

bending modes expected for ketenimine is incomplete. Hence, the spectral identification of ketenimine, despite considerable support, must remain inconclusive.

### Conclusions

The attack of the isoelectronic species  $\text{CH}_2$  and  $\text{NH}$  on the  $\text{C}=\text{C}$  bond of  $\text{C}_2\text{H}_4$  in an inert matrix leads to the complete stabilization of the corresponding cyclic species. However, the principal product of the  $\text{CH}_2$

+  $\text{C}_2\text{H}_2$  reaction in the matrix is the linear species allene. Considerable evidence also supports the stabilization of the previously unobserved species ketenimine in the corresponding reaction of  $\text{NH}$  with  $\text{C}_2\text{H}_2$ . A consideration of possible mechanisms for the formation of these species suggests that at least some of the  $\text{CH}_2$  and  $\text{NH}$ , initially in an excited singlet state, may be deactivated by the matrix to the ground triplet state before reaction with  $\text{C}_2\text{H}_2$ .

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## Compressibility of Gases. IV. The Burnett Method Applied to Gas Mixtures at Higher Temperatures. The Second Virial Coefficients of the Helium-Nitrogen System from 175° to 475°<sup>1</sup>

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The Burnett method of determining the compressibility factor of gases has been tested for the study of gaseous mixtures over a range of higher temperatures. Mixtures of helium and nitrogen were used at 175°, 250°, 325°, 400° and 475° and up to pressures slightly above 100 atmospheres. At each temperature, seven or more mixtures evenly spaced over the whole range of composition were measured. The results demonstrate the advantages of the method as judged by the values obtained for the second virial interaction coefficient,  $B_{12}$ , which is the quantity of central interest for mixtures. In addition to the rarity of such data in general, these values have especial interest because they lie on the high-temperature side of the maximum in  $B_{12}$  and their variation with temperature is not explained adequately by the existing theory of intermolecular interactions.

### Introduction

Previous experiments at this Laboratory<sup>2-4</sup> have revealed the advantages of the Burnett<sup>5</sup> method for obtaining compressibility data for gaseous mixtures. Those studies were limited to measurements at a single temperature (30°) and for that reason did not provide sufficient information for testing the agreement between second virial interaction coefficients determined from the compressibility data and those calculated from the intermolecular potential functions. The work reported here was undertaken to examine the potentialities of the Burnett method over a temperature range sufficiently wide to allow this comparison.

The helium-nitrogen system was chosen for the test. Despite the low magnitude of the molecular interactions in this system, the method has produced accurate data for it which are sufficiently fine-grained and extensive to call for refinement of the existing theory of the interaction of such non-polar molecules.

### Experimental

The two Burnett chambers had volumes of 100 and 300 ml. and were constructed of 19-9 DL stainless steel by the High Pressure Instrument Co. of Erie, Penna. Packless bellows valves especially designed for our work by Hoke Inc., were used successfully while immersed in the bath at 175°, but failed at higher temperatures. For the higher temperatures the system was altered so that the valves were external to the bath. For this purpose midget needle valves with Teflon packing were employed. This modification did not significantly increase the unavoidable small (ca. 1% of total) unthermostated volume associated with the line from the thermostated chambers to the pressure measuring equipment.

The thermostat was a 28 gallon salt-bath kept at constant temperature by a Wheelco model 407 Capacitrol and model 610 magnetic pilot amplifier which controlled the saturable core reactor employed to regulate the power supply to the heaters. The Capacitrol picked up its signal from a Chromel-Alumel thermocouple located in the bath. Fine control was obtained manually with a Variac placed in the voltage supply to the magnetic am-

plifier. To guide this manual control and to determine the absolute value of the temperature, a platinum resistance thermometer placed in the bath between the chambers was used with a Leeds and Northrup G-2 Mueller bridge, the operator being guided by the bridge balance. The platinum resistance thermometer and the precision resistor used to calibrate the bridge were both calibrated by the National Bureau of Standards. With this arrangement the temperature was maintained within  $\pm 0.01^\circ$  at 175° and 250° and  $\pm 0.02^\circ$  at the other temperatures.

All pressures were measured with the same dead-weight piston gage as used in the earlier studies.<sup>3,4</sup> A Ruska Instrument Co. model 2406 pressure differential diaphragm indicator was used as the null device. The sensitivity of the indicator was 0.001 atmosphere when determined at one atmosphere. Flexing of the diaphragm was used to exchange gas in the indicator and the line connecting it to the first chamber with the gas in that chamber; this also enhanced the mixing.

The effective area of the piston was obtained by balancing the gage against the ice-point vapor pressure of carbon dioxide, taken as 34.4009 atmospheres.<sup>6</sup>

The helium and nitrogen used in this study were analyzed with a mass spectrometer. Both were better than 99.8% pure and were used without further purification. The carbon dioxide was known to contain 0.16% water and traces of hydrocarbons. These impurities were removed by passing the gas into an evacuated high pressure cylinder containing magnesium perchlorate at 200°.

The starting pressure in each run was close to 100 atmospheres. The volumes of the chambers given above were such that ten or more expansions could be obtained before the pressure became too low. The high pressure readings were reproducible to 1 part in 20,000; however, there was greater variation for pressures below 20 atmospheres because of the 0.001 atmosphere limiting sensitivity of the diaphragm indicator.

### Results

In earlier articles<sup>2-4</sup> methods have been given for treating the series of pressure readings,  $p_0, p_1, p_2, \dots, p_r, p_{r+1}, \dots$ , obtained in the Burnett expansions. These methods all employ the fundamental relationship which exists for any pair of the readings and the corresponding values of  $Z$ , the compressibility factor

$$p_r/p_{r+1} = N(Z_r/Z_{r+1}) \quad (1)$$

where  $N$  is the ratio of the volume after expansion to that before. In particular, those articles have dealt with the evaluation of the virial coefficients,  $B, C, D, \dots$ , in the equation of state

$$Z_r = 1 + Bp_r + Cp_r^2 + Dp_r^3 + \dots$$

(6) O. C. Bridgeman, *J. Am. Chem. Soc.*, **49**, 1174 (1927).

(1) Based on a dissertation submitted in February, 1962, by Robert J. Witonsky in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) W. C. Pfefferle, Jr., J. A. Goff and J. G. Miller, *J. Chem. Phys.*, **23**, 509 (1955).

(3) R. C. Harper, Jr., and J. G. Miller, *ibid.*, **27**, 36 (1957).

(4) G. M. Kramer and J. G. Miller, *J. Phys. Chem.*, **61**, 785 (1957).

(5) E. S. Burnett, *J. Applied Mechanics, Trans. ASME*, **58**, A136 (1936).

and have put forth an important advantage of the experiment, namely, that it can be used to give the composition of any mixture directly, thereby eliminating the need for chemical analysis.

In the study described here, experiments were performed between 175° and 475° in intervals of 75°. The observed pressures were corrected for the unthermostated volume using a correction factor based on the equation of state of the gas. Since the correction factors required a knowledge of the compressibility factors, the quantities sought by the analysis, it was necessary to solve the equations by successive approximations. To reduce the labor of this procedure the calculations were done on an IBM 1620 computer.

Pure nitrogen and helium and their mixtures were studied at each temperature. At 175°, seven mixtures were used and above that temperature eight or nine mixtures. In each case the mixtures covered the whole range of concentrations in fairly even spacing. With each run, a plot of  $p_r/p_{r+1}$  against  $p_r$  was made. Figure 1 shows a few representative curves for the pure gases and three mixtures at 400°. It is interesting to note that the plots are linear for mixtures containing as much as 80% nitrogen. This general behavior was observed at all temperatures, with curvature commencing at lower nitrogen content as the temperature was lowered; however, even at 175° mixtures containing as much as 60% nitrogen showed no curvature up to 100 atmospheres.

Linearity of the pressure ratio plots suggested the use of a linear expression for the compressibility factor:  $Z_r = 1 + Bp_r$ . Schneider and Duffie<sup>7</sup> showed that their Burnett data for helium above 0° and up to 70 atmospheres could be described adequately by that equation. When the linear expression is substituted in eq. 1 there results the equation

$$p_r/p_{r+1} = B(N - 1)p_r + N \quad (2)$$

Equations of condition of the general form of eq. 2 were then used for the least-squares solutions for the best values of  $N$  and  $B$ . To test whether eq. 2 faithfully represented the data over the entire pressure range studied, a value of the volume ratio  $N$ , obtained by averaging the values of previous calculations, was imposed on the data and the second virial coefficient was calculated from each successive pair of pressures using eq. 2. The absence of any systematic trend in the values of  $B$  was accepted as the criterion for establishing this equation as adequate. Table I shows this test applied to a mixture containing almost 80% nitrogen. The agreement among the values of  $B$  is all that can be expected considering the accuracy of the individual pressure measurements. There is no indication that a quadratic term need be included in the expression for the compressibility factor. This table also emphasizes the greater uncertainty in pressure measurements at lower pressures.

TABLE I

$B$  CALCULATED FROM EQUATION 2 FOR THE MIXTURE WITH  $x_{He} = 0.2107$  AT 400°

$r$	$B \times 10^4, \text{atm.}^{-1}$	$r$	$B \times 10^4, \text{atm.}^{-1}$
0	4.07	5	3.98
1	4.06	6	4.14
2	4.05	7	3.38
3	4.08	8	3.99
4	4.12	9	4.41

This test failed for nitrogen-rich mixtures where the effect of the third virial coefficient became important. For these runs eq. 2 was applied to the low pressure linear region and the calculated values of  $B$  and  $N$  were

(7) W. G. Schneider and J. A. H. Duffie, *J. Chem. Phys.*, **17**, 751 (1949).

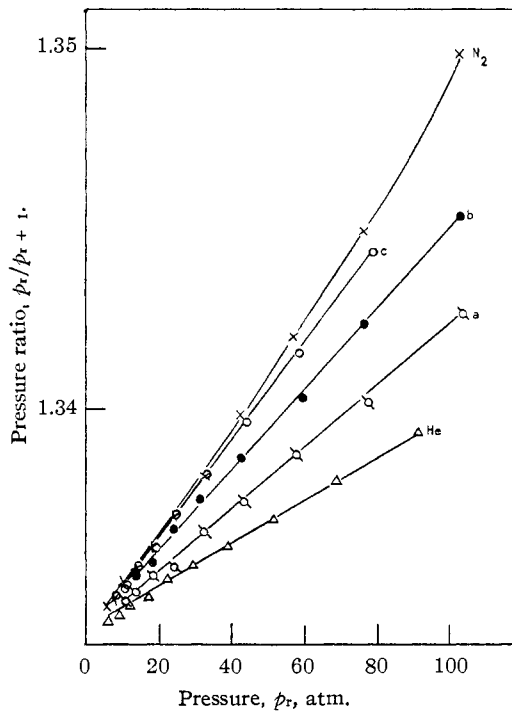


Fig. 1.—Pressure ratio plots for helium, nitrogen and three mixtures at 400°: curve a,  $x_{He} = 0.7998$ ; curve b,  $x_{He} = 0.5128$ ; curve c,  $x_{He} = 0.2107$ .

then imposed on equations of the form introduced in the earlier studies<sup>3,4</sup> to obtain  $C$

$$\ln(p_r/p_{r+1}) = \ln N + \alpha(p_r - p_{r+1}) + \beta(p_r^2 - p_{r+1}^2) \quad (3)$$

TABLE II

THE OBSERVED SECOND AND THIRD VIRIAL COEFFICIENTS FOR HELIUM-NITROGEN MIXTURES AT DIFFERENT TEMPERATURES

Mole fraction of helium	$B_{mix} \times 10^4$ (atm. <sup>-1</sup> )	$C_{mix} \times 10^7$ (atm. <sup>-2</sup> )	Mole fraction of helium	$B_{mix} \times 10^4$ (atm. <sup>-1</sup> )	$C_{mix} \times 10^7$ (atm. <sup>-2</sup> )
175°			250°		
1.0000	2.976	..	1.0000	2.485	..
1.0000	2.951	..	1.0000	2.486	..
0.8985	3.460	..	0.8999	3.010	..
.7703	3.905	..	.7142	3.704	..
.7123	4.211	..	.6058	4.056	..
.5427	4.840	..	.5184	4.237	..
.3635	4.898	..	.4139	4.462	..
.2425	4.789	1.85	.3439	4.500	0.22
.0992	4.083	4.44	.2103	4.574	0.83
.0000	3.883	5.12	.1036	4.382	2.31
			.0000	4.272	2.94
325°			400°		
1.0000	2.190	..	1.0000	1.754	..
0.8947	2.550	..	0.9027	2.151	..
.8021	2.889	..	.7998	2.569	..
.7028	3.204	..	.7241	2.755	..
.6097	3.543	..	.6199	2.996	..
.5126	3.790	..	.5128	3.359	..
.4121	3.997	..	.3974	3.731	..
.3086	4.260	..	.3069	3.882	..
.2034	4.307	0.58	.2107	4.062	0.77
.1069	4.414	0.66	.0000	4.237	1.38
.0000	4.243	2.06			
475°			475°		
1.0000	1.576	..	0.4008	3.270	..
0.9044	1.942	..	.3047	3.576	..
.7995	2.209	..	.2030	3.744	..
.7164	2.414	..	.1005	4.007	..
.6011	2.794	..	.0000	4.032	0.52
.5004	3.118	..			

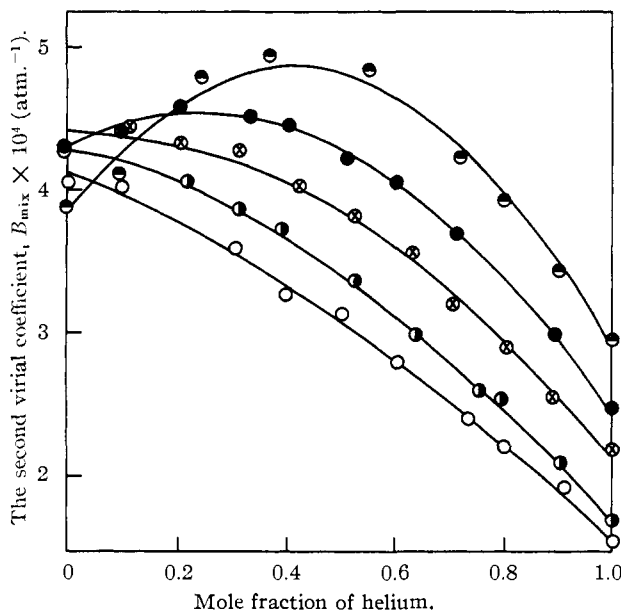


Fig. 2.— $B_{\text{mix}}$  vs. composition at: 175°, ●; 250°, ●; 325°, ⊗; 400°, ●; 475°, ○.

where  $C = \alpha^2/2 + \beta$  and  $B = \beta$ . When the effect of the third virial coefficient was important even at low pressures, the values of both  $B$  and  $C$  were obtained from the solutions of eq. 3.

The values for the virial coefficients determined as described above are given in Table II. The agreement of the second virial coefficients of helium obtained in the duplicate runs at 175° and 250° demonstrates the good reproducibility attainable with the Burnett experiment.

#### Discussion

Each set of pure gas and mixture second virial coefficients at a particular temperature was fitted by the method of least-squares to the well established relationship

$$B_{\text{mix}} = x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22} \quad (4)$$

where  $x_1$  and  $x_2$  are the mole fractions of components 1 and 2,  $B_{11}$  and  $B_{22}$  are the corresponding second virial coefficients for the pure gases, and  $B_{12}$  is the second virial interaction coefficient which is a property of the collision of the dissimilar molecules. Graphical comparisons of the observed and calculated values of  $B_{\text{mix}}$  are shown in Fig. 2 where the curves represent the values calculated from eq. 4. It is clear that one set of virial coefficients describes the results quite well over the entire composition range.

Although the present study was not primarily concerned with the pure gases, the pure gas second virial coefficients obtained can be used to indicate the absolute accuracy of our results as a whole because they can be compared with values in the literature. Table III shows part of this comparison. In it, the values of  $B_{\text{He}}$  obtained in our work are listed in two columns. The first gives the results obtained from the measurements of the pure gas and the second shows the least-squares values obtained from the measurements of the mixtures by application of eq. 4 to the whole set of  $B_{\text{mix}}$  values at each temperature. Here, and in the tables to follow, the errors shown for the mixture values are the errors indicated by the least-squares fit of the data to eq. 4. Both the pure gas and the mixture values are shown graphically at  $x_{\text{He}} = 1$  in Fig. 2, the latter being the intercepts of the curves.

This table also lists the results obtained by Schneider and Duffie<sup>7</sup> and by Holborn and Otto<sup>8</sup> for the reason

(8) L. Holborn and J. Otto, *Z. Physik*, **33**, 1 (1925).

TABLE III  
THE SECOND VIRIAL COEFFICIENT FOR HELIUM  $B_{\text{He}} \times 10^4$   
(ATM.<sup>-1</sup>)

$t$ , °C.	Present work		Schneider and Duffie	Holborn and Otto	Keesom adopted
	Pure gas	Mixtures			
175	2.96	$2.90 \pm 0.08$	3.04	3.03	2.91
250	2.49	$2.48 \pm .02$	2.54	2.51	2.40
325	2.19	$2.11 \pm .05$	2.17	2.12	2.04
400	1.75	$1.75 \pm .04$	1.89	1.83	..
475	1.58	$1.57 \pm .04$	1.66	..	..

that theirs are the only experimental studies of the compressibility of pure helium covering the range of temperature of interest here. Except for the 400° values, the figures given for these authors were obtained by interpolation, the smoothing formula given by Schneider and Duffie being used in treating their results.

The other careful studies of the compressibility of helium in the range 100–200° have produced results which confirm the absolute accuracy of our 175° value. The smoothed data of Gibby, Tanner and Masson<sup>9</sup> give  $B_{\text{He}} = 2.91 \times 10^{-4}$  atm.<sup>-1</sup> at 175°. Wiebe, Gaddy and Heins<sup>10</sup> made measurements at 100° and 200°. Interpolation of their figures gives the value,  $2.96 \times 10^{-4}$  atm.<sup>-1</sup>. The results of Michels and Wouters<sup>11</sup> at 100° and 150° extrapolate to  $2.98 \times 10^{-4}$  atm.<sup>-1</sup>. Recently, Silberberg, Kobe and McKetta,<sup>12</sup> using the Burnett experiment, obtained values at 100° and 200° which place the 175° value at  $3.00 \times 10^{-4}$  atm.<sup>-1</sup>.

The results obtained at Leiden by Keesom and others<sup>13</sup> are well known to be systematically lower than those of other workers at all temperatures above  $-150^\circ$ . In reviewing all of the data up to 1942 for  $B_{\text{He}}$  in the range  $-150^\circ$  to  $300^\circ$ , Keesom<sup>13</sup> noted that the values obtained at Berlin<sup>8</sup> were the highest, the lowest being the Leiden values, while the English<sup>9</sup> and American<sup>10</sup> results lay between. He then put forth a set of "adopted" values extending to  $300^\circ$  "in which due account is taken of all the material available." The last column in Table III shows values taken from that correlation made by Keesom.

Our results for  $B_{\text{N}_2}$  are given in Table IV where they are compared with values given by the formulations obtained by Keyes<sup>14</sup> and more recently by the National Bureau of Standards<sup>15</sup> by fitting the best compress-

TABLE IV  
THE SECOND VIRIAL COEFFICIENT FOR NITROGEN,  $B_{\text{N}_2} \times 10^4$   
(ATM.<sup>-1</sup>)

$t$ , °C.	Present work		Keyes	N.B.S.
	Pure gas	Mixtures		
175	3.88	$3.84 \pm 0.08$	3.63	3.61
250	4.27	$4.28 \pm .02$	4.18	4.19
325	4.24	$4.35 \pm .05$	4.32	4.35
400	4.24	$4.28 \pm .04$	4.26	4.32
475	4.03	$4.10 \pm .04$	4.12	4.19

sibility data up to 400° together with data for several other properties. The agreement is again such as to leave little to fear concerning the absolute accuracy of our work.

(9) C. W. Gibby, C. C. Tanner and I. Masson, *Proc. Roy. Soc. (London)*, **A122**, 283 (1929).

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

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

(12) I. H. Silberberg, K. A. Kobe and J. J. McKetta, *J. Chem. Eng. Data*, **4**, 314 (1959).

(13) W. H. Keesom, "Helium," Elsevier Press, New York, N. Y., 1942.

(14) F. G. Keyes, in "Temperature (Its Measurement and Control in Science and Industry)," Reinhold Publishing Corp., New York, N. Y., 1941, Chapter 1.

(15) J. Hilsenrath, *et al.*, "Tables of Thermal Properties of Gases," National Bureau of Standards Circular 564, U. S. Department of Commerce, 1955.

Of greater interest is the third quantity that is obtained by fitting the  $B_{\text{mix}}$  values to eq. 4, namely,  $B_{12}$ , the second virial interaction coefficient. Table V gives the values of this quantity in both atm.<sup>-1</sup> and cc./mole. Also shown are values calculated using parameters obtained<sup>16</sup> from transport property data and the exp-six potential function.

TABLE V  
THE SECOND VIRIAL INTERACTION COEFFICIENT,  $B_{\text{He-N}_2}$

$t$ , °C.	Present work		Calculated <sup>16</sup> cc./mole
	Atm. <sup>-1</sup> × 10 <sup>4</sup>	Cc./mole	
175	6.234 ± 0.104	22.92 ± 0.38	18.68
250	5.221 ± .045	22.41 ± .19	19.33
325	4.429 ± .085	21.73 ± .42	19.98
400	3.838 ± .064	21.20 ± .35	20.29
475	3.313 ± .056	20.33 ± .34	20.24

These parameters were obtained by Walker and Westenberg by fitting the exp-six potential to both their measurements of the temperature dependence of the coefficient of mutual diffusion for the helium-nitrogen system from 300° to 1100°K. and to part of the results of Amdur, Mason and Jordan<sup>17</sup> on the scattering of helium atoms with energies in the range 500–2100 e.v. by room temperature nitrogen. These calculated values will be discussed later.

Figure 3 shows the results in molar volume units. Included in the figure is the 30° value determined by Kramer and Miller<sup>4</sup> to be 21.83 cc./mole. Since there are no experimental measurements between 30° and 175°, the exact shape of the maximum is uncertain; nevertheless, it is apparent that our values lie on the high-temperature side of a maximum in  $B_{12}$ . Miller, Stroud and Brandt<sup>18</sup> have recently made determinations of the compressibility factor of a large number of helium-nitrogen mixtures at 21.1° using the Burnett method up to 272 atmospheres. We have made a least-squares fit of their data to eq. 4 which yields the value 19.75 cc./mole for  $B_{12}$ . This indicates the steepness of the rise on the low-temperature side of the maximum. Such a steep rise was also indicated by earlier, rougher estimates<sup>4,19,20</sup> of  $B_{\text{He-N}_2}$  at 25° and in the range -183° to -198°.

For systems where the intermolecular pair potential  $u$  is a function only of the separation  $r$ , the second virial coefficient can be expressed as

$$B(T) = 2\pi N \int_0^{\infty} [1 - \exp(-u/kT)] r^2 dr \quad (5)$$

where  $N$  is the Avogadro number. In order to obtain information about intermolecular forces from experimental second virial coefficient data, it is necessary to assume a functional form for the intermolecular potential which contains several adjustable parameters.

For spherical non-polar molecules the Lennard-Jones (6,12) potential has had wide application with considerable success. This potential has two adjustable parameters and can be written as

$$u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$$

where  $\epsilon$  is the depth of the potential minimum relative to  $u(\infty)$  and  $\sigma$  is a collision parameter, *i.e.*,  $u(\sigma) = 0$ . Equation 5 has been integrated analytically for the Lennard-Jones potential and extensive tables of the reduced second virial coefficient,  $B^*(T^*)$ , where  $T^* = kT/\epsilon$ , have been produced from the results.<sup>21</sup>

(16) R. E. Walker and J. Westenberg, *J. Chem. Phys.*, **29**, 1147 (1958).

(17) I. Amdur, E. A. Mason and J. E. Jordan, *ibid.*, **27**, 527 (1957).

(18) J. E. Miller, L. Stroud and L. W. Brandt, *J. Chem. Eng. Data*, **5**, 6 (1960).

(19) A. E. Edwards and W. E. Roseveare, *J. Am. Chem. Soc.*, **64**, 2816 (1942).

(20) I. van Itterbeek and W. van Doninck, *Proc. Phys. Soc. (London)*, **62B**, 62 (1949).

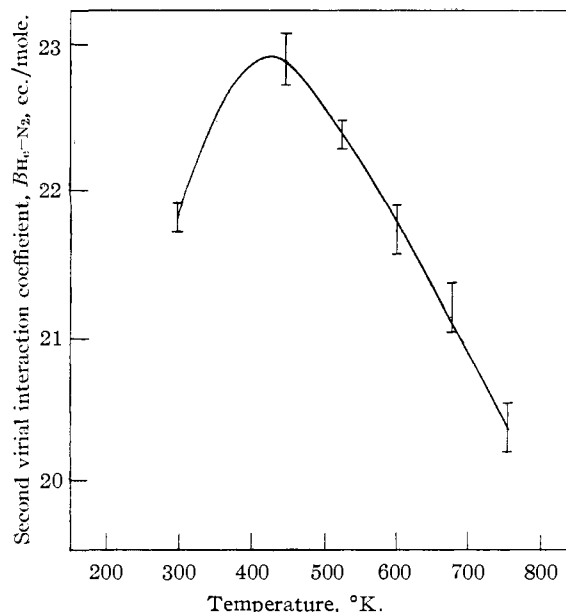


Fig. 3.— $B_{\text{He-N}_2}$  vs. temperature.

Another potential useful in studying systems where the only contribution to the attractive energy is a consequence of coupled induced dipoles is the modified Buckingham exp-six potential

$$u(r) = \epsilon \left(1 - \frac{6}{\alpha}\right)^{-1} \left\{ (6/\alpha) \exp \left[ \alpha \left(1 - \frac{r}{r_0}\right) \right] - \left(\frac{r_0}{r}\right)^6 \right\}$$

where  $\epsilon$  is the magnitude of the potential minimum,  $r_0$  is the position of the minimum, and  $\alpha$  is a parameter which determines the steepness of the repulsive term. This potential is more realistic than is the Lennard-Jones potential because there is theoretical justification for representing the repulsive term as an exponential and the application of it is more flexible because of the presence of the third parameter. The reduced second virial coefficient has been calculated for the modified Buckingham exp-six by Rice and Hirschfelder<sup>22</sup> for  $T^*$  from 0.40 to 400, and for  $\alpha$  from 12 to 15.

A convenient graphical method can be used in testing the applicability of a potential function and determining the adjustable parameters when the reduced virial coefficient has been calculated for the potential. This method is a modification of that of Lennard-Jones<sup>23</sup> with predetermined indices of attraction and repulsion and consists of plotting  $\log B^*$  against  $\log T^*$  on one sheet of square transparent paper and  $\log B$  against  $\log T$  on another sheet of the paper, both plots drawn to the same scale. If the potential is a suitable one the two curves can be brought into coincidence by parallel translation to both axes. The amount of translation in each direction will then determine the parameters. Figure 4 shows the result of this method when applied to the Lennard-Jones (6,12) potential. The circles represent the experimental values for the interaction coefficient and the curve represents the theoretical values superimposed on the data in the region of the maximum. It is apparent that no single set of parameters for this potential can describe the temperature dependence of  $B_{\text{He-N}_2}$  over the entire temperature range.

The discrepancy between the observed rate of decrease of  $B_{\text{He-N}_2}$  and the rate predicted by the (6,12) potential can be attributed to collisions that are considerably softer than those given by an inverse twelfth

(21) J. O. Hirschfelder, C. F. Curtis and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954.

(22) W. E. Rice and J. O. Hirschfelder, *J. Chem. Phys.*, **22**, 187 (1954).

(23) J. E. Jones, *Proc. Roy. Soc. (London)*, **A106**, 463 (1924).

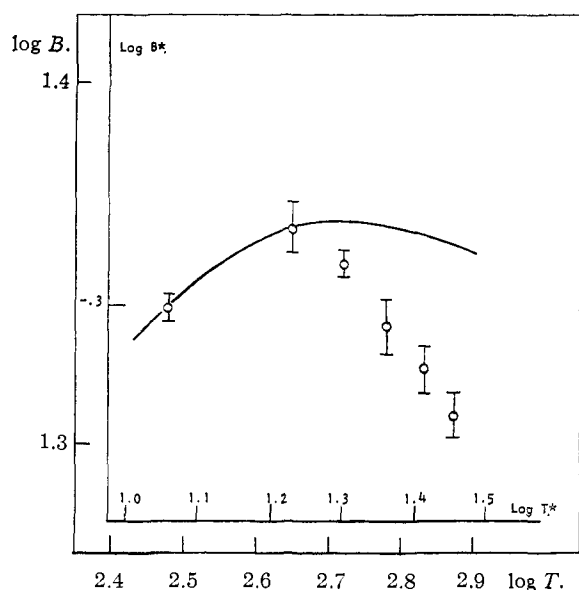


Fig. 4.—Test of fit for  $B_{\text{He-N}_2}$  using Lennard-Jones (6, 12) potential.

power repulsive term. Since the exp-six potential has a parameter  $\alpha$  which varies the repulsive term, an attempt was made to compare the data with values calculated using this potential. A graphical method devised by Mason and Rice<sup>24</sup> and similar to the method described above was employed. For this potential there exists a family of  $B^*$  vs.  $T^*$  curves, one for every value of  $\alpha$ . The curve best representative of the experimental points is selected, thereby fixing the value of  $\alpha$ , and parallel translation effects the determination of the other parameters. The best value of  $\alpha$  was 12; however, this potential was only a slight improvement over the (6,12) potential.

Walker and Westenberg<sup>16</sup> were able to fit their diffusion data quite well with the exp-six potential using the parameters  $\alpha = 12$ ,  $\epsilon/k = 31.9$  and  $r_0 = 3.80$  Å. The values for  $B_{\text{He-N}_2}$  calculated using these parameters in the exp-six potential are given in Table V. The agreement with our experimental values is good only at 475° and the direction of change with temperature is opposite to that which we observed. Since the diffusion data can be described also by a simple point center of repulsion potential, the attractive term in the intermolecular potential function is relatively unimportant in characterizing this transport property in this temperature range. On the other hand, the contribution the attractive term makes to the second virial coefficient is quite appreciable at these temperatures.

It is important to know whether the appreciable interpenetration of the particles on the high-temperature side of the maximum in the second virial interac-

tion coefficient is peculiar to the helium-nitrogen system or is more general. Unfortunately,  $p$ - $V$ - $T$  experiments which require accurate volume measurements are not readily extended to temperatures high enough to allow  $B$  to reach its maximum in most cases. The Burnett experiment, requiring only pressure measurements, does not suffer from this limitation and, as evidenced in the present study, can be extended to elevated temperature.

The discussion thus far has demonstrated that neither the (6,12) potential nor the exp-six potential is compatible with the observed behavior of the interaction coefficient. Some objection might be raised to the application of the simple orientation-independent expression for the second virial coefficient to the case of the nitrogen molecule. Certainly such a model ignores the importance of quadrupole orientation and anisotropy of the London forces.

Pople<sup>25</sup> has developed general expressions for the second virial coefficient for axially symmetric molecules such as nitrogen. Later, it has been shown<sup>26</sup> that since the multipole expansion of the potential function is not valid at small separation, the perturbation terms arising in the treatment of Pople should be separated into long and short range terms using a non-zero value for the limit of integration of the long range term. Since the exact form of the short-range directional forces is as yet unknown, only the effect of long-range directional forces could be determined. This was shown to be several per cent. of the spherically symmetric term for nitrogen at temperatures below 150° and gradually diminishing at higher temperatures.

The theory for determining the importance of orientation between a spherically symmetric atom and an axially symmetric molecule has not been extended to second virial coefficient theory. It is expected that the magnitude of long-range directional effects will be shown to be too small to explain the gap between the calculated values of  $B_{12}$  and those observed here. New developments in the theory of short-range forces may throw considerable light on this problem.

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