piston gauge were calibrated (to "vacuum" weight) by the Metrology Section of the National Research Council of Canada, as were also the scale pan of the gauge and the piston itself. The sum of these three weights constitutes (apart from the barometric pressure) the total loading on the piston. The scale pan is constructed partly of aluminum and partly of steel. To apply an air buoyancy correction, the steel and aluminum components are weighed separately. Then the buoyant force to be subtracted from the total vacuum weight can be represented as $m_b \rho_a / \rho_w$ where m_b includes the total vacuum weight, the weight of the aluminum component of the scale pan having been expressed as an equivalent vacuum weight of steel, and $\rho_a / \rho_w = \text{density of air} / \text{density of steel} = (1/\rho_w)(M_p/RT) = \text{constant} \times p/T$. Here M is the molecular weight of air of mean relative humidity, R the gas constant, p the corrected baro-

TABLE I. Summary of coefficients in the series equation, $PV = A_T + B_T P$, for helium.

Temperature °C	Volume expressed in terms of: Amagat units $B_T \times 10^3$ $\text{cm}^3/\text{mole}^*$				No. of runs
	A_T	$B_T \times 10^3$	A_T	B_T	
0	0.999475	0.525	22415.2	11.77	8
100	1.365369	0.509	30621.1	11.42	6
200	1.731262	0.494	38827.0	11.08	6
300	2.097156	0.480	47032.9	10.76	6
400	2.463050	0.466	55238.8	10.45	6
500	2.828943	0.452	63444.7	10.14	8
600	3.194837	0.438	71650.6	9.82	10
600 (second pipet at 0°C)		0.438			5

* The value of the normal volume used to convert to units of cm^3/mole was 22427.0 cm^3 , where the molecular weight of helium was taken as 4.00248 g and the normal density as $0.178467 \times 10^{-3} \text{ g/cm}^3$ (see reference 3).

³ W. H. Keesom, *Helium* (Elsevier Press, Amsterdam, 1942), Chapter II.

⁴ L. Holborn and J. Otto, *Zeits. f. Physik* **33**, 1-11 (1925); see also, J. Otto, *Zeits. f. Instrumentenk.* **48**, No. 6, 257-8 (1928).

⁵ R. Wiebe, V. L. Gaddy, and C. Heins, *J. Am. Chem. Soc.* **53**, 1721-5 (1931).

⁶ A. Michels and H. Wouters, *Physica* **8**, 923 (1941).

TABLE II. Comparison of second virial coefficient data for helium by various authors

Temperature °C	$B_T \times 10^3$ (Amagat units)				
	Michels and Wouters	Wiebe, Gaddy, and Heins	Keesom <i>et al.</i>	Holborn and Otto	Present measure- ments
0	0.529	0.522	0.501	0.524	0.525
100	0.506	0.504	0.480	0.508	0.509
200		0.478		0.494	0.494
300				0.468	0.480
400				0.452	0.466
500					0.452
600					0.438

metric pressure, and T ($^{\circ}\text{K}$) the temperature of the room. Actually it is found sufficiently accurate for a large number of measurements to take a mean value of p and T and use a corresponding constant mean value for ρ_a , the air density.

In order to correct the piston gauge constant C for variation in piston temperature, the relation $C_t = C_{30}[1 - 2.2 \times 10^{-5}(t - 30)]$ is employed, where C_t and C_{30} are the gauge constants at $t^{\circ}\text{C}$ and 30°C , and the coefficient of linear expansion of steel (of the piston) is taken to be $1.1 \times 10^{-5}/\text{deg}$. This value was verified by measuring the gauge constant C_t by balancing the piston gauge against the vapor pressure of carbon dioxide at 0°C and varying the temperature of the piston from 18° to 38°C . These measurements yielded $1.09 \times 10^{-5}/\text{deg}$ for the linear expansion coefficient of the piston.

The correction to the pressure due to the hydrostatic head in the oil line, which transmitted the pressure from the gauge to the mercury U-tube, amounted to about 17 mm Hg and was computed from the measured height of the oil and its measured density at room temperature.

The dead-space volume of the pipet assembly amounted to approximately 0.5 percent of the total volume and was slightly different when the gas was contained in the first pipet only from what it was when the gas was contained in both pipets. In order to apply a correction, the dead space in each case is subdivided into regions of uniform temperature. The volume and mean temperature of each region are measured separately. The procedures used in computing the dead-space correction factors are given in I. Although the total unheated volume is relatively small, it was found that in order to achieve an accuracy within one percent in the second virial coefficient, the correction had to be made with considerable accuracy, particularly at the higher temperatures; specifically, it was found necessary in making these corrections to use Eq. (2) instead of the perfect gas law. These difficulties could, however, be quite considerably reduced by using larger gas pipets. For the present measurements the pipet volumes were approximately 58 cc and 28 cc for the first and second pipets respectively. This ratio of volumes gives a convenient spacing of points on the pressure ratio-pressure plot.

The final corrected pressure in each case is obtained in international millimeters of mercury and converted to normal atmospheres (76 cm Hg, density 13.5951 g/cm^3 , $g = 980.665 \text{ cm/sec}^2$).

The pressure ratios are computed from the final corrected pressures and are plotted against the initial pressures (the pressures before expansion). The values of the slope and intercept, from which the second virial coefficient is computed, are obtained for each run from a least-squares fit. In doing this it is desirable to weight the ratios corresponding to higher pressures more heavily than those corresponding to lower pressures,

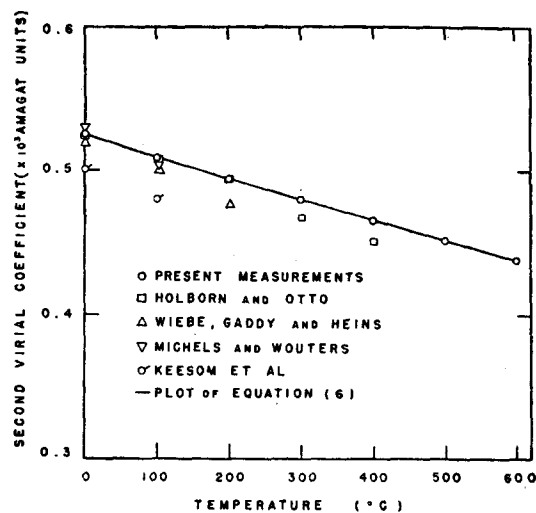


FIG. 1. Plot of second virial coefficient data.

since the relative precision with which the higher pressures can be measured with the piston gauge is greater. Accordingly each point is weighted in direct proportion to the pressure shown on the abscissa. The values of the second virial coefficients shown in Table I represent the mean of a number of plots at each temperature.

For the runs at 600°C with one pipet at 0°C , the procedure is identical except that a preliminary plot is first made of Eq. (5), omitting the last term on the left hand side. The slope and intercept obtained from this plot are then used as a first approximation in an iteration procedure to evaluate this term. After weighting each point as before, the final slope and intercept and thus the second virial coefficient are obtained from a least-squares fit.

ESTIMATE OF ERRORS

The error associated with measurement of the temperature, estimated to be $\pm 0.01^{\circ}\text{C}$, is negligible, particularly since for helium in the temperature range from 0°C to 600°C the second virial coefficient varies but slowly with temperature. It is therefore necessary to consider only errors associated with the pressure measurements.

The piston gauge was calibrated against the vapor pressure of pure carbon dioxide at 0°C . Bridgeman⁷ gives the precision of the vapor pressure at this temperature as $1/26,000$. A number of calibrations carried out during the course of the present measurements were reproducible to about $1/10,000$. These two factors combined may give rise to a maximum error in B of the order of 0.1 percent.

The sensitivity of the piston gauge was approximately 0.3 g, or (for the piston used) about 0.25 mm Hg. This gives rise to a slight scatter of the points on the straight line pressure ratio-pressure plot. In a typical

⁷ O. C. Bridgeman, J. Am. Chem. Soc. 49, 1174-1183 (1927).

plot of a single run the probable error in B , obtained by a least-squares fit, was 0.3 percent. (Part of this scatter may be attributable to small variations in the temperature of the dead space.) Averaging over several runs should reduce the error due to this cause to at least as low as 0.2 percent.

The source of greatest error, at least at the higher temperatures, is the dead-space volume. This is a consequence of the difficulty of measuring very small volumes accurately and the fact that the dead space is not at a uniform temperature. The latter difficulty can, to a large extent, be overcome by subdividing the dead space into smaller regions and measuring the temperature of each region. This subdivision must, however, not be carried too far, since then the error in measuring the volume of each region becomes large. Moreover, it introduces some uncertainty to assume that at the boundary of each region the temperature changes in a discontinuous manner, while throughout the particular region it remains uniform. Assuming a possible error in the dead-space temperature of 1° and a possible error in the dead-space volume of 20 percent, leads to a possible error in B at 600°C , due to the uncertainty in the dead-space correction, of approximately 0.5 percent. At 0°C the corresponding error in B is less than 0.1 percent.

In calculating the dead-space correction factor, Eq. (2) was employed rather than the perfect gas law. With the experimental arrangement employed, use of the perfect gas law would have led to an error in B at 600°C of 3 percent. In applying Eq. (2) to calculate the dead-space correction factor (see I), a rather cumbersome expression is obtained. It was found possible to replace this by the relation

$$F = F_0(1 - \alpha P), \quad (6)$$

where F is the dead-space correction factor, F_0 is the equivalent dead-space correction factor calculated from the ideal gas law, and α is a parameter evaluated empirically. The error introduced by the approximation (Eq. (6)) amounts only to about 0.1 percent in B at 600° .

Taking all errors into account the over-all possible

error in the mean value of B amounts at 600°C to about 1 percent, while at 0°C it is well within $\frac{1}{2}$ percent.

EXPERIMENTAL

Purification of Helium

The helium used for the present measurements was obtained from the Amarillo Helium Plant of the U. S. Bureau of Mines. It was stated to contain several percent of nitrogen and possibly a trace of hydrocarbon. It was found to contain, in addition, approximately 1.8 percent of hydrogen. To purify the helium it was passed first through a combustion tube at 450°C filled with copper and copper oxide turnings to remove hydrogen (and oxygen), then through a liquid air trap, and finally through two liquid air traps packed with granular charcoal. The latter were found to remove nitrogen (but not hydrogen) very effectively from the helium gas. Several batches of gas which had been twice passed slowly through the purification train were each analysed by a mass spectrometer for nitrogen and hydrogen content.⁸ The purified gas was found to contain in each case less than 0.02 percent nitrogen and 0.06 percent hydrogen.

Apparatus and Procedure

The apparatus used for the pressure and temperature measurements, and the procedure employed, are described in I. For the measurements at each temperature, the thermostat was adjusted exactly to the desired temperature to within 0.01° . In this manner a temperature correction of the final data to the even temperatures shown in Table I was avoided. Exact adjustment of the thermostat temperature was easily accomplished by adjusting the Wheatstone bridge used in the temperature control circuit.

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⁸ We are greatly indebted to Mr. M. H. Thomas and co-workers at the Chalk River Laboratories for carrying out these analyses.