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# THE EQUATION OF STATE OF HELIUM*

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## ABSTRACT

A brief review of the statistical theory of the equation of state is presented. Upon the basis of a recent quantum mechanical calculation of the interatomic energy, the second virial coefficient of helium has been calculated. With the use of the theoretically determined virial coefficient some properties of helium have been computed. A detailed comparison with experimental data is given.

## INTRODUCTION

THE past several years have seen a great advance in our understanding of intermolecular forces. The work of Heitler and London on the resonance interaction of two hydrogen atoms suggested the nature of the repulsive force operating at small intermolecular distances to determine the effective molecular cross-section. More recently the work of Eisenschitz and London followed by that of other investigators has permitted a calculation of the polarization force, operating at larger intermolecular distances to produce the van der Waals' attraction. However the theory has so far been subjected to no critical comparison with experiment. It is the object of the present paper to make such a comparison in the case of helium, the only gas for which a fairly accurate calculation of the intermolecular energy has been carried out.

## THEORY OF THE EQUATION OF STATE

Many empirical equations of state have been suggested for gases. All of them, however, may be expanded in the familiar virial form

$$\frac{pV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \cdots \tag{1}$$

where $p$ is the pressure, $V$ the volume of a gram-mol of gas, $R$ the ideal gas constant, and $T$ the absolute temperature. The coefficients, $B$, $C$, $\cdots$ are in general functions of the temperature.

Although a complete statistical theory of the equation of state has not been worked out in detail, it is possible under certain conditions to obtain a correlation between the second virial coefficient, $B$, and the intermolecular forces.

Above the critical temperature, it seems legitimate to assume that the fraction of the molecules in quantized collision states will be insignificant. Moreover, the Boltzmann distribution function may probably be regarded as

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valid for all gases until temperatures in the neighborhood of absolute zero are reached. Thus even in the case of hydrogen at a pressure of one atmosphere and a temperature of 2°K, both the Fermi-Dirac and the Bose-Einstein distribution functions give the same result as that of Boltzmann within a few percent insofar as the translational energy is concerned.[1] Subject to these limitations, it is possible to identify the sum of state with Gibbs' phase integral[2]

$$z = \int \cdots \int e^{-\bar{E}/kT} dq_1, \cdots dp_{3N} \tag{2}$$

where $\bar{E}$ is the total energy of a gas consisting of $N$ molecules averaged over all internal coordinates and $k$ is Boltzmann's constant. The integration is to be taken over all of the $6N$ dimensional momentum-configuration space available to the system. If the thermodynamic potential, $\psi$, (Helmholtz free energy function) is defined by the relation

$$\psi = E - TS$$

where $S$ is the entropy, Gibbs has shown that

$$\psi = -kT \ln z \tag{3}$$

Moreover,

$$\left(\frac{\partial \psi}{\partial V}\right)_T = -p. \tag{4}$$

The integral (2) may be evaluated in simple form under certain conditions.[3] It is to be assumed that the density of the gas is low enough so that molecular configurations in which the fields of more than two molecules overlap, are sufficiently rare that they may be ignored. In the case of neutral gas molecules where the molecular forces are effective only at very short range, this condition is often fulfilled even at relatively high densities. Under these circumstances it is possible to write

$$z = f(T) \prod_{n=1}^{N} (V - 2nB) \tag{5}$$

where

$$B = \tfrac{1}{2} \int \int \int (1 - e^{-\bar{\epsilon}/kT}) dx dy dz.$$

Here $\bar{\epsilon}$ is the mutual potential energy of two molecules and the integration is to be taken over all values of their relative coordinates. From Eqs. (3), (4), and (5), after expansion of the logarithm in powers of $B/V$, it is found that

$$\frac{pV}{RT} = 1 + \frac{B}{V} + \frac{4B^2}{3V^2} + \cdots$$

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[1] R. H. Fowler, Statistical Mechanics, p. 539 (1929).

[2] J. W. Gibbs, Elementary Principles in Statistical Mechanics (1902).

[3] F. G. Keyes, Chem. Rev. **4**, 175 (1929). K. F. Herzfeld, Müller-Pouillets Lehrbuch der Physik, Vol. **3**, Kinetische Theorie der Wärme, p. 167.

where the second term may be identified with that of the virial Eq. (1). If, as in the case of helium the molecules are spherically symmetrical

$$B = 2\pi N \int_0^\infty (1 - e^{-\epsilon(r)/kT})r^2dr \tag{6}$$

where $r$ is the distance between the two molecules.

Perhaps the most well known of empirical equations of state is that of van der Waals:

$$p = \frac{RT}{V - b} - \frac{A}{V^2}\cdot$$

It is of interest to see what form the intramolecular potential, $\epsilon$, must assume to be consistent with it. The virial Eq. (1) may be transformed into van der Waals' equation if $B/V$ is assumed to be very small relative to unity and

$$B = b - A/RT.$$

If the molecules are treated as rigid spheres of diameter, $\sigma$, it is obvious that when $r \leqq \sigma$, $\epsilon = \infty$, and formula (6) yields, after expansion of $e^{-\epsilon/kT}$;

$$B = b - A/RT$$

where

$$b = \frac{2\pi N\sigma^3}{3} = 4 \text{ (total volume of the molecules)}$$

and

$$A = A_0 + \sum_{n=1}^{\infty} A_n/(RT)^n; A_0 = -2\pi N^2 \int_\sigma^\infty \epsilon r^2 dr$$

$$A_n = -2\pi N^{n+2} \int_\sigma^\infty \epsilon^{n+1} r^2 dr.$$

It must be concluded, therefore, that the coefficient $A$ appearing in van der Waals' equation is not a constant, but a slowly varying function of the temperature. This conclusion is born out by experiment in the region of low temperatures where the sum $\sum_{n=1}^{\infty} An/(RT)^n$ may no longer be neglected. Moreover, experiment at high temperatures, invalidates the assumption of rigid molecules. Thus, it is found that $b$ is a slowly decreasing function of the temperature, a fact which can only be explained as due to an interpenetration of the molecules. Van der Waals' equation is therefore to be regarded as merely a first approximation even at small densities.[4]

## THE MOLECULAR FIELD

Empirical information furnished by the equation of state suggests that the general character of the force between two molecules may be conveniently represented by means of two potentials, $\epsilon_r$ and $\epsilon_a$. The potential $\epsilon_r$, which predominates at small molecular separations, must ascend steeply with in-

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[4] F. G. Keyes and R. S. Taylor, J. Am. Chem. Soc. **49**, 896 (1927).

creasing slope as two molecules approach and diminish rapidly as they recede, thus giving rise to a strong repulsive force at small intermolecular distances. The potential, $\epsilon_a$, nullified at small separations by $\epsilon_r$, must fall off less rapidly with the distance, giving rise to an attractive force at larger intermolecular separations. Thus the total intermolecular potential, $\epsilon$, might be written

$$\epsilon = \epsilon_r + \epsilon_a.$$

This representation is to be regarded as more or less schematic, since no sharply defined physical significance can be independently assigned to $\epsilon_r$ or $\epsilon_a$. Still, it has the advantage of suggesting two different types of molecular interaction which we believe to be effective in determining the intermolecular energy.

According to present quantum mechanical ideas, the "repulsive" potential, $\epsilon_r$, is to be regarded as arising from a resonance interaction between the molecules. A calculation of the resonance energy has so far been accomplished only for atomic hydrogen[5] and helium.[6] In the case of atomic hydrogen, the situation is complicated by the existence of two alternative modes of interaction, one of them giving rise to the repulsion of which we have spoken, and the other to valence union. Helium is, therefore, the only simple gas for which we have a knowledge of the repulsive field. Although a somewhat complicated function of the interatomic distance, the resonance energy in the range of importance in the thermal interaction of gas molecules may be adequately represented by the formula

$$\epsilon_r = \lambda e^{-cr}.$$

The "attractive" potential is to be regarded as arising from a mutual polarization of the molecules,[7] chiefly due to a rapidly pulsating field associated with the internal motion of the electrons in the molecule. The dominant term in this energy comes from the oscillating dipole. If terms from multipoles of higher order are ignored, the attractive potential has the form

$$\epsilon_a = -\frac{\beta}{r^6}\cdot$$

A general scheme for the calculation of $\epsilon_a$ has been developed by London and Eisenschitz.[8] They have made an exact calculation of the mutual energy of two hydrogen atoms as well as rough estimates in the case of some other gases.

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[5] Heitler and London, Zeits. f. Physik **44**, 455 (1927); Sugiura, Zeits. f. Physik. **45**, 484 (1927).

[6] Slater, Phys. Rev. **32**, 349 (1928).

[7] In 1920 Debye (Phys. Zeits. **21**, 178, 1920) suggested that the van der Waals attraction in gases had its origin in a mutual electrical polarization. Upon the basis of an electrostatic molecular model, he attempted to calculate the van der Waals $A$ constant for several gases in terms of their electrostatic multipole moments. That his theory was not very successful from a quantitative standpoint, is readily understandable in view of the inadequacy of the molecular model employed.

[8] Eisenschitz and London, Zeits. f. Physik **60**, 491 (1930); London, Zeits. f. Physik **63**, 245 (1930).

[9] Slater and Kirkwood, Phys. Rev. **37**, 682 (1931).

A calculation of the mutual energy of two helium atoms by another method has been carried out by Slater and Kirkwood.[9] They obtain for the total intermolecular potential of helium:

$$\epsilon = \left\{ 7.7e^{-2.43r/a_0} - \frac{0.68}{(r/a_0)^6} \right\} 10^{-10} \text{ ergs} \tag{7}$$

where $a_0$ is the Bohr radius of the hydrogen atom. In this expression, terms arising from variable multipole moments of higher order than the dipole have been neglected. Moreover, an error of a few percent in the coefficient of the exponential term is not unlikely since an approximate wave function was employed in its calculation.

## THE EQUATION OF STATE OF HELIUM

With the expression for the intermolecular potential given by Eq. (7), we have computed the second virial coefficient of helium at several temperatures, by graphical integration of Eq. (6). The results are listed in Table I together with experimental values of Holborn and Otto.[10] The theoretical values of the virial coefficient $B$ have been plotted as a function of the reciprocal temperature in Fig. 1, and as a function of the temperature in Fig. 2. For comparison, the experimental results of a number of investigators have been included.[11,12] From Table I it may be seen that the computed values of the virial coefficient, while consistently lower than the experimental ones of Holborn and Otto, do not differ from them by more than five or six percent between 100°K and 400°K. Below 50°K, the agreement between the two is not quite as close. This fact may probably be attributed as much to error in the experimental measurements as to error in the theoretical values of the virial coefficient. However, a real discrepancy at low temperatures might be expected if the proportion of molecules in quantized collision states became appreciable, for in that event, Gibbs' phase integral would cease to be an adequate representation of the sum of state and Eq. (6) would lose its validity. At present it is impossible to decide whether or not this effect is of im-

TABLE I. *Second virial coefficient of helium.*

| $T$ (°K) | $B$ (theory) cc/mol | $B$ (H and O) cc/mol |
|---|---|---|
| 350 | 10.80 | 11.60 |
| 300 | 11.14 | 11.80 |
| 250 | 11.34 | 11.95 |
| 200 | 11.58 | 11.95 |
| 100 | 10.75 | 10.95 |
| 20 | −6.94 | −4.00 |

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[10] Holborn and Otto, Zeits. f. Physik **33**, 1 (1925); **38**, 359 (1926).

[11] Nijhoff, Keesom, and Iliin, Leiden Communications **188C**, Oct. 1927.

[12] Onnes, Leiden Communications, Verslag Akad. Amsterdam **102a**, 495 (1907); **102c**, 741 (1908); Onnes and Boks, ibid **170a**, **170b**, (1924); Onnes and Van Agt, ibid **176b**, 625 (1925).

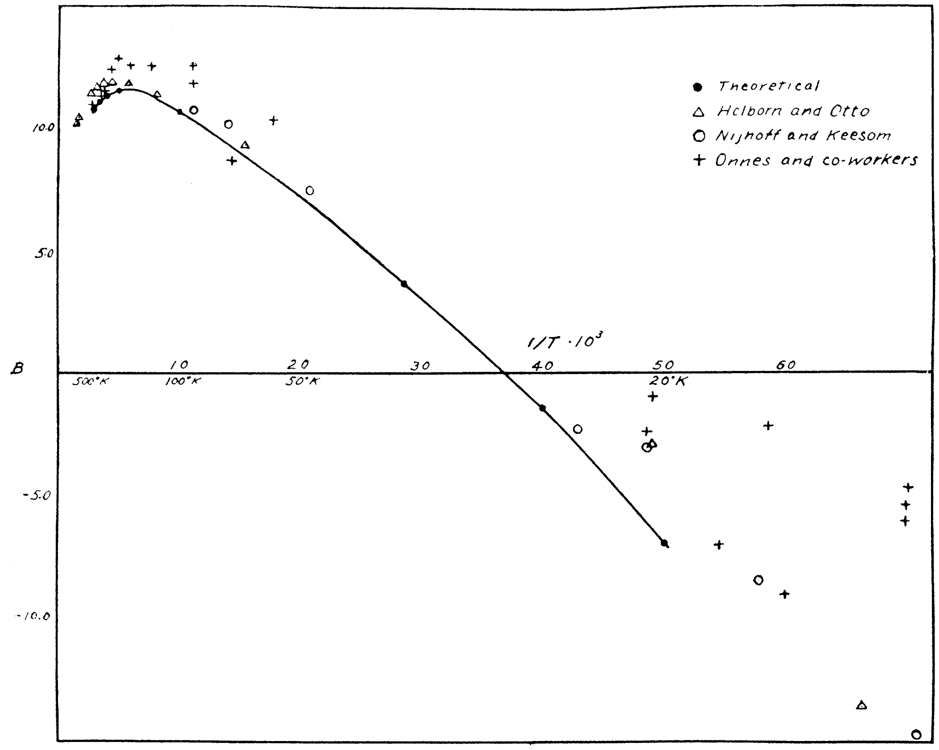

Fig. 1. The second virial coefficient of helium plotted as a function of the reciprocal temperature.

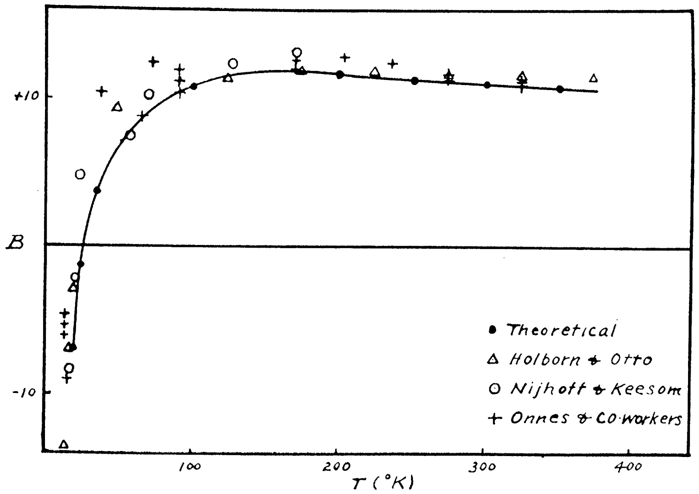

Fig. 2. The second virial coefficient of helium plotted as a function of the temperature.

portance because of inconsistency in the experimental values themselves in the low temperature region.

On the whole the agreement between the theoretical and experimental values of the virial coefficient is extraordinarily good. The slight discrepancy between them is not surprising in view of the approximations which were made in the calculation of the intermolecular energy, Eq. (7).

An examination of Fig. 1 shows that both the theoretical and experimental curves pass through a maximum at about 173°K. This phenomenon has been observed only in the case of helium, but presumably it should occur at sufficiently high temperatures for all gases. Thus, for hydrogen, neon, nitrogen and a number of other gases, the curve obtained by plotting $B$ against $1/T$ shows a decided concave bending in the region of high temperatures. The limitations of van der Waals' equation are clearly brought out in Fig. 1. Below 100°K, it would be possible to apply van der Waals' equation to helium, since in a narrow temperature range the relation between $B$ and $1/T$ may be approximated by a linear function. However, above 150°K, the van der Waals form of equation is entirely inadequate. Not only does the coefficient, $A$, cease to be constant, but it becomes very sensitive to temperature variation.

## SOME PROPERTIES OF HELIUM

In order to obtain a more detailed comparison with experiment, some properties of helium have been computed with the aid of the theoretically determined virial coefficients. By means of Eq. (1) the pressure has been calculated at several temperatures and volumes. The computed and experimental pressures are given in Table II.

TABLE II. *Helium pressures calculated from the first three terms of the theoretical virial. Expansion*: $p=(RT/V)(1+B/V+4B^2/3V^2.)$

| $V$ (liters/mol) | $p$ (calc.) | $p$ (obs.) | Δ |
|---|---|---|---|
| $t=200$°C | | | |
| 2.000 | 19.51 atm. | 19.52 atm. | −0.01 atm. |
| 0.400 | 99.60 | 99.82 | −0.22 |
| $t=100$°C | | | |
| 2.000 | 15.39 | 15.40 | −0.01 |
| 0.333 | 94.96 | 95.11 | −0.15 |
| $t=0$°C | | | |
| 2.000 | 11.27 | 11.27 | 0.00 |
| 0.250 | 93.97 | 94.12 | −0.15 |
| $t=-100$°C | | | |
| 2.000 | 7.15 | 7.15 | 0.00 |
| 0.200 | 75.45 | 75.66 | −0.21 |

The Joule-Thomson coefficient, $\mu$, may be expressed in terms of the virial coefficient $B$, and the heat capacity $C_p$ in the following manner:

$$\mu = -\frac{1}{C_p}\left[B + \frac{1}{T}\,\frac{dB}{d\left(\frac{1}{T}\right)}\right] = +\left(\frac{\partial T}{\partial p}\right)_H \tag{8}$$

At 25°C, $\mu$ is calculated to be $-0.061°$ atm.$^{-1}$. Moreover, between $+100°$ and $-100°$C, the value of $dB/d(1/T)$ is extremely small and therefore the temperature coefficient of $\mu$ is very small. Roebuck[13] has recently obtained the value $-0.06°$ atm.$^{-1}$ from measurements of the Joule-Thomson effect between $+100°$C and $-100°$C. The temperature variation in $\mu$ lay within his experimental error. A rough calculation of the Joule-Thomson inversion point leads to the temperature, 54°K. Although there is no reliable experimental determination with which to compare it the temperature 54°K is in accord with the fact that helium cannot be liquefied at the lowest temperature attainable by evaporating liquid nitrogen, about 70°K.

The thermodynamic temperature scale may be identified with the scale of the ideal gas thermometer. In order to reduce the scale of an actual gas thermometer to the thermodynamic temperature scale, corrections which are functions of the virial coefficients of the gas must be applied. We have used the theoretically determined values of $B$ in conjunction with recent measurements of the coefficient of expansion and the coefficient of pressure of helium[14] to determine the position of the freezing point of water under a pressure of one atmosphere on the absolute temperature scale. The coefficient of pressure of a gas at constant volume is defined as,

$$\alpha_v = \frac{p_{100} - p_0}{100 p_0}$$

where $p_0$ is the pressure at 0°C and $p_{100}$ the pressure at 100°C. It is easily shown that

$$T_0 = 1/\alpha_0$$

where $T_0$ represents the position of 0°C on the absolute temperature scale and $\alpha_0$ is the coefficient of pressure of an ideal gas, for which $pV = RT$. Moreover, it is possible to calculate $\alpha_0$ in terms of the $\alpha_v$ of an actual gas if its second virial coefficient is known.

$$\alpha_0 = \alpha_v + p_0(6.098 B_0 - 4.464 B_{100}) \cdot 10^{-7}$$

where $p_0$ is again the pressure at 0°C, $B_{100}$ the virial coefficient at 100°C expressed in cc/mol, and $B_0$ its value at 0°C. $\alpha_0$ may also be obtained from the coefficient of expansion in a similar manner. From the measurements of Heuse and Otto on helium, we compute for the average value of $\alpha_0$.

$$0.0036609 \text{ atm./}°$$

which corresponds to

$$T_0 = 273.16.$$

By linear extrapolation Heuse and Otto find that

$$T_0 = 273.16.$$

The International helium thermometer is defined as a constant volume gas thermometer in which the pressure of helium at 0°C is equal to that of a

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[13] J. R. Roebuck and H. Osterberg, Phys. Rev. **37**, 110 (A) (1931).

[14] W. Heuse and J. Otto, Ann. d. Physik [5] **2**, 1012 (1929).

one meter column of mercury at 0°C and standard gravity. The gas temperature is defined as

$$t_g = \frac{p_{t_g} - p_0}{p_{100} - p_0}\,.$$

The corresponding temperature on the absolute scale is of course

$$t = T - T_0.$$

The correction $\Delta t$ which must be added to the gas temperature $t_g$ to bring it into agreement with the absolute temperature scale may be computed from the second virial coefficient by means of the formula

$$\Delta t = 5.870\{3.731t_g(B_{100} - B_0) - (373.1 + t_g)(B_{t_g} - B_0)\}\cdot 10^{-5}$$

where the virial coefficients $B_{100}$, $B_0$, and $B_{t_g}$ are expressed in cc/mol. The corrections have been calculated for several temperatures. They are listed with those given by the Reichsanstalt in Table III.

TABLE III. *Corrections to international helium thermometer scale.*

| $t_g$ | $\Delta t$ (calc.) | $\Delta t$ (H and O) |
|---|---|---|
| 200 | +0.006 | +0.008 |
| 100 | 0.000 | 0.000 |
| 50 | −0.0003 | −0.001 |
| 0 | 0.000 | 0.000 |
| −100 | +0.009 | +0.009 |
| −200 | +0.032 | +0.028 |
| −250 | +0.051 | +0.043 |

L. Holborn and J. Otto, Zeits. f. Physik **38**, 359 (1926); **30**, 1 (1925).

Baxter and Starkweather[15] have measured the density of helium. Their value at 0°C and a pressure of one international atmosphere (pressure of a column of mercury 76 cm in height at 0°C and at standard gravity; $g = 980.665$ dynes $\sec^{-2}$) is

$$0.17847 \text{ g/liter}.$$

Using this density together with our value of $B$ at 0°C and taking the gas constant, $R$, as 0.08206 liter atm. the mean for a large number of gases, we calculate the atomic weight of helium as 4.0022. This is to be compared with the atomic weight 4.0020 obtained by Baxter and Starkweather from the density given above and their own compressibility measurements at low pressures.

In all of the cases which have been considered, the theoretically determined virial coefficient gives results which are in substantial agreement with experiment. When it is remembered that the calculation of the virial coefficient is based upon purely *a priori* considerations and depends upon experiment only through the values of certain universal atomic constants, it seems to furnish a striking confirmation of the present theory of intermolecular forces.

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[15] Baxter and Starkweather, Proc. Nat. Acad. Sci. **11**, 231 (1925).