Compressibility of the Binary Systems: Helium-Nitrogen and Carbon Dioxide–Ethylene

PEH SUN KU[1] and BARNETT F. DODGE
Department of Engineering and Applied Science, Yale University, New Haven, Conn.

The compressibility factors of nitrogen, helium, and four mixtures were determined at 38.5° and three mixtures at 100.0° C. and of carbon dioxide, ethylene and three mixtures at 100° C., using the Burnett method. The maximum pressures were in the range of 200 to 300 atm. Values of z are tabulated *vs.* the experimental values of pressure. Values of second, and in some cases, third virial coefficients were calculated for pure components and for mixtures and compared with literature values. Tests were made of four combining rules for calculation of the second interaction virial coefficient and the results compared with the values calculated from the experimental data.

THE BURNETT METHOD was selected for the compressibility measurements because of its simplicity and the fact that no direct measurement of volume or of mass—the two most difficult of the four variables to measure accurately—is required. It has the additional advantage for mixtures that the composition is obtained directly from the pressure measurements. The method is usually limited to conditions where only a single gaseous phase exists, but recently Burnett (*3*) outlined procedures for applying his method to systems of more than one phase. One possible disadvantage of the method is the fact that more than one set of pressure vessels is needed to cover properly a wide pressure range because with a fixed value of the volume ratio, N, the pressure intervals between expansions will not be well spaced in all pressure regions. Another point is that N is raised to the n'th power where n is the number of expansions, and, consequently, errors in it are magnified.

These two binary systems were chosen because one represents two gases of simple molecular structure and low critical temperatures, which might be expected to exhibit relatively small deviations from ideality and the other consists of gases of more complex structure and critical temperatures near the ambient and would consequently be expected to show marked deviation from ideal behavior but still not liquefy at supercritical pressures.

Previous compressibility measurements on the He-N_2 system have been made by Kramer and Miller (*7*), Miller, Stroud, and Brandt (*15*), Pfefferle, Goff, and Miller (*16*), Canfield, Leland, and Kobayashi (*4*), and Witonsky and Miller (*20*). The first and third sets of experimenters worked only at 30° C. and the second at 70° F.; Canfield, Leland, and Kobayashi covered the range from 0° to −140° C. at pressures to 500 atm., and Witonsky and Miller covered the temperature range 175° to 475° C. and pressures to about 100 atm. Measurements on pure He and N_2 have been made by a number of investigators but we will make comparison only with the measurements of Schneider and Duffie (*17*), Wiebe, Gaddy, and Heins (*19*), and Stroud, Miller, and Brandt (*18*) on helium and with those of Lunbeck, Michels, and Wolkers (*9*) and Michels, Wouters, and deBoer (*14*) on N_2.

No previous work has been reported on CO_2-C_2H_4 mixtures. Many investigations have been made on the pure components, but in this paper reference will be made only to the data of Michels *et al.* (*12, 13*) and MacCormack and Schneider (*10*) on CO_2 and Michels and Geldermans (*11*) on C_2H_4.

THEORETICAL BACKGROUND OF THE METHOD

This experimental method has been used by a number of investigators since it was originally proposed and tested by Burnett (*2*) so that a detailed description of it is unnecessary. The following brief outline of the procedure and the equations used should be sufficient to present the essential features of the method.

A series of expansions from one pressure vessel to a second one is made, each expansion being followed by an evacuation of the second vessel after thermal equilibrium has been established. The series of expansions is carried to as low a pressure as feasible, and the only measurements are of the pressure before and after each expansion and the temperature of the constant temperature bath in which the vessels are immersed. The pressure interval between successive expansions is governed by the relative volumes of the two vessels and is a function also of the pressure level and the compressibility. The choice of the relative volumes of the two vessels is based on a compromise. A relative volume which gives a desirable distribution of points in the high-pressure region will generally give too small a separation of points at low pressures. This is particularly true with a very compressible mixture such as CO_2 and C_2H_4. One way out of this difficulty is to use more than two vessels so that more than one value of volume ratio is available, and hence, one can choose a ratio best suited to a given pressure range.

In the case of a binary mixture, the two gases are charged separately to the larger of the two vessels. From the pressure measurement after each addition and the compressibility of one of the gases and that of the mixture (obtained in the subsequent series of expansions), the composition is easily calculated as follows:

$$P_A V = n_A z_A RT \tag{1}$$

$$P_M V = n_M z_M RT \tag{2}$$

Dividing 1 by 2

$$x_A = \frac{n_A}{n_M} = \frac{P_A z_M}{P_M z_A} \tag{3}$$

The following equation applies before and after the i'th expansion

$$\frac{P_i}{P_{i+1}} = N \frac{z_i}{z_{i+1}} \tag{4}$$

---

[1] Present address: General Electric Co., Space Technology Center, Valley Forge, Pa.

To obtain the value of the volume ratio, N, the pressure ratio is related to the absolute pressure either graphically or algebraically, and at the limit where $P \rightarrow 0$, $\frac{z_i}{z_{i+1}} \rightarrow 1.0$, and $\frac{P_i}{P_{i+1}} \rightarrow N$. In other words, N is the limiting value of the pressure ratio at $P = 0$. To obtain an accurate extrapolation, the volume calibration (determination of N) is made using a gas which gives a linear relation. Helium fulfills this condition admirably, is widely used for this purpose, and was the method used in this investigation.

Multiplying together all the pressure ratios given by Equation 4 from the initial pressure, P_0, to the final pressure, P_n, one gets

$$\frac{P_0}{P_n} = N^n \frac{z_0}{z_n} \tag{5}$$

or rearranging

$$z_n = \frac{N^n P_n}{(P_0/z_0)} \tag{6}$$

As $P_n \rightarrow 0$, $z_n \rightarrow 1.0$ and hence P_0/z_0 is the limiting value of N^iP_i *vs.* P_i at $P = 0$. This value is obtained by extrapolation either graphically or algebraically. Once P_0/z_0 is known, the z at any intermediate pressure in the expansion series may be obtained from Equation 4 rearranged to

$$z_{i+1} = z_i N \frac{P_{i+1}}{P_i} \tag{4a}$$

or as an alternative, one may use Equation 6 with the subscript n referring to any expansion.

This treatment has tacitly assumed that N is a constant independent of P at constant T. Burnett (2) used a jacketed vessel with a pressurized fluid in the annular space to balance the internal pressure and prevent distortion. The volume change of a cylindrical vessel owing to internal pressure can be calculated with sufficient accuracy from the theory of elasticity and such a calculation showed that the volume change of the vessels used in this investigation introduced a negligible error. The effect of temperature was eliminated by making the helium calibration runs at the same temperatures as those at which the runs on the mixtures were made.

With gases like CO_2 and C_2H_4, the plot of N^iP_i *vs.* P_i did not become linear at the lowest practicable pressures and graphical extrapolation to $P = 0$ is unreliable. In this case, an algebraic extrapolation was used based on the virial equation of state in the form

$$z = 1 + BP + CP^2 + DP^3 + \ldots. \tag{7}$$

APPARATUS AND EXPERIMENTAL TECHNIQUE

The general arrangement of the equipment is shown in Figure 1. The gases were supplied from commercial storage cylinders and compressed to the measuring vessels by a hand-operated piston pump using oil which worked against mercury in the liquid piston device, *H*, to compress the gas. Two sets of measuring vessels, designated V_1, V_2, and V_1', V_2', were used. The approximate volumes in milliliters were: $V_1 = 61$, $V_2 = 26$, $V_1' = 778$, $V_2' = 261$. The vessels were cylindrical with diameter ratios of 2 and constructed of 18-8 stainless steel.

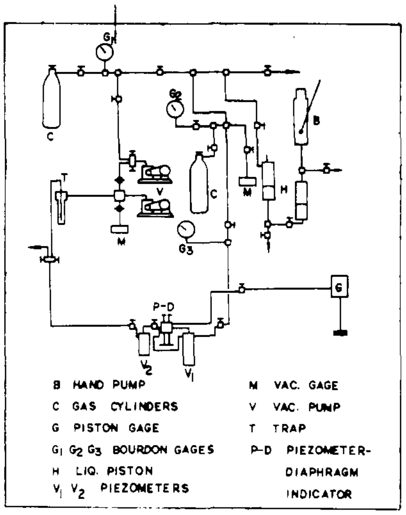

Figure 1. Arrangement of the equipment

Bourdon-spring gages were used for pressure indication, but the actual measurements were made with a piston gage having several piston-cylinder combinations which were calibrated by measurement of the vapor pressure of CO_2 at 0° C. using the value of Bridgeman (*1*). The oil in the piston-gage system was originally separated from the gas in the measuring vessels by a mercury U-tube provided with an electric-contact device to indicate pressure equalization. This arrangement was very sensitive but troublesome to operate, and there was always the danger of forcing some of the mercury into one of the measuring vessels thereby changing its volume. Consequently the mercury indicator was later replaced by a diaphragm-type of indicator (Ruska Instrument Corp.). In contrast to the mercury indicator, this instrument could support a large differential pressure which was a great advantage in ease of operation.

Because the mercury U-tube indicator was outside the constant temperature bath and the connections to it on the gas side constituted a part of the measuring volume at a temperature not precisely known, the effect of this was minimized by using relatively large measuring vessels. The diaphragm indicator, on the other hand, could be placed in the thermostat thus eliminating the volume correction and permitting the use of smaller vessels requiring less gas. This is the reason for the two sets of measuring vessels.

The measuring vessels were immersed in an oil bath whose temperature was held constant to ±0.01° to 0.02° C. and measured with a platinum-resistance thermometer and Mueller bridge.

The vacuum system, consisting of two pumps and a McLeod gage, was used to remove gas from the second measuring vessel after each expansion. It had sufficient capacity so that the residual gas left after a reasonable pumping time was calculated to have a negligible effect on the results.

The gases were of the highest purity obtainable in commercial cylinders and were used without further purification except in the case of the CO_2 used for piston-gage calibration which was purified by three distillations.

Mixtures of gases were made in the measuring vessels by introducing the gases separately as this permitted the determination of the composition without having to withdraw samples for analysis. Complete mixing, which sometimes took several hours, was indicated by constancy of pressure.

TREATMENT OF EXPERIMENTAL DATA

The graphical method was used for the determination of N and of P_0/z_0. A combination of Equation 4 and 7 gives

$$\frac{P_i}{P_{i+1}} = N + (N-1)\,BP_i + \left(N - \frac{P_{i+1}}{P_i}\right) CP_i^2 + \ldots. \tag{8}$$

In Equation 8, N is a constant which is determined graphically from helium runs by an extrapolation to zero pressure. Equation 8 can be rearranged into a linear form,

$$Y_i = B + CX_i \qquad (9)$$

where $Y_i = (R_i - N)/(N - 1)P_i$ and $X_i = (N - R_i^{-1})P_i/(N - 1)$, R_i, stands for the pressure ratio P_i/P_{i+1}. The virial coefficients, B and C were determined graphically from Equation 9. The compressibility factors, z, reported are based on Equation 6 using the N value obtained graphically from the calibrations with helium. In the case of CO_2–C_2H_4, the measurements were made after the substitution of the diaphragm indicator for the mercury U-tube on the piston pressure gage, and no volume calibration with

Table I. Mole Fractions of Helium-Nitrogen Mixtures

At 38.5° C.					
0% Helium		16.0% Helium		31.4% Helium	
Pressure, atm.	Compressibility factors, *z*	Pressure, atm.	Compressibility factors, *z*	Pressure, atm.	Compressibility factors, *z*
280.179	1.13487	249.224	1.12833	254.046	1.14281
194.849	1.06532	163.934	1.06725	167.235	1.08178
139.869	1.03222	110.778	1.03706	112.756	1.04882
102.026	1.01631	75.877	1.02144	76.999	1.02991
75.022	1.00872	52.314	1.01267	52.960	1.01862
54.995	0.99810	36.211	1.00796	36.582	1.01177
40.689	0.99677	25.107	1.00497	25.330	1.00741
30.139	0.99659	17.427	1.00308	17.569	1.00479
22.332	0.99674	12.108	1.00211	12.199	1.00324
16.552	0.99718	8.412	1.00116		
12.268	0.99760	5.848	1.00076		
9.094	0.99813				
6.740	0.99857				
4.995	0.99891				
3.703	0.99957				
56.4% Helium		86.0% Helium		100% Helium	
295.143	1.17435	285.777	1.15308	288.497	1.12733
209.121	1.12313	203.701	1.10941	207.002	1.09188
149.672	1.08503	146.763	1.07891	149.829	1.06670
108.266	1.05941	106.554	1.05731	109.114	1.04857
78.892	1.04201	77.782	1.04180	79.827	1.03546
57.772	1.02994	57.008	1.03064	58.595	1.02591
42.451	1.02156	41.900	1.02248	43.113	1.01889
31.261	1.01541	30.863	1.01658	31.780	1.01374
23.067	1.01134	22.771	1.01240	23.461	1.01017
17.038	1.00830	16.816	1.00916	17.334	1.00740
12.595	1.00610	12.429	1.00679	12.816	1.00539
9.316	1.00448	9.194	1.00526	9.481	1.00394
6.894	1.00334	6.803	1.00402	7.017	1.00295
5.103	1.00247	5.035	1.00302	5.195	1.00227
3.780	1.00232	3.728	1.00243	3.847	1.00183
				2.849	1.00150
At 100° C.					
0% Helium		17.8% Helium		51.3% Helium	
208.106	1.09082	213.294	1.10528	211.221	1.10972
149.140	1.05501	152.720	1.06803	151.898	1.07702
108.346	1.03435	110.705	1.04484	110.144	1.05397
79.321	1.02197	80.852	1.02983	80.369	1.03789
58.336	1.01433	59.339	1.02002	58.911	1.02672
43.073	1.00958	43.680	1.01333	43.312	1.01873
31.788	1.00670	32.224	1.00888	31.915	1.01307
23.508	1.00473	23.804	1.00578	23.554	1.00902
17.395	1.00335	17.600	1.00359	17.403	1.00616
12.882	1.00274	13.022	1.00209	12.867	1.00394
9.543	1.00177	9.640	1.00123	9.522	1.00265
7.070	1.00128	7.139	1.00064	7.049	1.00168
5.241	1.00094	5.289	1.00037	5.220	1.00105
3.884	1.00071	3.919	1.00035	3.866	1.00064
				2.865	1.00063
67.2% Helium		100% Helium			
215.479	1.10717	230.383	1.08111		
155.157	1.07591	167.154	1.05860		
112.604	1.05379	121.955	1.04234		
82.193	1.03807	89.362	1.03076		
60.251	1.02696	65.669	1.02225		
44.300	1.01902	48.364	1.01604		
32.627	1.01288	35.670	1.01133		
24.078	1.00876	26.349	1.00819		
17.790	1.00588	19.480	1.00590		
13.154	1.00375	14.406	1.00398		
9.733	1.00232	10.664	1.00296		
7.205	1.00136	7.896	1.00220		
5.336	1.00085	5.847	1.00162		
3.958	1.00053	4.335	1.00211		
2.933	1.00035				

helium was made. Consequently, N was determined from the curve fitting to Equation 8 based on a statistical method described by Deming (*5*). Details are given by Ku (*8*). This gave a set of slightly differing N values, and instead of using an average, we chose to use that value which resulted from a run that was carried to the lowest pressure. This was believed to be the most accurate value.

RESULTS AND DISCUSSION

Compressibility factors for the He-N_2 system as a function of pressure along various isotherms are given in Table I. The values for 38.5° C. are plotted in Figure 2 to show the trends. The compressibility factors at 100° C. show similar trends and are not plotted. Similar results for CO_2-C_2H_4 are presented in Table II. The actual experimental pressure rather than smoothed values are tabulated. The constants in the virial equations for the mixtures are given in Table III and plotted in Figures 3 and 5. The great dissimilarity of the two systems is evident by comparing Figure 2 with Figure 4; the latter shows the values of z *vs.* P for CO_2-C_2H_4.

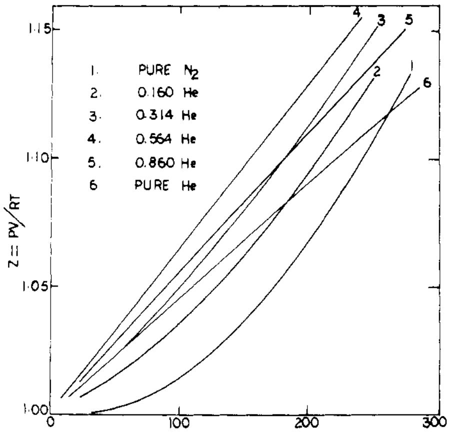

Figure 2. Compressibility factors *vs.* pressure for He-N_2 mixtures at 38.5° C.

The trends shown in Figure 3 are similar to those reported by Kramer and Miller (*7*) and Miller, Stroud, and Brandt (*15*), but their temperatures were different so that the values are not directly comparable.

Values of the coefficient B for the pure gases are compared with those of other investigators in Table IV. The agreement is about as good as would be expected considering the fact that the true value of B is based on an extrapolation to $P = 0$, and our measurements of P in the low-pressure range were less precise than at higher pressures. Furthermore, some of the literature values are based on an extrapolation from values well above 1 atm. The B given by some investigators is simply the coefficient of the second term in an infinite series expansion, and its value will depend on the number of terms used. The values of z for N_2 agree well with those reported by Lunbeck, Michels, and Wolkers (*9*), the difference being of the order of 0.001 to 0.002. The authors' experimental values of z for CO_2 are compared with those of Michels and Michels (*12*) and for ethylene with data of Michels and Geldermans (*11*) in Figure 6.

Values of the interaction parameter, B_{12}, were calculated from the well known relation

$$B_{12} = \frac{B_M}{2x_1x_2} - \tfrac{1}{2}\left[\frac{x_1}{x_2}B_1 + \frac{x_2}{x_1}B_2\right] \qquad (10)$$

There was considerable scatter in the values calculated in this way at 38.5° but much less at 100° C. Application of the method of least squares using the B_1 and B_2 values from this work as given in Table IV, yielded the values shown in Table V. The standard deviation of B_{12} at 38.5° C. is $\pm 0.86 \times 10^{-4}$, while at 100° C. it is $\pm 0.39 \times 10^{-4}$. Only four mixtures in one case and three in the other were investigated, which is probably fewer than desirable to ensure good values of the interaction coefficients. In evaluating B_{12} from a set of mixture data by the least squares method, one can

Table II. Mole Fractions of Carbon Dioxide–Ethylene Mixtures at 100° C.

Carbon Dioxide					
0%		0%		11.9%	
Pressure, atm.	Compressibility factors, z	Pressure, atm.	Compressibility factors, z	Pressure, atm.	Compressibility factors, z
260.429	0.7582	208.777	0.6945	254.365	0.7424
159.917	0.6609	141.356	0.6676	160.708	0.6660
116.795	0.6853	106.349	0.7131	118.913	0.6996
89.724	0.7474	81.071	0.7717	90.568	0.7565
67.997	0.8042	61.145	0.8264	68.495	0.8122
50.849	0.8538	45.421	0.8715	51.053	0.8595
37.569	0.8956	33.246	0.9056	37.511	0.8965
27.213	0.9209	24.098	0.9319	27.234	0.9241
19.630	0.9431	17.333	0.9516	19.633	0.9457
14.063	0.9592	12.387	0.9655	14.050	0.9608
10.027	0.9710	8.833	0.9774	10.016	0.9725
		6.261	0.9836	7.112	0.9803
		4.431	0.9882	5.040	0.9862
		3.131	0.9915	3.564	0.9902
				2.519	0.9937
24.8%		69.5%		100%	
260.263	0.7390	262.947	0.6722	247.905	0.6014
165.675	0.6678	175.832	0.6381	175.132	0.6030
122.695	0.7022	132.862	0.6845	135.759	0.6638
93.369	0.7586	101.964	0.7458	105.683	0.7337
70.575	0.8141	77.424	0.8040	80.841	0.7967
52.576	0.8610	57.821	0.8525	60.660	0.8487
38.580	0.8969	42.657	0.8928	44.759	0.8891
28.030	0.9251	31.019	0.9217	32.603	0.9194
20.192	0.9417	22.368	0.9436	23.532	0.9422
14.448	0.9612	16.056	0.9617	16.856	0.9581
10.295	0.9724	11.460	0.9745	12.015	0.9696
7.311	0.9802	8.145	0.9832	8.538	0.9782
5.181	0.9862			6.057	0.9852

Table III. Constants for the Mixture in the Equation:

$$z = 1 + BP + CP^2$$

He-N_2 Mixtures

38.5° C.			100° C.		
Mole fraction of He	$B \times 10^4$ atm.$^{-1}$	$C \times 10^6$ atm.$^{-2}$	Mole fraction of He	$B \times 10^4$ atm.$^{-1}$	$C \times 10^6$ atm.$^{-2}$
0.0	-1.069	2.110	0.0	1.951	-1.238
0.160	2.053	1.339	0.178	3.704	-0.685
0.314	3.667	0.884			
0.564	5.274	0.320	0.513	5.012	-0.221
0.860	5.387	-0.008	0.672	4.989	-0.097
1.000	4.552	-0.0376	1.000	3.662	-0.011

CO_2-C_2H_4 Mixtures, 100° C.[a]

Mole Fraction of CO_2	$B \times 10^3$ atm.$^{-1}$	$C \times 10^6$ atm.$^{-2}$
0.00	-2.85	-3.37
0.119	-2.96	2.55
0.248	-2.95	3.00
0.695	-2.71	1.95
1.00	-2.53	-0.172

[a] For this system the virial equation with two constants is limited to a pressure of about 100 atm.

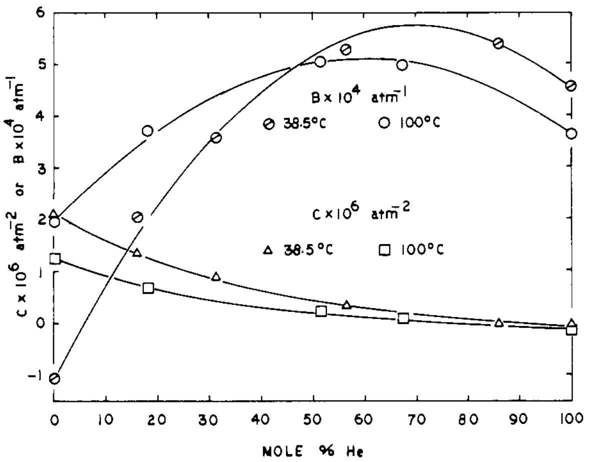

Figure 3. Virial coefficients of He-N_2 mixtures as a function of composition

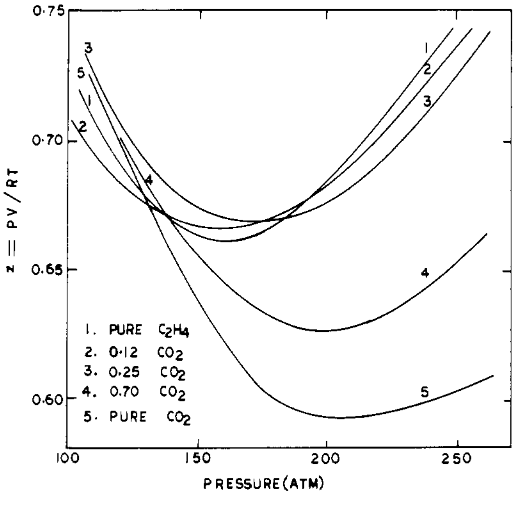

Figure 4. Compressibility factors vs. pressure for CO_2–C_2H_4 mixtures at 100° C.

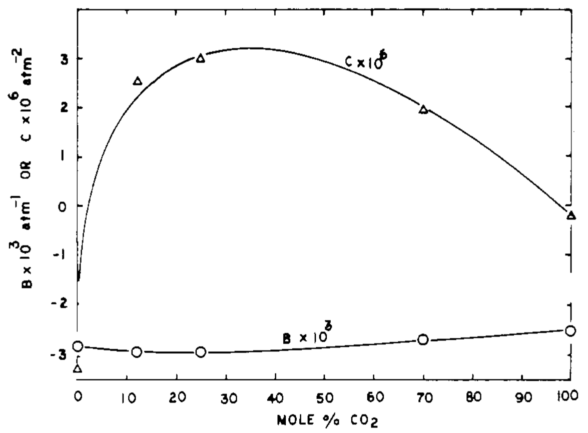

Figure 5. Variation of second and third virial constants with mole % of CO_2 in the CO_2–C_2H_4 mixtures

Table IV. Comparison of Values of B of the Pure Components in This Work with Those in the Literature

Gas	Temp., ° C.	Coefficients $B \times 10^4$, atm.$^{-1}$ This work	Literature values		
He	38.5	4.55	4.55 (*17*)	4.49 (*19*)	4.35 (*18*)
He	100.0	3.66	3.73 (*17*)	3.69 (*19*)	
N_2	38.5	-1.069	-1.036 (*14*)		
N_2	100.0	1.95	2.057 (*14*)		
CO_2	100.0	-25.3	-23.90 (*12*)	-23.46 (*10*)	
C_2H_4	100.0	-28.6	-26.37 (*11*)		

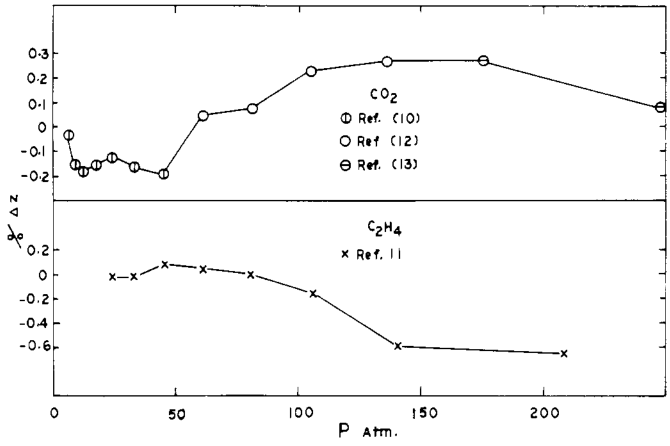

Figure 6. Percentage deviation between z values of the authors and those of some previous investigators

proceed in either of two ways: treat all three coefficients as variables and solve for them from three simultaneous equations, or take B_1 and B_2 as fixed from previous data on the pure components and evaluate B_{12} only. These two procedures can lead to very different results. When only a few mixtures are investigated, as in the present case, the second method is preferred. In Table VI, there are assembled all the existing data in two different units on the interaction coefficient of the He-N_2 system as a function of temperature. The data for B_{12} in volume units are plotted in Figure 7, and the curve was drawn quite arbitrarily through the points (the last three values of Witonsky and Miller (*20*) are not plotted, but they would fall smoothly on an extension of the curve). The values in the range 290° to 400° K. are still somewhat uncertain. The present values lie below the line, and the value of Miller, Stroud, and Brandt (*15*) is even further below the line. If, however, one plots B_{12} in pressure units (Figure 8), the authors' results appear to fall better in line with the results at lower and higher temperatures.

Table V. Comparison of Calculated and Experimental Values of the Interaction Second Virial Coefficient

Temp., °C.	System	Value of $B_{12} \times 10^4$ in Atm.$^{-1}$				
		Exptl	Eq. 11	Eq. 12	Eq. 13	L-J[a]
38.5	He-N_2	8.61	1.77		0.027	7.20
100.0	He-N_2	7.24	3.15	3.06	3.07	6.15
100.0	CO_2–C_2H_4	−30.4	−26.95	−26.9	−26.9	−26.3

[a] Calculated from Lennard-Jones potential by methods of Hirschfelder, Curtiss, and Bird (*6*). Quantum effects allowed for in case of He. [b] Inapplicable.

Table VI. Second Virial Interaction Coefficient, B_{12}, of the He-N_2 System as a Function of Temperature

T, °K.	B_{12}, Cc./G. Mole	B_{12}, Atm.$^{-1}$ × 10^4	Ref.
133.15	13.80	12.63	(*14*)
143.14	15.31	13.03	(*14*)
158.15	16.50	12.70	(*14*)
183.15	17.85	11.88	(*14*)
223.13	20.16	11.00	(*14*)
273.15	21.66	9.67	(*14*)
294.25	19.75	8.18	(*15*)[a]
303.15	21.83	8.79	(*7*)
311.7	22.02	8.61	This work
373.2	22.17	7.24	This work
448	22.92	6.23	(*20*)
523	22.41	5.22	(*20*)
598	21.73	4.43	(*20*)
673	21.20	3.84	(*20*)
748	20.33	3.31	(*20*)

[a] This value is given in (*20*) but based on the measurements of (*15*).

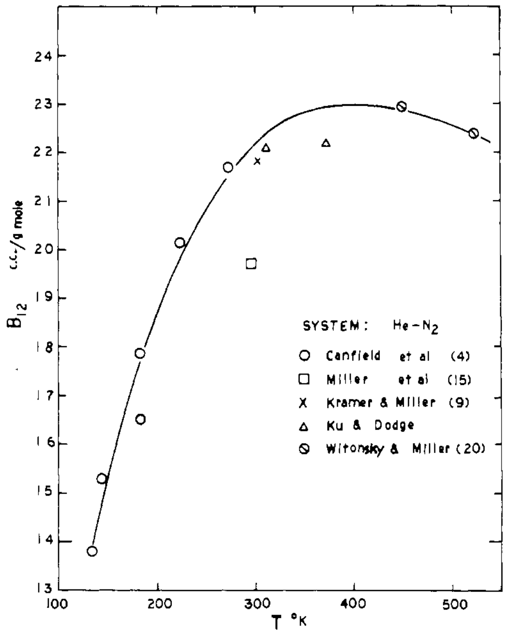

Figure 7. Second interaction virial coefficient in volume units as a function of temperature

There are three commonly used rules for obtaining B_{12} from B_1 and B_2, which are expressed in the following equations:

$$B_{12} = \frac{B_1 + B_2}{2} \tag{11}$$

$$B_{12} = (B_1B_2)^{1/2} \tag{12}$$

$$B_{12} = \tfrac{1}{8}\,(B_1^{1/3} + B_2^{1/3})^3 \tag{13}$$

Each of these predicts that B_{12} has a value between those of B_1 and B_2. Hence, they cannot apply either to the He-N_2 system or the CO_2–C_2H_4 one since B_{12} is larger than either B_1 or B_2 in the case of He-N_2 and smaller in the case of CO_2–C_2H_4. To show the extent of the error involved, Table V compares the values of B_{12} calculated by each of these equations with the experimental values obtained from the least squares treatment of the B_M *vs.* x_1 curve and also with the values of B_{12} calculated from the Lennard-Jones potential using conventional rules for combining force constants. These constants are tabulated by Hirschfelder, Curtiss, and Bird (*6*). Quantum effects were allowed for in the case of He.

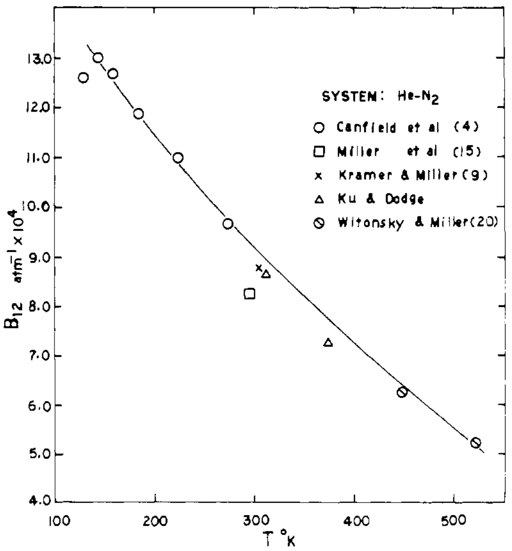

Figure 8. Second interaction virial coefficient in pressure units as a function of temperature

In the case of He-N_2, the three combining rules given by Equations 11, 12, and 13 are grossly in error, but the rule based on the Lennard-Jones force constants is in fair agreement with the experimental values. Close agreement is hardly to be expected in view of the purely empirical combining rules used. In the case of CO_2–C_2H_4, all of the rules are in fair agreement with the experimental values which is to be expected since B_1 and B_2 are not very different.

An error analysis was made which shows that the pressure measurements have an error of about 0.02%. The value of N has an uncertainty of 1.05×10^{-4}. As a result of the small error in N, the volume should be accurate to 0.015%. The temperature of the bath was controlled to 0.01° at 38.5° C. and 0.02° at 100° C. The over-all uncertainty in the compressibility factors was estimated to be about 0.06%. The results on the pure components in this work are comparable to 0.0 to 0.2% with the existing data.

ACKNOWLEDGMENT

Thanks are due to R. W. Southworth and R. H. Bretton of this department and to graduate students A. G. Blake and T. Y. Chen for assistance in computer programming and for helpful suggestions.

NOMENCLATURE

B, C, D = coefficients in the virial equation of state
N = ratio of volumes of pressure vessels = $(V_1 + V_2)/V_1$
n = number of moles
P = pressure
R = gas constant; pressure ratio, defined in Equation 9
T = absolute temperature
V = volume
X = defined in Equation 9
x = mole fraction
Y = defined in Equation 9
z = compressibility factor

Subscripts and Exponents

A = component A
i = designating number of any expansion, $i = 1, 2 \ldots n$
M = mixture
n = denoting last expansion
o = initial condition
1, 2 = components, pressure vessels

LITERATURE CITED

(1) Bridgeman, O.C., *J. Am. Chem. Soc.* **49**, 1174–83 (1927).
(2) Burnett, E.S., *J. Appl. Mech.* **3**, A136–40 (1936).
(3) Burnett, E.S., *U. S. Bur. Mines, Rept. Invest.* **6267** (1963).
(4) Canfield, F.B., Leland, T.W., Kobayashi, R., *Advan. Cryog. Eng.* **8**, 146–57 (1963).
(5) Deming, E.W., "Statistical Adjustment of Data," Wiley, New York, 1948.
(6) Hirschfelder, J.O., Curtiss, C.F., Bird, R.B., "Molecular Theory of Gases and Liquids," Wiley, New York, 1954.
(7) Kramer, G.M., Miller, J.G., *J. Phys. Chem.* **61**, 785–8 (1957).
(8) Ku, P.S., D. Eng. dissertation, Yale University, 1960.
(9) Lundbeck, R.J., Michels, A., Wolkers, G.J., *Appl. Sci. Res., Sec.* **A3**, 197–210 (1952).
(10) MacCormack, K.E., Schneider, W.G., *J. Chem. Phys.* **18**, 1269–72 (1950).
(11) Michels, A., Geldermans, M., *Physica* **9**, 967–73 (1942).
(12) Michels, A., Michels, C., *Proc. Roy. Soc. (London)* **153A**, 201–14, (1935).
(13) Michels, A., Michels, C., Wouters, H., *Ibid.*, 214–24 (1935).
(14) Michels, A., Wouters, H., deBoer, J., *Physica* **1**, 587–94 (1934).
(15) Miller, J.E., Stroud, L., Brandt, L.W., J. Chem. Eng. Data **5**, 6–9 (1960).
(16) Pfefferle, W.C., Jr., Goff, J.A., Miller, J.G., *J. Chem. Phys.* **23**, 509–13 (1955).
(17) Schneider, W.G., Duffie, J.A., *Ibid.*, **17**, 751–4 (1949).
(18) Stroud, L., Miller, J.E., Brandt, L.W., J. Chem. Eng. Data **5**, 51–2 (1960).
(19) Wiebe, R., Gaddy, V.L., Heins, C., Jr., *J. Am. Chem. Soc.* **53**, 1721–25 (1931).
(20) Witonsky, R.J., Miller, J.G., *Ibid.*, **85**, 282–6 (1963).

Received for review April 7, 1965. Accepted January 10, 1967. This work was supported by funds from Contract Nonr-609(06) with the office of Naval Research, from a National Science Foundation Grant and by a fellowship grant from Yale University.

Densities of Sodium-Ammonia Solutions

SAM NAIDITCH, OSCAR A. PAEZ, and JAMES C. THOMPSON[1]
Unified Science Associates, Inc., Pasadena, Calif.

Densities of sodium-ammonia solutions have been determined from −60° to 60° C., for compositions of 0.08 to 12 mole % sodium. Volumes were measured dilatometrically and corrected for loss of solvent by vaporization. Compositions were determined from electrical conductivities or by gas analysis, then densities at −33.8° C. were obtained from published density-composition data. From these densities and ratios of volumes to those at −33.8° C., densities were established at all other temperatures. Densities decrease with increasing metal concentration; the effect is smaller at higher temperatures. Over the range studied, the excess volumes of the solutions decrease continuously with increasing temperature, from 45 cc. per mole Na at −60° C. to zero just above 60° C.

SPECIFIC conductivities of sodium-ammonia solutions were measured in this laboratory from −60° to 190° C. (*8*); densities were required for conversion of these data into equivalent conductivities. There were excellent data in the literature for densities at the boiling point of ammonia (−33.8° C.) from 1.2 to 5.2*M* (*6*) and 0.6 to 1.2*M* (*2*). At other temperatures, the most complete set was that of Kikuti (*3*), who measured the densities of 1.5 to 5.2*M* solutions from −30° to 30° C. Since these data were not extensive enough for the present study, densities were determined over a wider range of temperatures and concentrations. The strength of glass was a limiting factor; cells frequently ruptured near 60° C., because of the high vapor pressures of the solutions—of the order of 25 atm.

EXPERIMENTAL

Sample Preparation and Stability. Stable sodium-ammonia solutions were prepared in a borosilicate glass, bakeable vacuum system. Sodium (U.S. Industrial Chemical 99.95%+, nitrogen packed) was triply-distilled, encapsulated, and sealed onto the system. The sample cells were calibrated, cleaned, sealed onto the vacuum system, and vacuum baked. Ammonia (Matheson 99.99%) was passed through an activated charcoal trap, stored overnight at −78° C. over sodium, then vacuum fractionated. The sodium was distilled onto a recess above the cell, the purified ammomia was condensed onto the sodium, and the solution was allowed to overflow into the cell. Then, the filled cells were chilled with liquid nitrogen, evacuated, sealed-off, and stored at dry-ice temperature. Samples prepared in this manner are stable to at least 165° C. (*8*).

About 85% of the cells ruptured between 40° and 60° C. because of the high vapor pressures of ammonia at these temperatures. Volumes and conductivities of those cells that survived at 60° C. were remeasured on cooling. The low temperature data obtained prior to heating were reproduced on cooling; this established that there had been no measurable decomposition in these cells.

---

[1] Present address: The University of Texas, Austin, Tex.