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Determination of Intermolecular Forces from the Joule-Thomson Coefficients

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(Received February 2, 1938)

The energy of interaction between nonpolar molecules is determined inductively from a study of the experimental Joule-Thomson coefficients. These coefficients have been measured very accurately for some substances, and in these cases our method of analysis is preferable to other methods which utilize less accurate data. It follows from classical statistical mechanics that:

$$\mu_0 = (-2\pi N/C_p^0)$$
$$\times \int_0^\infty r^2 [1 - (1 - E(r)/kT) \exp(-E(r)/kT)] dr.$$

Here μ_0 and C_p^0 are the Joule-Thomson coefficient and specific heat at constant pressure, respectively, both extrapolated to zero pressure; N is Avogadro's number; k is Boltzmann's constant; and $E(r)$ is the energy of interaction of two molecules separated by a distance r.

This integral is evaluated using the Lennard-Jones form for the potential energy, $E(r) = -cr^{-6} + lr^{-s}$. Here c, l, and s are varied so as to give the best agreement with the experimental μ_0. The numerical tables required for these analyses are given. Helium and argon are studied in detail. The necessary quantum corrections are made for helium and shown to be negligible for argon. The Joule-Thomson studies of Roebuck and Osterberg are found to be in accord with other PVT measurements. It is shown that all substances having a mutual potential energy of the Lennard-Jones form with the same value for s, satisfy the theorem of corresponding states. Consequently, at low pressures, the Boyle point, T_B, is proportional to the Joule-Thomson inversion point, T_I, and $T_B = 0.532 T_I$. This relationship is verified in the case of N_2.

I. INTRODUCTION

THE interaction between the individual molecules of a substance is evidenced by a variety of physical and chemical properties such as the deviations from the ideal gas laws, the behaviour of liquids and crystals, the solubilities and tendencies for adsorption, etc. The investigation of any of these properties should be useful in determining the forces of attraction and repulsion between the molecules. Lennard-Jones[1] has been successful in analyzing these forces through a study of the experimental second virial coefficients. In this paper we extend his methods to utilize the accurate data which are available for the Joule-Thomson coefficients. A formulation based on statistical mechanics gives an explicit relationship between the Joule-Thomson coefficients and the energy of interaction between the molecules. This energy of interaction may be expressed in the form:

$$E(r) = -c/r^6 + l/r^s \qquad (1)$$

as a compromise between accuracy of representation and tractability in use. Here $E(r)$ is a function of the separation between the molecules, r, but not a function of the temperature. c, l,

and s are parameters which are adjusted so as to obtain the best fit with the experimental data. In this paper, we give a detailed comparison of the experimental Joule-Thomson coefficients for helium and argon with the theoretical formulation and present numerical tables which will aid in making similar analyses for other substances. The calculated and the experimental Joule-Thomson coefficients should agree if the function corresponds to the true interaction energy, but other functions may exist which would fit the data equally well. Quantum mechanics may be used to decide which are the more reasonable ones. The statistical formulae must be corrected to take into account the nonclassical interactions between the molecules. These corrections are sometimes appreciable as in the case of helium at low temperatures. For heavier molecules at reasonably high temperatures these corrections are negligible. In such cases we might expect the theorem of corresponding states to apply, and the properties of one gas would be simply related to those of another gas. This theorem is valid if the potential energy between a pair of molecules can be expressed in the form:

$$E(r) = E_0 f(r/r_0),$$

where E_0 and r_0 are characteristic constants of the molecules, and $f(r/r_0)$ is a universal function.

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[1] Lennard-Jones, Chapter X of Fowler's *Statistical Mechanics* (Cambridge University Press, 1936), and more recently, Physica **4**, 941 (1937).

The potential energy of Eq. (1) is of this form if s is supposed to have the same value for all substances under consideration.

II. RELATIONS BETWEEN THE JOULE-THOMSON, THE FREE EXPANSION, AND THE VIRIAL COEFFICIENTS

The imperfection of a gas is due to the attractions and repulsions of the molecules. Both the Joule-Thomson and the virial coefficients are direct measures of these forces and both become zero for a perfect gas. There are a number of ways of defining the virial coefficients,[2] but for the purposes of this paper we shall use the form of the equation of state:

$$pV = RT(1 + Bp + Cp^2 + Dp^3 + \cdots). \quad (2)$$

Here B, C, D, $\cdots$ are called the second, third, fourth, $\cdots$ virial coefficients and are functions of the temperature but not of the pressure. In this equation, p is the pressure in atmospheres, T is the absolute temperature, V is the molal volume in cm³, and R is the gas constant per mole, i.e. $R = 82.07$. It is easy to show that these virial coefficients are related to the Joule-Thomson coefficient,

$$\mu \equiv (\partial T / \partial p)_H \quad (3)$$

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[2] Virial coefficients are defined in the literature according to the three equations of state: (1). as from Eq. (2). (2). the equation $pV = A_p + B_p p + C_p p^2 + \cdots (2')$. Here it is obvious that $A_p = RT$ and that B_p, $C_p \cdots$ are equal to RT times our B, C, $\cdots$ respectively. (3). the equation of state given in powers of $1/V$, $pV = A_v + B_v/V + C_v/V^2 + \cdots (2'')$. Here again $A_v = RT$ but the relationship of the higher virials to our B, $C \cdots$ are not so obvious. To find these relations it is necessary to substitute for $1/V$ in $(2'')$ $1/V = p(RT)^{-1}(1 + Bp + Cp^2 + \cdots)^{-1}$ from Eq. (2), expand the right-hand side of the equation in powers of p, and equate the coefficients in this expansion to the corresponding virial coefficients of Eq. (1). Thus we find

$$B = B_v/R^2T^2, \qquad C = C_v/R^3T^3 - B_v^2/R^4T^4,$$
$$D = D_v/R^4T^4 - 3C_vB_v/R^5T^5 + 2B_v^3/R^6T^6.$$

The value of R which is used by different workers is another source of confusion. In theoretical treatments it is customary to express R in molal units whereas experimental workers prefer to express R so that $pV = 1$ at unit pressure and 0°C. The conversion of R from these experimental to the molal units then involves the use of all of the virial coefficients. Kammerlingh-Onnes and his co-workers at Leiden have adopted the international atmosphere as their unit of pressure. Holborn and Otto and their colleagues at Berlin have adopted 1 meter of mercury $= 1000/760$ atmos. as their unit of pressure. In this country, the Amagat units have become popular. Here the int. atm. is the unit of pressure, as in the Leiden units, but the unit of density is the density of nitrogen at 0°C and 1 atmos. (1.2506 grams per liter).

where H is the enthalpy or heat content of the gas. From thermodynamics[3] it may be shown that

$$\mu = -(\partial H / \partial p)_T / C_p \quad (4)$$

where C_p is the specific heat at constant pressure. But since

$$(\partial H / \partial p)_T = V - T(\partial V / \partial T)_p$$
$$= -T^2[(\partial / \partial T)(V/T)]_p \quad (5)$$

it follows that

$$\mu = T^2[(\partial / \partial T)(V/T)]_p / C_p. \quad (6)$$

Both the numerator and the denominator of (6) may be expressed in terms of the virial coefficients. By integrating the relation $V = (\partial F / \partial p)_T$, with respect to pressure where F is the free energy (or thermodynamic potential) and using Eq. (2), we obtain

$$F = F^0 + RT \log p + RTBp + (1/2)RTCp^2$$
$$+ (1/3)RTDp^3 + \cdots. \quad (7)$$

Here F^0 is the constant of integration which is a function of temperature but not of pressure.[4] Since $C_p = -T(\partial^2 F / \partial T^2)_p$, it follows from (7) that

$$C_p = C_p^0 - RT\left[p\frac{d^2(BT)}{dT^2} + (1/2)p^2\frac{d^2(CT)}{dT^2} \right.$$
$$\left. + (1/3)p^3\frac{d^2(DT)}{dT^2} + \cdots \right], \quad (8)$$

where C_p^0 is the specific heat at zero pressure. In terms of C_v^0, the specific heat at constant volume for infinite volume, $C_p^0 = C_v^0 + R$. In cases where neither C_p^0 nor C_v^0 can be obtained directly from experimental measurements with sufficient accuracy, it is often convenient to make use of spectroscopic information by means of the equation:[5]

$$C_v^0 = R[(\partial / \partial T)T^2(\partial / \partial T)(\log f)]_v, \quad (9)$$

where f is the partition function for the molecule, or the sum of all of the quantum states each multiplied by its Boltzmann factor, i.e., expo-

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[3] See for example Lewis and Randall, *Thermodynamics* (McGraw-Hill 1923), pp. 68, 162 and 163.
[4] The super- or subscript, zero, is used throughout this paper to denote the value of the quantities at zero pressure.
[5] Fowler, *Statistical Mechanics*, second edition (1936), p. 197, Eq. (611).

nential of minus the energy of the state divided by kT. At reasonably high temperatures $C_v{}^0$ usually does not deviate appreciably from its classical value of $(3/2)R$ for monatomic molecules, $(5/2)R$ for diatomic, etc. At very low temperatures, quantum effects occur and at very high temperatures for di- and polyatomic molecules, the specific heat of internal vibrations appears, but even in these cases the evaluation of $C_v{}^0$ to the desired accuracy should not be the source of any great amount of difficulty. The numerator of Eq. (6) is readily obtained from (1) so that we finally derive the Joule-Thomson coefficient in terms of the virial coefficients

$$\mu = \frac{RT^2[dB/dT + p\,dC/dT + p^2\,dD/dT + \cdots]}{C_p{}^0 - RT\left[p\dfrac{d^2(BT)}{dT^2} + (1/2)p^2\dfrac{d^2(CT)}{dT^2} + (1/3)p^3\dfrac{d^2(DT)}{dT^2} + \cdots\right]}. \tag{10}$$

For the purpose of making our analysis, it is more convenient to expand the right side of Eq. (10) in a Maclaurin series in powers of pressure so that

$$\mu = \mu_0 + p(\partial\mu/\partial p)^0{}_T + (1/2)p^2(\partial^2\mu/\partial p^2)^0{}_T + \cdots, \tag{11}$$

where μ_0 is the Joule-Thomson coefficient extrapolated to zero pressure $(\partial\mu/\partial p)^0{}_T$ is its derivative with pressure at constant temperature evaluated at zero pressure, and $(\partial^2\mu/\partial p^2)^0{}_T$ is its corresponding curvature at zero pressure. Here

$$\mu_0 = \frac{R}{C_p{}^0}T^2\frac{dB}{dT} \tag{12}$$

an equation similar to that obtained by Whitelaw.[6] This relation is particularly useful because it enables us to determine the second virial coefficient regardless of the magnitude of the third, fourth, etc. virials. Similarly

$$\left(\frac{\partial\mu}{\partial p}\right)^0{}_T = \frac{RT}{C_p{}^0}\left[T\frac{dC}{dT} + \mu_0\frac{d^2(BT)}{dT^2}\right] \tag{13}$$

and

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[6] Whitelaw, Physica **1**, 749 (1934).

$$\left(\frac{\partial^2\mu}{\partial p^2}\right)^0{}_T = \frac{RT}{C_p{}^0}\left[2T\frac{dD}{dT} + \mu_0\frac{d^2(CT)}{dT^2} + 2\left(\frac{\partial\mu}{\partial p}\right)^0{}_T\frac{d^2(BT)}{dT^2}\right]. \tag{14}$$

Most of our analysis will be concerned with the second virial coefficient and with μ_0. Later we shall use Eq. (13) to show how the potential energy between pairs of molecules, leads to approximately the correct pressure dependence of the Joule-Thomson coefficient when we obtain the potential from a study of μ_0 as a function of temperature.

If μ_0 is known as a function of temperature, we can integrate Eq. (12) to obtain the second virial coefficient except for a constant of integration:

$$B = \int_{T_0}^{T}(C_p{}^0\mu_0/RT^2)dT + (B)_{T_0}. \tag{15}$$

Here T_0 is any convenient temperature. Whitelaw used this equation to show that the data of Roebuck and Osterberg for the Joule-Thomson coefficients of helium were consistent with the second virial coefficients determined by other workers. The constant of integration of Eq. (15) could be evaluated on the reasonable supposition that as the temperature becomes infinite, B approaches zero. But unfortunately the temperatures at which the Joule-Thomson effect have been studied are not sufficiently high to make such an extrapolation accurate. We shall therefore resort to an indirect method of obtaining this constant. First we use the Joule-Thomson coefficient to determine the interaction energy between a pair of molecules. Then substituting this mutual potential energy expression into the statistical mechanical formula for B, Eq. (19), we obtain the absolute value of the second virial coefficient at any temperature. Because statistical mechanics is developed in terms of molecular models, it is often capable of giving more information from the same data than could be obtained from thermodynamics alone. As a matter of fact we will show that using a rather good form for the potential energy, the Boyle point at low pressures is 0.532 times the temperature of inversion of the Joule-

Thomson effect. When T_0 is taken to be the Boyle point, the constant of integration in Eq. (15) is $(B)_{T_0} = 0$.

The coefficient of free expansion, $\eta \equiv (\partial T/\partial p)_U$ where U is the internal energy of the gas, is another thermodynamical property closely related to the Joule-Thomson coefficient. Roebuck[7]

has shown that

$$\eta = \frac{\mu C_p + [(\partial/\partial p)(pV)]_T}{C_p - [(\partial/\partial T)(pV)]_p}. \qquad (16)$$

Using Eqs. (2), (8) and (10) it is easy to show that this is equivalent to the relation:

$$\eta = \frac{\mu_0 C_p{}^0 + RTB + pR(d(CT^2)/dT) + p^2(R/T)(d(DT^3)/dT) + \cdots}{C_v{}^0 - Rp(d/dT)T(d(BT)/dT) - (1/2)(Rp^2/T)(d/dT)T^2(d(CT)/dT) + \cdots}. \qquad (17)$$

And the coefficient of free expansion extrapolated to zero pressure has the simple form:

$$\eta_0 = \frac{\mu_0 C_p{}^0}{C_v{}^0} + \frac{RTB}{C_v{}^0} = \frac{RT}{C_v{}^0} \frac{d(BT)}{dT}. \qquad (18)$$

III. RELATIONS BETWEEN THE THERMODYNAMIC PROPERTIES AND THE INTER-MOLECULAR ENERGY

Fowler[8] and others have shown that, if the molecules in the gas interact as one would expect on the basis of classical mechanics, the second virial coefficient is related to the energy of interaction of a pair of molecules $E(r)$ in the following way:

$$B = \frac{2\pi N}{RT} \int_0^\infty r^2 [1 - \exp(-E(r)/kT)] dr, \qquad (19)$$

where r is the separation between a pair of molecules, k is Boltzmann's constant and N is Avogadro's number. Substituting this expression for B into Eq. (12), we find that the Joule-Thomson coefficient extrapolated to zero pressure is

$$\mu_0 = \frac{-2\pi N}{R} \left(\frac{R}{C_p{}^0} \right)$$

$$\times \int_0^\infty r^2 \left[1 - \left(1 - \frac{E(r)}{kT} \right) \exp \left(-\frac{E(r)}{kT} \right) \right] dr. \qquad (20)$$

Since $C_p{}^0$ and $C_v{}^0$ are usually expressed in units

of the gas constant R, it is convenient to retain the ratios $\left(\dfrac{R}{C_p{}^0} \right)$ and $\left(\dfrac{R}{C_v{}^0} \right)$ in the formulae. Similarly from (19) and (18), the coefficient of free expansion extrapolated to zero pressure is

$$\eta_0 = -\frac{2\pi N}{R} \left(\frac{R}{C_v{}^0} \right) \int_0^\infty r^2 \frac{E(r)}{kT} \exp \left(-\frac{E(r)}{kT} \right) dr. \qquad (21)$$

These equations permit us to determine $E(r)$ inductively if we know the experimental values of B, μ_0, or η_0 at different temperatures. Conversely, if we know the energy of interaction $E(r)$ either from theoretical or other experimental considerations, they permit us to calculate the thermodynamic properties of the substance. Lennard-Jones[9] has confined his analysis to a study of B whereas we find it equally as convenient to study μ_0 for which very accurate experimental data are available.

Before introducing any complicated expressions for the potential energy it is instructive to examine the gross properties of the second virial, Joule-Thomson, and free expansion coefficients. For this purpose we introduce a simple potential energy function which contains the essential features. Such a function is one first used by Herzfeld and Goeppert-Mayer.[10] Here, as shown in Fig. 1,

$E(r) = \infty$	when	r is less than r_0,
$E(r) = -D$		r lies between r_0 and r_a,
$E(r) = 0$		r is greater than r_a.

When this function is inserted into Eqs. (19),

[7] Roebuck, Proc. Am. Acad. Sci. **64**, 287 (1930).
[8] R. H. Fowler, *Statistical Mechanics*, second edition (Cambridge Press, 1936) Chapter 8; Proc. Camb. Phil. Soc. **22**, 861 (1925). Also Ursell, Proc. Camb. Phil. Soc. **23**, 685 (1927).

[9] Lennard-Jones, Chapter X of Fowler's *Statistical Mechanics* (1936) and more recently, Physica **4**, 941 (1937).
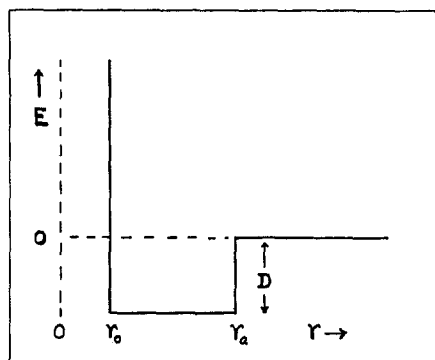[10] Herzfeld and Goeppert-Mayer, Phys. Rev. **46**, 995 (1934).

FIG. 1. The energy of interaction, E, as a function of the internuclear separation, r, for idealized molecules. This function was used by Herzfeld and Goeppert-Mayer.

(20) and (21), we obtain:

$$B = \frac{2\pi N}{3RT} r_0{}^3 \left[1 - \frac{r_a{}^3 - r_0{}^3}{r_0{}^3} \{ \exp (D/kT) - 1 \} \right]. \quad (22)$$

$$\mu_0 = \frac{-2\pi N}{3R} \left(\frac{R}{C_p{}^0} \right) r_0{}^3 \left[1 - \frac{r_a{}^3 - r_0{}^3}{r_0{}^3} \right.$$

$$\left. \times \left\{ \left(1 + \frac{D}{kT} \right) \exp (D/kT) - 1 \right\} \right], \quad (23)$$

$$\eta_0 = \frac{2\pi N}{3R} \left(\frac{R}{C_v{}^0} \right) r_0{}^3$$

$$\times \left[\left(\frac{r_a{}^3 - r_0{}^3}{r_0{}^3} \right) \frac{D}{kT} \exp (D/kT) \right]. \quad (24)$$

Here we see that B, μ_0, and η_0 are all proportional to the cube of the collision diameter, r_0. At low temperatures, the exponential term due to the attraction between the molecules, D, is of paramount importance, whilst at high temperatures it approaches unity. At high temperatures, B and μ_0 are only slightly affected by the attraction between the molecules and the limiting values are the same as for rigid spheres. The free expansion, η_0, seems to be very sensitive to the exact form for the potential energy for even at high temperatures it involves a characteristic of the attractive part of the potential, $(r_a{}^3 - r_0{}^3)D$. From (24) it seems that η_0 could never be negative, and this assertion is made in a number of the texts. However, as evidence of the sensitivity of the free expansion to the potential function, it may be cited that this conclusion is

not borne out when a more accurate potential is used. As a matter of fact Roebuck and Osterberg[11] have found that for helium it is actually negative at high temperatures.

As Wigner[12] and Slater[13] have pointed out, quantum-mechanical interactions between the molecules in the gas will introduce two types of corrections to the classical virial coefficient of Eq. (19). The first correction is due to the Pauli exclusion principle which requires that two similar molecules interacting must obey either the Bose-Einstein or the Fermi-Dirac statistics. The use of these statistics is well known in the case where the molecules are like atoms, and their interaction results in the formation of an ortho or para diatomic molecule. Just as in this case, the Bose, Fermi, and classical statistics lead to the same distributions when the thermal energy, kT, becomes large compared with the separation between the energy levels of rotation of the two molecules as a unit. Gropper[14] and recently Beth and Uhlenbeck[15] have considered this effect, and they were able to show that this correction is negligible except for the lightest molecules at the lowest temperatures. The second quantum-mechanical effect, however, leads to corrections which are sufficiently large to warrant consideration in any critical study of the properties of gases. It is due to the formation of double molecules when the relative kinetic energy of the colliding molecules is less than the potential energy of their attraction. The double molecules, just like diatomic species, possess discrete rotational and vibrational states for their relative motions and therefore have quite a different energy distribution from what one would expect classically. Uhlenbeck and Beth[16] have developed the correction terms to the second virial theorem so that we are able to correct the error due to this cause. According to Uhlenbeck and Beth:

$$B = B_{\text{class}} + B_q + \cdots, \quad (25)$$

where B_{class} is the B of Eq. (19) and B_q is the quantum-mechanical correction involving the

[11] Roebuck and Osterberg, Phys. Rev. **45**, 332 (1934).
[12] E. Wigner, Phys. Rev. **40**, 749 (1932).
[13] J. C. Slater, Phys. Rev. **38**, 237 (1931).
[14] Gropper, Phys. Rev. **50**, 963 (1936); **51**, 1108 (1937).
[15] Beth and Uhlenbeck, Physica **4**, 915 (1937).
[16] Uhlenbeck and Beth, Physica **3**, 729 (1936).

lowest power of h. The series converges rapidly for high temperatures and therefore it will suffice to consider B_q:

$$B_q = \frac{N^2 h^2}{24\pi R M k^3 T^4} \int_0^\infty r^2 \left(\frac{\partial E}{\partial r}\right)^2 e^{-E(r)/kT} dr. \quad (26)$$

Here h is Planck's constant and M is the molecular weight of the gas. The absolute magnitude of this correction for helium and argon at various temperatures will be discussed in a later section.

The second virial coefficients for two isotopic molecules provide a direct measurement of the quantum correction. For this case $E(r)$ and hence B_{class} is the same for the two molecules, but the quantum correction according to Eq. (26) involves the mass as well as the potential energy of the molecules. If the subscripts 1 and 2 refer to these isotopes and $(B)_1$ and $(B)_2$ are the second virial coefficients as determined experimentally, the quantum correction for isotope 1 is:

$$(B_q)_1 = [(B)_1 - (B)_2]/(1 - M_1/M_2). \quad (27)$$

K. Schäfer[17] has measured the second virial coefficients for H_2 and for D_2 so that we can compare the calculated with the experimental quantum corrections in this case. Using the Lennard-Jones potential with the energy of repulsion varying inversely with the twelfth power of the separation, we calculate $(B_q)_{H_2}$ = 0.0056 at 45^0A. From Eq. (27), $B_{H_2} - B_{D_2}$ is equal to $\frac{1}{2}(B_q)_{H_2}$ or 0.0028 whereas Schäfer finds this difference to be 0.0015. The agreement is as good as could be expected considering that the higher terms in Eq. (25) become important at low temperatures. As in the case of helium, these terms will make the quantum correction smaller than B_q. Schäfer has also calculated the quantum corrections for H_2 but unfortunately he attributed the total quantum correction to the discrete states with energy less than that of the separated molecules. Wigner[12] has shown that the quantum correction arising from the states of greater energy is equally important and, therefore we cannot regard the excellent agreement which Schäfer obtained as significant.

[17] K. Schäfer, Zeits. f. physik. Chemie **B36**, 85 (1937); **B38**, 187 (1937).

IV. THE FORM OF THE ASSUMED POTENTIAL ENERGY FUNCTION

The form which we assume for the potential energy function for use in the statistical mechanical formulae must be a compromise between accuracy and tractability. Lennard-Jones[18] has recently published a discussion of the various forms which are currently considered. At large separations both theory and experiment point to an energy of attraction varying as the inverse sixth power of the separation. Margenau[19] has shown that, at least in the case of hydrogen atoms and perhaps quite generally, an inverse eighth power attraction becomes important at slightly smaller separations. As the molecules approach they reach a point of minimum energy and repel each other on closer contact. It is only in the cases of interaction between two hydrogen,[20] two helium[21] atoms, and two neon atoms[22] that quantum-mechanical calculations for the repulsive energy are available. In these calculations as well as in the experimental studies of crystal lattice energies[23] it appears that the energy of repulsion decreases exponentially with the separation. In a study of van der Waals energy, however, we are only interested in the variation of this energy over a small range of separations, and therefore it will be permissible to approximate the exponential behavior by a repulsion energy varying as an inverse power. We therefore use the Lennard-Jones[24] potential

$$E(r) = -c/r^6 + l/r^s. \quad (1)$$

With this function, Lennard-Jones has shown how to integrate the expression for the second virial coefficient, (18), in terms of a rapidly converging series. The use of an exponential repulsion in formula (18) is possible and has actually been used by Kirkwood and Keyes[25] for helium and by Herzfeld[26] for argon, but the work

[18] Lennard-Jones, Physica **4**, 941 (1937).
[19] H. Margenau, Phys. Rev. **38**, 747 (1931).
[20] Eisenschitz and London, Zeits. f. Physik **60**, 491 (1930); H. Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).
[21] Slater and Kirkwood, Phys. Rev. **37**, 682 (1931); Slater, Phys. Rev. **32**, 349 (1928); Margenau, Phys. Rev. **38**, 747 (1931).
[22] Bleick and Mayer, J. Chem. Phys. **5**, 252 (1934).
[23] Born and Mayer, Zeits. f. Physik **75**, 1 (1932).
[24] Lennard-Jones, see for example Fowler's *Statistical Mechanics*, Chapter X and for his later work reference 18.
[25] Kirkwood and Keyes, Phys. Rev. **37**, 832 (1931).
[26] K. Herzfeld, Phys. Rev. **52**, 374 (1937).

entailed is sufficient to prevent its general application. The analysis which we make in this paper is directed at making subsequent analyses of the forces between molecules easy to perform. The Lennard-Jones potential is sufficiently flexible as to approximate the true potentials when the three constants c, l, and s are properly chosen, and yet it is easy to apply.

Substituting (1) into (19), Lennard-Jones obtained an expression equivalent to:

$$B = (2\pi N/3RT)r_0{}^3 F_s(E_{min}/kT) \qquad (28)$$

where $r_0 = (l/c)^{1/(s-6)}$ is the internuclear separation for which $E(r)$ is zero, and

$$E_{min} = -(1-6/s)c(6c/sl)^{6/(s-6)} \qquad (29)$$

is the minimum value for the potential energy of the two molecules with respect to the separated molecules as zero. The factor $2\pi Nr_0{}^3/3RT$ in Eq. (28) will be recognized as the second virial coefficient for rigid elastical molecules of collision diameter, r_0. F_s is then the correction factor to take into account the attraction between the molecules and the change of the collision diameter with temperature. Previous analyses[18] have shown that for many molecules s varies between 9 and 12, and the virial coefficients calculated with various values of s lie so close together that it is ·difficult to tell which value of s gives the best fit with experiment. The $F_s(E_{min}/kT)$ are rapidly converging infinite series which must be tabulated for various values of s and of E_{min}/kT. Fortunately, only a few values of s need be considered, and once these functions have been evaluated, they may be used in the analysis of many different substances. The function F_s of Eq. (28) has the explicit form:

$$F_s = y^{3/s-6}\left\{ \Gamma\left(\frac{s-3}{s}\right) - \sum_{n-1}^{\infty} c_n(s)y^n \right\}, \qquad (30)$$

where

$$y = \left(-\frac{E_{min}}{kT}\right)^{(s-6)/s} \frac{s}{6^{6/s}(s-6)^{(s-6)/s}}$$

$$= \frac{c}{l^{6/s}(kT)^{(s-6)/s}} \qquad (31)$$

and $\qquad c_n(s) = 3\Gamma\left(\frac{6n-3}{s}\right)\bigg/ sn! \qquad (32)$

Lennard-Jones has published some of his curves for F_s but it is not possible to read them to the accuracy which is necessary in making an analysis. However, the values of F_s can be readily calculated using the values of $c_n(s)$ which are given in Table I.

Substituting the above expression for B into Eq. (11) and differentiating we obtain:

$$\mu_0 = \frac{2\pi Nr_0{}^3}{3R}\left(\frac{R}{C_p{}^0}\right)G_s(E_{min}/kT), \qquad (33)$$

where

$$G_s = y^{3/s-6}\left\{ -\frac{3+s}{s}\Gamma\left(\frac{s-3}{s}\right) + \sum_{n=1}^{\infty} d_n(s)y^n \right\} \qquad (34)$$

and

$$d_n(s) = \frac{3}{s^2 n!}[(3+s)+n(s-6)]\Gamma\left(\frac{6n-3}{s}\right). \qquad (35)$$

The values of $d_n(s)$ and of G_s are given in Tables I and II, respectively, while in Fig. 2, G_s is plotted against y. Since G_s is the correction factor of the Joule-Thomson coefficient to take into account the attractions between the molecules and the decrease in collision diameter as the collisions become harder, this figure shows us the qualitative trends in the change of the Joule-Thomson effect with temperature. We see plainly that at low temperatures μ_0 is positive; at a higher temperature it becomes negative and finally approaches zero. A similar study for F_s would show that $-B$ exhibits an analogous change with temperature.

In making the analysis with the Lennard-Jones potential, we fitted the experimental values of μ_0 at two temperatures, T_1 and T_2. From Eq. (33) it follows (if $C_p{}^0$ remains constant in this temperature range) that

$$(\mu_0)_{T_1}/(\mu_0)_{T_2} = G_s(E_{min}/kT_1)/G_s(E_{min}/kT_2). \qquad (36)$$

Different values of E_{min} were then tried to find the one which gives the value of the ratio agreeing with the experimental one. The value of G_s for this value of E_{min}/kT was then substituted into (33) to give $r_0{}^3$, the other constant characteristic of the molecular interaction. Fig. 2 is useful in deciding on a rough value of E_{min} to try as a first approximation.

TABLE I.

n	$c_n(9)$	$c_n(12)$	$c_n(15)$	$d_n(9)$	$d_n(12)$	$d_n(15)$
1	$8.9302 \cdot 10^{-1}$	$9.0640 \cdot 10^{-1}$	$9.1817 \cdot 10^{-1}$	1.488367	1.58620	1.65271
2	$1.66667 \cdot 10^{-1}$	$1.5318 \cdot 10^{-1}$	$1.4892 \cdot 10^{-1}$	$3.33333 \cdot 10^{-1}$	$3.44647 \cdot 10^{-1}$	$3.57408 \cdot 10^{-1}$
3	$5.0152 \cdot 10^{-2}$	$3.7766 \cdot 10^{-2}$	$3.3333 \cdot 10^{-2}$	$1.17022 \cdot 10^{-1}$	$1.03858 \cdot 10^{-1}$	$1.00000 \cdot 10^{-1}$
4	$1.65374 \cdot 10^{-2}$	$9.5735 \cdot 10^{-3}$	$7.3938 \cdot 10^{-3}$	$4.40996 \cdot 10^{-2}$	$3.11140 \cdot 10^{-2}$	$2.66178 \cdot 10^{-2}$
5	$5.55556 \cdot 10^{-3}$	$2.3604 \cdot 10^{-3}$	$1.5523 \cdot 10^{-3}$	$1.66667 \cdot 10^{-2}$	$8.85156 \cdot 10^{-3}$	$6.51966 \cdot 10^{-3}$
6	$1.85749 \cdot 10^{-3}$	$5.5845 \cdot 10^{-4}$	$3.0606 \cdot 10^{-4}$	$6.19163 \cdot 10^{-3}$	$2.37344 \cdot 10^{-3}$	$1.46907 \cdot 10^{-3}$
7	$6.1250 \cdot 10^{-4}$	$1.2645 \cdot 10^{-4}$	$5.6731 \cdot 10^{-5}$	$2.24582 \cdot 10^{-3}$	$6.00642 \cdot 10^{-4}$	$3.06350 \cdot 10^{-4}$
8	$1.98413 \cdot 10^{-4}$	$2.7424 \cdot 10^{-5}$	$9.9206 \cdot 10^{-6}$	$7.93651 \cdot 10^{-4}$	$1.43977 \cdot 10^{-4}$	$5.95238 \cdot 10^{-5}$
9	$6.3063 \cdot 10^{-5}$	$5.7079 \cdot 10^{-6}$	$1.6431 \cdot 10^{-6}$	$2.73273 \cdot 10^{-4}$	$3.28201 \cdot 10^{-5}$	$1.08443 \cdot 10^{-5}$
10	$1.96603 \cdot 10^{-5}$	$1.1427 \cdot 10^{-6}$	$2.5872 \cdot 10^{-7}$	$9.17482 \cdot 10^{-5}$	$7.14171 \cdot 10^{-6}$	$1.86276 \cdot 10^{-6}$
11	$6.0125 \cdot 10^{-6}$	$2.2053 \cdot 10^{-7}$	$3.8864 \cdot 10^{-8}$	$3.00625 \cdot 10^{-5}$	$1.4886 \cdot 10^{-6}$	$3.03141 \cdot 10^{-7}$
12	$1.80483 \cdot 10^{-6}$	$4.1119 \cdot 10^{-8}$	$5.5872 \cdot 10^{-9}$	$9.62576 \cdot 10^{-6}$	$2.9811 \cdot 10^{-7}$	$4.6932 \cdot 10^{-8}$
13	$5.3212 \cdot 10^{-7}$	$7.42 \cdot 10^{-9}$	$7.7083 \cdot 10^{-10}$	$3.01533 \cdot 10^{-6}$	$5.76 \cdot 10^{-8}$	$6.9375 \cdot 10^{-9}$
14	$1.54167 \cdot 10^{-7}$	$1.299 \cdot 10^{-9}$		$9.25002 \cdot 10^{-7}$	$1.072 \cdot 10^{-8}$	
15	$4.3927 \cdot 10^{-8}$	$2.2 \cdot 10^{-10}$		$2.78204 \cdot 10^{-7}$	$1.9 \cdot 10^{-9}$	

TABLE II.

$-E_{min}/kT$	y	G_9	$-E_{min}/kT$	y	G_{12}	$-E_{min}/kT$	y	G_{15}
0.006352	0.35	-0.43328	0.002500	0.10	-0.43310	0.002210	0.05	-0.48391
.009482	.40	$-.45919$	.008100	.18	$-.52372$	.007017	.10	$-.57005$
.013500	.45	$-.47491$	.010000	.20	$-.53659$	.022279	.20	$-.61486$
.018519	.50	$-.47997$	.015625	.25	$-.55596$	.043790	.30	$-.57983$
.032000	.60	$-.45588$	.022500	.30	$-.55967$	.10260	.50	$-.37065$
.050815	.70	$-.38205$	.040000	.40	$-.52784$	.1840	.7098	.00000
.062501	.75	$-.32468$	.050625	.45	$-.49456$	.22456	.80	.20287
.1175	.9256	.00000	.062500	.50	$-.45062$	.24358	.84	.30125
.14815	1.00	.20365	.075625	.55	$-.39634$	.27326	.90	.45865
.15264	1.01	.23439	.090000	.60	$-.33206$	.32572	1.00	.74804
.15722	1.02	.26594	.12250	.70	$-.17371$	.44141	1.20	1.43554
.25600	1.20	.99355	.14062	.75	$-.07966$	.57064	1.40	2.28705
.40652	1.40	2.24584	.1555	.7887	.00000	.71289	1.60	3.33463
.50001	1.50	3.10764	.16000	.80	.02446	.78874	1.70	3.94520
.52027	1.52	3.30334	.19360	.88	.21249	.86975	1.80	4.62245
.54107	1.54	3.50766	.20250	.90	.26369	1.03410	2.00	6.21054
.72786	1.70	5.50317	.25000	1.00	.54607			
			.30250	1.10	.87459			
			.36000	1.20	1.25327			
			.49000	1.40	2.18167			
			.64000	1.60	3.38508			
			.65610	1.62	3.52330			
			.7225	1.70	4.12008			
			.8100	1.80	4.94199			
			1.0000	2.00	6.96632			

Using (18) we can combine F_s and G_s to form η_0. Thus:

$$\eta_0 = \frac{2\pi N r_0^3}{3R}\left(\frac{R}{C_v^0}\right)[F_s + G_s]$$

$$= \frac{2\pi N r_0^3}{3R}\left(\frac{R}{C_v^0}\right)H_s, \quad (37)$$

where $H_s = F_s + G_s$

$$= y^{3/s-6}\left[-\frac{3}{s}\Gamma\left(\frac{s-3}{s}\right) + \sum_{n=1}^{\infty} e_n(s)y^n\right] \quad (38)$$

and

$$e_n(s) = \frac{3}{s^2 n!}\Gamma\left(\frac{6n-3}{s}\right)[3 + n(s-6)]. \quad (39)$$

From these equations we see that at sufficiently high temperatures, i.e. small values of y, H_s and hence η_0 will become negative, in agreement with the observations of Roebuck and Osterberg. It is interesting to note that this was not the case in (24) when the collision diameter was assumed to be rigid.

V. THE EQUATION OF CORRESPONDING STATES

It follows from Ursell's[8] development of the virial coefficients, that if $E(r)$ has the form

$$E(r) = E_0 f(r/r_0)$$

where E_0 and r_0 are constants characteristic of the molecule and $f(r/r_0)$ is a universal function for all substances, the theorem of corresponding states is valid. In the case of the Lennard-Jones form for the potential energy this would mean that s has the same value for many nonpolar substances. The equation of state can then be written in terms of reduced variables, P', V', T':

$$P'V'/T' = 1 + (P'/T')F_s(1/T') + \cdots, \quad (40)$$

where $P' = p/(E_{\min}/\frac{2}{3}\pi r_0{}^3)$, $V' = V/(\frac{2}{3}\pi N r_0{}^3)$,

$T' = Tk/E_{\min}$.

This equation has the important consequence that all of the properties of the substance which depend only on the equation of state will have the same values when expressed in these universal parameters. The virial, compressibility, and expansion coefficients are of this nature. From Eqs. (12) and (18) we see that $\mu_0 C_p{}^0$ and $\eta_0 C_v{}^0$ involve only the second virial coefficient and its derivatives and therefore have the same form for most nonpolar substances. The theorem of corresponding states is also useful in connection with the pressure dependent parts of the Joule-Thomson and free expansion coefficients which involve the specific heat $C_v{}^0$, a function of the internal configuration of the molecule, as well as the variables of state. Thus from Eq. (10) we see that:

$$\mu = r_0{}^3 f_1(P', T')/[(C_v{}^0/R) - f_2(P', T')], \quad (41)$$

where f_1 and f_2 are universal functions of the reduced pressure and temperature. To the approximation that $(C_v{}^0/R) = \frac{3}{2}$ for monatomic molecules, all of these substances would have a universal form for their Joule-Thomson coefficient; similarly diatomic molecules would fall into another class, etc. The relationship between these classes is given by (41). A knowledge of the functions f_1 and f_2 obtained from the experimental or theoretical study of Joule-Thomson coefficients for monatomic and diatomic gases should therefore be useful in predicting the Joule-Thomson coefficients for polyatomic molecules. Similarly from Eq. (16) it follows that:

$$\eta = r_0{}^3[(C_v{}^0/R)g_1(P', T')$$
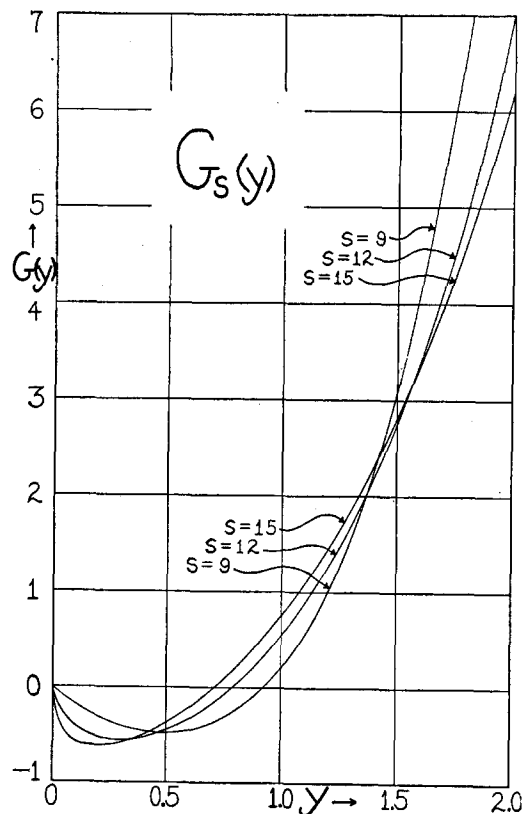$$- g_2(P', T')]/[(C_v{}^0/R) + g_3(P', T')]. \quad (42)$$

FIG. 2. G_s is plotted as a function of y. Since y is inversely proportional to the $(s-6)/s$ power of the temperature, small values of y correspond to high temperatures. The Joule-Thomson coefficient extrapolated to zero pressure is proportional to these G_s for all nonpolar substances to which the Lennard-Jones potentials apply.

The functions f and g occurring in (28) and (29) can be obtained explicitly from Eqs. (10) and (17) with the aid of (40).

One immediate application of the theorem of corresponding states is a connection between the temperatures for the Boyle point and for the (lower) Joule-Thomson inversion at low pressures. These points occur for different universal values of T'.

$$T_I/T_B = T'_I/T'_B, \quad (43)$$

where I and B refer to the inversion and Boyle points respectively. It follows that T_I/T_B should be very nearly the same for all nonpolar substances. Table III shows the values for this ratio which we obtained when the potential energy function was taken to be of the Lennard-Jones form with different values of s. Thus in the case of N_2 where the measurements of Roebuck and

Osterberg[27] give $T_I = 623^\circ A$, we would expect the Boyle point to lie between 333° and $.329^\circ A$. Actually the experimental determinations recorded in the *International Critical Tables* show that it is $325^\circ A$ which is satisfactory agreement.

VI. Analysis of the Joule-Thomson Data for Helium

Helium is one of the simplest gases to study. Its critical temperature is so low that at room temperature helium molecules behave almost like elastic billiard balls with little attraction between each other. Extensive theoretical and experimental studies of helium have been made. The only disagreeable feature of helium is the importance of the quantum-mechanical corrections which have to be made in its equation of state. Uhlenbeck and Beth inserted the Lennard-Jones potential into their equation and found that at $100^\circ A$ the quantum correction B_q is 11 percent of the classical second virial coefficient and that it is still 3 percent of B_{class} at $300^\circ A$. Their numerical values for B_q can be expressed in the form: $B = B_{\text{class}} + B_q$ where

$$B_q = 1.13T^{-2} + 33T^{-3}. \qquad (44)$$

Substituting this expression for the second virial coefficient into (12)

$$\mu_0 = (\mu_0)_{\text{class}} + (\mu_0)_q$$

where $\quad (\mu_0)_q = -0.90T^{-1} - 40T^{-2}. \qquad (45)$

Here $(\mu_0)_q$ is the correction term to be added to the classical expression $(\mu_0)_{\text{class}}$ to obtain the experimental value μ_0. Comparing this correction term with the experimental results of Roebuck and Osterberg[28] we obtain Table IV. If this quantum correction is correct at least as to

approximate magnitude, it becomes apparent that an analysis of the law of force between two helium molecules based on the classical statistical mechanical formulae would lead to an apparent potential energy quite different from reality. Wigner[12] has pointed out that the quantum-mechanical correction is extraordinarily sensitive to the exact form for the potential energy between the molecules. It is therefore difficult to estimate the accuracy of the Uhlenbeck and Beth quantum-mechanical correction and of the corresponding correction to the Joule-Thomson coefficient. We are particularly troubled by the discrepancy between the Uhlenbeck and Beth results and those of Kirkwood[29] who performed a similar analysis and obtained much smaller correction terms. Tentatively, we shall accept the Uhlenbeck and Beth results in our analysis, with the reservation that future work in this field may change the values of $(\mu_0)_q$ appreciably. We fitted the $(\mu_0)_{\text{class exp}}$ of Table IV with the aid of Eq. (39) and obtained a revised Lennard-Jones potential for helium which gives excellent agreement with the Roebuck and Osterberg determinations. The column marked $(\mu_0)_{\text{class calc}}$ was obtained with this function,

$$E(r) = -15.22 \times 10^{-61}/r^6 \\ + 4.39 \times 10^{-106}/r^{12} \text{ ergs.} \quad (46)$$

This potential bears a striking resemblance to that of Slater and Kirkwood,

$$E(r) = -16.2 \times 10^{-61}/r^6 \\ + 7.7 \times 10^{-10} \exp(-1.28r \times 10^8) \text{ ergs}, \quad (47)$$

which was obtained from quantum-mechanical computations. Our potential gives $E_{\text{min}} = -13.2 \times 10^{-16}$ ergs and $r_0 = 2.57A$ whereas the Slater and Kirkwood function gives $E_{\text{min}} = -14.4 \times 10^{-16}$ ergs and $r_0 = 2.58A$. Kirkwood and Keyes[25] have

Table III.

	BOYLE POINT		INVERSION POINT		T INVERSION
					—————
	$-E_{\text{min}}$		$-E_{\text{min}}$		T BOYLE
s	$\overline{kT_B}$	y_B	$\overline{kT_I}$	y_I	
9	0.2195	1.1400	0.1175	0.9256	1.8683
12	.2924	1.0815	.1555	0.7887	1.8803
15	.3476	1.0398	.1840	0.7098	1.8895

Table IV.

$T^\circ A$	$(\mu_0)_{\text{exp}}$	$(\mu_0)_q$	$(\mu_0)_{\text{class exp}}$	$(\mu_0)_{\text{class calc}}$
80.9	−0.0365 deg. atm.⁻¹	−0.0172 deg. atm.⁻¹	−0.0193	−0.0200
88.9	− .0410	− .0152	− .0258	− .0257
116.8	− .0497	− .0106	− .0381	− .0384
172.1	− .0557	− .0066	− .0491	− .0498
273.1	− .0599	− .0038	− .0561	− .0568
297.5	− .0601	− .0034	− .0567	− .0574
374.2	− .0621	− .0027	− .0594	− .0590
472.6	− .0616	− .0021	− .0595	− .0595
575.5	− .0568	− .0017	− .0551	− .0585

[27] Roebuck and Osterberg, Phys. Rev. **48**, 450 (1935).
[28] Roebuck and Osterberg, Phys. Rev. **43**, 60 (1933).

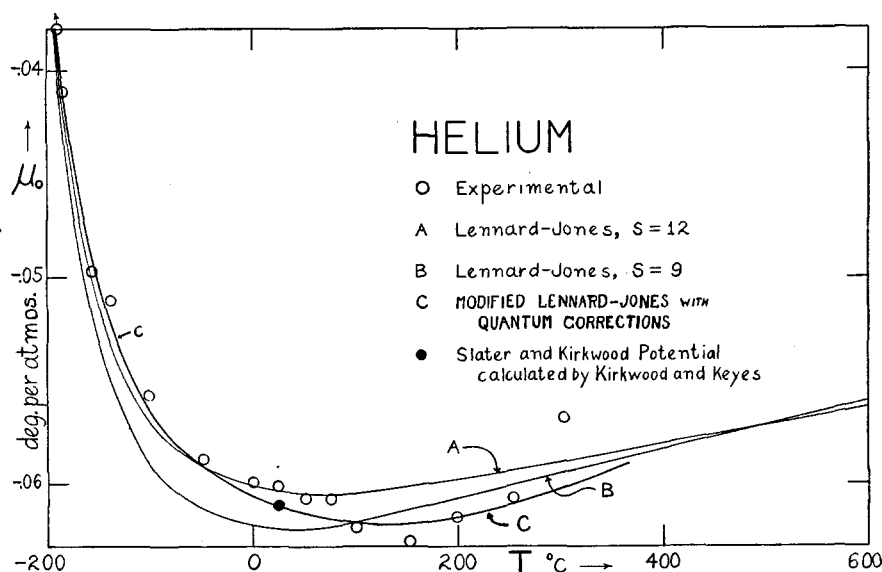[29] J. Kirkwood, Physik. Zeits. **33**, 39 (1932).

FIG. 3. The Joule-Thomson coefficient for helium is plotted as a function of tempera-
ture. The curves A and B were derived from the Lennard-Jones potentials in which
the constants were adjusted so as to fit the experimental values of the second virial
coefficient. The minimum in the Joule-Thomson coefficient indicates that the collision
diameter of helium decreases with increasing temperature.

used the Slater and Kirkwood potential to
compute the second virial coefficient. Their
agreement with experiment is good, and this
agreement would be further improved if the
Uhlenbeck and Beth quantum corrections were
used in place of those calculated by Kirkwood.
Margenau[30] believes this to be fortuitous since
he has shown that the induced dipole-quadrupole
terms, which are neglected in the Slater-Kirkwood
potential, are appreciable.

In Fig. 3 we have plotted:

1. The experimental Joule-Thomson coefficients of
Roebuck and Osterberg.

2. The curves A and B obtained from the Lennard-
Jones potentials with $s=9$ and $s=12$ from an analysis of
the second virial coefficient neglecting quantum effects.

3. Curve C, our results using the modified Lennard-
Jones function (μ_0 class calc) to which is added the quan-
tum corrections $(\mu_0)_q$.

At the comparatively high temperatures in
which we are interested, i.e., over 173^{0}A, the effect
of the attractive part of the potential curve is
negligible, and for all practical purposes the heli-
um molecules could be thought of as elastic billiard
balls. Because the repulsive part of the poten-

tial curve is now the important one, the Joule-
Thomson coefficient is negative, and the second
virial coefficient is positive. But the collision
diameter of the helium molecule decreases
with the increased violence of the average
collisions as the temperature is raised, and this
gives rise to two rather interesting effects. The
coefficient of free expansion becomes negative,
and the Joule-Thomson coefficient passes through
a minimum value. Neither of these effects could
be caused in any other way. From the Slater and
Kirkwood potential we see that the collision
diameter, i.e., the value for r when $E(r)=\frac{1}{2}kT$,
at room temperature is a half an angstrom
smaller than at very low temperatures so that
these qualitative arguments are sound.

Mayer and Harrison have recently computed
the values of the third virial coefficient using the
Lennard-Jones potential with $s=12$ and they
have kindly made their results available to us
in a private communication. Substituting their
values for C into Eq. (12) it follows that
$(\partial\mu/\partial p)^0_T=0.0005$. Of course, this computation
is made neglecting the quantum corrections.
Actually, to within the accuracy of their measure-
ments, Roebuck and Osterberg did not observe
any change of μ with pressure. It, therefore,

[30] Margenau, Phys. Rev. **38**, 1785 (1931); Proc. Nat.
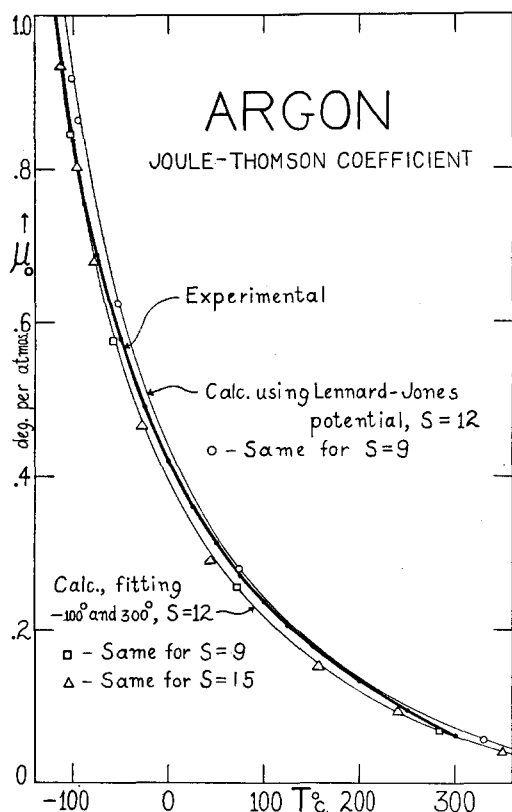Acad. **18**, 56 (1932) and **18**, 230 (1932).

FIG. 4. The Joule-Thomson coefficient for argon is plotted as a function of temperature. The heavy line is from the experimental measurements of Roebuck and Osterberg. The line above the experimental curve is obtained from the Lennard-Jones potentials in which the constants were adjusted to fit the second virial coefficient data. The lower curve is an attempt to fit the Roebuck and Osterberg results by making the calculated and experimental results agree at −100°C and 300°C.

appears that the quantum correction is much more important in the case of third virials than it is for the second. Perhaps this might be expected since the third virial coefficient arises from three-body collisions. These collisions can be thought of as two-body collisions between double and single molecules. Since quantum considerations make these double species considerably less probable than would be expected on classical grounds, the third virial coefficient will be correspondingly smaller.

VI. ANALYSIS OF THE JOULE-THOMSON DATA FOR ARGON

Argon, like helium, is a simple gas on which to test our methods of analysis. In some respects it

is easier to study because the quantum corrections are negligibly small at ordinary laboratory temperatures. Unfortunately, the interactions between two argon molecules have not been studied theoretically, and our analysis must proceed purely inductively. Lennard-Jones has studied the second virial coefficients for argon and constructed potential functions which fit this data. But the absolute value of the second virial coefficient is difficult to measure accurately because it involves a knowledge of the volume of the gaseous system to many significant figures. Perhaps the inaccuracy of this constant is best illustrated by a direct comparison between the values of B for 0°C of Kammerlingh-Onnes[31] and of Holborn and Otto[32] which on conversion to our units are -7.3860×10^{-4} atmos.$^{-1}$ and -9.8509×10^{-4} atmos.$^{-1}$, i.e., a difference of 25 percent. The experimental measurement of the Joule-Thomson coefficient has the advantage that it provides a direct measurement of the imperfection of the gas in which this imperfection appears as a first rather than a second-order effect. Roebuck and Osterberg[33] have made some excellent measurements of the Joule-Thomson coefficient which we shall utilize. Their results for μ_0 are plotted in Fig. 4. An excellent empirical representation of their data is obtained by using the Herzfeld-Goeppert-Mayer potential where $r_0 = 3.43$A, $r_a = 9.53$A and $D = 2.37 \times 10^{-15}$ erg per molecule, the constants having been derived by fitting minus 100°, 100°, and 300°C. The Joule-Thomson coefficient calculated by Eq. (23) for this function agrees to within the experimental accuracy with the R. and O. data, but unfortunately we can attach little theoretical significance to it because the separation r_a at which the attractive potential ceases to be large is at a distance far in excess of any theoretical inter-

TABLE V.

T	$(\partial\mu/\partial p)^0_T$ calc.	$(\partial\mu/\partial p)^0_T$ obs.
573.2	−0.0007 deg/atmos.^{2}	−0.0002 deg/atmos.^{2}
473.2	− .0011	− .0005
373.2	− .0015	− .0009
273.2	− .0015	− .0012
173.2	− .0015	− .0030

[31] Kammerlingh Onnes and Crommelin, Leiden Communication 118b, 24 (1910).
[32] Holborn and Otto, Zeits. f. Physik 33, 1 (1925).
[33] Roebuck and Osterberg, Phys. Rev. 46, 785 (1934).

action potential. The general characteristic that the potential should be shallow and that the attraction should extend over a large separation, may, however, have some significance. The Lennard-Jones curves, obtained by adjusting the constants in the potential energy function to fit the second virial data, agree with the experimental Joule-Thomson data at medium high temperatures but diverge at lower and higher temperatures. We changed these constants so as to fit the Joule-Thomson data at both 300°C and −100°C, but for no value of s, lying between 9 and 15 did the curves agree with R. and O. for the intermediate points. These curves are also shown in Fig. 4. It therefore appears that the experimental data is sufficiently accurate to warrant the use of a potential function more accurate than the Lennard-Jones type. Herzfeld[26] has recently computed the second virial coefficient for argon using the potential energy function which he and Goeppert-Mayer found to agree with crystal structure data. This function contains an exponential repulsion term instead of the inverse power, and it would be interesting to see how closely this potential would give results agreeing with Roebuck and Osterberg.

The quantum corrections are small in the case of argon. By substituting the Lennard-Jones potential with $s=12$ into Eq. (26) we find that at the lowest temperature that we are interested in, i.e., $T=173.2A$, B_q is only 2.54×10^{-5} which is less than one percent of the experimental second virial coefficient. This quantum correction would be even smaller by a factor of ten if argon molecules were rigid spheres with no attractions between the molecules. From the calculation at 173.2°A we estimate B_q by the form $B_q = 0.76 T^{-2}$. It follows that the quantum correction for μ_0 at 173.2°A is only $(\mu_0)_q = -0.0035$ or one-half of one percent of the experimental Joule-Thomson coefficient. Since this correction becomes smaller at higher temperatures it can be neglected. In Fig. 4, this quantum correction is roughly the width of the heavy black line.

The pressure dependence of the Joule-Thomson effect requires a knowledge of the higher virial coefficients as shown by Eqs. (10) to (14). Using Professor Joseph Mayer's and Miss Harrison's values for the third virial coefficients obtained from the Lennard-Jones potential with an inverse
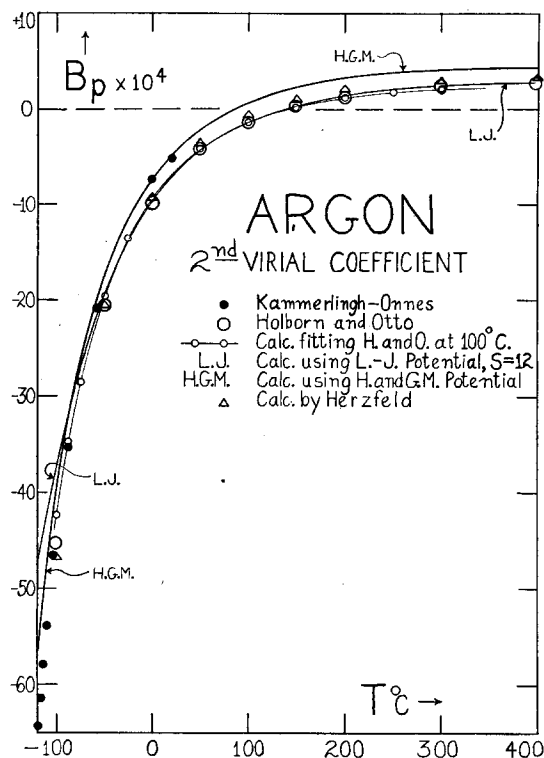

FIG. 5. The second virial coefficient of argon is plotted as a function of the temperature. The experimental points of Kammerlingh-Onnes and of Holborn and Otto are compared with the values calculated in different ways from the Joule-Thomson measurements of Roebuck and Osterberg. The values calculated by Herzfeld from a potential energy obtained from crystal structure data are also plotted.

twelfth power repulsion made, we obtained the values given in Table V of the change of the Joule-Thomson coefficient with pressure at zero pressure. The agreement between the calculated and the observed values is right as to the order of magnitude and the general trend, but the discrepancy is larger than we had anticipated. We have plotted in Fig. 5 the experimental second virial measurements of Kammerlingh-Onnes and of Holborn and Otto. Then we have drawn four curves. The first is a curve which we obtained by integrating the Joule-Thomson coefficients of R. and O. by Eq. (14) and evaluating the constant to fit H. and O's. second virial for $T=100°C$. The second is the curve obtained by the use of the Lennard-Jones potential with $s=12$. The third is that which we obtained from Eq. (32) using the Herzfeld-Goeppert-Mayer potential with constants derived from Joule-
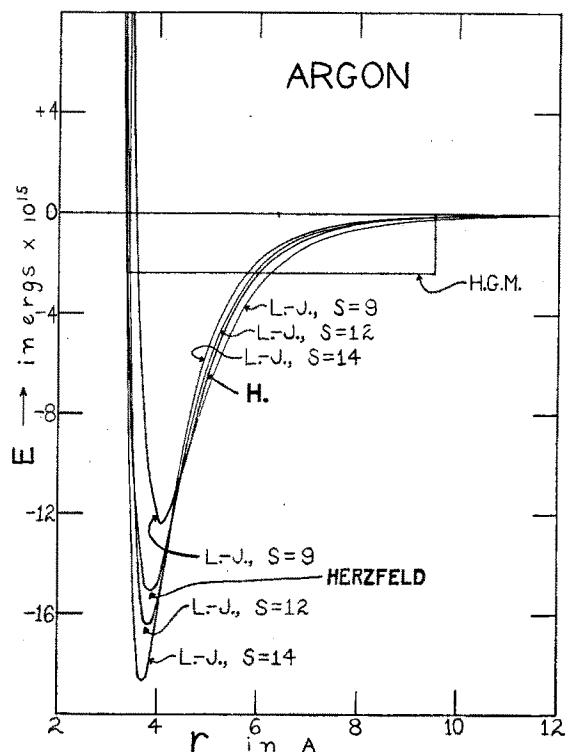
FIG. 6. The potential energy, E, of two colliding argon atoms is plotted as a function of their separation, r. The Lennard-Jones curves for $s=9$, 12, and 14 fit the experimental second virial and Joule-Thomson data equally well. The Herzfeld function is obtained from crystal structure observations. The Herzfeld and Goeppert-Mayer function which is quite different from any of these, still fits this data.

Thomson data. The fourth is that obtained by Herzfeld using his potential (with r in A):

$$E(r) = -1.11 \times 10^{-10} r^{-6}$$
$$+ 1.34 \times 10^{-9} \exp(-r/0.345) \text{ ergs.}$$

where the constants have been evaluated from a study of crystal structure. Of all of these functions, Herzfeld's seems to give the best agreement with experiment. The R. and O.

curve, obtained by the integration and experimental evaluation of the integration constant, agrees nicely with all of H. and O.'s experimental data. The Lennard-Jones curve is satisfactory, compared with H. and O.'s data, at high temperatures, but deviates appreciably at the lower temperatures which is the same effect which we noticed in studying the Joule-Thomson effect. The H.G.M. potential results in agreement with Kammerlingh-Onnes.

In Fig. 6 we have plotted the potential energy function for argon. The Lennard-Jones curves all give about the same agreement with the Joule-Thomson data. The Herzfeld function is probably the most accurate. From the great difference between these functions we see the inherent uncertainty involved in the inductive method of determining the potential energy curves. The fact that the Herzfeld Goeppert-Mayer function also gives a good fit, makes this indeterminancy more apparent. The convergence of the inductive and of the theoretical approach should improve this situation. We should obtain from quantum mechanics at least some of the constants for the potential energy function as, for example, the van der Waals attractive potential, $-c/r^6$, and probably the Margenau inverse eighth power attraction term. Theoretical considerations should also determine the best form of the remainder of the potential and this will involve the only parameters to be determined from experiment.