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THE EQUATION OF STATE FOR BINARY MIXTURES OF METHANE AND NITROGEN

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Introduction

The experimental work here reported was carried out during the years 1923 and 1924 for the purpose of ascertaining whether or not the equation of state which represented the separate gases, nitrogen and methane, was also capable of representing the data for mixtures of the two gases. The measurements have been found to give an affirmative answer and in addition yield the interesting result that the constants of equations of state for the mixtures are linear functions of the constants for the pure gases and the compositions of the mixtures. More explicitly, the β, α, and l constants for the mixtures appear to be given within a reasonably good approximation by the equations $\beta_{N_2}W_{N_2} + \beta_{CH_4}W_{CH_4}$, $\alpha_{N_2}W_{N_2} + \alpha_{CH_4}W_{CH_4}$, $l_{N_2}W_{N_2} + l_{CH_4}W_{CH_4}$ where the β_{N_2}, β_{CH_4}, etc., represent constants for the separate components and the W's refer to the masses of the constituents. The A constant is of the same form in the square root of the constants of the separate gases, namely, $(\sqrt{A}_{N_2}W_{N_2} + \sqrt{A}_{CH_4}W_{CH_4})^2$.

The stated relation between the constants of the separate gases and the composition has been obtained by neglecting the "curvature" of the isometrics. Actually this introduces relatively only a small error in computing the *pressures* since the departure of the gaseous mixtures from isometric linearity is small in the region of 0 to 200°. It is of course possible to allow for the isometric curvature in the manner already used for N_2,[1] CO_2,[2] CH_4[3] and $(C_2H_5)_2O$.[4] The detailed consequences for the additive rule of constants when allowance is made for the isometric curvature will be presented in a later paper.

It will be clear that the additive rule is a further step in the direction of providing a basis for the development of a more general mass action expression for chemical reactions in the gaseous phase. Already, in fact, Lewis and Gillespie[5] have applied the rule to their data on ammonia–nitrogen mixtures. Keyes[6] has also used the above additive equation of state constants rule to compute the Haber equilibrium to 1000 atmospheres

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[1] Keyes and Taylor, THIS JOURNAL, **49**, 896 (1927).

[2] Bridgeman, *ibid.*, **49**, 1130 (1927).

[3] Keyes and Burks, *ibid.*, **49**, 1403 (1927).

[4] Beattie, *ibid.*, **49**, 1123 (1927).

[5] Lewis and Gillespie, *ibid.*, **47**, 305 (1925); **48**, 28 (1926); **49**, 1146 (1927).

[6] Keyes, *ibid.*, **49**, 1393 (1927).

in a somewhat different manner (and, all things considered, a tolerable agreement with the observational material for the equilibrium results).

The choice of gases for the present investigation depends among other things upon the chemical indifference of methane in the presence of nitrogen. Both gases were, moreover, in the experimental temperature range of the apparatus available, well above their respective critical temperatures—a matter of importance from the point of simplicity of interpretation because of the nearly linear character of the isometrics at higher temperatures. The gases are, moreover, both of the non-polar type. The quality of the gases employed was similar in every way to the gases employed for the measurements of pure methane and nitrogen.[7] It is of interest to note also that not only were the gases for the "mixtures" measurements made with gases of identical quality as those used to obtain the constants for the pure gases but the same apparatus was used alike for pure gases and mixtures. The consistency of the data as a whole should accordingly be favored.

The Experimental Data

Tables I, II and III give the data for three mixtures, two of which are nearly of the same composition. The first row in each table records the

TABLE I

PRESSURE, VOLUME, TEMPERATURE DATA FOR THE NITROGEN–METHANE MIXTURE
0.6956 G. OF NITROGEN—0.3044 G. OF METHANE
Pressure in International atmospheres; volumes in cc. per g.

Volume, cc./g.	0°	50°	100°	150°	200°	
30	31.640	38.172	44.664	51.126	57.591	Obs.
	31.664	38.149	44.635	51.120	57.606	Calcd.
25	37.756	45.711	53.634	61.513	69.381	Obs.
	37.782	45.688	53.594	61.500	69.406	Calcd.
20	46.812	56.998	67.146	77.220	87.281	Obs.
	46.855	56.972	67.089	77.206	87.323	Calcd.
15	61.681	75.810	89.886	103.823	117.737	Obs.
	61.759	75.783	89.807	103.831	117.855	Calcd.
12	76.349	94.723	113.010	131.113	149.225	Obs.
	76.476	94.694	112.912	131.130	149.348	Calcd.
10	90.952	113.864	136.643	159.246	181.658	Obs.
	91.101	113.811	136.521	159.231	181.941	Calcd.
8	112.929	143.254	173.483	203.305	233.066	Obs.
	113.088	143.121	173.153	203.186	233.218	Calcd.
6	150.927	195.529	239.853	283.615	327.443	Obs.
	150.575	194.448	238.321	282.194	326.067	Calcd.

$$p^{\text{atm.}} = \frac{3.5950}{v - \delta}\,T - \frac{3434.9}{(v + 0.2094)^2}$$

$$\log_{10}\delta = 0.37861 - \frac{0.5951}{v}$$

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

Table II

Pressure, Volume, Temperature Data for the Nitrogen–Methane Mixture 0.3101 G. of Nitrogen—0.6899 G. of Methane

Pressure in International atmospheres; volumes in cc. per g.

Specific volume	0°	50°	100°	150°	200°	
29.946	37.700	45.994	54.227	62.424	70.592	Obs.
	37.682	45.894	54.107	62.319	70.532	Calcd.
24.946	44.662	54.814	65.036	74.920	84.913	Obs.
	44.665	54.723	64.781	74.839	84.897	Calcd.
19.946	54.823	67.948	80.918	93.821	106.684	Obs.
	54.868	67.826	80.784	93.742	106.700	Calcd.
14.946	71.113	89.484	107.710	125.792	143.701	Obs.
	71.275	89.426	107.577	125.728	143.879	Calcd.
11.946	86.974	110.899	134.726	158.570	182.031	Obs.
	87.102	110.905	134.708	158.511	182.314	Calcd.
9.946	102.359	132.464	162.645	192.505	222.069	Obs.
	102.531	132.451	162.371	192.291	222.211	Calcd.

$$p^{\text{atm.}} = \frac{4.4383}{v - \delta}T - \frac{6660.4}{(v + 0.5113)^2}$$

$$\log_{10} \delta = 0.49721 - \frac{0.937}{v}$$

Table III

Pressure, Volume, Temperature Data for the Nitrogen–Methane Mixture, 0.2969 G. of Nitrogen—0.7031 G. of Methane

Pressure in International atmospheres; volumes in cc. per g.

Volume, cc./g.	0°	50°	100°	150°	200°	
40	28.868	34.972	41.038	47.075	53.084	Obs.
	28.900	34.954	41.008	47.062	53.115	Calcd.
35	32.750	39.811	46.821	53.803	60.738	Obs.
	32.790	39.787	46.784	53.781	60.778	Calcd.
30	37.843	46.220	54.514	62.773	70.988	Obs.
	37.898	46.183	54.469	62.754	71.040	Calcd.
25	44.819	55.089	65.260	75.360	85.414	Obs.
	44.898	55.048	65.198	75.348	85.498	Calcd.
20	55.002	68.262	81.353	94.371	107.308	Obs.
	55.098	68.178	81.258	94.338	107.418	Calcd.
15	71.298	89.910	108.283	126.483	144.608	Obs.
	71.393	89.715	108.037	126.359	144.681	Calcd.
12	87.008	111.450	135.606	159.515	183.313	Obs.
	86.935	110.951	134.967	158.982	182.998	Calcd.
10	102.360	133.203	163.655	193.779	223.800	Obs.
	103.042	133.200	163.360	193.519	223.677	Calcd.

$$p^{\text{atm.}} = \frac{4.46475}{v - \delta}T - \frac{6803.6}{(v + 0.4)^2}$$

$$\log_{10} \delta = 0.51760 - \frac{1.0371}{v}$$

observed pressures and the row immediately beneath the pressures computed by the respective equations (based directly on the data) placed at the bottom of each table. The isometrics are not strictly linear for the mixtures. For the pure gases the isometrics of nitrogen show very little curvature in the temperature region 0–200°, while the methane isometrics show pronounced enough curvature to be treated quantitatively.[3] The isometrics of the mixtures show less curvature as the amount of methane diminishes, as would perhaps be expected. The pressures evidently are well represented by the equations, which are of the same general form as may be used for representing the pressures of the pure gases.

Figs. 1 and 2 give a survey of the additive volumes rule[8] (Leduc's rule) and the additive pressures rule (Dalton's rule).[9] The even pressures for Fig. 1 were obtained by graphical treatment, while Fig. 2 contains the observational material taken directly from Tables I and III. It is quite evident that the agreement of these computed volumes or pressures does not accord with the observed volumes or pressures. It is to be noted, however, that the additive volumes relation gives better accord with the experimental data than the additive pressures. For both additive relations the agreement improves as higher temperatures are approached. In every instance also the observed volumes for constant pressures and the

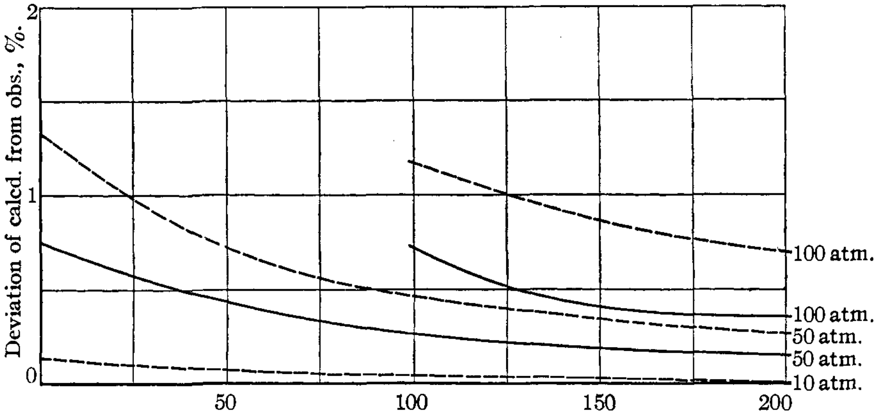

Fig. 1.—The calculated numbers are obtained from the formulas $v_{\text{calcd.}} = 0.3044 v_{CH_4} + 0.6956\ v_{N_2}$ and $v_{\text{calcd.}} = 0.7031\ v_{CH_4} + 0.2969\ v_{N_2}$, where v_{CH_4} and v_{N_2} are the volumes of the pure gases under the same pressure and temperature as the mixture. The ordinates are the percentage differences between observed and "calculated" or $[(v_{\text{obs.}} - v_{\text{calcd.}})/v_{\text{obs.}}] \times 100$.

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[8] The "calculated" volumes (cc. per g. of mixture) are obtained by using the measured or experimental volumes for methane and nitrogen, v_{CH_4}, v_{N_2}, in the formula $v_{\text{calcd.}} = v_{CH_4}\ 0.3044 + v_{N_2}\ 0.6956$.

[9] The "calculated" pressures (atm. for volumes in cc./g.) are obtained by using the measured or experimental pressures for methane and nitrogen, p_{CH_4}, p_{N_2}, in the formula $p_{\text{calcd.}} = p_{CH_4}\ 0.30444 + p_{N_2}\ 0.69555$.

observed pressures for constant volumes are greater than those computed by these rules.

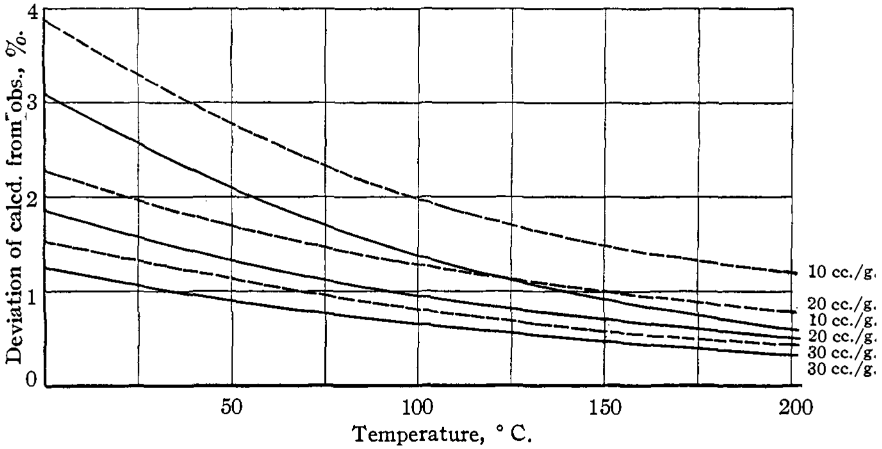

Fig. 2.—The calculated numbers are obtained from the formulas $p_{\text{calcd.}} = 0.3044\, p_{CH_4} + 0.6956\, p_{N_2}$ and $p_{\text{calcd.}} = 0.741\, p_{CH_4} + 0.2969\, p_{N_2}$, where p_{CH_4} and p_{N_2} are the pressures of the pure gases under the same volume and temperature as the mixture. The ordinates are the percentage differences between observed and "calculated" or $[(p_{\text{obs.}} - p_{\text{calcd.}})/p_{\text{obs.}}] \times 100$.

Relations between the Equation of State Constants

Table IV contains the equation of state constants for pure nitrogen in the second column and those for methane in the third column. The remaining columns contain the constants for the mixtures noted at the top of each column. The horizontal rows of constants marked "calcd." are computed using the following linear relations between the constants for the pure gases and the composition of the mixtures where the *W*'s are the weights of gases composing a gram of mixture. The constants given in the table for pure methane, it should be stated, are those obtained by ignoring the curvature of the isometrics of methane. It is clear that

TABLE IV

CONSTANTS FOR EQUATIONS FOR PURE GASES AND MIXTURES

Units: cc. per g. International atmospheres

	N_2	CH_4	CH_4, 70.31%	CH_4, 68.99%	CH_4, 30.44%
$A_{\text{obs.}}$	1650.5	10151.4	6803.6	6660.4	3434.9
$A_{\text{calcd.}}$	....	....	6872.8	6741.8	3472.6
$\beta_{\text{obs.}}$	1.65	3.961	3.293	3.142	2.391
$\beta_{\text{calcd.}}$	....	....	3.275	3.245	2.354
$\alpha_{\text{obs.}}$	0.992	2.857	2.388	2.158	1.370
$\alpha_{\text{calcd.}}$	....	....	2.304	2.279	1.560
$l_{\text{obs.}}$	0.313	0.536	0.400	0.511	0.209
$l_{\text{calcd.}}$	....	....	0.470	0.467	0.381
R	2.9286	5.1173	4.4675	4.4383	3.5950

very good agreement obtains between the "synthetic" constants and those determined directly from the observational data. Tables V and VI give a sufficient survey of the accuracy with which the equations of state computed from the constants of the pure gases for two of the mixtures give the pressures of the mixtures compared with the observed pressures.

TABLE V

PRESSURES FOR THE 30.44 WEIGHT PER CENT. METHANE MIXTURE COMPUTED WITH THE "SYNTHETIC" EQUATION OF STATE AND COMPARED WITH THE MEASURED PRESSURES

Volume, cc./g.	0°	50°	100°	150°	200°	
30	31.603	38.077	44.551	51.025	57.499	Calcd.
	31.640	38.172	44.664	51.126	57.591	Obs.
20	46.732	56.817	66.902	76.987	87.073	Calcd.
	46.812	56.998	67.146	77.220	87.281	Obs.

$$p^{\text{atm.}} = \frac{3.5950}{v - \delta} T - \frac{3472.6}{(v + 0.381)^2}$$

$$\log_{10} \delta = 0.37181 - \frac{0.678}{v}$$

TABLE VI

PRESSURES FOR THE 70.31 WEIGHT PER CENT. METHANE MIXTURE COMPUTED WITH THE "SYNTHETIC" EQUATION OF STATE AND COMPARED WITH THE MEASURED PRESSURES

Volume, cc./g.	0°	50°	100°	150°	200°	
30	37.846	46.130	54.413	62.697	70.980	Calcd.
	37.843	46.220	54.514	62.773	70.988	Obs.
20	55.029	68.106	81.183	94.259	107.336	Calcd.
	55.002	68.262	81.353	94.371	107.308	Obs.

$$p^{\text{atm.}} = \frac{4.4675}{v - \delta} T - \frac{6872.8}{(v + 0.47)^2}$$

$$\log_{10} \delta = 0.51521 - \frac{1.00}{v}$$

This is the first time within the knowledge of the writers that information has been obtained by direct experiment concerning the combination rule of the constants of the equations of state of mixtures (in terms of the constants and masses of the constituent gases). The scheme (1) has, however, been used by van der Waals and others.

$$\begin{aligned} A &= (\sqrt{A}_{\text{N}_2}W_{\text{N1}} + \sqrt{A}_{\text{CH}_4}W_{\text{CH}_4})^2 \\ \beta &= \beta_{\text{N}_2}W_{\text{N}_2} + \beta_{\text{CH}_4}W_{\text{CH}_4} \\ \alpha &= \alpha_{\text{N}_2}W_{\text{N}_2} + \alpha_{\text{CH}_4}W_{\text{CH}_4} \\ l &= l_{\text{N}_2}W_{\text{N}_2} + l_{\text{CH}_4}W_{\text{CH}_4} \end{aligned} \qquad (1)$$

It is quite possible that the combination scheme will be less simple for molecules whose "diameters" are less nearly equal than is the case for nitrogen and methane. Attention should be called in the case of these mixtures to the fact that the interaction constant of van der Waals for these nitrogen–methane mixtures has been successfully represented by the relation $A_{12} = \sqrt{A_{N_2}A_{CH_4}}$. In a later paper the theoretical conditions under which this can be true will be discussed.

Summary

1. Experimental data for three mixtures of nitrogen and methane have been obtained for the temperature range 0 to 200° and to pressures amounting to 200 or 300 atmospheres.

2. The equation of state for each mixture has been found to be the same in form as that applying to the pure gases.

3. The constants of the equations of state representing the mixtures were found to be linear functions of the constants of nitrogen and methane and compositions of the mixtures as follows: $A = (\sqrt{A}_{N_2}W_{N_2} + \sqrt{A}_{CH_4}W_{CH_4})^2$; $\beta = \beta_{N_2}W_{N_2} + \beta_{CH_4}W_{CH_4}$; $\alpha = \alpha_{N_2}W_{N_2} + \alpha_{CH_4}W_{CH_4}$; $l = l_{N_2}W_{N_2} + l_{CH_4}W_{CH_4}$.

4. The generalized equation of state based on the present results for a mixture of n gases would be written

$$p = \frac{\Sigma R_1 W_1 T}{v - \Sigma \beta_1 W_1 e^{-\frac{\Sigma \alpha_1 W_1}{v}}} - \frac{(\Sigma \sqrt{A}_1 W_1)^2}{(v + \Sigma l_1 W_1)^2}.$$

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

EQUILIBRIUM IN THE REACTIONS OF TIN WITH WATER VAPOR AND CARBON DIOXIDE

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The reactions of metals and their oxides with water vapor, together with the corresponding reactions with carbon dioxide, offer an indirect method of study of the water–gas equilibrium. Conversely, the equilibrium data pertaining to the latter reaction may be used to test the consistency of results obtained in the systems involving the metals. A series of such inter-comparisons in the case of iron and its oxides[1] revealed a large difference between the directly and indirectly determined values of the water–gas equilibrium constant. In view of the close agreement of the two sets of indirect determinations with each other it appears probable that the directly obtained data are in error. It remains desirable, however, to test this conclusion by further experiments. With that object the work here described was undertaken.

The equilibria selected for study may be represented by the following equations

$$Sn(l) + 2H_2O(g) = SnO_2(s) + 2H_2;\ K_1 = (H_2)/(H_2O) \tag{1}$$

$$Sn(l) + 2CO_2 = SnO_2(s) + 2CO;\ K_2 = (CO)/(CO_2) \tag{2}$$

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[1] Eastman and Evans, THIS JOURNAL, **46**, 888 (1924).