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AN EQUATION OF STATE FOR GASEOUS MIXTURES. I. APPLICATION TO MIXTURES OF METHANE AND NITROGEN

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1. Introduction

Recently a new equation of state has been proposed by O. C. Bridgeman and the author[1] and applied to the compressibility data on the ten gases helium, neon, argon, hydrogen, nitrogen, oxygen, air, carbon dioxide, methane and ethyl ether. The measured pressures were reproduced over the experimentally measured temperature range and for a wide range of densities with an average deviation of 0.18% for all ten gases. This equation of state is

$$p = \frac{RT(1 - \epsilon)}{V^2} [V + B] - \frac{A}{V^2} \tag{1}$$

where $A = A_0 (1 - a/v)$; $B = B_0 (1 - b/v)$; $\epsilon = c/VT^3$; R is the gas constant and A_0, a, B_0, b and c are constants whose values depend upon the kind of gas under consideration.

In the present paper this equation is applied to the comprehensive set of data taken by Keyes and Burks on mixtures of methane and nitrogen, by the use of a simple rule for the calculation of the values of the constants of the mixture from those of the pure component gases. The agreement between the observed and calculated pressures is good and leads to the expectation that the method used for the calculation of the values of the constants in the case of the methane and nitrogen mixtures will also apply to other gaseous mixtures.

In his treatment[2] of binary systems, van der Waals assumed that the equation of state of a gaseous mixture was of the same general form as that for a pure gas, *i. e.*

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

He suggested that the value of the b constant for a mixture of two gases could be calculated by "linear combination" of the b values for the pure gases

$$b_x = b_1 (1 - x) + b_2 x$$

where x is the mole fraction of the second component. However, through-

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[1] Beattie and Bridgeman, This Journal, **49**, 1665 (1927); *ibid.*, **50**, 3133, 3151 (1928). A comprehensive treatment of the equation of state and a detailed comparison with the compressibility data are given in *Proc. Am. Acad. Arts Sci.*, **63**, 229 (1928).

[2] Van der Waals, "Die Continuität des Gasförmigen und Flüssigen Zustandes," Part II, Barth, Leipzig, 1900.

out his book van der Waals employed the relation deduced from kinetic theory by Lorentz[3]

$$b_x = b_1 (1 - x)^2 + 2 b_{12}x (1 - x) + b_2x^2$$

in which

$$b_{12} = \left(\frac{1}{2} \sqrt[3]{b_1} + \frac{1}{2} \sqrt[3]{b_2}\right)^3$$

If, however, b_{12} can be represented as the average of b_1 and b_2

$$b_{12} = (b_1 + b_2)/2$$

the Lorentz equation for b_x reduces to the linear combination rule of van der Waals.

For the cohesive constant van der Waals used the relation

$$a_x = a_1(1 - x)^2 + 2a_{12}x(1 - x) + a_2x^2$$

a_{12} being an interaction constant which cannot in general be calculated from a_1 and a_2.

Galítzine[4] applied an equation of the Clausius type to Andrews'[5] data on mixtures of nitrogen and carbon dioxide and calculated the interaction constant by the relation $a_{12} = \sqrt{a_1a_2}$; the complete expression for a_x becoming

$$a_x = a_1 (1 - x)^2 + 2\sqrt{a_1a_2}x(1 - x) + a_2x^2$$

or

$$\sqrt{a_x} = \sqrt{a_1}(1 - x) + \sqrt{a_2}x$$

i. e., the square root of the a constant is linearly combined. He also used the same method of combination for the b constant.

Somewhat later D. Berthelot[6] proposed that in the application of van der Waals' equation to binary mixtures, the parameters b_x and $\sqrt{a_x}$ for the mixture be obtained by linear combination of the b and $\sqrt{a}$ constants of the component gases. This method was criticized by van der Waals,[7] who believed than in general the properties of a mixture cannot be calculated from those of the component gases, because a_{12} cannot be obtained from the constants of the pure gases. This view is also held by Happel,[8] who shows that a_{12} cannot be calculated from a_1 and a_2 unless some assumption is made regarding the law of the attractive force between the unlike molecules of the gas mixture.

Trautz and Emert[9] have measured the increase in pressure resulting from mixing two gases for many binary systems at about one atmosphere

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[3] Lorentz, *Wied. Ann.*, **12**, 127, 660 (1881).

[4] Galitzine, *ibid.*, **41**, 770 (1890).

[5] Andrews, *Phil. Trans. Roy. Soc., London*, **178A**, 45 (1887).

[6] D. Berthelot, *Compt. rend.*, **126**, 1703, 1857 (1898).

[7] Van der Waals, *ibid.*, **126**, 1856 (1898). Later this criticism, which was founded on the critical behavior of gas mixtures, was for the most part withdrawn (*cf.* "Continuität," Vol. II, p. 156).

[8] Happel, *Ann. Physik*, **26**, 95 (1908).

[9] Trautz and Emert, *Z. anorg. allgem. Chem.*, **150**, 277 (1926).

and at several temperatures. They computed the values of a and b of the van der Waals' equation for the pure gases at each temperature by means of van Laar's[10] temperature functions. The constants for the mixtures were obtained from these values, using the Lorentz method of combination for b, and the Galatzine–Berthelot method for a. The experimental results were explained reasonably well, although not within the experimental error.

Keyes and Burks[11] have presented a series of measurements on mixtures of methane and nitrogen and have treated these data by means of the Keyes equation for a non-associating gas

$$p = \frac{RT}{V - \beta e^{-\alpha/V}} - \frac{A}{(V + l)^2}$$

They found that the values of the constants obtained by passing an equation of state through the compressibility data on the mixtures could be calculated from the constants for the pure gases and the compositions of the mixtures when each of the constants R, β, α, $\sqrt{A}$, l, was combined linearly.

Dalton's law of the additivity of pressures at constant volume and temperature has been the basis of much of the treatment of gas mixtures, although this principle has long been known to hold only approximately for real gases. Amagat,[12] from a study of his measurements of the compressibility of oxygen, nitrogen and air to 3000 atmospheres, found that at constant temperature and pressure the pV product for air could be obtained by linear interpolation between the pV products of the pure gases. Since the pressure is the same throughout, this rule states that the volume of a gas mixture is given by the sum of the volumes of the component gases, each measured under the total pressure of the mixture. In this form, the Amagat law of the additivity of volumes at constant pressure and temperature was studied by Leduc,[13] who claimed that it was quite exact for mixtures of the permanent gases. Penning[14] has used the exactness of this relation for air as a test of the accuracy of his measurements, and Holborn and Otto[15] have employed the rule to calculate the compressibility of pure neon from measurements on a neon–helium mixture containing 28% of helium. Keyes and Burks[11] have shown that the Amagat law is a better approximation than Dalton's

[10] Van Laar, "Die Zustandsgleichung von Gasen und Flüssigkeiten," L. Voss, Leipzig, **1924**.

[11] Keyes and Burks, THIS JOURNAL, **50**, 1100 (1928).

[12] Amagat, *Ann. chim. phys.*, [5] **19**, 384 (1880); *Compt. rend.*, **127**, 88 (1898).

[13] Leduc, *Compt. rend.*, **126**, 218 (1898). The Amagat law is sometimes called Leduc's law, *cf.*, however *ibid.*, **127**, 88 (1898).

[14] Penning, *Archives Neerlandaises*, III A, **7**, 172 (1923); *Comm. Phys. Lab. Univ. Leiden*, No. 166.

[15] Holborn and Otto, *Z. Physik*, **23**, 77 (1924).

law for methane–nitrogen mixtures and the same has been found true for oxygen–argon mixtures by Masson and Dolley[16] although the reverse was the case for argon–ethylene and oxygen–ethylene mixtures. Gillespie[17] has demonstrated that the Lewis and Randall[18] rule, which can be taken as the additivity of fugacity for gaseous mixtures at constant pressure and temperature, is correct only if the Amagat law holds.

Verschoyle[19] has shown that in the isothermal expansion

$$pV = A + Bp + Cp^2$$

the constants B and C for mixtures of hydrogen and nitrogen are not linear functions of the compositions but lie on smooth curves. Lennard-Jones and Cook,[20] from a consideration of the interaction between molecules, obtain for the B coefficient of a mixture the relation

$$B'_x = B'_{11}(1-x)^2 + 2B'_{12}x(1-x) + B'_{22}x^2$$

in which B'_{12} arises from the interaction of molecules of unlike species. A relation for the temperature dependence of B'_{12} is deduced and compared with the experimental results, with substantial agreement.

2. Calculation of the Values of the Constants for Gaseous Mixtures

It seems reasonable to suppose that the equation of state of a given gaseous mixture would be of the same general form as that for a pure gas and that the values of the constants could be obtained from the compressibility data in the same manner as from similar data on a pure gas. Whether the constants so obtained can be computed with sufficient accuracy for purposes of thermodynamic calculation from the values of the constants of the pure gases and the composition of the mixture is a question which must be settled experimentally. In the present paper a simple method for calculating the values of the constants of a mixture is studied from the standpoint of the experimental measurements on methane–nitrogen mixtures.

Kinetic theory considerations lead in general to quadratic equations such as those deduced by Lorentz for the calculation of the equation of state constants of a binary mixture from those of the component gases. If the interaction constant (*i. e.*, b_{12} or a_{12}) can be taken as the average of the constants of the pure gases, the equation for combining the constants reduces to a linear one; while if the interaction constant can be taken as the square root of the product of the constants of the pure gases, the rule

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[16] Masson and Dolley, *Proc. Roy. Soc., London,* **103A,** 524 (1923).

[17] Gillespie, THIS JOURNAL, **47,** 305 (1925).

[18] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923,** p. 226. See also Bichowsky, THIS JOURNAL, **44,** 116 (1922).

[19] Verschoyle, *Proc. Roy. Soc., London,* **111A,** 552 (1926).

[20] Lennard-Jones and Cook, *ibid.,* **115A,** 334 (1927).

reduces to linear combination of the square roots of the constants. The former assumption is more logical when the constant contains the dimension of density to the first power and the latter when the constant contains the dimension of density squared.

It is proposed that the values of the constants of Equation 1 for mixtures can be obtained from the constants of the pure gases by linear combination for those constants in which the dimension of density is contained to the first power, namely, a, B_0, b, c and R, and by linear combination of the square root of the constant A_0, in which the dimension of density is contained to the second power.

The volume V of Equation 1 may be (a) the total volume of n moles of the mixture, (b) the volume of an average mole or (c) the volume of one gram of the mixture.

(a) When V is the volume of n moles consisting of n_1 moles of Gas 1, n_2 moles of Gas 2, etc., the rule of combination becomes

$$\begin{aligned}
A_{om} &= (n_1\sqrt{A_{01}} + n_2\sqrt{A_{02}} + n_3\sqrt{A_{03}} + \ldots)^2 &&= (\Sigma n_1\sqrt{A_{01}})^2 \\
a_m &= n_1a_1 + n_2a_2 + n_3a_3 + \ldots &&= \Sigma(n_1a_1) \\
B_{om} &= n_1B_{01} + n_2B_{02} + n_3B_{03} + \ldots &&= \Sigma(n_1B_{01}) \\
b_m &= n_1b_1 + n_2b_2 + n_3b_3 + \ldots &&= \Sigma(n_1b_1) \\
c_m &= n_1c_1 + n_2c_2 + n_3c_3 + \ldots &&= \Sigma(n_1c_1) \\
R_m &= n_1R + n_2R + n_3R + \ldots &&= \Sigma(n_1R)
\end{aligned} \tag{2}$$

where the subscript m refers to the value of the constant for the mixture, the subscript 1 refers to Gas 1, and the summation extends over all of the gases in the mixture.

(b) When V is the volume of an average mole of the mixture, the number of moles n_1, n_2, etc., of the relations given under (a) are replaced by the mole fractions x_1, x_2, . . . of the gases composing the mixture.

(c) When V is the volume of one gram, the constants are combined according to the methods given in Equation 2, the mole numbers n_1, n_2, . . . being replaced by w_1, w_2, . . . where w is the weight fraction and the values of the constants R_1, A_{01}, a_1, B_{01}, etc., are the appropriate values for one gram of the pure Gas 1.

It is now possible to write the complete equation of state for a mixture. Using for instance the relations (2) we obtain

$$p = \frac{\Sigma(n_1)RT\,(1 - \epsilon)}{V^2}\,[V + B] - \frac{A}{V^2} \tag{3}$$

where $A = (\Sigma n_1\sqrt{A_{01}})^2[1 - \Sigma(n_1a_1)/V]$, $B = \Sigma(n_1B_{01})[1 - \Sigma(n_1b_1)/V]$, and $\epsilon = \Sigma(n_1c_1)/VT^3$. When a mixture of a given composition is studied it is more convenient to calculate from Equation 2 the values of the constants for the mixture, and use these values in Equation 1, the mixture then being treated as a pure substance. When, however, the effect of a variation in composition is considered, the general equation of state of mixtures (3) or its counterpart using the mole fraction or weight fraction must be used.

3. The Virial Equation of State for Mixtures

Since the equation of state (3) is completely algebraic, it can be rearranged into the virial form

$$pV = \Sigma(n_1)RT + \frac{\beta_m}{V} + \frac{\gamma_m}{V^2} + \frac{\delta_m}{V^3} \tag{4}$$

where

$$\beta_m = \Sigma(n_1)RT\Sigma(n_1B_{01}) - (\Sigma n_1\sqrt{A_{01}})^2 - \left(\frac{\Sigma(n_1)R\Sigma(n_1c_1)}{T^2}\right)$$

$$\gamma_m = -\Sigma(n_1)RT\Sigma(n_1B_{01})\Sigma(n_1b_1) + (\Sigma n_1\sqrt{A_{01}})^2\Sigma(n_1a_1) - \left(\frac{\Sigma(n_1)R\Sigma(n_1B_{01})\Sigma(n_1c_1)}{T^2}\right)$$

$$\delta_m = \frac{\Sigma(n_1)R\Sigma(n_1B_{01})\Sigma(n_1b_1)\Sigma(n_1c_1)}{T^2}$$

The parameters β_m, γ_m and δ_m are algebraic functions of temperature, the mole numbers and the values of the constants of the gases composing the mixture. For a mixture of constant composition these parameters depend only on the temperature. By use of Equation 4 most of the usual thermodynamic equations can be integrated and hence many of the more important properties of gas mixtures calculated.[21]

The second virial coefficient β_m for a binary mixture can be written in the form obtained by Lennard-Jones and Cook[20]

$$B'_x = B'_{11}(1 - x)^2 + 2\,B'_{12}x(1 - x) + B'_{22}x^2$$

where $B'_x = \dfrac{\beta_m}{\Sigma(n_1)^2RT}$ and x is the mole fraction of the second constituent. By comparison with Equation 4, it can be seen that

$$B'_{11} = B_{01} - A_{01}/RT - c_1/T^3$$

$$B'_{22} = B_{02} - A_{02}/RT - c_2/T^3$$

$$2B'_{12} = B_{01} + B_{02} - 2\sqrt{A_{01}A_{02}}/RT - (c_1 + c_2)/T^3$$

Thus by use of the method of combining the constants given in Section 2, it is possible to calculate the value of B'_{12} from the equation of state constants of the pure gases composing the mixture and also determine its temperature variation.

4. Comparison of the Equation of State for Mixtures with the Experimental Data

It is generally true that two sets of pressure–volume–temperature data taken by different observers on the same gas do not agree with each other to the same order of accuracy as the consistency of each group of measurements within itself. Hence for a study of gas mixtures, the observations on the pure gases as well as on the mixtures should be made in the same apparatus. There exist several sets of data which fulfil this condition but in almost every case the investigator studied so few isotherms that it is not possible by a treatment of these data alone to obtain reliable constants for the pure gases.

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[21] *Cf.* Beattie, *Phys. Rev.*, **31**, 680 (1928); *ibid.*, **32**, 691, 699 (1928).

In the bibliography on the compressibility of gas mixtures given by Pickering,[22] the only measurements which are complete enough to test an equation of state for mixtures are those of Bartlett, which will be treated later.

Recently Keyes and Burks have measured the compressibility of methane[23] and three mixtures of methane and nitrogen[23,24] for five isotherms from 0 to 200° and for pressures extending to about 250 atmospheres. Using the same apparatus, Smith and Taylor[25] had previously measured the compressibility of pure nitrogen over the same temperature and pressure range. There is thus presented a complete series of pressure–volume–temperature data extending from pure nitrogen to pure methane covering the same temperature and pressure range. They were taken in the same apparatus using the same methods for calculating the results and hence the relative values should be very good, probably better than the absolute values.

In a previous publication,[1] the data of Smith and Taylor on pure nitrogen and of Keyes and Burks on pure methane have been considered, and the constants of the equations of state, based on these two sets of measurements alone, determined in units of international atmospheres, liter per mole and degrees Kelvin. Since all of the original data of these two groups of observers are in the volume unit of cubic centimeters per gram, the constants have been calculated to this basis. In Table I are given these values of the constants for the pure gases, together with those for the

TABLE I

VALUES OF THE EQUATION OF STATE CONSTANTS FOR NITROGEN, METHANE AND THEIR MIXTURES

Units: international atmospheres; cc. per gram; degrees Kelvin (T°K. = t°C + 273.13). Compositions are in weight fractions. The values of the constants for the mixtures are calculated from the constants of the pure gases and the compositions by means of the relations (2).

Gas	$\Sigma(w_1R_1)$	$(\Sigma w_1\sqrt{A_{01}})^2$	$\Sigma(w_1a_1)$	$\Sigma(w_1B_{01})$	$\Sigma(w_1b_1)$	$\Sigma(w_1c_1)$
Nitrogen	2.92904	1457.5	0.6382	1.5398	−0.5740	2.00×10^6
69.556% N_2; 30.444% CH_4	3.59572	3048.2	.7961	2.1321	− .7006	3.827×10^6
31.014% N_2; 68.986% CH_4	4.43974	5894.4	.9961	2.8819	− .8610	6.139×10^6
29.69% N_2; 70.31% CH_4	4.46873	6008.7	1.0030	2.9076	− .8665	6.219×10^6
Methane	5.11890	8860.0	1.157	3.4852	− .9900	8.00×10^6

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[22] Pickering, "International Critical Tables," McGraw-Hill Book Co., New York, **1928**, Vol. III, p. 17.

[23] Keyes and Burks, THIS JOURNAL, **49**, 1403 (1927).

[24] Burks, "Thesis," Massachusetts Institute of Technology, Cambridge, Mass., **1924**.

[25] Smith and Taylor, THIS JOURNAL, **45**, 2107 (1923); *ibid.*, **48**, 3122 (1926).

TABLE II

COMPARISON OF THE OBSERVED PRESSURES WITH THOSE CALCULATED FROM THE EQUATION OF STATE FOR NITROGEN

For each isometric the observed pressures are given in the first horizontal line, and the observed minus the calculated pressures in the second. The latter values subtracted from the former give the pressures calculated from the equation of state.

Vol. cc./g.	Temp., °C.	0	49.98	100	152.34	200	Av. dev.	
		Pressures, atmospheres					Atm.	%
23.1195	obs.	34.18	41.01	47.81	54.93	61.38		
	obs.−calcd.	0.02	0.04	0.05	0.06	0.05	0.044	0.090
20.1039	obs.	39.25	47.14	55.09	63.32	70.84		
	obs.−calcd.	0.02	0.00	0.05	0.03	0.04	.028	.050
17.0883	obs.	46.05	55.50	65.02	74.81	83.77		
	obs.−calcd.	−0.03	−0.03	0.07	0.02	0.02	.034	.056
14.0728	obs.	55.84	67.47	79.28	91.44	102.55		
	obs.−calcd.	−0.01	−0.10	0.04	0.01	0.03	.038	.052
11.0572	obs.	70.98	86.29	101.70	117.68	132.20		
	obs.−calcd.	0.00	−0.08	0.01	0.00	−0.01	.020	.022
9.0468	obs.	86.71	106.13	125.56	145.77	163.91		
	obs.−calcd.	−0.04	−0.06	0.05	0.10	−0.07	.064	.052
7.0364	obs.	111.96	138.26	164.40	191.61	216.15		
	obs.−calcd.	0.08	0.09	0.13	0.16	0.01	.094	.060
5.0260	obs.	160.22	200.15	240.05	281.96	319.53		
	obs.−calcd.	1.25	0.92	0.97	1.45	1.44	1.206	.520
			Total average deviation to 5 cc./g.				.191	.113
			Total average deviation to 7 cc./g.				.046	.055

TABLE III

COMPARISON OF THE OBSERVED PRESSURES WITH THOSE CALCULATED FROM THE EQUATION OF STATE FOR METHANE

For each isometric the observed pressures are given in the first horizontal line and the observed minus the calculated pressures in the second. The latter values subtracted from the former give the pressures calculated from the equation of state.

Vol. cc./g.	Temp., °C.	0	50	100	150	200	Av. dev.	
		Pressures, atmospheres					Atm.	%
40	obs.	32.30	39.42	46.47	53.49	60.49		
	obs.−calcd.	−0.02	0.02	0.03	0.04	0.04	0.030	0.062
35	obs.	36.51	44.76	52.94	61.04	69.16		
	obs.−calcd.	−0.04	0.01	0.04	0.02	0.04	.030	.060
30	obs.	42.00	51.81	61.51	71.14	80.75		
	obs.−calcd.	−0.05	0.01	0.03	0.03	0.02	.028	.050
25	obs.	49.44	61.50	73.45	85.26	97.05		
	obs.−calcd.	−0.06	−0.01	0.04	0.00	−0.01	.024	.040
20	obs.	60.13	75.78	91.24	106.54	121.81		
	obs.−calcd.	−0.07	−0.02	0.01	−0.02	−0.02	.028	.040
15	obs.	76.88	99.00	120.85	142.43	163.97		
	obs.−calcd.	−0.03	−0.07	−0.05	−0.12	−0.13	.080	.062
12	obs.	92.69	121.95	150.88	179.41	207.95		
	obs.−calcd.	0.15	−0.05	−0.05	−0.15	−0.06	.092	.068
10	obs.	107.95	145.08	181.84	218.12	254.27		
	obs.−calcd.	0.53	0.09	0.10	0.07	0.19	.196	.142
				Total average deviation			.064	.066

mixtures calculated by the relations of Equation 2, using the weight fractions determined by analysis.

In Tables II to VI are presented the comparison of the observed pressures with those calculated from the equations of state for mixtures, and in Table VII is given a summary of the results. The "Observed Pressures" listed are the original unsmoothed values.

TABLE IV

COMPARISON OF THE OBSERVED PRESSURES WITH THOSE CALCULATED FROM THE EQUATION OF STATE FOR A MIXTURE CONTAINING 69.556% OF NITROGEN AND 30.444% OF METHANE BY WEIGHT

For each isometric the observed pressures are given in the first horizontal line and the observed minus the calculated pressures in the second. The latter values subtracted from the former give the pressures calculated from the equation of state.

Temp., °C. Vol. cc./g.		0	50	100	150	200	Av. dev. Atm.	 %
		Pressures, atmospheres						
30	obs.	31.64	38.17	44.66	51.13	57.59		
	obs.−calcd.	0.04	0.08	0.10	0.11	0.13	0.092	0.202
25	obs.	37.76	45.71	53.63	61.51	69.38		
	obs.−calcd.	0.07	0.11	0.15	0.17	0.19	.138	.252
20	obs.	46.81	57.00	67.15	77.22	87.28		
	obs.−calcd.	0.12	0.18	0.26	0.28	0.32	.232	.340
15	obs.	61.68	75.81	89.89	103.82	117.74		
	obs.−calcd.	0.24	0.33	0.47	0.52	0.59	.430	.470
12	obs.	76.35	94.72	113.01	131.11	149.23		
	obs.−calcd.	0.40	0.54	0.76	0.88	1.07	.730	.630
10	obs.	90.95	113.86	136.64	159.25	181.66		
	obs.−calcd.	0.65	0.84	1.13	1.39	1.53	1.108	.798
8	obs.	112.93	143.25	173.48	203.31	233.07		
	obs.−calcd.	1.19	1.46	2.04	2.44	2.90	2.006	1.138
6	obs.	150.93	195.53	239.85	283.62	327.44		
	obs.−calcd.	2.88	3.59	4.77	5.83	7.20	4.854	2.000
			Total average deviation to 6 cc./g.				1.199	0.729
			Total average deviation to 8 cc./g.				0.677	.547

TABLE V

COMPARISON OF THE OBSERVED PRESSURES WITH THOSE CALCULATED FROM THE EQUATION OF STATE FOR A MIXTURE CONTAINING 31.014% OF NITROGEN AND 68.986% OF METHANE BY WEIGHT

For each isometric the observed pressures are given in the first horizontal line and the observed minus the calculated pressures in the second. The latter values subtracted from the former give the pressures calculated from the equation of state.

Temp., °C. Vol. cc./g.		0	50	100	150	209	Av. dev. Atm.	 %
		Pressures, atmospheres						
29.9456	obs.	37.70	45.99	54.23	62.42	70.59		
	obs.−calcd.	0.00	0.01	0.03	0.02	0.00	0.012	0.022
24.9456	obs.	44.66	54.81	65.04	74.92	84.91		
	obs.−calcd.	−0.01	−0.01	0.14	−0.02	−0.05	.046	.070
19.9456	obs.	54.82	67.95	80.92	93.82	106.68		
	obs.−calcd.	−0.01	0.01	−0.01	−0.05	−0.08	.032	.034
14.9456	obs.	71.11	89.48	107.71	125.79	143.70		
	obs.−calcd.	0.03	−0.05	−0.05	−0.09	−0.23	.090	.076

Table V (*Concluded*)

Vol. cc./g.	Temp., °C.	0	50	100	150	200	Av. dev. Atm.	Av. dev. %
		Pressures, atmospheres						
11.9456	obs.	86.97	110.90	134.73	158.57	182.03		
	obs. − calcd.	0.29	−0.09	−0.23	−0.16	−0.36	.226	.176
9.9456	obs.	102.36	132.46	162.65	192.51	222.07		
	obs. − calcd.	0.52	−0.11	−0.14	−0.20	−0.40	.274	.192
7.9456	obs.	126.04	165.87	206.42	246.51	286.10		
	obs. − calcd.	1.85[a]	0.19	0.12	0.07	−0.18	.140	.065
6.9456	obs.	143.52	191.02	239.94	288.11	335.68		
	obs. − calcd.	3.28[a]	0.74	0.81	0.79	0.57	.728	.293
				Total average deviation			.181	.113

[a] These two deviations were not included in the averages.

Table VI

Comparison of the Observed Pressures with those Calculated from the Equation of State for a Mixture Containing 29.69% of Nitrogen and 70.31% of Methane by Weight

For each isometric the observed pressures are given in the first horizontal line and the observed minus the calculated pressures in the second. The latter values subtracted from the former give the pressures calculated from the equation of state.

Vol. cc./g.	Temp., °C.	0	50	100	150	200	Av. dev. Atm.	Av. dev. %
		Pressures, atmospheres						
40	obs.	28.87	34.97	41.04	47.08	53.08		
	obs. − calcd.	0.00	0.03	0.05	0.06	0.04	0.036	0.084
35	obs.	32.75	39.81	46.82	53.80	60.74		
	obs. − calcd.	0.00	0.04	0.06	0.08	0.06	.048	.096
30	obs.	37.84	46.22	54.51	62.77	70.99		
	obs. − calcd.	0.01	0.06	0.08	0.10	0.09	.068	.120
25	obs.	44.82	55.09	65.26	75.36	85.41		
	obs. − calcd.	0.02	0.08	0.12	0.13	0.11	.092	.134
20	obs.	55.00	68.26	81.35	94.37	107.31		
	obs. − calcd.	0.06	0.14	0.18	0.20	0.19	.154	.186
15	obs.	71.30	89.91	108.28	126.48	144.61		
	obs. − calcd.	0.16	0.25	0.32	0.33	0.34	.280	.260
12	obs.	87.01	111.45	135.61	159.52	183.31		
	obs. − calcd.	0.37	0.42	0.54	0.61	0.67	.522	.392
10	obs.	102.36	133.20	163.66	193.78	223.80		
	obs. − calcd.	0.70	0.74	0.92	1.05	1.26	.934	.580
				Total average deviation			.267	.232

Table VII

Summary of the Average Deviations of the Pressures Calculated by the Equation of State from the Observed Pressures

Gas	Temp. range, °C.	Max. press., atm.	Vol. range, cc./g.	No. of points	Total av. dev. Atm.	Total av. dev. %
N_2	0 to 200	216	23 to 7	35	0.046	0.055
69.556% N_2 + 30.444% CH_4	0 to 200	233	30 to 8	35	.677	.547
31.014% N_2 + 68.986% CH_4	0 to 200	336	30 to 7	38	.181	.113
29.69% N_2 + 70.31% CH_4	0 to 200	224	40 to 10	40	.267	.232
CH_4	0 to 200	254	40 to 10	40	.064	.066

5. Discussion of the Results

It may be well to emphasize that the values of the constants for the mixtures were calculated by means of the relations (2) from the constants of the pure gases and the composition of the mixtures, *and were not derived by passing an equation through the mixture data.*

The volume of the piezometer used in all the measurements of Smith and Taylor and of Keyes and Burks was about 13 cc., and hence for specific volumes below 7 cc. per gram the total volume of the gas was small—from 2 to 3 cc. At these large densities, a small error in the specific volume makes a large error in the pressure. Therefore, in taking the "Total Average Deviations" the two isometrics below 7 cc. per gram were not included. With this exception and two points in Table V all the measured pressures were used in taking the averages.

The equation reproduces the measured pressures for the pure gases nitrogen and methane very satisfactorily, as can be seen by an examination of Table VII. Two independent sets of measurements were made by Keyes and Burks with mixtures containing about 70% methane. The equation of state for mixtures reproduced these data with average deviations of 0.11 and 0.23%, which is again a very satisfactory result. It will be noticed that for the 70.31% methane mixture, all the deviations are positive and increase in a regular manner with the density, which could be explained by a slight error in the measured composition and hence account for the somewhat larger average deviation. The average deviation for the 30% methane mixture, which was not checked, is larger than for either of the others, being 0.55%. This could be explained on the basis of an error in the composition of the mixture, especially as the deviations are all positive and progress in a regular manner with the density. A small variation in the values of the constants A_{0m} and B_{0m} for a mixture, due to a variation in the assumed composition, will cause a large variation in the calculated pressure at the larger densities.

The question of whether or not the method of combining the constant used in the case of methane and nitrogen will prove satisfactory for other gas mixtures must be settled by further experimental work. If the equation of state constants for the two gases composing a mixture have about the same values, it may be impossible to conclude that one method of combining the constants is better than any one of several other possible methods. In the case of methane and nitrogen the B_0 constants (on a molal basis) are not so very different from each other; but for all of the ten pure gases so far treated[1] the B_0 constant does not show a wide variation (with the exception of ethyl ether). The A_0 constant for methane is about twice that for nitrogen (on a molal basis), which represents a rather wide variation. Thus it is believed that the method of combining constants used in the present paper for methane and nitrogen will hold for many other gas mixtures.

6. Summary

The equation of state proposed by Beattie and Bridgeman has been applied to mixtures of methane and nitrogen by use of a simple method for calculating the values of the constants of the mixture from those for the pure gases. The constants R, a, B_0, b and c which contain the dimension of density to the first power are combined linearly, thus $B_{0x} = B_{01}(1 - x) + B_{02}x$; the A_0 constant contains the dimension of density to the second power and hence the square root of A_0 is combined linearly, $A_{0x} = [\sqrt{A_{01}}(1 - x) + \sqrt{A_{02}}x]^2$.

It is concluded that it is possible to write a single equation by means of which pressures for the entire series of mixtures of methane and nitrogen, including the pure gases, can be calculated from the temperature, density and composition.

The satisfactory nature of the agreement between observed and calculated pressures for the mixtures of methane and nitrogen leads to the expectation that this method of combining the constants will prove applicable to mixtures of other gases. The general equation of state for mixtures is presented in Equation 3 and the virial form in Equation 4. This equation of state is completely algebraic and can be used for the integration in terms of elementary functions of many thermodynamic relations.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE FORMATION OF OZONE IN THE ELECTRICAL DISCHARGE AT PRESSURES BELOW THREE MILLIMETERS[1]

BY JAMES K. HUNT

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Ozone formation in the electrical discharge has been studied chiefly at atmospheric pressures under conditions which give a non-uniform distribution of ionization. The purpose of this investigation was the study of the factors involved in the formation of ozone in an electrical discharge at low pressures, under conditions of somewhat greater uniformity. Pressures below three millimeters of mercury were employed and a high precision in the chemical analysis was demanded for these minute quantities of ozone.

In a previous communication from this Laboratory[2] the influence of the electrodes was studied down to 14 mm. and the ratio of electrode area to

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[1] This communication is based on a thesis submitted for the degree of Doctor of Philosophy at the University of Wisconsin in 1926, under the direction of Farrington Daniels.

[2] Newsome, THIS JOURNAL, 48, 2035 (1926).