I. Compressibility and an Equation of State for Gaseous Ammonia

II. Compressibility of a Gaseous Mixture of Ammonia and Methane

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Abstract of the Thesis

I. COMPRESSIBILITY AND EQUATION OF STATE FOR GASEOUS AMMONIA

II. COMPRESSIBILITY OF THE GASEOUS MIXTURE METHANE- AMMONIA

by
Charles M. Apt

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The compressibility of ammonia was measured in the region of from 150° to 300° and from one mole per liter to ten moles per liter. The results were fitted to the Beattie-Bridgeman equation of state over the same range of temperature but from one to eight moles per liter in density. The average overall deviation of the calculated to the observed pressures came to 0.244 per cent.

In addition, the compressibility of the polar gas mixture, containing 70.151 mole per cent methane and 29.849 mole per cent ammonia, was measured.

From the Beattie-Bridgeman constants for the pure ammonia and the pure methane, equation of state constants for the mixture were calculated, using two different sets of combining rules. In one case, using the "non polar" combining rules, the average overall per cent deviation in the observed to the calculated pressures amounted to 1.089 per cent. This result was considerably improved upon by the application of "polar" combining rules. These rules, obtained by W. H. Stockmayer, resulted from a theoretical study on the second virial coefficients of polar gases. The overall per cent deviation found on applying these rules amounted to 0.707 per cent.

From the compressibility measurements on the pure ammonia, the second and third virial coefficients were determined for that gas by the method of least squares. These virial coefficients were then compared with those calculated using both the Lennard-Jones and the Stockmayer potential. Both potentials gave good agreement for the second virial coefficients. However, for the third virial coefficients, only the Stockmayer potential gave results in fair agreement with those observed.

Thesis supervised by: James Alexander Beattie

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Biographical Note

Charles Maurice Apt was born in New York City on June 15, 1923. He received both his primary and secondary education in the public schools of that city.

In June 1941 he received the Charles Hayden Memorial Scholarship to New York University. After attending that university for one year, he was conscripted into the United States Army. He served for a period of over three years both in the United States and in the European Theater of Operations.

In the fall of 1946, after being honorably discharged from the Army, he returned to college. He received his B.A. from Oxford University in 1949 and commenced his graduate studies at the Massachusetts Institute of Technology in september of that year. His thesis was carried out under the supervision of Professor J.A. Beattie.

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To his co-worker John F. Connolly, whose experimental skill and careful attention to detail, helped in a very real way to bring this work to a successful conclusion, he is indeed grateful.

I. Introduction

The main purpose of the present investigation was to study the behaviour of gas mixtures, especially of polar with non-polar gases. Such a study is of interest for several reasons. For theoretical purposes, it serves to give a greater understanding of the forces operating between polar and non-polar molecules. Then too, in many industrial processes involving gaseous reactions at high pressures, it is necessary to be able to calculate the equilibrium constants. Processes such as the manufacture of ammonia and methanol may be taken as examples. Gillespie (1, 2) has shown that, with a knowledge of the equilibrium constant K_p^* for the gaseous reaction occuring at low pressure, and with an equation of state for the gaseous mixture, one could calculate the high pressure equilibrium constants.

To obtain an equation of state for gas mixtures was our main concern. It has been the practice in this laboratory, to determine the equation of state of a gas mixture from the equations of state obeyed by the pure gases. For this purpose the Beattie-Bridgman equation of state (3) has been used to fit the pure gases. This method for obtaining an equation of state for a gaseous mixture involves two assumptions. First, it is assumed that the equation of state obeyed by the gas mixture will have the same form as that of the pure gases. Secondly, it is assumed that the parameters appearing in the equation of state for any gas mixture, can be expressed as a function of composition and the parameters appearing in the equation of state for the pure gases. To test this latter assumption, for a gas mixture made up of polar with non-polar gases, mixtures of methane and ammonia were studied.

The compressibility of pure methane had already been measured by Keyes and Burks (10) and the Beattie-Bridgman equation of state constants were calculated by Beattie and Bridgman (3) and corrected by Stockmayer (11) for the revised atomic weights of the elements carbon, hydrogen, and nitrogen. The compressibility of pure ammonia was measured in the course of the present investigation, for though there exists in the literature (4,5,6,7,8,9) a great deal of data on ammonia, nevertheless there were no data available on the compressibility of ammonia, over the range of density and temperature required in this study.

In addition to the measurements made on the pure ammonia, the compressibilities of two mixtures composed of methane and ammonia were determined, one of which is reported in this thesis, the other will be found in a thesis by Connolly (12).

When the compressibility measurements had been made, the pure ammonia was fitted to the Beattie-Bridgman equation of state (3) in the region of from one to eight moles per liter in density and from 150° to 300° C. We used for the equation of state for the methane the one obtained from the measurements of Keyes and Burks (10).

From the equation of state constants of the pure ammonia and the pure methane, we then calculated the equation of state constants for the mixtures of methane and ammonia using two different methods. In each case, the pressures of the mixtures were calculated from the equations of state obtained, and these pressures were compared with the observed, measured pressures and the over-all per cent deviations were determined.

In addition to the study on the mixtures, some theoretical calculations were made utilizing the compressibility measurements on the pure ammonia. Thus the second and third virial coefficients determined from the experimental measurements on the pure ammonia, were compared with the theoretical values obtained by using both the Stockmayer potential (14) and the Lennard-Jones potential (25).

II. Experimental Procedure

The apparatus used to measure the compressibility of gases is fully described in the literature (31). The method used consists in confining a weighed amount of gas in an all-steel bomb, by means of mercury. During the course of the measurements the bomb is placed in an oil thermostat where temperature is controlled by means of a phase shifting thyratron circuit which operates a resistance heater located in the bath. The temperatures range from 150 to 300° C.

Pressures are measured on an Amagat dead weight gauge. The pressure is transmitted from the confined gas by means of mercury. The pressures range covered in these experiments was from 30 to 400 atmospheres.

Volumes are measured by means of a mercury injector which, when calibrated, can be used to add or remove from the bomb known amounts of mercury. By this means, the volumes may be so adjusted that even densities may be set during the course of the measurements at any given isotherm. The injector is placed in an oil bath, the temperature of which is regulated at 30° C.

Temperatures are measured by means of a platinum resistance thermometer, and the resistances are measured on a Mueller Bridge.

Details of the apparatus and its calibration are given in the Appendices (A, B) as are the corrections which are applied in order to obtain the corrected volumes and pressures.

III. Compressibility and Equation of State of Ammonia

The ammonia used in this research was obtained from the Matheson Corporation, and had the stated purity of 99.9%. The gas was further purified by treatment with sodium to remove any traces of water and by low temperature fractionation as described in Appendix (C).

An attempt was made to determine the vapor pressure of the ammonia at a series of temperatures. However, during the course of our measurements at the 30° isotherm, it was noted that the pressure varied with the vapor volume, indicating the presence of a permanent gas. The first loading was discarded. Before the second loading the gas was again purified in a manner described above and greater precautions were taken to remove any of the impurities that were present. We still found that the vapor pressure curve was not flat at the 30° isotherm, indicating again the presence of some permanent gases. An estimate was made as to the amount of impurity present and it was found to be about 0.02 mole per cent. It was concluded that, although some impurity was present, the amount was negligible for our purposes. We therefore proceeded to measure the compressibility of the gaseous ammonia above its critical point, starting at 150° and proceeding in steps of 25° to 300° and at densities of 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0 moles per liter. The measured compressibilities are given in Table I.

It was found in the course of these measurements, that at the higher temperatures, some of the ammonia had decomposed. At 300° this amounted to between 0.2 to 0.3 per cent, at 275° to about 0.2 per cent, at 250° to about 0.1 per cent, and below 250° the amount of decomposition was negligible.

Measurements have been made in the past on the compressibility of ammonia which overlap part of the region studied in this investigation. Thus Beattie and Lawrence (8) report measurements on ammonia which cover the range of from 150° to 300° and from 1 to 3 moles per liter in density. Their measurements, interpolated to our measured densities, are compared to those reported here in Table II where it is seen that the average over-all per cent deviation is 0.292. The experimental error is given as 0.3 per cent.

J.S. Kasanowsky (9) has also reported measurements on the compressibility of ammonia at temperatures ranging from 200° to 300° and at pressures of from 30 to over 1500 atmospheres. At four different densities his measurements overlap the region studied in this investigation. In Table III his measurements are compared with those obtained in the present work, where it is found that the average over-all per cent deviation is 0.425%. He reports his over-all experimental error as 0.5%.

For the measured densities, pressures, and temperatures given in Table I, the equation of state constants were calculated using the method of Beattie and Bridgman (3) and discussed briefly in the Appendix (E). It was found that a satisfactory fit could be obtained for ammonia for the density range of from 1 to 8 moles per liter inclusive. The constants obtained are given in Table IV.

The molecular weight used was 17.032 grams and this was obtained from the 1950 reports in the Journal of the American Chemical Society (28) on the atomic weights of the elements.

In Table V the observed pressures and the deviation of the observed from the calculated pressures are given. In Table VI the average deviation of the calculated pressures from the measured pressures are given, as are the percentage deviations, for each of the isometrics.

Table I

Compressibility of Gaseous Ammonia

Temp. °C. (Int.)	150	175	200	225	250	275	300
Density, moles/liter	Pressure, standard atmospheres						
1.0	31.42	33.76	36.05	38.33	40.56	42.80	44.96
1.5	44.84	48.55	52.17	55.73	59.26	62.75	66.12
2.0	56.88	62.08	67.14	72.08	76.96	81.79	86.45
2.5	67.65	74.45	81.03	87.45	93.75	100.01	106.03
3.0	77.26	85.74	93.93	101.91	109.72	117.48	124.93
3.5	85.80	96.05	105.93	115.53	124.92	134.24	143.19
4.0	93.38	105.46	117.08	128.38	139.42	150.36	160.85
4.5	100.10	114.06	127.49	140.53	153.27	165.90	178.03
5.0	106.04	121.92	137.21	152.06	166.55	180.94	194.93
6.0	115.91	135.75	154.86	173.45	191.63	209.65	226.98
7.0	123.58	147.47	170.54	193.04	215.10	236.98	285.03
8.0	129.56	157.56	184.71	211.33	237.34	263.30	288.37
9.0	134.27	166.41	197.74	228.49	258.91	289.04	318.26
10.0	138.09	174.39	210.01	245.17	280.03	314.80	348.71

Table II

Comparison of the pressures obtained by Apt and Connolly with those obtained by interpolation from the measurements of Beattie and Lawrence for gaseous ammonia

Temp. °C. (Int.)		150	175	200	225	250	275	300
Density, moles/liter		Pressures, standard atmospheres						
1.0	Apt and Connolly	31.42	33.76	36.05	38.33	40.56	42.80	44.96
	Beattie and Lawrence	31.47	33.80	36.12	38.41	40.66	42.92	45.11
	A. &C. - B. & L.	-0.05	-0.04	-0.07	-0.08	-0.10	-0.12	-0.15
1.5	Apt and Connolly	44.84	48.55	52.17	55.73	59.26	62.75	66.12
	Beattie and Lawrence	44.92	48.64	52.28	55.89	59.42	62.88	66.35
	A. & C. - B. & L.	-0.08	-0.09	-0.11	-0.16	-0.16	-0.13	-0.23
2.0	Apt and Connolly	56.88	62.08	67.14	72.08	76.96	81.79	86.45
	Beattie and Lawrence	56.99	62.24	67.34	72.34	77.23	82.00	86.77
	A. & C. - B. & L.	-0.11	-0.16	-0.20	-0.26	-0.27	-0.21	-0.32
2.5	Apt and Connolly	67.65	74.45	81.03	87.45	93.75	100.01	106.03
	Beattie and Lawrence	67.75	74.64	81.23	87.76	94.11	100.32	106.43
	A. & C. - B. & L.	-0.10	-0.19	-0.20	-0.31	-0.36	-0.31	-0.40
3.0	Apt and Connolly	77.26	85.74	93.93	101.91	109.72	117.48	124.93
	Beattie and Lawrence	77.46	85.92	94.34	102.43	110.29	118.05	125.42
	A. & C. - B. & L.	-0.20	-0.18	-0.41	-0.52	-0.57	-0.57	-0.49

Total average deviation (atmos.) is .226

Total average per cent deviation is .292

Table (III)

Comparison of the Pressures Obtained by J.S. Kasarnowsky with those Obtained by Interpolation from the Measurements of Apt and Connolly for Gaseous Ammonia

Temp.	°C. (int.)	200	225	250	275	300
Density, mole/liter			Pressures, standard atmospheres			
3.216	Apt and Connolly	99.92	107.88	116.36	124.79	132.87
	J.S. Kasarnowsky	100.2	108.6	117.0	125.4	133.8
	A. & C. - J.S.K.	-0.98	-0.72	-0.64	-0.61	-0.93
5.000	Apt and Connolly	137.21	152.06	166.55	180.94	194.73
	J.S. Kasarnowsky	138.3	152.5	166.7	181.0	195.2
	A. & C. - J.S.K.	-1.09	-0.44	-0.15	-0.06	-0.47
6.667	Apt and Connolly	165.54	186.64	207.40	227.98	247.79
	J.S. Kasarnowsky	166.0	186.8	207.5	228.2	249.0
	A. & C. - J.S.K.	-0.46	-0.16	-0.10	-0.22	-1.21
10.000	Apt and Connolly	210.01	245.17	280.03	314.80	348.71
	J.S. Kasarnowsky	208.0	243.3	278.6	313.9	349.2
	A. & C. - J.S.K.	+2.01	+1.87	+1.43	+0.90	-0.49

Total average deviation (atmos.) is 0.747

Total average per cent deviation is 0.425

Table (IV)

Values of Constants for the Beattie-Bridgman Equation of State for Gaseous Ammonia

$$P = RT\ (1 - \varepsilon)/V^2 \quad V + B \quad - A/V^2$$

$$A = A_o(1 - a/V)$$

$$B = B_o(1 - b/V)$$

$$\varepsilon = c/VT^3$$

Units; normal atmospheres, liter per mole, °K ($T°K = t°C + 273.13$)

$R = 0.08206$

$A_o = 5.936$

$a = 0.05244$

$b = 0.05281$

$c = 100 x 10^4$

$B_o = 0.08970$

Molecular weight of ammonia = 17.032 grams

Table (V)

Comparison of the Pressures Calculated from the Equation of State with the Observed Pressures for Gaseous Ammonia

Temp. °C. (int.)		150	175	200	225	250	275	300
Density, moles/liter.					Pressures, standard atmospheres			
1.0	obsd.	31.42	33.76	36.05	38.33	40.56	42.80	44.96
	obsd-calc.	-0.13	-0.07	-0.05	-0.04	-0.06	-0.08	-0.17
1.5	obsd.	44.84	48.55	52.17	55.73	59.26	62.75	66.12
	obsd-calc.	-0.23	-0.11	-0.05	-0.04	-0.05	-0.08	-0.23
2.0	obsd.	56.88	62.08	67.14	72.08	76.96	81.79	86.45
	obsd-calc.	-0.32	-0.12	-0.01	-0.00	-0.03	-0.08	-0.29
2.5	obsd.	67.65	74.45	81.03	87.45	93.75	100.01	106.03
	obsd-calc.	-0.39	-0.09	-0.05	-0.07	-0.02	-0.05	-0.33
3.0	obsd.	77.26	85.74	93.93	101.91	109.72	117.48	124.93
	obsd-calc.	-0.42	-0.04	+0.14	+0.13	+0.10	+0.02	-0.34
3.5	obsd.	85.80	96.05	105.93	115.53	124.92	134.24	143.19
	obsd-calc.	-0.41	+0.06	+0.28	+0.31	+0.20	+0.09	-0.33
4.0	obsd.	93.38	105.46	117.08	128.38	139.42	150.36	160.85
	obsd-calc.	-0.35	+0.18	+0.41	+0.44	+0.32	+0.18	-0.33
4.5	obsd.	100.10	114.06	127.49	140.53	153.27	165.90	178.03
	obsd-calc.	-0.26	+0.32	+0.56	+0.58	+0.43	+0.28	-0.28
5.0	obsd.	106.04	121.92	137.21	152.06	166.55	180.94	194.93
	obsd-calc.	-0.14	+0.44	+0.69	+0.70	+0.52	+0.38	-0.25
6.0	obsd.	115.91	135.75	154.86	173.45	191.63	209.65	226.98
	obsd-calc.	+0.01	+0.56	+0.77	+0.76	+0.59	+0.45	-0.20
7.0	obsd.	123.58	147.47	170.54	193.04	215.10	236.98	285.03
	obsd-calc.	-0.23	+0.21	+0.36	+0.37	+0.27	+0.28	-0.31
8.0	obsd.	129.56	157.56	184.71	211.33	237.34	263.30	288.37
	obsd-calc.	-1.32	-1.03	-0.90	-0.74	-0.74	-0.41	-0.67

Table VI

Density, moles/liter	Av. dev. (atmos.)	Av. per cent dev.
1.0	.086	0.225
1.5	.113	0.210
2.0	.121	0.177
2.5	.143	0.174
3.0	.177	0.185
3.5	.240	0.218
4.0	.316	0.256
4.5	.387	0.286
5.0	.446	0.301
6.0	.477	0.281
7.0	.290	0.156
8.0	.830	0.459

Total average deviation (atmos.) from 1 to 8 moles per liter = .302

Total average per cent deviation from 1 to 8 moles per liter = 0.244

IV. Virial Coefficients for Ammonia

A. Second Virial Coefficients from the Stockmayer Potential

Instead of using a closed form for the equation of state, such as that used by Beattie and Bridgman, Kamerlingh-Onnes (46) has shown that compressibility measurements may be correlated by using an equation of state of the type:

$$PV = RT + B/V + C/V^2 + \dots \qquad (1)$$

Here B is known as the second virial coefficient and C is the third virial coefficient. Both B and C and the higher terms are functions of the temperature.

In the present work, for calculating these virial coefficients, use is made of the function Bv which is defined as:

$$B_v = V(PV - RT) = B + C/V + \dots \; (2)$$

In equation (2) B and C are the second and third virial coefficients respectively. To determine B and C it was assumed that B_v may be expressed in terms of the density in the following way:

$$B_v = B + C/V + D/V^3 \qquad (3)$$

The constants B, C and D are determined by the method of least squares. It is obvious that the constants B and C are the second and third virial coefficients appearing in equation (1) under the assumption that the term in $1/V^3$ takes care of the higher terms. In Table VII the values of B_v are given and the deviations of these values from those calculated by the method of least squares are listed underneath. In Table VIII values for RT are given and the corresponding thermodynamic temperatures are tabulated.

The values for B, C, and D of equation (3) are given, for the seven temperatures from 150° to 300° in Table IX.

It has been shown, for example, by the application of the virial theorem of Clausius that B may be expressed by (13):

$$B = 1/2 \; N\int_{v} (1 - \exp. \; (-W(q)/kT)\;) \; dv \qquad (4)$$

where the integral is taken over volume, N is Avogadro's number and W(q) is the mutual potential energy of a pair of molecules as a function of their space co-ordinates q, and dv is the volume element in phase space.

Stockmayer (14) used for the complete potential energy between a pair of polar molecules the equation:

$$W(q) = \lambda r^{-s} - cr^{-6} - p^{2} r^{-3} g \qquad (5)$$

where λ and c are constants, r is the intermolecular distance, p is the dipole moment, which for ammonia is given (15-19) as 1.46d, and g is the geometrical factor of the form:

$$g = 2 \cos\theta_1 \, , \cos\theta_2 \; - \sin.\theta_1 \sin\theta_2 \cos\varphi \qquad (6)$$

This potential may also be written in the form:

$$W(q)/kT = (4/T) \; (R_{ij}^{-12} - R_{ij}^{-6} - {}^{t}1/\sqrt{2} \; R_{ij}^{-3} g) \qquad (7)$$

where $R_{ij} = r_{ij}/r_o$, ${}^{t}1 = 1/8 \; (p^2/ \; (r_o)^3)$, and $= {}_{k}T/\varepsilon'$. ε' and r_o are the energy and the distance characteristic of non polar part, if p is equal to zero, then r_o is the distance at which W(q) = 0, and $-\varepsilon$ is the minimum value of W(q). The angles given in equation (6) θ_1 , θ_2 and φ , specify the inclinations of the two dipole axes to the intermolecular axis, the azimuthal angle between them.

Equation (4) may be rewritten in the form:

$$B(T) = N/4 \int_{0}^{\infty} \int_{\Omega} (\; 1 - \exp(-W(q)/_{k}T \;) \; r^{2} \, dr \, d\Omega$$

where

$$\int_{\Omega} d\Omega = \int_{0}^{2\pi}\int_{0}^{\pi}\int_{0}^{\pi} \sin\theta_1 \sin\theta_2 \; d\theta_1 d\theta_2 d\varphi = 8\pi \qquad (8)$$

and solving the integral using the Stockmayer potential given in equation (5) above, the solution obtained is:

$$B(T) = b_o(4/\gamma')\left[\Gamma(3/4) - 1/4\sum_{n=1}^{\infty}\sum_{k=0}^{\leq n} 2^n/n!\binom{n}{k}\frac{\Gamma(2n-2k21/4)}{T^{\left(\frac{n+k}{2}\right)}}\, t_1^{2k}\; G_k\right]$$

where;

$$G_k = 1/(2k+1)\sum_{j=0}^{K}\binom{k}{j}\, 3\gamma'/(2j+1) \qquad (9)$$

$$\gamma = k^{T}/\varepsilon'$$

$$b_o = 2/3\,(\pi N r_o^3)$$

$$t_1 = 1/\sqrt{8}\,(p^2/\varepsilon'(r_o')^3)$$

Rowlinson (20, 21) defines the function $B_p{}^{(o)}_2(T)$ such that

$$B(T) = b_o\, B_p{}^{(o)}_2(T) \qquad (10)$$

and tables of this function as well as tables of the function $\gamma'/t_1\, B_p{}^{(o)}_2(T)$ are given by him in the references listed above. He also sets out a method of curve fitting for the Stockmayer potential. This method was used in the present calculations.

Both the calculated and observed second virial coefficients are given in Table X. In the first column are the values obtained in the present work, in the second column are the values obtained by Lawrence (22) from his measurements on the compressibility of ammonia, by the extrapolation of the B_v values given by equation (2). That is, in the B_v versus $1/V$ plots he made, he extrapolated the curves so obtained to $1/V = 0$. The intercepts are the second virial coefficients for the various temperatures. The agreement between these two sets of measured values of B(T) is quite good. In the third column of Table X are found the theoretical values of B(T).

The agreement between the observed second virial coefficients and those calculated using the Stockmayer potential is very good.

The parameters used to fit the second virial coefficients to Stockmayer's potential are given in Table XI. These parameters were used to construct the series of potential energy curves, 1, 2, and 3 of Figure 1. Curve number 1 is the one obtained when P, the dipole moment, is equal to zero. We would then have just the Lennard-Jones potential. In the case where the dipoles are oriented so that they exert a maximum of attraction on one another, the depth of the minimum is greatly increased. This is seen in curve 2 where the depth of the minimum is nearly 6 times that of curve 1. On the other extreme, when the dipoles are so oriented that they exert a maximum of repulsion on one another, then the potential energy curve obtained is one of pure repulsion. This may be seen in curve 3.

Table (VII)

Values of B(V,T) for Ammonia, $B(V,T) = V(pV - RT)$ (observed)

$$B(V,T) = B(T) + C(T)/V + D(T)/V^3$$

(calculated, see Table (IX))

Temp. °C (int.)		150	175	200	225	250	275	300
Temp. °K		423.183	448.198	473.214	498.231	523.248	548.264	573.278
RT, liter-atmos./mole		37.7241	36.7767	38.8293	40.8821	42.9348	44.9875	47.0400
Density, mole/liter		B(V,T), liters^2 -atmos/mole^2						
1.0	obsd.	-3.30410	-3.01670	-2.77930	-2.55210	-2.37480	-2.18750	-2.08000
	obsd.-calc.	-0.00515	-0.00686	-0.01361	-0.00866	-0.02328	-0.02317	-0.03823
1.5	obsd.	-3.22053	-2.94000	-2.69953	-2.48587	-2.28540	-2.18750	-1.97333
	obsd.-calc.	+0.00092	+0.00033	+0.00159	-0.00180	+0.00895	+0.00709	+0.00961
2.0	obsd.	-3.14205	-2.86835	-2.62965	-2.42105	-2.22740	-2.04625	-1.90750
	obsd.-calc.	+0.00239	+0.00295	+0.00742	+0.00412	+0.01032	+0.00973	+0.01741
2.5	obsd.	-3.06564	-2.79868	-2.56692	-2.36084	-2.17392	-1.99340	-1.85120
	obsd.-calc.	+0.00244	+0.00423	+0.00680	+0.00607	+0.00788	+0.00939	+0.01674
3.0	obsd.	-2.99027	-2.73223	-2.50643	-2.30403	-2.12050	-1.94250	-1.79890
	obsd.-calc.	+0.00228	+0.00308	+0.00480	+0.00541	+0.00628	+0.00801	+0.01340
3.5	obsd.	-2.01709	-2.66680	-2.44674	-2.24957	-2.06954	-1.89520	-1.75103
	obsd.-calc.	+0.00090	+0.00187	+0.00305	+0.00335	+0.00328	+0.00410	+0.00721
4.0	obsd.	-2.84478	-2.60292	-2.38982	-2.19678	-2.01995	-1.84938	-1.70688
	obsd.-calc.	-0.00020	+0.00022	-0.00025	+0.00073	+0.00017	-0.00003	-0.00085
4.5	obsd.	-2.77327	-2.54000	-2.33293	-2.14516	-1.97218	-1.80462	-1.66173
	obsd.-calc.	-0.00080	-0.00111	-0.00219	-0.00179	-0.00334	-0.00377	-0.00579
5.0	obsd.	-2.70322	-2.47854	-2.27746	-2.09402	-1.92496	-1.75990	-1.61880
	obsd.-calc.	-0.00139	-0.00247	-0.00398	-0.00337	-0.00579	-0.00594	-0.01056
6.0	obsd.	-2.56763	-2.35862	-2.16988	-1.99563	-1.83275	-1.67430	-1.53500
	obsd.-calc.	-0.00200	-0.00326	-0.00554	-0.00550	-0.00738	-0.00853	-0.01398
7.0	obsd.	-2.43854	-2.24423	-2.06663	-1.90071	-1.74374	-1.59046	-1.45409
	obsd.-calc.	-0.00128	-0.00192	-0.00307	-0.00350	-0.00360	-0.00424	-0.00758
8.0	obsd.	-2.31614	-2.13521	-1.96756	-1.80824	-1.65841	-1.50938	-1.37422
	obsd.-calc.	+0.00191	+0.00296	+0.00497	+0.00492	+0.00649	+0.00736	+0.01260

Table (VIII)

Values of RT for Absolute Thermodynamic Temperatures

$T^{o}C$ (Int.)	$T^{o}C$ (th.)	RT
150	423.183	34.7241
175	448.198	36.7767
200	473,214	38.8293
225	498.231	40.8821
250	523.248	42.9348
275	548.264	44.9875
300	573.278	47.0400

The thermodynamic centigrade temperatures were calculated from the equation recommended by the 8th General Conference of the International Committee on Weights and Measures.

$$t(th) = t(int) + t/100(t/100-1)\ (.04217 - .00007481t)$$

$$T = t(th) + 273.16.$$

Table (IX)

Second and Third Virial Coefficients of Ammonia

$$pV = RT + B(T)/V + C(T)/V^2 + D(T)/V^4$$

Temp. °C (Int.)	B(T) liter^2-atmos. per mole^2	C(T) liter^3-atmos. per mole^3	D(T) x10^4 liter^5-atmos. per mole^5
150	-3.4547566	+ 0.15603054	-2.1783784
175	-3.1496547	+ 0.14002648	-2.1234934
200	-2.8957059	+ 0.13024572	-2.3200428
225	-2.6629700	+ 0.11974363	-2.1121777
250	-2.4667501	+ 0.11546634	-2.3804932
275	-2.2741257	+ 0.11003279	-2.3999670
300	-2.1607335	+ 0.11932069	-3.5284451

Table (X)

Comparison of the Observed Second Virial Coefficients with those Calculated Using Stockmayer's Potential for Polar Gases, for Gaseous Ammonia.

T° (therm.)	B(T), cc/mole present investigation	B(T), cc/mole Lawrence	B(T), cc/mole calculated
423.183	99.5	99.7	99.3
448.198	85.6	85.7	86.4
473.214	74.6	74.7	74.6
498.231	65.1	65.4	65.4
523.248	57.5	57.5	57.5
548.264	50.6	50.7	50.6
573.278	45.9	44.5	45.9

The average deviation is ± 0.2 cc/mole

Table XI

The Parameters Used for the Fitting of the Stockmayer Potential Are:

$t_1 = 1.2$

$\varepsilon'/k = 284.6$

$b_o = 20.17\ \mathrm{cm}^3/\mathrm{mole}$

$r_o = 2.5190\ \mathrm{x}10^{-8}\ \mathrm{cm}.$

$\varepsilon' = 3.9289\ \mathrm{x}10^{-14}$ ergs/degree

$p = 1.46$ Debeye

In the curve fit it was necessary to assume at one stage that the values B(T) could be represented by the equation:

$$B(T) = AT^s$$

and a plot is made of log B(T) against log.T, and the slope of the best straight line is then given by s. This quantity is necessary in the curve fitting process so it is given here:

$$s = 2.6$$

B. Third Virial Coefficient for Ammonia and Stockmayer's Potential.

C(T), the third virial coefficient, provides a more severe test of molecular models than the second virial coefficient B(T), in that it is more sensitive to the shape of the potential. This will be seen in the comparison that is made between the agreement of the observed values of the second virial coefficients and those obtained from the Stockmayer or Lennard-Jones potential with the agreement obtained between the observed values of the third virial coefficients and those calculated using the Stockmayer or Lennard-Jones potential.

The third virial coefficient is given by:

$$C(T) = - N^2/3 \iint f_{12} f_{13} f_{23} \, dr_1 \, dr_2 \qquad (11)$$

where;

$$f_{ij} = (\exp(-W(q)ij/kT - 1)$$

where W(q)ij is the energy of interaction of molecule i and j and depends on their distance apart and their relative orientation and is given by equation (5).

Hirschfelder, Bird, Spotz, and Curtiss (23) have calculated the third virial coefficients for gases obeying the Lennard-Jones potential,

$$W(q)/kT = (4/\tau') \left[R_{ij}^{-12} - R_{ij}^{-6} \right] \qquad (12)$$

using high speed calculators. Rowlinson (23) has carried out the calculations for the polar part so that combining the work of Hirschfelder, Bird, Spotz, and Curtiss with his own, he constructed a table of values for the third virial coefficients for the Stockmayer potential in terms of the parameters t_1 and τ, which parameters are obtained on fitting the second virial coefficient.

In Table XII are given the third virial coefficients as determined from experiment by the method of least squares, and the third virial coefficient as determined by the calculations of Rowlinson et al.

The agreement between the observed and the calculated third virial coefficients may be considered fair. One must take into account firstly that the accuracy of the calculated values is not given in Rowlinson's paper. Secondly, the experimental values of the third virial coefficient were obtained from a three turn polynomial, while generally good enough to give B(T), it does not yield the best values of C(T). If one looks, for example, at the values of B(T) and C(T) obtained from experimental measurements by Hirschfelder et al., one sees that with more terms in the polynomial the second virial coefficient changes very little whereas there are sizable changes in the values of C(T) (23).

Table XII

Comparison of the Measured Third Virial Coefficients With Those Calculated Using Stockmayer's Potential for Polar Gases, for Gaseous Ammonia.

T^{o} (therm.)	C(T) $cc^2/mole^2$ observed	C(T) $cc^2/mole^2$ calculated
423.183	4493.4	3300
448.198	3807.5	2970
473.214	3354.3	2630
498.231	2929.0	2300
523.248	2689.3	2020
548.264	2445.9	1800
573.278	2536.6	1610

C. Second Virial Coefficients from the Lennard-Jones Potential.

For comparison with the Stockmayer potential, calculations of the second virial coefficient of ammonia were made for the Lennard-Jones potential (25) which may be written as:

$$W(q) = \lambda r^{-12} - \mu r^{-6}$$

$$= 4\varepsilon\left[(\sigma/r)^{-12} - (\sigma/r)^{-6}\right]$$

$$\varepsilon = \lambda/\mu 4 \quad \text{ergs}$$

$$\sigma^6 = \lambda/\mu \quad \text{cm.}^6$$

$$\theta = \varepsilon/k \quad {}^{\circ}K$$

$$\beta = 2\pi N \sigma^3/3$$

The method used for obtaining the parameters of the potential was the one given by Stockmayer and Beattie (26) who found that in the range of θ/T of 0.2 to 1.0, B(T) could be represented by the equation:

$$B(T) = \beta\left(\frac{\theta}{T}\right)^{1/4}(1.064 - 3.602\ \theta/T) \qquad (14)$$

From a plot of $BT^{1/4}$ against $1/T$ β and θ may be determined since $-3.602\beta\theta^{5/4}$ is the slope and $1.064\beta\theta^{1/4}$ is the intercept on the $BT^{1/4}$ axis at $1/T = 0$ of the best straight line through the experimental points.

From a graph obtained by the method mentioned above it was

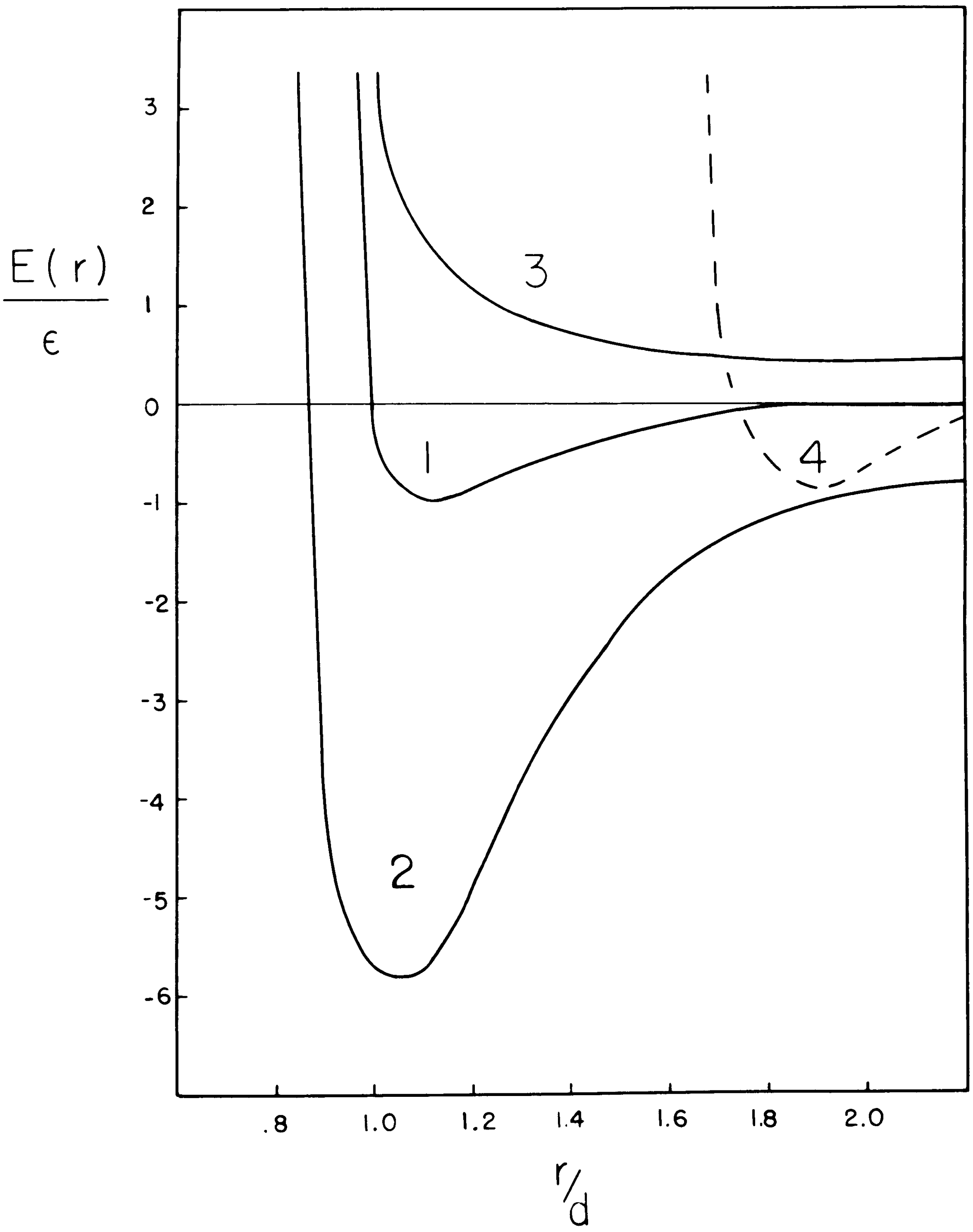


Figure 1

found that

$$-369.003 = -3.602\,\beta\,\Theta^{5/4}$$

and

$$428.8 = 1.064\,\beta\Theta^{1/4}$$

then

$$\Theta = 254.199$$

$$\beta\Theta^{1/4} = 403.0$$

and then the equation becomes

$$B(T) = 403.0/T^{1/4}(1.064 - 915.621/T) \quad (15)$$

which was used to calculate the second virial coefficients.

The results are shown in Table XII and these are compared with the observed second virial coefficients whence it is found that the average over-all deviation is ±0.84 cc/mole.

In Table XIII the parameters of the Lennard-Jones potential are given. From these parameters, curve 4 of figure 1 was plotted. Here it may be noticed that, although the value of ε obtained using Stockmayer's potential has nearly the same value as that obtained using the Lennard-Jones, r_0, the value of r when $E(r) = 0$, is nearly twice as large for the Lennard-Jones potential.

The second virial coefficient is not nearly so sensitive to the form of the potential energy function used as is the third. Thus we find that the calculated values of the second virial coefficient using the Lennard-Jones potential gives almost as good agreement with observed values as does Stockmayer's. However, great differences are encountered on examining the third virial coefficient.

Table XIII

Comparison of the Observed Second Virial of Ammonia With Those Calculated Using the Lennard-Jones Potential

T° (therm.)	B(T) cc/mole Observed	B(T) cc/mole Calculated
423.183	99.5	97.7
448.198	85.6	85.7
473.214	74.6	75.3
498.231	65.1	66.0
523.248	57.5	57.8
548.264	50.6	50.5
573.278	45.9	43.9

Over-all average deviation is ±0.84

Table XIV

Lennard-Jones Parameters

$\varepsilon = 350.9203 \times 10^{-16}$ ergs

$\mu = 8.9860 \times 10^{-58}$ ergs cm^6

$\lambda = 5.7526 \times 10^{-102}$ ergs cm^{12}

$\sigma = 4.3091$ Å

$r_o = 2^{1/6}\sigma = 4.8368$ Å

Where

$N = 6.023 \times 10^{23}$

$k = 1.3805 \times 10^{-16}$ erg deg.$^{-1}$

were obtained from Birge (45).

D. Third Virial Coefficient from the Lennard-Jones Potential.

Using the parameters obtained by fitting the Lennard-Jones potential for the second virial coefficients and the tables set up by Hirschfelder, Bird, Spotz, and Curtiss (23), the third virial coefficients were calculated. These calculated values are given in Table XV.

The agreement between the observed and the calculated values of the third virial coefficients, as is shown in Table XV, is quite poor. One may say, therefore, on comparing the agreement found here with that found using the Stockmayer potential, that this latter potential is the more realistic one in this case.

Table XV

Comparison of the Observed and the Calculated Third Virial Coefficients for Gaseous Ammonia Using the Lennard-Jones Potential

T° (therm.)	$C(T)$ $cc^2/mole^2$ Observed	$C(T)$ $cc^2/mole^2$ Calculated
423.183	4,500	10,250
448.198	3,800	9,800
473.214	3,400	9,400
498,231	2,900	9,000
523.248	2,700	8,700
548.264	2,400	8,500
573.278	2,500	8,200

V. Compressibility and Equation of State for the Gas Mixture Ammonia-Methane

A. Introduction

The methane used in this investigation was obtained from the Phillips Petroleum Company and had the stated purity of 99.5%. The gas was further purified by low temperature fractionation as described in Appendix (C). The ammonia was obtained from the Matheson Corporation and purified in a manner as described above and in Appendix (C).

The mixture reported on here consisted of 29.849 mole per cent ammonia and 70.151 mole per cent methane. The measured compressibility of this mixture is given in Table XVI.

Here, as in the case of the measurements on the pure ammonia, decomposition was found to occur at the higher temperatures amounting to 0.17% at the highest temperature, i.e., at 300°, and becoming progressively less at the lower temperatures, being negligible at 250° and below.

B. Non-Polar Combination

The equation of state constants for the mixture, A_{om}, a_m, B_{om}, b_m and c_m were obtained in two different ways. In the first method, using what we termed to be the non-polar combining rules, A_{o12} and c_{12} were obtained by a square-root method, B_{o12} from a Lorentz combination, and a_{12} and b_{12} from a linear combination of the equation of state constants of the pure components, methane and ammonia.

Thus;

$$A_{om} = (\Sigma_i x_i A_{oi}{}^{1/2})^2$$

$$B_{om} = 1/8 \Sigma_i \Sigma_j x_i x_j \ (B_{oi}{}^{1/3} + B_{oj}{}^{1/3})^3 \qquad (16)$$

$$= x_1^2 B_{o1} + 1/4 x_1 x_2 (B_{o1}^{1/3} + B_{o2}^{1/3})^3 + x_2^2 B_{o2}$$

$$c_m = (\sum_i x_i c_i^{1/2})^2$$

$$a_m = x_1 a_1 + x_2 a_2$$

$$b_m = x_1 b_1 + x_2 b_2$$

so that the equation of state for n_i moles of gas may be written as;

$$p = \frac{\sum_i n_i RT}{V} + \frac{(\sum_i n_i)^2 \beta_m}{V^2} + \frac{(\sum_i n_i)^3 \gamma_m}{V^3} + \frac{(\sum_i n_i)^4 \delta_m}{V^4} \qquad (17)$$

$$\beta_m = RTB_{om} - A_{om} - \frac{RC_m}{T^2}$$

$$\gamma_m = RTB_{om} b_m + A_{om} - \frac{RB_{om} c_m}{T^2}$$

$$\delta_m = \frac{RB_{om} b_m c_m}{T^2}$$

General physical considerations indicate the square root combination for the attractive constant A_o, which corresponds to the a in Vander Waals equation, and the Lorentz for the repulsive constant B_o, which corresponds to b in the Van der Waals equation, this latter type of combination corresponding to the averaging of the radii of the molecules.

In addition, in a study on the compressibility of gaseous mixtures of methane and normal butane, Beattie, Stockmayer, and Ingersoll (27) found that the above combination rules could be used to reproduce the compressibilities of the mixtures almost as well as the equation of state represented the properties of the pure gases.

Before these rules could be applied to the mixture reported here, the equation of state constants for the pure methane had to be corrected for the revised atomic weights of the element. In the 1950 report of the Committee on Atomic Weights of the American Chemical Society (28), the atomic weight of carbon is given as 12.010 grams and that of hydrogen as 1.008 grams. This gives for the molecular weight of methane 16.042 grams. The equation of state constants for methane calculated by Beattie and Bridgman were based on a molecular weight of 16.0308 grams. This meant that all of the constants had to be recalculated on the basis of the new molecular weights. Dimensional analysis shows that R, a, b, B_o, and c may be corrected by multiplying these constants by the ratio of the molecular weights and that A_o, which is given in terms of liters ^{2}-atmos. per mole^2 had to be corrected by multiplication by the square of the ratio of the molecular weights. This was done by Stockmayer (11) and the corrected constants for methane are given in Table XV.

In Table XVII there may be found the measured compressibilities of the gas mixture and the deviation of the observed pressures from those calculated using the "non-polar" combination rules, as set out in equation (16) above, are given in Table XVIII. Here it is found that the average over-all percent deviation is 1.07.

The equation of state constants for the mixture using the "non-polar" combination rules are given in Table XIX.

Table (XVI)

Compressibility of the Gaseous Mixture Methane-Ammonia
Consisting of 29.849 Mole Per Cent Ammonia and
70.151 Mole Per Cent Methane

Temp. °C (int.)	150	175	200	225	250	275	300
Density, moles/liter	Pressure, standard atmosphere						
1.0	33.89	36.06	38.22	40.37	42.51	44.68	46.83
1.5	50.34	53.69	57.03	60.35	63.66	67.02	70.33
2.0	66.52	71.12	75.70	80.24	84.78	89.37	93.91
2.5	82.49	88.39	94.28	100.10	105.91	111.80	117.63
3.0	98.27	105.56	112.81	119.98	127.13	134.39	141.61
3.5	113.92	122.66	131.34	139.92	148.48	157.18	165.83
4.0	129.51	139.75	149.94	159.97	170.02	180.18	190.33
4.5	145.06	156.90	168.64	180.22	191.81	203.53	215.23
5.0	160.64	174.12	187.50	200.67	213.87	227.25	240.55
6.0	192.11	209.13	225.95	242.58	259.18	276.02	292.84
7.0	224.37	245.21	265.83	286.15	306.55	327.15	347.71
8.0	257.94	282.99	307.72	332.05	356.53	381.17	405.87
9.0	293.30	323.02	352.16	380.91			
10.0	331.17	365.85	399.89				

Table (XVII)

Comparison of the Pressures Calculated from the "Non-Polar" Combining Rules with the Observed Pressures for the Gaseous Mixture 29.849 Mole Per Cent Ammonia, 70.151 Mole Per Cent Methane

Temp. °C (int.)		150	175	200	225	250	275	300
Density, mole/liter		Pressures, standard atmospheres						
1.0	obsd.	33.89	36.06	38.22	40.37	42.51	44.68	46.83
	obsd.-calc.	+0.14	+0.10	+0.06	+0.02	-0.04	-0.06	-0.11
1.5	obsd.	50.34	53.69	57.03	60.35	63.66	67.02	70.33
	obsd.-calc.	+0.37	+0.30	+0.23	+0.14	+0.05	+0.01	-0.07
2.0	obsd.	66.52	71.12	75.70	80.24	84.78	89.37	93.91
	obsd.-calc.	+0.69	+0.59	+0.47	+0.33	+0.19	+0.10	-0.03
2.5	obsd.	82.49	88.39	94.28	100.10	105.91	111.80	117.63
	obsd.-calc.	+1.12	+0.95	+0.79	+0.57	+0.35	+0.22	+0.04
3.0	obsd.	98.27	105.56	112.81	119.98	127.13	134.39	141.61
	obsd.-calc.	+1.62	+1.40	+1.16	+0.87	+0.57	+0.39	+0.18
3.5	obsd.	113.92	122.66	131.34	139.92	148.48	157.18	165.83
	obsd.-calc.	+2.19	+1.90	+1.59	+1.20	+0.82	+0.60	+0.34
4.0	obsd.	129.51	139.75	149.94	159.97	170.02	180.18	190.33
	obsd.-calc.	+2.85	+2.47	+2.08	+1.58	+1.12	+0.80	+0.49
4.5	obsd.	145.06	156.90	168.64	180.22	191.81	203.53	215.23
	obsd.-calc.	+3.57	+3.11	+2.62	+2.02	+1.47	+1.08	+0.69
5.0	obsd.	160.64	174.12	187.50	200.67	213.87	227.25	240.55
	obsd.-calc.	+4.35	+3.79	+3.21	+2.48	+1.83	+1.40	+0.92
6.0	obsd.	192.11	209.13	225.95	242.58	259.18	276.02	292.84
	obsd.-calc.	+6.13	+5.39	+4.56	+3.64	+2.75	+2.18	+1.63
7.0	obsd.	224.37	245.21	265.83	286.15	306.55	327.15	347.71
	obsd.-calc.	+8.21	+7.25	+6.24	+5.06	+4.06	+3.35	+2.68
8.0	obsd.	257.94	282.99	307.72	332.05	356.53	381.17	405.87
	obsd.-calc.	+10.67	+9.58	+8.38	+6.97	+5.85	+5.02	+4.34

Table XVIII

Deviations "non-polar" Combination

Density, moles/liter	Av. dev. (atmos.)	Av. per cent dev.
1.0	.076	.194
1.5	.167	.303
2.0	.343	.467
2.5	.577	.629
3.0	.884	.799
3.5	1.234	.954
4.0	1.627	1.100
4.5	2.080	1.248
5.0	2.569	1.384
6.0	3.754	1.671
7.0	5.264	1.979
8.0	7.529	2.339

Total average deviation (atmos.) from 1 to 8 moles per liter = 2.153

Total average per cent deviation from 1 to 8 moles per liter = 1.089

Table XIX

Equation of State Constants Obtained by Using the "Non-Polar" Combining Rules on the Pure Gases, Methane and Ammonia

	Methane	Ammonia	Mixture
R	0.082117	0.08206	0.08210
A_o	2.2801	5.936	3.19165
B_o	0.05591	0.08970	0.065441
b	-0.01588	0.05281	0.004623
a	0.01856	0.05244	0.028673
c	12.84×10^4	100×10^4	30.2348×10^4

C. Polar Combining Rules

The set of combining rules given above made no special concessions for the fact that one of the species present in the mixture was polar. Stockmayer (29) arrived at a method for combining equation of state constants for polar gas mixtures from considerations based on the evaluation of the second virial coefficient of polar gases. The potential he used was quite similar to (5) above with the repulsive term omitted. The potential he used may be written as;

$$W(q) = \kappa r^{-6} - p^{2} g r^{-3} \qquad (r \geqslant r_0)$$

$$W(q) \rightarrow \infty \qquad (r < r_0)$$

Substituting this potentia 1 in equation (8) gives for the solution of the second virial coefficient, B(T) ,

$$B(T) = (2\pi N r_0^3/3) \left[1 - \sum_{n=1}^{\infty} \sum_{m=0}^{\leq n/2} Q_{mn} \, (\kappa/r_0^6 kt)^n \left[p^2 r_c^3/\kappa\right]^{2m} \right] \quad (18)$$

where N is Avogodro's number, k is the Boltzmann constant and Q_{mn} are numbers whose definition need not be given here. This equation may be rewritten with abbreviations to give:

$$B(T) = (2\pi N\sigma^3/3) \left[1 - yF(yx) \right] \quad (19)$$

$$y = \kappa/r_0^6 \, kT$$

$$x = p^2 \sigma^3/\kappa$$

and

$$F(xy) = \sum_{n=0}^{\infty} \sum_{m=0}^{m \leq n/2} Q_{mn} \, y^{n-1} x^{2m}$$

He compared the form of B(T) given in equation (19) above with that obtained from the Beattie-Bridgman equation of state where;

$$B(T) = B_o - A_o/RT - c/T^3 \qquad (20)$$

or more exactly with the form given by Keyes (30)

$$B(T) = B_o - A/RT \exp D/T^2 \qquad (21)$$

For non-polar substances, these two forms are essentially equivalent. Then, as will be seen, A is equal to A_o and D is equal to D_o, substituting for D_o the quantity Rc/A_o and expanding the exponential of equation (21) keeping the first two terms we get (20). It should be noted here, however, that this latter step is strictly true only when Rc/A_oT^2 is small, as is usually found for non-polar substances.

For the theoretical equation (19) to be in accord with the empirical equation (21) it is necessary that log F(xy) be a linear function of y^2 for constant x. This indeed was found for a given range of temperatures, which is in the region of experimental investigation. A more detailed study of the function log F(xy) showed that the function F(xy) could adequately be represented over the range mentioned above by the equation;

$$F(xy) = (1.160 + 0.282x^2) \exp (0.067y^2 + 0.159x^2y^2) \qquad (22)$$

This equation is to be compared with (21) whence B_o, A, and D can be related to the parameters k, r_o, and p. It was thus evident that A and D could be written as a sum of two parts one of which depends on and r_o and this may be called the non-polar part, and the other which depends on p^2 and may be called the polar part i.e.,

$$A = A_o + A_{polar} \qquad (23)$$

$$D = D_o + D_{polar}$$

Further identification of the equations listed above leads to the following relationships:

$$B = 2\pi N r_o^3 /3$$

$$A_o/RB_o = 1.16\kappa /r_o^6 k$$

$$A \text{ polar}/RB_o = 0.282p^4 /\kappa k \qquad (24)$$

$$D_o = 0.067 (\kappa/\sigma^6 k)^2$$

$$D\text{polar} = 0.159 (p^2/\sigma^3 k)^2$$

Since only A and D and not their component are determined when using Keyes empirica l equation for B(T) (21), a knowledge of p is needed before A_o, A_p, and D_o and D_p can be calculated. Assuming p to be known, then these constants are given by:

$$A_o = 1/2 (A + (A^2 - 0.756p^4)^{1/2})$$

$$A_p = 1/2(A - (A^2 - 0.756p^4)^{1/2}) \qquad (25)$$

$$D_p = 13.6p^4/B_o^2$$

$$D_o = D - D_p$$

This last set of equations can be obtained from the equations already given by some manipulation. The constants A and A_o are in the units of liters^2-atmos. pe5 mole^2, B_o in liters per mole, and p is in Debeye units (10^{-18}e.s.u.).

The method used for combining the constants was to combine A_{o1} and

A_{o2} quadratically, B_1 and B_2 by a Lorentz combination, a_{12} and b_{12} were obtained by a linear combination. A little more work was required to get c_{12}. To calculate c_{12} we first calculate D_{01} and D_{o2} from the following equations:

$$D_1 = Rc_1/A_1$$

$$D_2 = Rc_2/A_2$$

Then D_{p1} was calculated from,

$$D_{p1} = 13.6\ p^4/\ B_o^2$$

and

$$D_{o1} = D_1 - D_{p1} \tag{26}$$

where subscript 1 stands for ammonia and 2 for methane. So that

$$D_{p2} = 0 \quad \text{and } A_{p2} = 0$$

and (27)

$$D_{02} = Rc_2/A_2$$

Then the interaction constants were obtained in the following way:

$$D_{o12} = (D_{o1} \times D_{o2})^{1/2}$$

$$D_{p12} = (D_{p1} \times D_{p2})^{1/2} = 0$$

$$A_{p12} = (A_{p1} \times A_{p2})^{1/2} = 0 \tag{28}$$

$$A_{o12} = (A_{o1} \times A_{o2})^{1/2}$$

so that the c_{12} constant is obtained by

$$c_{12} = \frac{A_{012} \quad D_{012}}{R} \tag{29}$$

From the above sets of equations the equation of state constants were obtained from the following:

$$\begin{aligned} A_{om} &= x_1^2 A_{o1} + 2x_1x_2A_{o12} + x_2^2 A_{o2} \\ cm &= x_1^2 c_{o1} + 2x_1x_2c_{o12} + x_2^2 c_{o2} \\ B_{om} &= x_1^2 B_{o1} + 1/4x_1x_2(B_{o1}^{1/3} + B_{o2}^{1/3})^3 + x_2^2 B_{o2} \\ a_m &= x_1 a_1 + x_2 a_2 \\ b_m &= x_1 b_1 + x_2 b_2 \end{aligned} \tag{30}$$

Using this last set of equations a set of equation of state constants were calculated whose values are given in Table XX.

The values of the pressures calculated from these equation of state constants are compared with those measured in Table XXI. In the following table the average deviation in the pressures is given and the average per cent deviations are given for each of the isometrics. Here it is seen that the over-all per cent deviation has been reduced from 1.08% to 0.70% or an improvement in the fit of better than 0.3%.

In view of Rowlinson's recent work on the third virial coefficient for polar gases (24), the combining rules for polar gases ought to be re-examined. At the time Stockmayer published his set of combining rules only the second virial coefficients for polar gases had been worked out. Thus these rules did not take into account the effects of the third virial coefficient. When due account is taken of the third virial coefficient, it is hoped that the combining rules obtained will allow one to calculate more accurately the pressures of polar mixtures.

Table (XX)

Equation of State Constants Obtained on Applying the Stockmayer "Polar" Combining Rules

$A_{om} = 3.17227$

$a_m = 0.028673$

$B_{om} = 0.065441$

$b_m = 0.004623$

$c_m = 25.1068 \times 10^4$

Table (XXI)

Comparison of the Pressures Calculated from the Stockmayer Combining Rules with the Observed Pressures for the Gaseous Mixture 29.849 Mole Per Cent Ammonia, 70.151 Mole Per Cent Methane

Temp. °C (int.)		150	175	200	225	250	275	300
Density, mole/liter		Pressures, standard atmospheres						
1.0	obsd.	33.89	36.06	38.22	40.37	42.51	44.68	46.83
	obsd.-calc.	+0.09	+0.06	+0.03	-0.02	-0.08	-0.10	-0.14
1.5	obsd.	50.34	53.69	57.03	60.35	63.66	67.02	70.33
	obsd.-calc.	+0.27	+0.21	+0.14	+0.06	-0.03	-0.06	-0.15
2.0	obsd.	66.52	71.12	75.70	80.24	84.78	89.37	93.91
	obsd.-calc.	+0.51	+0.42	+0.32	+0.18	+0.05	-0.03	-0.16
2.5	obsd.	82.49	88.39	94.28	100.10	105.91	111.80	117.63
	obsd.-calc.	+0.84	+0.69	+0.54	+0.33	+0.13	-0.01	-0.17
3.0	obsd.	98.27	105.56	112.81	119.98	127.13	134.39	141.61
	obsd.-calc.	+121	+1.01	+0.80	+0.52	+0.24	+0.08	-0.11
3.5	obsd.	113.92	122.66	131.34	139.92	148.48	157.18	165.83
	obsd.-calc.	+1.62	+1.37	+1.09	+0.74	+0.38	+0.17	-0.07
4.0	obsd.	129.51	139.75	149.94	159.97	170.02	180.18	190.33
	obsd.-calc.	+2.10	+1.77	+1.43	+0.96	+0.54	+0.24	-0.05
4.5	obsd.	145.06	156.90	168.64	180.22	191.81	203.53	215.23
	obsd.-calc.	+2.61	+2.23	+1.79	+1.24	+0.72	+0.37	+0.02
5.0	obsd.	160.64	174.12	187.50	200.67	213.87	227.25	240.55
	obsd.-calc.	+3.16	+2.69	+2.17	+1.50	+0.91	+0.52	+0.09
6.0	obsd.	192.11	209.13	225.95	242.58	259.18	276.02	292.84
	obsd.-calc.	+4.39	+3.77	+3.05	+2.21	+1.41	+0.90	+0.41
7.0	obsd.	224.37	245.21	265.83	286.15	306.55	327.15	347.71
	obsd.-calc.	+5.79	+5.01	+4.15	+3.10	+2.21	+1.60	+1.01
8.0	obsd.	257.94	282.99	307.72	332.05	356.53	381.17	405.87
	obsd.-calc.	+7.45	+6.60	+5.62	+4.38	+3.42	+2.71	+2.15

Table (XXIa)

Deviations, Stockmayer combination

Density, moles/liter	Av. dev. (atmos.)	Av. percent dev.
1.0	.074	.182
1.5	.131	.232
2.0	.239	.324
2.5	.387	.426
3.0	.567	.522
3.5	.777	.615
4.0	1.013	.703
4.5	1.283	.791
5.0	1.577	.872
6.0	2.306	1.051
7.0	3.267	1.253
8.0	4.619	1.509

Total average deviation (atmos.) from 1 to 8 moles per liter is 1.353

Total average percent deviation from 1 to 8 moles per liter is .707

A. Apparatus

1. Introduction

The compressibility apparatus used in this laboratory is described by J.A. Beattie (31) in the literature.

Figure (2) gives a general diagram of the apparatus. In this figure is shown the compressibility bomb, F, whose volume is about 200 cc. enclosed in the thermostat, G. The volume of the bomb is controlled by the introduction of mercury from the compressor, C, which is located in an oil bath regulated at 30° C. The compressor is connected to the bomb by means of a series of steel capillaries as shown. The temperature of the thermostat is controlled by means of the platinum resistance thermometer, T'. Temperatures are measured by the platinum resistance thermometer T. Pressures are measured on an Amagat type gauge shown at B. The pressure is transmitted from the bomb to the tip of the needle in the riser-block, D, by mercury, and from here to the gauge by oil.

2. Measurement of pressure

The pressure is measured on an Amagat dead weight gauge. The model used in this laboratory is the one developed by F.G. Keyes (32).

Pressure is transmitted from the tip of the needle in the riser-block, D, to the gauge by means of oil. The piston floats in oil in the close fitting cylinder. On top of the cylinder rests a cross arm to which the scale pans are connected. Onto these scale pans are placed the weights to balance the pressure exerted by the gas. These weights are then converted to normal atmospheres by multiplication by the gauge constant which is determined from the vapor pressure of pure carbon dioxide at 6° C. The vapor pressure at this temperature is taken as 34.401 normal atmospheres.

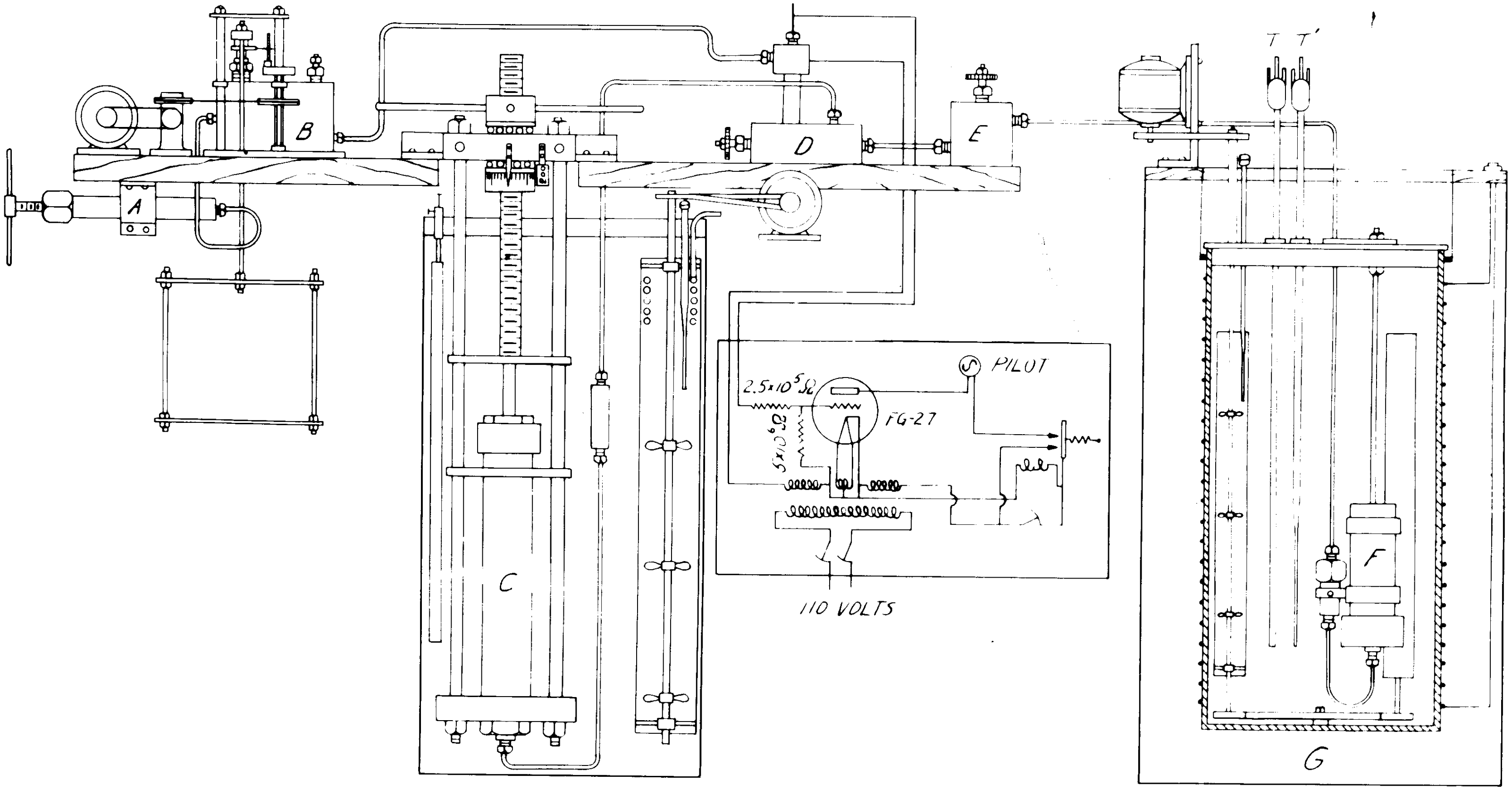


Figure 2.

In order to insure that the piston will float freely in the oil, it is rotated backwards and forwards 30 times a minute through an angle of 60°. At the end of each stroke there is a short time during which the piston is floating freely in the oil, as may be shown by the breaking of an electrical circuit.

A small amount of oil is continuously leaking out from around the piston. This oil is replaced by means of the oil injector shown in figure (1) at A.

The riser-block, D, is used for the detection of pressure equilibrium. It consists of a steel tube 3/16 " inner diameter into the top of which projects an electrically insulated needle. Just above the tip of the needle is the oil which transmits the pressure to the gauge, below the oil is the mercury. A balance is reached when the oil mercury interface is located so that there is a making and breaking of electrical contact in the grid circuit of the thyratron. This may be seen by the flickering of pilot light.

The pressure exerted by the gas is given by the relation;

$$P_{gas} = P + P_{bar.} + P_{level} + P_{mem.} - P_{hg.}$$

1) P is the pressure measured at the Amagat gauge.

2) $P_{bar.}$ is the barometric pressure which is read from a barometer to the nearest tenth of a millimeter.

3) P_{level} is the correction for differences in oil levels and mercury levels, reduced to normal atmospheres. The oil head is very small. The mercury head correction is divided into two parts, first, the height of the mercury column at room temperature, and secondly the height of the column at the temperature of the bath.

The mercury level inside the steel bomb is calculated from the sectional area of the bomb. These heights were read off a plot determined by Hadlock (33). In this plot the distance from the top surface of the steel bomb to the mercury surface inside the bomb is plotted against the gas volume, mv.

4) $P_{meniscus}$ is a 1 mm. correction for the capillary depression at the oil-mercury surface in the riser block.

5) $P_{Hg.}$ is the vapor pressure of mercury corrected for the effect of pressure, i.e.,

$$2.303 \log_{10} \frac{P_{Hg.}}{P_{oHg.}} = V(P_{gas} - P_{oHg.})$$

P_{oHg} is the vapor pressure of mercury at the temperature of the bath and is obtained from the International Critical Tables. V is the molal volume of mercury at T^{o} K.

At each temperature the pressures are measured for the densities of from 1 to ten moles per liter with increasing densities and checked by repeating the measurements for decreasing densities.

The over-all accuracy of the pressure measurements is from .01% in the low pressure region and room temperature to .03% in high pressure, high temperature region.

3. Control and measurement of volume.

Volume is controlled and measured by the addition or removal of mercury, by means of the compressor, C, as shown in Figure 2. The compressor consists of a cold rolled steel cylinder 1 1/16" internal diameter into which fits a smooth piston made of one inch drill rod. The piston enters the cylinder through a packing gland at the top, this packing gland is made tight by cloth dipped into ceresine wax which is confined between hard rubber rings and compressed between steel rings by a cap nut. The piston is pinned to 1 1/2" threaded rod which passes through a Tobin bronze nut. A guide plate at the junction of the piston and threaded rod keeps the piston from rotating and allows vertical travel only. A heavy yoke keeps the assembly firmly anchored together. The Tobin bronze nut is turned between two roller bearings by five attached spokes. To the nut is geared a revolution counter and from a calibrated dial on the nut, thousandths of a turn can be estimated. A steel capillary of 1/8" diameter runs from the bottom of the bomb to the riser block and then to the bomb. The piston, as stated above, is one inch in diameter and has a vertical travel of 16 3/8", which corresponds to about 294 turns of the nut and to about 210 cc.'s of mercury.

The compressor is set in an oil bath which is regulated to a temperature of 30° with a maximum variation of .005° C. The temperature in the bath is measured on a Beckman thermometer which was calibrated against the platinum resistence thermometer.

The cumulative volume, V, of mercury forced out at 30°C. and one atmosphere is expressed by the equation:

$$V = ac + dc$$

where a and d are constants determined by calibration and c is the number of turns.

Since, in this work it is desirable to obtain compressibility measurements along isometrics as well as along the isothermals, it is necessary to set a series of volumes. This is done by calculating the compressor settings from the following formula:

$$V_{p,t} = ac + dc = V_b - mvd_t/d_{30} - \Delta V - D_1 + D_2 + D_3 \qquad (32)$$

V_b is the bench volume (See appendix B on calibrations). m is the number of moles of substance in the bomb, v is the specific molal volume. Thus mv is the desired volume for the sample of gas; d_t is the density of the mercury at t°C, d_{30} is the density at 30°C.

ΔV is the correction determined in the blank run for the effect of the bomb temperature t and the pressure p on the setting of the mercury compressor.

D_1 is the correction for the change of compressibility of the steel piston withdrawn. This is calculated knowing the compressibility of mercury ($1/V \frac{\partial}{\partial T}\left(\frac{\partial V}{\partial p}\right)$) which is 5.5×10^{-9} per atmosphere per degree centigrade, and from the compressibility ($1/V \frac{\partial V}{\partial p}$) of steel which is 5.8×10^{-7} per atmosphere. Thus the following formula is used to calculate D_1:

$$D_1 = \left[5.8 \times 10^{-7} + 5.5 \times 10^{-9}\,(t-30)\right](p-1)\,mv \qquad (33)$$

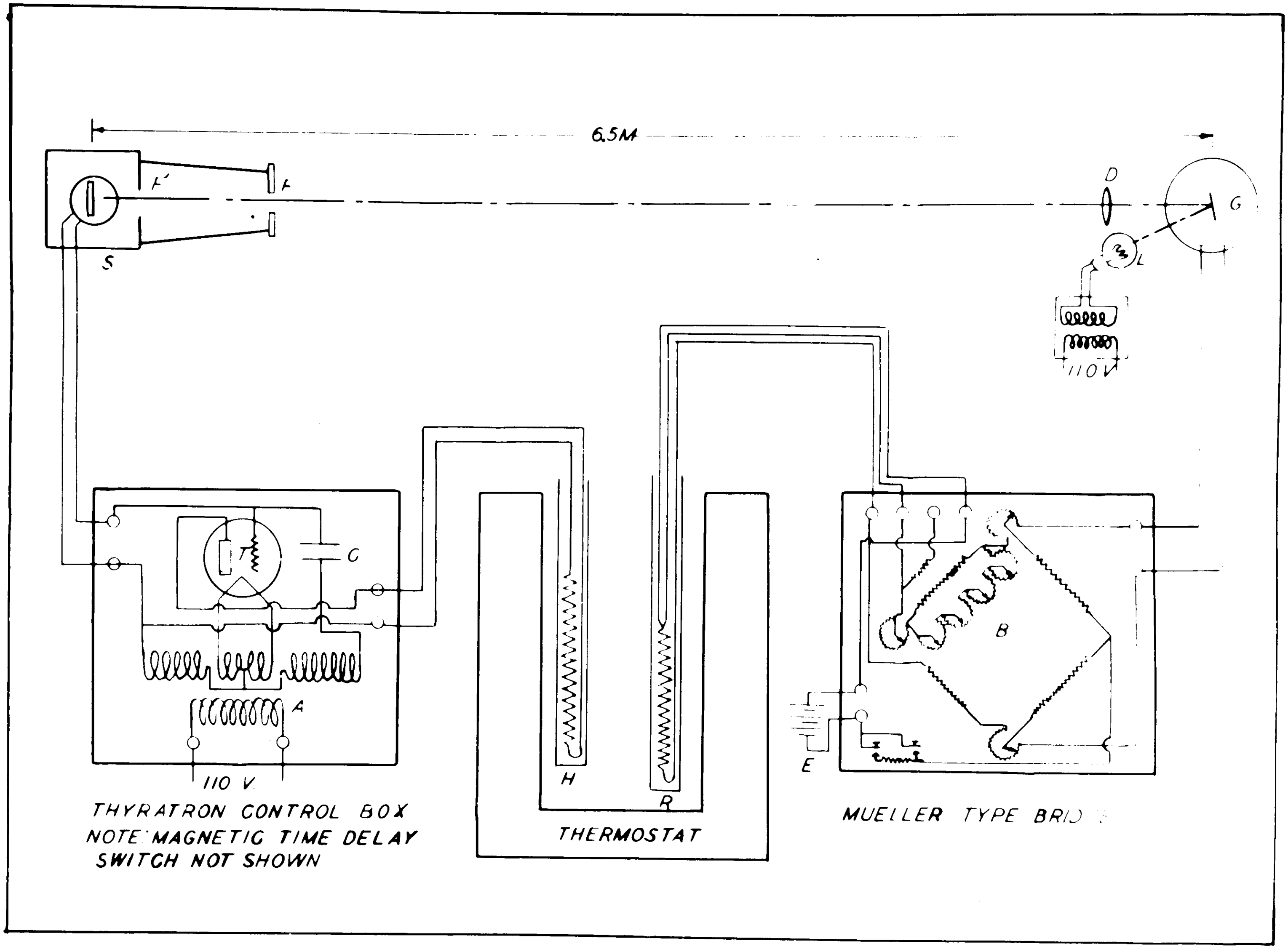
D_2 corrects for the volume of liquid mercury lost as vapor, for the determination the relation used is:

$$D_2 = \frac{200.6\ p_{hg.}\ mv}{RT\,d_t} \qquad (34)$$

where $p_{hg.}$ is the vapor pressure of mercury at T° K and a total pressure p. This correction is negligible for temperatures below 200° C.

D_3 is the correction for the variation with temperature of the volume (2.4 cc.'s) of mercury in the riser block, bomb stop cock, and capillaries, at room temperature, and amounts to .004 ml/°C.

D_1, D_2, and D_3 are all very small and can be calculated with a certainty

6.5M
F'
F
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D
G
L
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T
C
A
110 V
THYRATRON CONTROL BOX
NOTE MAGNETIC TIME DELAY
SWITCH NOT SHOWN
H
R
THERMOSTAT
B
E
MUELLER TYPE BRI

Figure 3

of .001 ml. The largest uncertainties and the most difficult to estimate are in the estimation of the volume. Due to hysteresis, it is felt that the volume can be measured to no better than .05% at the higher pressures and quite often the uncertainty is as great as .1%.

4). Temperature control.

The temperature control system is shown in figure (3). A flat type platinum resistance thermometer, R, is placed in the bath and its resistance is balanced on a Wheatstone bridge which is connected to a galvanometer, C. A beam of light from a source, L, reflects from the galvanometer mirror to a selenium cell, S, in a dark box 6.5 meters away. The variation of resistance of the selenium cell, with light intensity, is used to control the current input to the internal heater, H, by means of a phase shifting thyratron circuit, In addition there are external heaters which are operated manually with a 5 ampere variac. The external heaters are used to bring the bath up to about one degree of the desired temperature when the regulating circuit is brought in for the final control. The temperature can be controlled to .001° C by adjusting the resistances in the bridge. As a means to obtain constant voltage for both the external and internal heaters a one K.V.A. constant voltage transformer was used.

The high temperature bath, G, figure (2), is used over the range from 150° C to 300° C inclusive. It uses Socony Vacuum S/V Valrex oil A, which is a heavy cylinder lubricating mineral oil. The temperature regulation of this bath is exactly as described above. The cover of the bath is packed with glass wool, this gives thermal insulation as well as reducing the amount of fumes coming out of the bath at high temperatures. The level of oil in the bath is maintained constant as the temperature of the bath is increased by sucking out the expanded oil with a vacuum into a trap made from a ten liter pyrex spherical flask.

For the range of 0° to 125 °C another oil bath is used. In this temperature control is described above. Here however an oil of low viscisity is used. The stirring mechanicsm in this bath is driven by a 1/4 horsepower motor.

5). Measurement of temperature.

The temperature are measured by means of a strain free platinum resistance thermometer of the mica cross type (34). The thermometers are calibrated at the ice point of water, 0° C, the steam point of water 100°C, and the boiling point of sulpher, 444.6°C.

Interpolation is maee by the use of the Callendar forumula;

$$t = \frac{R_t - R_o}{\alpha R_o} + \delta \frac{t}{100} \left(\frac{t}{100} - 1\right) \qquad (35)$$

t, is the temperature in degrees centigrade on the international Platinum resistance thermometer scale. R_t and R_o are the given electrical resistances of the platinum thermometers at t° C and 0° respectively, α and δ are constants, which are determined at the steam and sulpher boiling points.

Resistances are measured on a Mueller bridge (35). This bridge is regulated at a temperature of 30° C. A commutator device is used to eliminate from the measurements the resistances of the leads up to the platinum resistance wire. The temperatures obtained are in degrees centigrade on the international scale.

A given constant temperature can be read with a given platinum resistance thermometer with a precision of .002°C. The deviations of the readings of a single platinum resistance thermometer from the international platinum resistance thermometer scale increase above 100°C to a maximum of .01°C to .02°C at 325°C.

6. Compressibility and weighing bombs.

The all steel bomb shown in figure (4) at A is used for substances whose vapor pressure is above 15 atmospheres at 30°C. It is made of chrome vanadium steel and has a volume of about 200 cc.

The gold washer assembly, C, is used to seal the bomb off after it is evacuated for blank run or after it is loaded with the gas to be studied in the compressibility run. The washer, C, is screwed down by means of the screw driver assembly, shown at A.

For an evacuation or a loading the steel capillary connecting the bomb to the fitting, B, is straightened, and in place of the fitting the screw driver assembly is used to connect the bomb to the vacuum line by means of a de Khotinsky seal. By this method the bomb may be evacuated and then sealed off or the gases to be studied are loaded into the bomb before sealing off.

When the gold washer is screwed down, so sealing off the bomg, the screw driver assembly is then removed and the fitting, B, is attached. This fitting then connects the bomb by means of steel capillaries, via the bomb stop cock, and the riser block, to the compressor.

This whole assembly is then evacuated up to the gold washer, before mercury is run in from the compressor, and the measurements begun. The gold washer can then be punctured by applying pressure from the compressor, then mercury is run into the bomb to compress the gas which floats on top of it.

The details of the screw driver assembly are given by R. Barriault in his thesis (36).

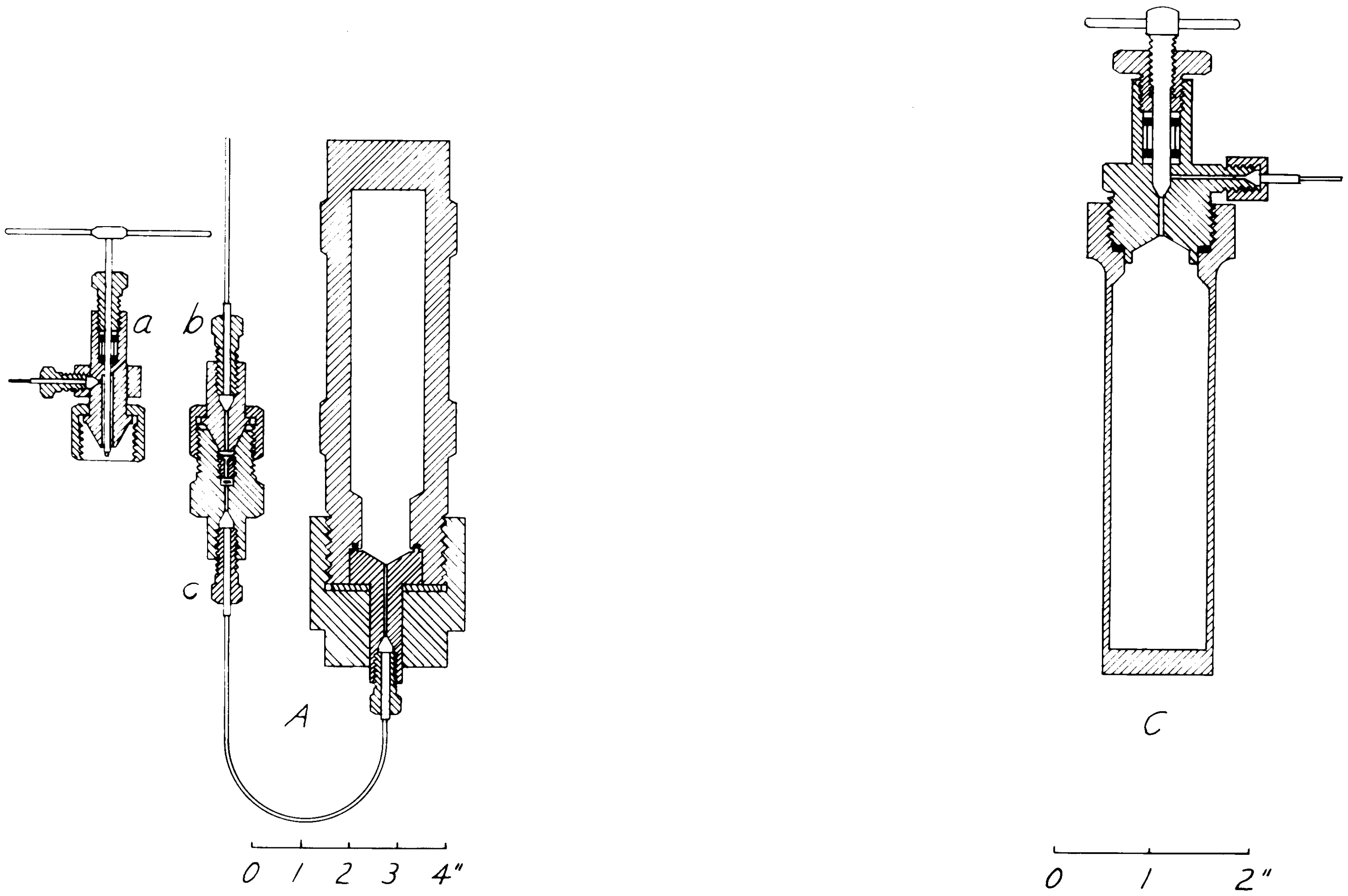

Figure 4

Part, C, of figure (4) shows the weighing bomb used to weigh the gas samples. A second of almost identical outside dimensions is used as a tare to reduce air buoyancy corrections to a minimum. The bomb is attached to the vacuum line by means of a de Khotinsky seal, and then evacuated, then it is rinsed out with the substance to be studied several times, before it is loaded with approximately the desired mass of substances to be studied.

7). The overall accuracy of the measurements.

The total overall uncertainty in the compressibility obtained by the apparatus described above increases from .03% at the lower pressures and temperatures to 0.1 to 0.2% at the higher temperatures and pressures.

B. Calibration

1). Construction and calibration of platinum resistance thermometer.

At the start of this research Programa new platinum resistance thermometer was constructed. The details of the construction are given by J. A. Beattie (34).

The platinum resistance thermometer was then calibrated by determining its resistance at three temperatures. These temperatures are, the ice point of water, 0°C, the steam point of water, 100°C and the boiling point of sulfur, 444.6. (37, 38, 39). Corrections are made for the barometric pressure at all three temperatures. Additional corrections were made, at the ice point for, the depth of immersion, of the thermometer, and at the sulfur point for the increase in pressure due to the thermometer windings.

Temperatures are calculated from the measured resistances by means of the Callendar formula (35). The constants α and δ are then calculated from the measured resistences at the steam point and the sulfur boiling point.

2). Calibration of the thermometer bridge L. and N. #93263

Before calibrating the platinum resistance thermometer the Leeds and Northrup thermometer bridge was calibrated. This was last done by S. W. Levine and D. R. Douslin (40).

The bridge was calibrated against itself by comparing the resistances with the .0001 ohm resistance, which we take to be correct. The measurements carried out in this calibration are described by Douslin and Levine (40). At the completion of the calibration the standard was changed from the .0001 ohm to the 100 ohm resistance and the required conversions were made.

The corrections that were obtained are listed in table XXIII which is to be compared with the table XXIV where the values listed are those calculated from the formula given by Douslin and Levine (40). This formula was developed by them after reviewing past calibrations. The equation is:

$$d = d_o - m \qquad (36)$$

where d is the correction for any month, d_o is the correction for the month of May, 1946, is a constant for each decade contact, and m is the number of months since May 1946.

The bridge has been designed so that the upper arm resistances may be balanced by a built in slide wire resistance. To compensate for the lead and shunt resistances in the variable resistances a fixed resistance was built into the bridge. However, the lead and shunt resistances do not remain constant with time so that a correction factor must be taken into account to compensate for the inequality. Douslin and Levine found this factor to be - .00052 ohms, Barriault and Brierly (36) found the factor to be - .00048 ohms. The value used in the present work was - .00060, so that R_t was calculated from

$$R_t = \frac{R_n + R_r}{2} - .00060 \qquad (37)$$

where R_n and R_r are the resistances read on the bridge for the normal and reverse positions.

Table XXII

History of Platinum Resistance Thermometer Number (   )

Date	R_0
Aug. 1950	22.3630
Dec. 1950	22.3636
March 1950	22.3640
May 1951	22.3644
Nov. 1951	22.3654
Jan. 1952	22.3656
Feb. 1952	22.3658
March 1952	22.3664
April 1952	22.3665
May 1952	22.3668

$$\alpha = .003926 \pm 1$$

$$\delta = 1.4967 \pm 2$$

Table (XXIII)

Corrections for L. and N. Bridge #93263 from Calibration of July 1950

	Decades					
	10	1	.1	.01	.001	.0001
Contacts						
1	-173	+ 132	+26	-2	0	0
2	-175	+ 253	+42	-3	0	-+1
3	-594	+ 380	+59	-5	-2	+1
4	-367	+ 504	+76	-6	-1	+2
5	-309	+ 627	+90	-5	-1	+3
6	- 89	+ 754	+104	-5	-1	+3
7	+ 60	+ 871	+121	-5	-1	+4
8	+275	+ 993	+136	-6	0	+4
9	+547	+1112	+152	-6	+1	+4

Table (XXIV)

L. and N. Bridge #93263 Corrections to the Decades

Values given in the chart must be multiplied
by 10^{-5} to give the correction in ohms

Determined Aug. 17, 1950

	Decades					
Contacts	10	1	.1	.01	.001	.0001
1	-174	+136	+27	-1	0	0
2	-180	+260	+43	-2	0	+1
3	-630	+390	+60	-3	0	+1
4	-388	+517	+77	-4	0	+2
5	-322	+642	+90	-5	0	+3
6	- 99	+769	+106	-5	0	+4
7	+ 48	+888	+124	-5	0	+5
8	+262	+1012	+140	-6	0	+6
9	+540	+1133	+157	-6	0	+6

Correction for time elapsed since calibration of May 1946 are determined by the equation

$$\Delta_t = \Delta_o - \alpha m$$

Δ_t = Correction to be applied at any time t.

Δ_o = Correction determined for May 1946

m = Months elapsed since May 1946

α = Constant determined for the above calibration. See Douslin and Levine notebook #1 p.140

3). Calibration of piston gauge #21.

The apparatus used in this calibration is described by Bridgman (41). Before the calibration could be started it was necessary to reload the carbon dioxide bomb. For this bone dry 99.9% pure carbon dioxide was used, which was obtained from Matheson Corporation. The gas from the tank was passed over phosphorus pentoxide and then through a U-tube immersed in a freezing mixture made up of acetone-solid carbon dioxide. The gas was then solidified with liquid nitrogen and purified by low temperature fractionation.

The gauge is calibrated by noting the weight that is required to balance the pressure exerted by the liquid carbon dioxide at 0° C. The vapor pressure of the liquid CO_2 at this temperature was taken to be 26,144.7 mm Hg. at the surface of the liquid. The following corrections were then added to obtain the corrected vapor pressure.

1) CO_2 (g) head at zero degrees centigrade was -3.14 mm Hg.
2) CO_2 (g) head at room temperature -1.84 mm Hg.
3) Difference in length of the needle contact in the riser block circuit in terms of mm Hg. + .40.
4) Oil level correction + 7.09 mm Hg.
5) Barometric pressure 754.2 mm Hg.

The gauge constant at 30.6° was then obtained as follows:

1) The weights on the pan including the whole pan assembly 12,681.628 gms.
2) The corrected vapor pressure of the liquid CO_2 was 25,393.01 mm Hg.

Thus:

$$C_{30.6} = \frac{25,393.01}{12,681.628} = 2.002346$$

This gauge constant, $C_{30.6}$ was then converted to C_{30} by

$$C_{30} = \frac{C_{\tau}}{1 - 2.2x_{10}^{5} (t - 30)}$$

The values of the constant C_{30} so obtained were:

1) 2.00235
2) 2.00205
3) 2.00241

The average of these three values is 2.00227. The chart that gave the conversion from the weights on the pan to atmospheres was the one which was calculated by Douslin and Levine (40). They used for the gauge constant the value 2.00435 mm Hg. per gram weight. It was therefore necessary to change all of our pressures at the end of our runs by the following relation:

$$P' = \frac{2.00227}{2.00435} P = 0.99896 P$$

In Table XXV the history of the gauge constants for piston #21 is given.

4) Calibration of the mercury compressor.

A full calibration of the mercury compressor was last carried out By Douslin and Levine (40) For the present research only an over-all check was deemed necessary.

A fine glass tip was cemented onto the steel capillary which is connected to the compressor. Then the mercury was forced out of the comprdssor until the reading on the compressor vernier showed that 290 turns had been taken out.

This total amount of mercury was then weighed and found to be

first weighing 2,807.070 gms.

second weighing 2,807.066 gms.

These weights compared favorably with those obtained by Douslin and Levine which were

first weighing 2,807.087 gms.

second weighing 2,806.984 gms.

It was therefore decided that we should use their calibration.

5) Blank runs.

As mentioned previously compressor settings are obtained from the equation,

$$V_p^t = ac + dc = V_b - mv \frac{d_t}{d_{30}} - \Delta V - D_1 + D_2 + D_3 \qquad (39)$$

The meaning of the various terms appearing in the above formula has already been given.

In order to determine ΔV, a "blank run" is made. This blank run is used to determine, for a series of pressures at each bomb temperature from 25°C to 300°C, at intervals of 25°, the effect of pressure and temperature on the apparent volume of the apparatus, including the mercury.

Table XXV

History of Gauge Constant, C_{30}, for Piston Gauge #21

Date	C_{30}
1927	2.00184
1931	2.00291
1935	2.00355
1938	2.00268
1942	2.00482
1948	2.00435
1952	2.00227

Before the blank run is started the compressibility bomb is evacuated at 400° C for a period of ten days. The gold washer is then screwed down and the bomb is removed from the line. The bomb capillary is then joined on at the riser block.

In addition the compressor is filled with clean mercury before starting on the blank run. The compressor vernier is then set at zero and the steel capillary from the compressor is joined on to the riser block.

This system, from the riser block to the gold washer, is evacuated through the riser block. Mercury is then forced in from the compressor until contact is made with the needle in the riser block. The oil line, which had connected the riser block to the vacuum system, is then disconnected from the vacuum line and is jointed to the Amagat gauge.

The zero set is then obtained by determining the volume necessary to fill the capillaries up to the gold washer. The zero set was carried out at room temperature under a series of pressures from 5 to 35 atmospheres. Then a graph was plotted of volume in cc's versus pressure in atmospheres and the volume at ten atmospheres was interpolated from the curve obtained.

The system from the riser block to the amagat gauge was then closed off by means of a stopcock, and the system put under pressure from the compressor. When the gold washer was pierced more mercury was run in to fill the bomb. The bench volume, V_b, may then be determined by placing the bomb filled with mercury into the thermostat, and, with the thermostat regulating at 30° C, the pressure is varied from 5 to 35 atmospheres. As in the case with the zero set, a plot of volume in cc's versus pressure in atmosphere is made and the volume at 10 atmospheres is interpolated from the curve, this represents the volume of mercury injected into the bomb at 30° and 10 atmospheres.

The difference between the bench volume and the zero set volume is the apparent bomb volume at 30°C and 10 atmospheres. Similar measurements were carried out with temperatures ranging from 25°C to 300°C at intervals of 25 degrees. At every 50°, however, the behaviour of the system was studied under a larger range of pressures, i.e., the pressure range covered was from 5 to 410 atmospheres.

The quantity ΔV was determined from the equation

$$\Delta V = V_b - V_p, t \tag{40}$$

where V_b is the bench volume and $V_{p,t}$ is determined from the equation

$$V_{p,t} = ac + dc \tag{41}$$

Where a and d are constants determined on calibrating the compressor, as mentioned above, a and c is the number of turns. We found that the results could be represented by the equation,

$$\Delta V_{p,t} = 0.10309 + 0.02777399\,(t-25) - (\,.0021126 + .0000011303\,(t-25)\,) \times (p-10) \tag{42}$$

$$+ \Delta_t \qquad + \Delta_p$$

where Δ_t is a deviation independent of pressure and Δ_p is a deviation independent of temperature. These deviations were plotted up and these plots were used for interpolation. The values of Δ_t and Δ_p

are given in Table XXVI.

During the course of the work it became necessary to open and clean the bomb. Because of this, a new partial blank run was carried out to determine the corrections to be applied to the equation (42). It was found that the above equation could be corrected by the following equation:

$$\Delta V'_{p,t} = \Delta V_{p,t} + .289\ (1 - d_t/d_{30}) - 10^{-5}\ (t-30) \qquad (43)$$

where d_t/d_{30} is the ratio of the densities of mercury at t° C to the density at 30° C, and $\Delta V_{p,t}$ is given by equation (42) above.

At the conclusion of the 300° degree blank run, the bomb was removed from the high temperature bath and placed in the low temperature bath and the 30° isotherm redetermined. The results obtained showed good agreement with the original 30° isotherm, which meant that mercury neither leaked out of the system nor was there any gas given off by the walls of the bomb during the blank run determinations.

The bench volume and zero set volume, determined prior to the measurement of the compressibility of ammonia, were 203.649 and 3.274, to give a bomb volume of 200.375 cc.

Before making a new compressibility run a new V_b bench volume must be determined. This is obtained by adding the new zero set volume to the originally determined bomb volume.

Figure 5 shows the work sheet used for the blank run.

BLANK RUNS

TEMP. 100 °C

Date May, 12 1951

Observer C. M. Apt

Dir	Compressor	T_G °C	BAR. mm	T_R °C
D	281.219	26.8	755.3	25.9
U	281.225	26.8	755.3	25.9
D	281.245	26.8	755.3	25.9
U	281.250	26.8	755.3	25.9
D	281.264	26.8	755.3	25.9
U	281.270	26.9	755.3	25.9
D	281.326	26.8	755.3	25.9
U	281.332	26.8	755.3	25.9
D	281.379	26.8	755.3	25.9
U	281.384	26.8	755.3	25.9
D	281.768	26.8	755.3	25.9
U	281.772	26.8	755.3	25.9
D	282.149	26.8	755.3	25.9
U	282.151	26.8	755.3	25.9
D	282.529	26.8	755.3	25.9
U				
D				
U				
D				
U				

WTS.	Aver. Comp.	Volume cc	WT. P. Atm	Total P Atm	$\triangle V$
S.P.	281.222	201.309	5.4184	7.1422	+2.017
S.P $5B_1$	281.248	201.328	11.4005	13.1243	+1.998
S.P. $10B_1$	281.267	201.341	17.3828	19.1066	+1.985
S.P. $25B_1$	281.329	201.386	35.3291	37.0528	+1.940
L.P.	281 382	201.424	50.6357	52.3595	+1.902
L.P. $50B_{1-2}$	281.770	201.701	170.2712	171.9950	+1.625
L.P. $50B_{1-4}$	282.150	201.973	289.9075	291.6312	+1.353
L.P. $50B_{1-6}$	282.529	202.245	409.5433	411.2671	+1.081

N 31.0914

Control R 29.8033

Aver. T_R 25.9

R 31.2082

R_o 22. 3644

Aver. Bar. 755.3

Aver T_G 26.8

Figure 5

Table XXVI

All Steel Bomb Calibration Deviations (Residuals)

$t^{\circ}C$	Δ_t ml.	P atm.	Δ_p ml.
25	- .051	7.27	+ .010
50	- .020	13.24	+ .007
75	+ .004	19.22	+ .006
100	+ .019	37.17	+ .002
125	+ .027	52.49	.000
150	+ .030	172.12	- .002
175	+ .025	291.76	.000
200	+ .018	411.40	+ .002
225	+ .011		
250	- .004		
275	- .019		
300	- .040		

C. Purification, weighing, and loading of sample.

The ammonia used in this research was obtained from Matheson Corporation. The stated purity of the gas was 99.9%. The gas was further purified by low temperature fractionation in a glass apparatus of the type described by Simard (42).

The procedure used was to take the gas from the tank and condense it to the liquid in a glass vessel immersed in a freezing mixture made up of acetone and solid CO_2. This condensation took place in the presence of sodium so as to remove any traces of water an oxygen. Then 70 cc's of the ammonia was distilled over to another vessel and the rest discarded. This 70 cc. sample was condensed to the solid and pumped on with the mercury diffusion pump for about an hour, then redistilled three times, the initial and final 10 cc. of distillate being discarded each time. The discarded portions were removed by pumping. After the weighing bomb had been evacuated and then rinsed with some of the substance to be studied, the approximately correct amount of ammonia, taken from the middle portion of the remaining sample, was condensed into the weighing bomb. After having been closed, the weighing bomb was allowed to warm up to room temperature.

The weighing bomb was then removed from the line and weighed against its tare over a period of some days to test for leakage.

For the mixture of ammonia and methane, the ammonia was handled exactly as described above, the methane, obtained from the Phillips Petroleum Company, of stated purity 99.5%, treated in a somewhat similar fashion, except that the treatment with sodium was omitted. When both components had been loaded into their respective weighing bombs, the two filled weighing bombs were then weighed against each other.

The loading of the compressibility bomb was performed in an apparatus quite similar to that described by Simard (42), modified to include inlets for both weighing bombs. In the case of the ammonia compressibility run, the ammonia was then condensed into the compressibility with liquid nitrogen. When all the ammonia had been transferred the residual pressure was measured on a McLeod gauge, and a correction was made for the amount of ammonia lost in the glass system. Then the gold washer was screwed down, closing off the compressibility bomb. The weighing bomb which had contained the ammonia was again weighed against its tare so that, by difference, the amount of ammonia loaded into the bomb could be calculated, taking into account the above mentioned correction.

For the mixture the ammonia was transferred first and before this weighing bomb was removed from the line the vapor pressure was noted. To remove the weighing bomb mercury is run up into a cut-off, this cut-off enabling us to remove the weighing bomb in the course of the loading while at the same time isolating the compressibility bomb which was immersed in the liquid nitrogen, and the glass tubing joining the bomb to the system is cut. This weighing bomb, which contained the ammonia, was then weighed against that containing the methane. To the difference in weight obtained from this weighing, a correction had to be applied for the loss of ammonia ahead of the cut-off. Then the weighing bomb containing the methane was connected on to the system, this system up to the bomb was evacuated, the mercury in the cut-off was run down, and the methane was allowed to distill over to the compressibility bomb. When the methane had distilled over, the residual pressure in the system was determined on a McLeod gauge, and then corrections were determined for the loss of ammonia and methane at this stage. The gold washer was then screwed down and the compressibility bomb was transferred to the thermostat, and connected via the riser block to the compressor and the piston gauge.

After the methane was loaded, and the compressibility bomb sealed off, the two weighing bombs, which were now empty, were weighed against each other, and taking into account the losses of gas mentioned above, the mass of gas in the compressibility bomb could then be calculated. It is believed that this method determines the mass of each component to 0.3 to 0.4 milligrams, which amounts to a maximum error of about 0.03% in the composition.

D. Calculations for a Compressibility Run

Calculations for a compressibility run are made on a mimeographed work sheet as shown in Figure 6.

At the top of the sheet is noted the temperature of the bath, density in moles per liter, and the final corrected pressure determined for this one point.

The items in the first column on the left are used to determine the compressor setting for the desired density. From equation (39) which re-written to

$$ac + dc = \sum_1 - \sum_2 + D_3 \qquad (44)$$

ΔV is calculated from equation (42) with the required corrections given in equation (43). D_2 is calculated from equation (34) and D_3 is a correction of -.004 ml. for each degree of room temperature below 250°C. $_{mv}$ is the volume of the sample calculated from the total number of moles of the sample for the particular density setting. When $\sum_1$, and $\sum_2$, and d_3 have been determined, they are subtracted algebraically from the bench volume, V_b, and the result, $V_{p,t}$ is divided by a of equation (44) above, to give the approximate setting of the compressor. With this approximate number of turns determined, reference is then made to a deviation plot, of turns vs. volume in cc, to determine the correction term, dc, in the equation (44) above. This new $V_{p,t}$ is once again divided by a and the desired compressor setting is calculated.

In the right hand column, T_g is the temperature of the gauge, T_r the room temperature, T_r and T_g differ due to frictional heating of the gauge. $\sum_1$ is made up of the sum of the barometric pressure and H_r, the mercury head at room temperature, corrected to 0°C and standard gravity by the factor,

$$F = \frac{g_{M.I.T.}\, d_t}{g_o\, d_o}$$

where g_o is standard gravity, d_t is the density of mercury at t°C., and d_o is the density of mercury at 0°C. $\sum_2$ is the sum of the mercury head at the temperature of the termostat, H_t , and the mercury hydrostatic head in the bomb, H_b corrected in the same way as $\sum_1$. The oil head and capillary depression are combined into a single correction since they are constant. The total pressure, not including the gauge pressure, then becomes;

$$\Delta P_{mm.} = \sum 1\ \text{corr.} + \sum 2\ \text{corr.} - \text{oil head} + \text{cap. dep.} - \text{Hg. V.P.}$$

$$\Delta P_{atm.} = \frac{\Delta P_{mm}}{760}$$

In the next to the last column are listed the weights on the pan, and in the last column these weights are converted to atmospheres. To obtain the corrected pressure we add $\Delta P_{atm.}$ to the measured pressure as determined from the pan weights.

To calculate the term ΔV it is necessary to have the total pressure. This is in the first instance estimated, then ΔV is calculated, the compressor setting is made, and the total pressure is measured and ΔV is re-calculated using this pressure. From the new ΔV a new compressor setting is calculated and the pressure redetermined. This process is repeated until there is no further change in ΔV. It has been found that convergence to the correct value of ΔV is very rapid.

275	TEMP.	P.V.
4	LEN. M/L	
150.5156	PRESS. ATM. CORR.	DATE: **March, 16 1952**

				WTS.	ATM.
V_B	203.649	T_g	26.2	L.P.	50.6364
D_2	.0030	T_R	25.4	$50B_1$	59.8184
$\sum_1$	203.6520	BAR.	747.9	$25B_2$	29.9093
		H_R	410.4	$5B_1$	5.9821
$mv \frac{d_t}{d_{30}}$	45.8524	$\sum_1$	1158.3	500 gms.	1.3194
ΔV	6.4792	$\sum_1$ corr.	1152.7	200 "	.5279
D_1	.0139			100 "	.2638
$\sum_2$	52.3455	H_t	182.5	100 "	.2638
		H_B	69.5	50 "	.1319
D_3	-.0002	$\sum_2$	252.0	5 "	.0132
		$\sum_2$ corr.	239.7	2 "	.0053
$V_{p,t}$	151.3063	oil head	(0)	1 "	.0026
T app.	211.4	CAP. DEP.		1 "	.0026
d_c	-.0051	Hg V. P.	146.8		
		$\sum_1 + \sum_2$	1392.4		
Turns	211.375	ΔP mm	1245.6		
		ΔP atm.	1.6389	ΔP	1.6389
				TOTAL	150.5156

Figure 6

E. Calculations for the Beattie- Bridgman Equation of State

A full discussion on the procedure used for the fitting of the Beattie-Bridgman equation of state to compressibility measurements on gases is given in reference (43).

Practically all theoretical equations of state which express P as a function of V and T can be written in generalised form as;

$$P = T\Psi(V) - \phi(V) - F(V,T) \qquad (45)$$

The Beattie-Bridgman equation can be written as;

$$P = \frac{RT(1-\mathcal{E})}{V^2}(V + B) - \frac{A}{V^2} \qquad (46)$$

in which

$$A = A_o(1 - a/V) \qquad (47)$$

$$B = B_o(1 - b/V) \qquad (48)$$

$$\mathcal{E} = c/VT^3 \qquad (49)$$

where A_o, a, B_o, b, and c are the five constants to be determined.

Equation (45) can be put in the form;

$$P' = P + F(V,T) = T\Psi(V) - \phi(V) \qquad (50)$$

where we may consider P' as the corrected pressure since it varies linearly with temperature at constant density. In generalized form then;

$$\Psi(V) = \frac{R(V + B)}{V^2} \qquad (51)$$

$$\phi(V) = \frac{A}{V^2} \qquad (52)$$

$$F(V,T) = \frac{c\Psi(V)}{VT^2} \qquad (53)$$

Returning to equation (45) and substituting (53) we get that;

$$P = T\Psi(V) - \varphi(V) - \frac{c\Psi(V)}{VT^2}$$

$$\left(\frac{\Delta P}{\Delta T}\right)_V = \frac{P_2 - P_1}{T_2 - T_1} = \psi(V) + \frac{c\psi(V)}{V}\left(\frac{T_2 + T_1}{T_1^2\,T_2^2}\right)$$

$$\text{let} \quad \alpha = \left(\frac{T_1 + T_2}{T_1^2\,T_2^2}\right)\frac{c}{V}$$

$$\text{then} \quad \psi(V) = \left(\frac{\Delta P}{\Delta T}\right)_V - \alpha\psi(V)$$

$$\text{or} \quad \psi(V) = \left(\frac{\Delta P}{\Delta T}\right)_V \frac{1}{1 + \alpha}$$

so that

$$P' = P + c\left(\frac{\Delta P}{\Delta T}\right)_V \frac{1}{1 + \alpha}$$

The procedure used to fit the results, is to determine c first. This we did by taking as our first c value, that used by Beattie and Lawrence (44) to fit the values of the compressibility of ammonia. This value was 4.75×10^6. This value did not straighten the higher isometrics so two other values of c were chosen one of which was 100×10^4 the other 200×10^4. Calculations were carried out for all isometrics for each of the two c values. To calculate $\left(\frac{\Delta P}{\Delta T}\right)_V$, we consider the two extreme temperatures and their pressures for each isometric. Using these two c values, P' was calculated at each isometric for all temperatures, the best straight line through these points gives $\psi(V)$ and $\varphi(V)$ as the slope and intercept for that isometric.

The next step involves the calculation of B, where B is given by the relationship;

$$B = \frac{V^2\psi(V)}{R} - V \qquad (54)$$

By equation (48), B is assumed to be a linear function of the density. Thus the B values are calculated from (54) above. These values are then plotted against the density and the best straight line through these points is determined. This gives as the slope B_ob and as the intercept B_o, so that b could then be calculated. See Figure (7).

Finally, the function A is given by;

$$A = V^2\varphi(V) \qquad (55)$$

where φ (V) is calculated from the equation

$$\varphi(V) = T\psi'(V) - P + \frac{c\,\psi'(V)}{VT^2} \qquad (56)$$

and ψ' (V) is recalculated from equation (51) above, i.e.

$$\begin{aligned} B &= B_o(1 - b/V) \\ \psi'(V) &= R/V^2(V + B) \end{aligned} \qquad (57)$$

The values of A determined by (55) are plotted against the density and the best straight line gives, by equation (47) above, A_o as intercept and aA_o as the slope from which a may be calculated. See Figure (8).

The values of A_o, a, B_o, b and c were taken to give the best fit at the higher densities. The entire calculation was carried out for each of the two c values mentioned above. It was found that for c equal to 100 x 10^4

a better fit was obtained. The values of the Beattie-Bridgman equation of state constants are given in Table IV on page 11.

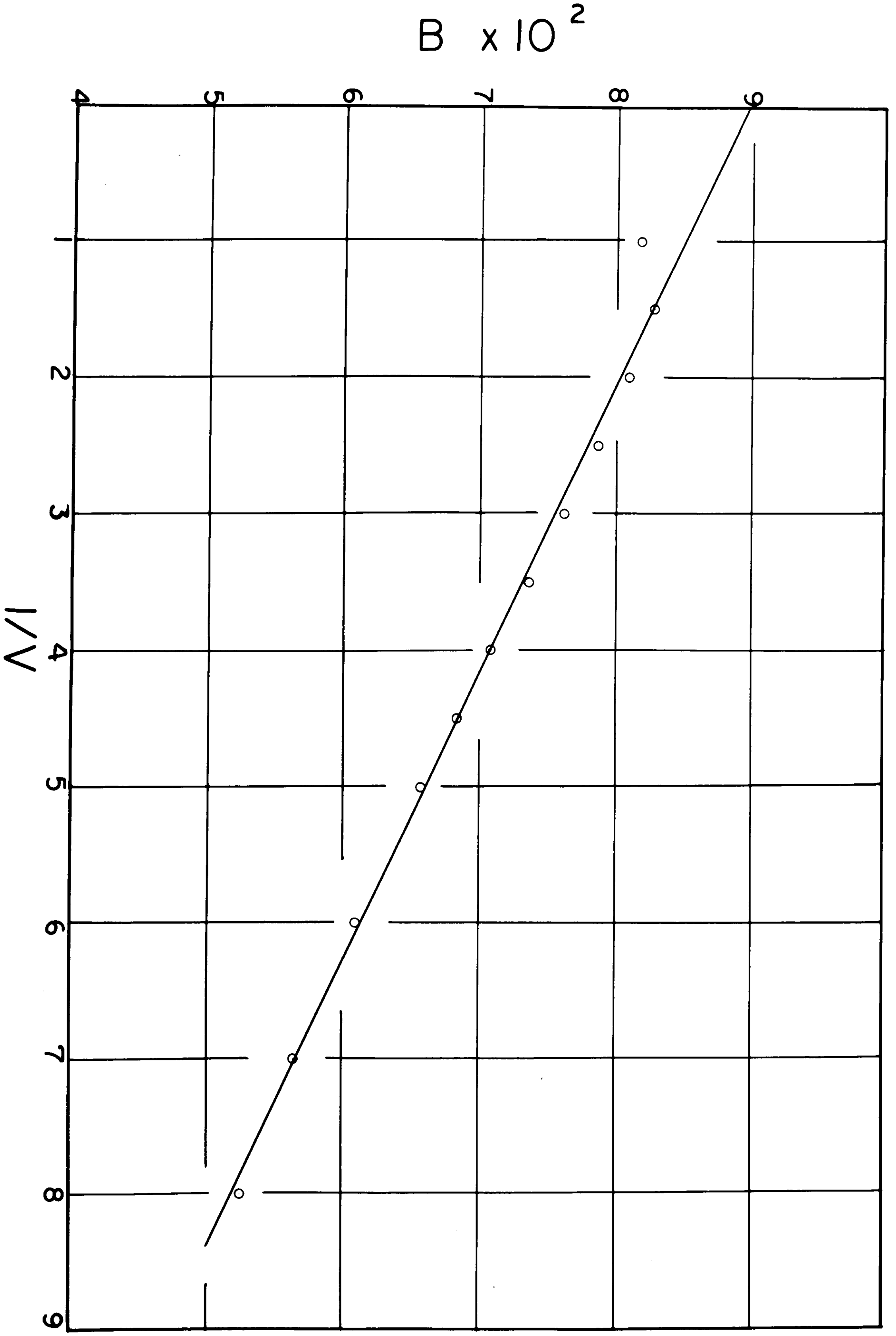

Figure 7

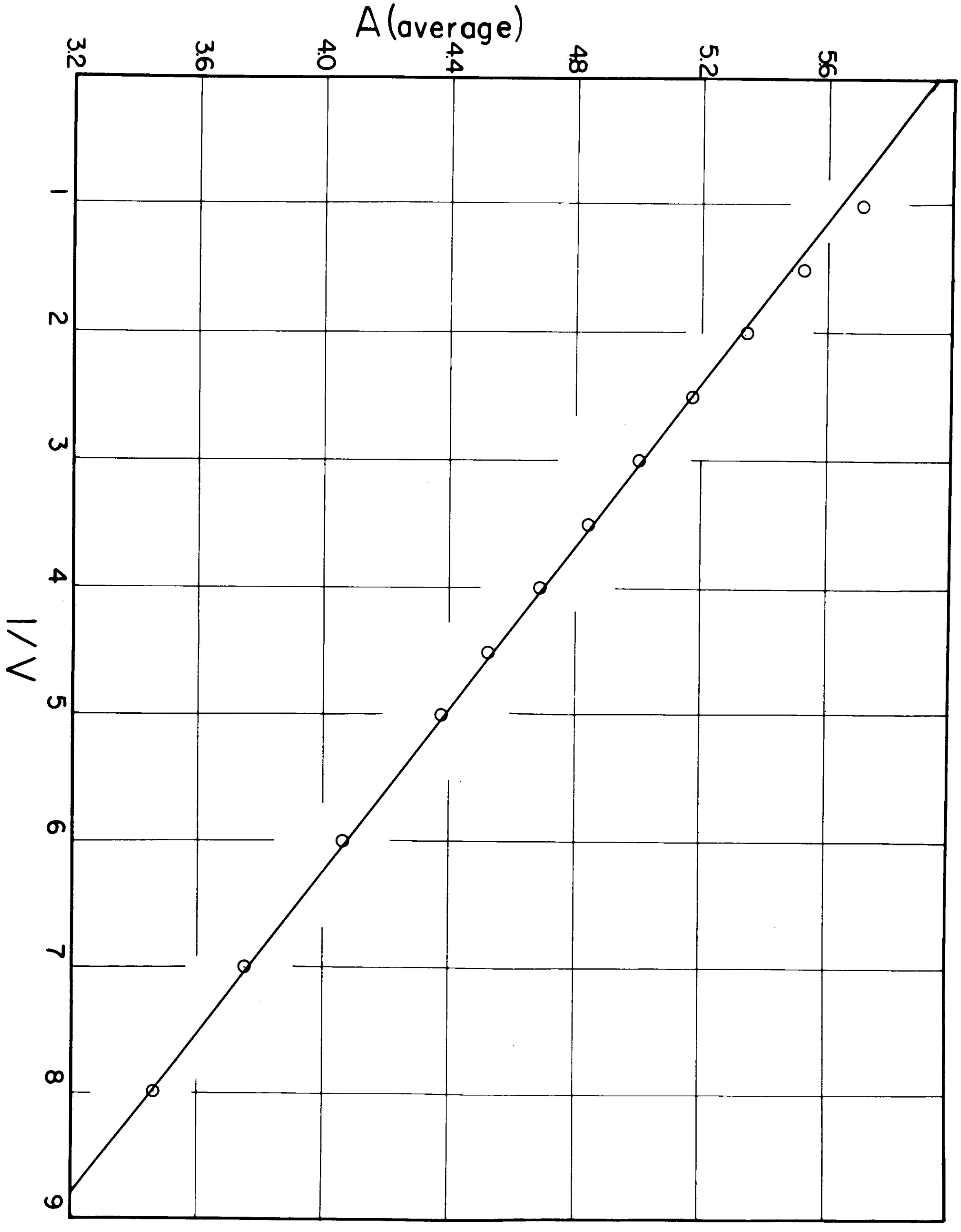

Figure 8

Summary

The work reported in this thesis concerns itself mainly with the study of the behavior of gaseous mixtures in which one of the components has a permanent dipole moment.

In carrying out this study, it was necessary to measure the compressibility of pure ammonia and to fit the results to the Beattie-Bridgeman equation of state. The equation of state constants obtained for the pure ammonia combined with those determined by J.A. Beattie for pure methane were then used to calculate the equation of state constants for the gaseous mixture of metane and ammonia. For this calculation two methods were used. In the first method no account was taken of the fact that one of the components was polar. In the second method, the combining rules used were determined by W.H. Stockmayer after a study on the second virial coefficients for polar gases. This latter method gave better results and, with the knowledge of the third virial coefficients for polar gases now available, it may be hoped that these rules may be improved so that pressures of gaseous mixtures containing polar components may be reckoned with higher accuracy.

In addition to the study on the mixtures, from the measurements on the compressibility of pure ammonia, the second and third virial coefficients were obtained. These were compared with the theoretical values calculated using both the Stockmayer and the Lennard-Jones potentials. While both of these potentials are able to reproduce with a good deal of accuracy, the second virial coefficients, only the Stockmayer potential gives reasonable values for the third. Since the third virial coefficient is much more sensitive to the shape of the potential used, The Stockmayer potential appears to be much more realistic for polar gases.

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