CHEMICAL EQUILIBRIA IN NON-IDEAL GASES WHOSE ISOMETRICS ARE LINEAR

BY FREDERICK G. KEYES

Introduction

Until recently there have existed no data whereby any theoretical formulation of chemical equilibria in the case of real gases might be tested. The publication of the experimental results on the ammonia synthesis from the elements by Larson and Dodge[1] and by Larson,[2] therefore, supplies valuable material for comparison with the calculations based on a formulation of actual gas equilibria already some ten years old.

Besides the numerical data pertaining to a given equilibrium, there are required also the fundamental constants of the equation of state for the mixtures of gases entering into the chemical interaction. The studies dealing with the equation of state problem at this Laboratory have established that for a single invariable molecular species, the pressure is a linear function of the temperature as higher temperatures are approached. It is further indicated, on the basis of experimental data soon to be published, that where the curvature of the isometrics can be accurately measured, the departure from linearity is explainable by assuming a quasi-association or aggregation of the single species to double or perhaps higher-order species.[3] In the presentation which is to follow, it will be

[1] Larson and Dodge, THIS JOURNAL, 45, 2918 (1923).

[2] Larson, ibid., 46, 367 (1924).

[3] It is clear that if aggregation is admitted as the reason for the curvature of the isometrics as small volumes and low temperatures are approached, the linearity of the isometrics must logically be viewed as a limiting condition arrived at only as higher temperatures and larger volumes are reached. However, the curvature is so small at relatively small volumes that it is legitimate for many purposes to ignore the curvature of the isometrics.

assumed that single molecular species alone of the reacting gases are present, reserving for a later paper the discussion of the manner in which aggregation of one or more of the reacting gases affects the equilibrium.

The Equation of State of Mixed Gases

The equation of state for a single species under conditions of high temperature and not too small volumes has been shown to be very approximately as follows.

$$p = \frac{RT}{v - \beta e^{-\alpha/v}} - \frac{A}{(v + l)^2} \tag{1}$$

The existing data pertaining to mixtures are far too meager to enable a definite conclusion to be drawn regarding the form of the equation of state for mixtures. The data available do show, however, that neither Dalton's additive pressure nor Leduc's additive volume propositions are true in general.

The desire to extend the thermodynamic treatment of gaseous reactions to high pressures led several years ago to a systematic experimental investigation of the isometrics of nitrogen-methane mixtures. Non-reactivity, large differences in the individual equation of state constants and convenience of experimental temperature range (0–200°) were factors which determined the choice of these two gases. The complete data obtained by Dr. H. G. Burks are now about ready for publication and the data[4] indicate that mixtures of these two gases follow the form of Equation 1 which represents the individual gases. Moreover, the constants for the mixtures are given within the limits of experimental error by the following equations.

$$
\begin{aligned}
A_{\text{mix.}} &= (\sqrt{A}_{\text{CH}_4} n_{\text{CH}_4} + \sqrt{A}_{\text{N}_2} n_{\text{N}_2})^2 \\
\beta_{\text{mix.}} &= \beta_{\text{CH}_4} n_{\text{CH}_4} + \beta_{\text{N}_2} n_{\text{N}_2} \\
\alpha_{\text{mix.}} &= \alpha_{\text{CH}_4} n_{\text{CH}_4} + \alpha_{\text{N}_2} n_{\text{N}_2} \\
l_{\text{mix.}} &= l_{\text{CH}_4} n_{\text{CH}_4} + l_{\text{N}_2} n_{\text{N}_2}
\end{aligned}
\tag{2}
$$

A generalized equation of state based on this result will be used in the calculation of the increase of the equilibrium constant (K_p) of the ammonia synthesis with pressure. The equation is as follows.

$$p = \frac{RT\Sigma n_1}{V - \Sigma n_1 \beta_1 e^{\Sigma \alpha_1 n_1/v}} - \frac{(\Sigma n_1 \sqrt{A_1})^2}{(V + \Sigma n_1 l_1)^2} \tag{3}$$

The Potential Energy of Gases

The potential energy of a gas will be defined as the integral $\int_{\infty}^{v} (\partial U/\partial v)_T dv$, where U is the internal energy of the gas and v the volume. The thermodynamic equation $(\partial U/\partial v)_T = T^2[(\partial P/T)/\partial T]_v$ makes possible the computation of the potential energy, and using Equation 1 there results $-A/(v + l)$. Equation 3, on the other hand, gives

$$-(\Sigma n_1 \sqrt{A_1})^2/(V + \Sigma n_1 l_1) \tag{4}$$

4 Burks, *Thesis*, Massachusetts Institute of Technology, **1924**.

The potential energy[5] as obtained through Equation 1 or 3 is a function of the volume alone, aside from the numbers of the different molecular species in the case of a mixture. The departure from linearity of the isometrics, as already stated, has been assumed to be due to a quasi-association or aggregation,[6] an effect which enters appreciably only as lower temperatures are approached, or at high pressures.

The Specific Heat Capacity of Gases

The specific heat of one component in a mixture of gases has always been assumed to be independent of the presence of the other gases, although the truth of the assumption is not self-evident. Moreover, it is conspicuous that one of the most evident failures of the classical kinetic gas theory is in connection with the accounting it gives of the specific heat capacity of even a pure gas. On the other hand, the general problem of obtaining an adequate theory of the specific heat capacity of gases is of fundamental importance in completing our knowledge of chemical equilibria. Indeed, the present expedient of employing for heat capacities linear or quadratic expansions with temperature necessarily reduces the formulations of equilibria to a semi-empirical procedure, whereby extrapolation is made highly uncertain.[7] In this paper the usual assumption of additivity of heat capacities will be retained.

The Entropy of an Actual Gas

The general equation for the increment of the entropy is

$$dS = (dU + dW)/T \tag{5}$$

where U is the internal energy and W the reversible work performed by the system. Where dW is given by $p\,dv$, Equation 5 becomes, for a substance of Species 1, where C_{v_1} is the constant-volume heat capacity,

$$dS = C_{v_1}\frac{dT}{T} + \left(\frac{\partial p}{\partial T}\right)_v dv \tag{6}$$

The derivative $(\partial p/\partial T)_v$ may be found from Equation 1. Substituting in Equation 5, and integrating, gives

[5] Recent attempts to measure the potential energy directly (Joule's experiment) have met with some success in the case of carbon dioxide. See Keyes and Sears, *Proc. Nat. Acad. Sci.*, **2**, 38 (1925).

[6] Keyes, THIS JOURNAL, **46**, 1584 (1924).

[7] Many formulations of physicochemical problems are based on empirical equations for gaseous heat capacities wherein the actually observed or apparent specific-heat data are employed. Evidently in certain instances as, for example, the heat capacities of water, carbon dioxide and hydrogen, a correction should be applied to the observed data to correct for the heat absorbed due to dissociation of the molecule. Moreover, in recent papers attempting to account for the "vibrational specific heat" of hydrogen, "uncorrected" experimental values of the heat capacity of hydrogen have been employed at temperatures approaching 2000°, whereas, according to the existing values for the dissociation of hydrogen, a considerable fraction of the apparent heat capacity is due to heat absorbed by the dissociating molecule.

$$S_1 = \int_0^T C_{v_1} \frac{\mathrm{d}T}{T} + R \int \frac{\mathrm{d}v}{v - \delta_1} + S_1^\circ \qquad (6')$$

where S_1° is the entropy constant for gas number 1. Evidently, since C_{v_1} is not generally known as a function of the temperature, $\int C_{v_1} \mathrm{d}T/T$ cannot be evaluated. The term $R \int \mathrm{d}v/(v - \delta)$ is also given by $R \log (v - \delta)$ only as a first approximation.[8]

The change in entropy of a perfect gas, on mixing with other perfect gases, was calculated by Gibbs.[9] Expressed in words, the Gibbs proposition asserts that the entropy of a gas in a mixture at fixed pressure and temperature is the same as it would be if it alone occupied the volume of the mixture. Each of two gases, for example, n_1 moles and n_2 moles at the same pressure and temperature p and T, are contained in compartments of volume V_1 and V_2 of a container with a removable partition. The equations of state of the two gases, considered perfect, are $V_1 = (RT/p)n_1$ and $V_2 = (RT/p)n_2$. The entropies are, therefore, given by the following (Equation 6) equations, where S_1°, S_2° are constants.

$$S_1 = n_1 \int C_{v_1}(\mathrm{d}T/T) + R\, n_1 \log V_1/n_1 + n_1 S_1^\circ \qquad (7)$$
$$S_2 = n_2 \int C_{v_2}(\mathrm{d}T/T) + R\, n_2 \log V_2/n_2 + n_2 S_2^\circ \qquad (8)$$

After the partition is withdrawn mixing takes place, the pressure and temperature remaining unaltered. The total volume V containing the two gases is now $V = V_1 + V_2$, and the equation of state of the mixture $V = (RT/p)(n_1 + n_2)$. According to Gibbs' proposition the entropies are

$$S_1' = n_1 \int C_{v_1}(\mathrm{d}T/T) + R\, n_1 \log V/n_1 + n_1 S_1^\circ \qquad (9)$$
$$S_2' = n_2 \int C_{v_2}(\mathrm{d}T/T) + R\, n_2 \log V/n_2 + n_2 S_2^\circ \qquad (10)$$

The equations of state of the separate gases and the mixture give the following relations, since p and T are the same before and after mixing: $V_1/n_1 = V_2/n_2 = V/(n_1 + n_2)$ and $V/n_1 = V/(n_1 + n_2)x_1$; $V/n_2 = V/(n_1 + n_2)x_2$, where x_1 is $n_1/(n_1 + n_2)$, the mole fraction. Therefore, the difference between Equations 7 and 9, 8 and 10 gives at once $Rn_1 \log x_1$, $Rn_2 \log x_2$, which are the magnitudes of the entropy change of mixing.

An actual gas is assumed to have molecules of finite size producing a "volume effect" in the equation of state and a universal attraction, the origin of the cohesive pressure. In Equation 1 the volume effect δ

[8] The integral $\int \mathrm{d}v/(v - \delta)$ has not been obtained in terms of ordinary functions. As far as required for the present application to the ammonia equilibrium, the approximation is sufficient. It has been found, moreover, that the complete value of the integral differs but little from the approximation until quite small volumes are approached. The complete integral, in fact, differs from $R \log (v - \delta)$ by $R \int \mathrm{d}\delta/(v - \delta)$, where $\mathrm{d}\delta = (\alpha\delta/v^3)\mathrm{d}v$. Approximately, the latter integral is of the order of $-\alpha\beta/2v^2$.

[9] Gibbs, Scientific Papers, Longmans, Green and Co., New York, 1906, vol. I, pp. 156, 165.

is a function of the volume because of the "sponginess"[10] of the molecules and the cohesive pressure contains a constant (l) related to a modification in the law of attraction due to the dependence of the molecular polarization on density.

The conception of a perfect gas carries with it the notion of a molecule of such small dimensions that the space for the motion and action of the molecules is the volume of the container. The term ($v - \delta$), on the other hand, in the case of an actual gas may be taken to represent physically the volume of the gas diminished by the "volume effect" of the molecules and termed the action space (Ω). The term $p + A/(v + l)^2$ represents the sum of the hydrostatic pressure and a pressure (cohesive pressure) acting in the same direction as the hydrostatic pressure. It is proposed to designate this sum by π.

The equations of the pure gases will now be written $\pi_1\Omega_1 = RT\,n_1$, $\pi_2\Omega_2 = RT\,n_2$, and the mixtures as $\pi\Omega = RT\Sigma n_1$. Thus it is clear that if π and T are held constant, $\Omega_1/n_1 = \Omega_2/n_2 = \Omega/\Sigma n_1$. The entropy equation of n_1 moles of a single gas may also be written from Equation 6'.

$$S_1 = n_1 \int C_{v_1}(\mathrm{d}T/T) + R\,n_1 \log \Omega_1/n_1 + n_1\,S_1{}^\circ \tag{11}$$

If it is assumed that a proposition similar to that of Gibbs is true for an actual gas in which π and T are maintained the same before and after mixing, the entropy of Gas 1 in the mixture of Gases 1 and 2, for example, will become

$$S_1' = n_1 \int C_{\pi_1}(\mathrm{d}T/T) + R\,n_1 \log \Omega/n_1 + n_1\,S_1{}^\circ \tag{12}$$

The difference in entropy is as before, $R\,n_1 \log x_1$, it being understood that π and T instead of p and T were maintained the same before and after mixing. The entropy Equations 11 and 12 evidently become identical with Equations 7 and 9, as the volume increases indefinitely and π then becomes identical with p.

The entropy Equation 11 in generalized form will be used in the computation of the equilibrium equation of an actual gas. The internal energy U may be easily obtained through the equation $U_1 = \int C_{v_1}\,\mathrm{d}T + (\partial U_1/\partial v)_T \mathrm{d}v + U_1{}^\circ$, in which the second term of the right-hand member is given for a mixture by Equation 4. The two fundamental equations required are, therefore,

$$S = \Sigma n_1 \int C_{v_1}(\mathrm{d}T/T) + R\Sigma n_1 \log \Omega/n_1 + \Sigma n_1\,S_1{}^\circ \tag{13}$$

$$U = \Sigma n_1 \int C_{v_1}\,\mathrm{d}T - (\Sigma n_1\sqrt{A_1})^2/(V + \Sigma n_1 l_1) + \Sigma n_1\,U_1{}^\circ \tag{14}$$

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[10] Professor T. W. Richards long ago introduced the idea of atomic compressibility. In the equation of state (1) the δ term depends on a similar conception in which the distances between the atoms are considered variable and responsive to variations in the intensity of the electromagnetic field, due to the varying density of the molecules produced by changes in volume. The atoms, for the purpose of mathematical simplification in the calculation of δ, were assumed of invariable "size," it being considered that their "hardness" is very likely great in comparison with that of the molecules.

The Equilibrium Equation

The free-energy equation of Helmholtz will be used because of the form of Equation 1. The equation requires the total energy of the mixture as well as the entropy of the mixture. Equations 13 and 14 may, therefore, be substituted in the free-energy equation $F = U - TS$, giving the following equation.

$$F = \Sigma n_1 \int C_{v1} \, dT - \frac{(\Sigma n_1 \sqrt{A_1})^2}{(V + \Sigma n_1 l_1)} + \Sigma n_1 U_1{}^\circ - T\Sigma n_1 \int C_{v1} \frac{dT}{T} - RT\Sigma n_1 \log \frac{\Omega}{n_1}$$
$$- T\Sigma n_1 S_1{}^\circ \quad (15)$$

For equilibrium, $\delta F_{T,v} = 0$. In carrying out the variation, it is to be noted that the variations δn_1, δn_2, etc., are proportional to whole numbers ν_1, ν_2, etc., which are the numerical coefficients in the chemical equation, with respect to which reaction equilibrium is assumed. Equation 15, on rearrangement following the variation operation, becomes

$$\Sigma \nu_1 \log x_1 = -\frac{\Sigma \nu_1 U_1{}^\circ}{RT} - \frac{\Sigma \nu_1}{RT} \int C_{v1} \, dT + \frac{\Sigma \nu_1}{R} \int C_{v1} \frac{dT}{T} + \frac{2\,\Sigma \nu_1 \sqrt{A_1}\,\Sigma n_1\, A_1}{RT(V + \Sigma n_1 l_1)}$$
$$- \frac{\Sigma n_1}{\Omega}\, \Sigma \nu_1 \beta_1 e^{-\Sigma n_1 \alpha_1 / V} - \frac{(\Sigma n_1 \sqrt{A_1})^2\, \Sigma \nu_1 l_1}{RT(V + \Sigma n_1 l_1)^2} + \frac{\Sigma n_1}{\Omega}\, \Sigma n_1 \beta_1 e^{-\Sigma n_1 \alpha_1 / V}\, \frac{\Sigma \nu_1 \alpha_1}{V}$$
$$+ \frac{\Sigma \nu_1\, S_1{}^\circ - R\Sigma \nu_1}{R} + \Sigma \nu_1 \log \frac{\Omega}{\Sigma n_1} \quad (16)$$

Equation 16 at large volume becomes

$$\Sigma \nu_1 \log x_1 = -\frac{\Sigma \nu_1 U_1{}^\circ}{RT} + \Sigma \nu_1 \log \frac{RT}{p} - \frac{\Sigma \nu_1 \int C_{v1} dT}{RT} + \frac{\Sigma \nu_1 \int C_{v1} \dfrac{dT}{T}}{R} + \frac{(\Sigma \nu_1 S_1{}^\circ - \Sigma \nu_1 R)}{R}$$
$$(17)$$

which is the usual perfect gas equilibrium equation except for the fact that the specific-heat terms have been retained in the integral form. If C_{v1}, C_{v2}, etc. are constant, $\Sigma \nu_1 \int C_{v1} dT / RT$ becomes $\Sigma \nu_1 C_{v1}/R$, and $(\Sigma \nu_1 \int C_{v1} dT/T)/R$ becomes[11] $\Sigma \nu_1 Cv_1/R \log T$, whereupon Equation 17 reduces to

$$\Sigma \nu_1 \log x_1 = -\frac{\Sigma \nu_1 U_1{}^\circ}{RT} + \Sigma \nu_1 \log \frac{RT}{p} + \frac{\Sigma \nu_1 C_{v1}}{R} \log T + \frac{-\Sigma \nu_1 C_{v1} + \Sigma \nu_1 S_1{}^\circ - \Sigma \nu_1 R}{R}$$

It is readily seen from Equation 17, as has been many times pointed out,[12] that a knowledge of the entropy constants and heats of reaction of the reacting gases would enable chemical equilibria to be calculated without actual equilibria data. It is to be emphasized, however, that a knowledge of the $S_1{}^\circ$ constants alone would not be sufficient to formulate correctly

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[11] The specific heat at constant volume has been used, since for substances whose isometrics are linear in the absolute temperature C_v is a temperature function only, as may be seen at once from the equation $\partial C_v/\partial v = T\partial p^2/\partial T^2$. The constant pressure specific heat, on the other hand, is complicated; $C_p = C_v + R/1 - \alpha\delta/v^2 - 2A/RT\cdot(v - \delta)^2/(v + l)^3$ from Equation 1.

[12] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 453.

a chemical equilibrium in the absence of a knowledge of the correct functional form relating C_v to the temperature.

Application to the Ammonia Equilibrium

The prevailing custom employed to represent equilibrium compositions of a gaseous mixture requires the computation of the quantity $\Sigma\nu_1 \log x_1 p$, where p is the total pressure of the equilibrium mixture. This quantity may easily be found from Equation 16 by adding $\Sigma\nu_1 \log p$ to each side of the equation. Operating similarly with respect to Equation 17 and subtracting the latter from the former gives an equation for the logarithm of the ratio of the ordinary equilibrium constants K_p and K_{p_0}, where the latter refers to the equilibrium constant as p approaches zero. The general equation becomes

$$\Sigma\nu_1 \log px_1 - \Sigma\nu_1 \log p_0x_1 = \frac{2\Sigma\nu_1\sqrt{A_1}\,\Sigma n_1\sqrt{A_1}}{RT(V + \Sigma n_1 l_1)} - \frac{\Sigma n_1}{\Omega}\Sigma\nu_1\beta_1 e^{-\Sigma n_1\alpha_1/V}$$

$$+ \Sigma\nu_1 \log\frac{p}{\pi} - \frac{(\Sigma n_1\sqrt{A_1})^2\,\Sigma\nu_1 l_1}{RT(V + \Sigma n_1 l_1)^2} + \frac{\Sigma n_1}{\Omega}\Sigma n_1\beta_1 e^{-\Sigma n_1\alpha_1/V}\frac{\Sigma\nu_1\alpha_1}{V} \qquad (18)$$

The tangent of the log K_p/K_{p_0}, p curve as p approaches 0 becomes, from Equation 18,

$$\log K_p/K_{p0} = \frac{2\Sigma\nu_1\sqrt{A_1}\cdot\Sigma n_1\sqrt{A_1}}{\Sigma n_1 R^2 T^2}\,p - \frac{\Sigma\nu_1\beta}{RT}\,p - \frac{\Sigma\nu_1}{(\Sigma n_1)^2}\frac{(\Sigma n_1\sqrt{A_1})^2}{R^2 T^2}\,p \qquad (19)$$

an equation which is not identical, except for the term involving β, with a special equation obtained by Gillespie[13] through considerations leading from the fugacity rule of Lewis and Randall.[14] This is to be expected, however, since the treatment employed to obtain Gillespie's equation depends, among other things, on assuming the additivity of volumes of the gases composing the equilibrium mixtures, whereas Equation 19 is a special equation obtained by combining the constants of the individual gases according to Equations 2 above, giving Equation 3.

It may be pointed out that although the pressure of a gaseous mixture at very large volumes ought to be given approximately by assuming either additive volumes or additive constants, nevertheless, the form of the resulting mass-action laws at low pressures is not the same.

The constants of the gases pertaining to the ammonia synthesis are given in Table I together with the other quantities required in computing the quantity K_p/K_{p_0}. Argon is included because of its presence in the equilibrium mixture used by Larson and by Larson and Dodge.

The constants for hydrogen and nitrogen are substantially the same that Gillespie has used to compute the K_p/K_{p_0} ratio. The constants for ammonia are, however, different and depend on recent and extensive p-v-T data for ammonia obtained by Lawrence.[15] The ammonia molecule

[13] Gillespie, THIS JOURNAL, **48**, 28 (1926).

[14] Ref. 12, p. 226.

[15] Lawrence, *Thesis*, Massachusetts Institute of Technology, **1924**.

TABLE I

CONSTANTS FOR THE GAS IN THE REACTION $^3/_2H_2 + ^1/_2N_2 = NH_3$

A_{H_2}	$= 0.159 \times 10^6$	$\sqrt{A_{H_2}}$	$= 0.3987 \times 10^3$	β_{H_2}	$= 19.4$	α_{H_2}	$= 5.9$
A_{N_2}	$= 1.288 \times 10^6$	$\sqrt{A_{N_2}}$	$= 1.135 \times 10^3$	β_{N_2}	$= 49.5$	α_{N_2}	$= 30.3$
A_{NH_3}	$= 5.68 \times 10^6$	$\sqrt{A_{NH_3}}$	$= 2.383 \times 10^3$	β_{NH_3}	$= 81.4$	α_{NH_3}	$= 110.1$
A_A	$= 1.58 \times 10^6$	$\sqrt{A_A}$	$= 1.257 \times 10^3$	β_A	$= 51.0$	α_A	$= 0$

l_{H_2}	$= -2.4$	$\Sigma\nu_1\sqrt{A_1}$	$= 1217.4$	$R = 82.06$ cc./atm./mole
l_{N_2}	$= 6.2$	$\Sigma\nu_1\beta_1$	$= 27.55$	
l_{NH_3}	$= 31.5$	$\Sigma\nu_1\alpha_1$	$= 86.1$	
l_A	$= -10.0$	$\Sigma\nu_1 l_1$	$= 32.0$	

possesses, like the water molecule, a natural or permanent electric moment in distinction from the hydrogen or nitrogen molecule which possess no permanent moments. The aggregation effect is relatively large in consequence for ammonia, and the constants in Table I were obtained after "correcting" the isometrics for curvature. As a matter of fact, when the curvature of the isometrics is neglected, the A and β values both are large as compared with those obtained from the more nearly linear isometrics at high temperatures where Equation 1 applies with great exactness.

From Equation 18 there results the following equation for the ammonia equilibrium, using the constants from Table I.

$$\log_{10} K_p/K_{p0} = 12.886 \frac{\Sigma n_1\sqrt{A_1}}{T(V + \Sigma n_1 l_1)} - 11.965 \frac{\Sigma n_1}{\Omega} e^{-\Sigma n_1\alpha_1/V} + \log_{10} \pi/p$$
$$- 0.16936 \frac{\Sigma(n_1/A_1)^2}{T(V + \Sigma n_1 l_1)^2} + 37.393 \frac{\Sigma n_1}{\Omega V} \Sigma n_1\beta_1 e^{-\Sigma n_1\alpha_1/V} \quad (20)$$

By means of this equation the numbers in the last column of Table II

TABLE II

AMMONIA EQUILIBRIUM DATA OBSERVED AND CALCULATED FROM EQUATION 20

t, °C.	p, atm.	NH₃, %.	n_{H_2}	n_{N_2}	n_{NH_3}	Σn_1	G. L. P. K_p/K_{p0} obs.	G. H. P. K_p/K_{p0} obs.	K_p/K_{p0} calcd.
375	50	19.44	1.1018	0.3268	0.3463	1.7814	1.0500		1.030
	100	30.95	0.8669	.2486	.5029	1.6248	1.1400		1.096
450	50	9.17	1.3532	.4106	.1787	1.9489	1.041		1.011
	100	16.35	1.1728	.3505	.2990	1.8287	1.095		1.039
	300	35.50	0.7851	.2213	.5574	1.5702	1.344[a]	1.537	1.283
	600	53.60	.5076	.1289	.7425	1.3854	1.993[a]	2.280	2.097
	1000	69.40	.3138	.0642	.8717	1.2560	3.705[a]	4.238	5.889
475	50	7.13	1.4089	.4292	.1416	1.9861	1.029		1.008
	100	12.98	1.2546	.3778	.2444	1.8832	1.068		1.028
	300	31.00	0.8660	.2482	.5035	1.6242	1.358[a]	1.472	1.227
	600	47.50	.5935	.1574	.6852	1.4425	1.819[a]	1.972	1.858
	1000	63.50	.3817	.0868	.8264	1.3013	3.106[a]	3.366	4.113
500	50	5.58	1.4526	.4438	.1125	2.0152	1.028		1.005
	100	10.40	1.3207	.3998	.2004	1.9273	1.053		1.021
	300	26.20	0.9587	.2791	.4417	1.6859	1.310[a]	1.349	1.177
	600	42.10	0.6757	.1848	.6304	1.4973	1.724[a]	1.777	1.688

[a] Extrapolated.

were computed, using for the "n" values computed from the equilibrium data of Larson and Dodge, and of Larson.   The formulas used to compute the number of moles are given below where a is the percentage of ammonia formed from the original gaseous mixture containing 0.3% of argon, 76.2% of hydrogen and 23.5% of nitrogen.   Moles of ammonia = 2.1277 $100/(100 + a) = y$; moles of hydrogen = $0.12127 + {}^3/_2 (1 - y)$; moles of nitrogen = $1/_2 (1 - y)$; moles of argon = 0.0064; total moles = 2.1277 $100/(100 + a)$.
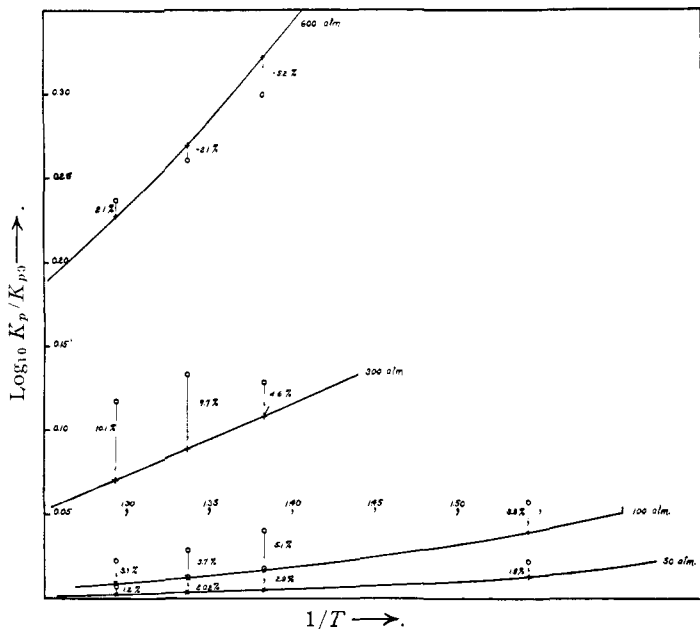

Fig. 1.—The ammonia equilibrium experimental results of Larson and Dodge, and of Larson, —— O; computed values from Equation 20, —— +.

Table II contains for comparison also the K_p/K_{p_0} ratio computed from the equations given by Gillespie,[16] which represent the first series (Larson and Dodge) of measurements of the equilibrium to 100 atm. and the second series (Larson) to 1000 atm.   There is a discontinuity between the two series and for this reason two columns are given in Table II headed G. L. P. and G. H. P., referring to Gillespie's equations representing the low-pressure data and the high-pressure data.   The low-pressure equation has been used to extrapolate to the three higher pressures for comparison purposes.   In general, the computed ratios at 50, 100 and 300 atm. are lower than those observed, while at 600 atm. the computed ratios lie between the two "observed" ratios at the two temperatures

[16] Gillespie, *J. Math. Phys., Mass. Inst. Techn.*, **4**, 84 (1925).

450 and 475°. The 1000-atm. ratios, however, are much larger than the observed. It is of interest to observe that at higher pressures the equilibrium-constant ratio shows a large variation with a comparatively small change in the equilibrium composition. For example, at 450° and 1000 atm. an increase in the percentage of ammonia from 68.4 to 71.0 changes the ratio from 4.24 to 4.85. Including the 100-atm. pressure range, the calculated and observed ratios are in accord within 5%, while in the high-pressure range the ratios are in agreement as regards order of magnitude. The percentage of ammonia deduced from the calculated ratios is not, however, greatly different from the observed amounts of ammonia at 300, 600 and 1000 atm. Fig. 1 exhibits the logarithm of the computed ratios for constant pressures plotted against the reciprocal of the absolute temperature.

The tedious computations necessary to secure the material for Table II were made by Miss Charlotte T. Perry, for whose assistance the writer is deeply grateful.

Summary

1. A generalized equation of state for mixtures is given applicable to gases whose isometrics are linear. This equation is based on experimental results obtained for binary mixtures of nitrogen and methane.

2. An equation for the entropy of a gaseous mixture is given which becomes identical with the familiar entropy equation for perfect gases at low pressures. By means of the entropy equation and the energy equation, a general expression for the equilibrium constant (K_p) is deduced by using the thermodynamic function $F = U - TS$, the free energy for temperature and volume as independant variables.

3. Comparison of the K_p/K_{p_0} equation (ratio of K_p at p atm. to K_{p_0} at zero pressure) with the experimental results of Larson and Dodge and of Larson for the ammonia synthesis indicates tolerable agreement to 600 atm. The computed results (K_p/K_{p_0}) are lower than the experimental results by several per cent. to 100 atm. The calculated ratios (K_p/K_{p_0}) at the three temperatures for which equilibrium measurements exist at high pressures (Larson) are in agreement as regards order of magnitude, the ratios observed and calculated being as follows.

t, °C.		300 atm.	600 atm.	1000 atm.
450,	obs.	1.537	2.280	4.238
	calcd.	1.283	2.097	5.889
475,	obs.	1.472	1.972	3.366
	calcd.	1.227	1.858	4.113
500,	obs.	1.349	1.777	
	calcd.	1.177	1.688	

4. Experimentally, log K_p/K_{p_0} is practically linear in $1/T$. This cannot be strictly true for the computed values of log K_p/K_{p_0} (Equation

20); nevertheless, numerically the linear relation does hold rather closely over temperature range 375 to 500° (Fig. 1).

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THE ISOMETRICS OF GASEOUS METHANE

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Introduction

The interest which attaches to an accurate knowledge of the properties of methane is two-fold. First, it belongs to that class of substances, of which nitrogen, hydrogen and oxygen are further examples, which in the sense of their dielectric behavior[1] may be said to possess no natural or permanent electrical moment. Secondly, relative to the other members of the above class of substances, the constants A, β, α and l of the equation of state are large, making it very suitable as a component with, for example, nitrogen in binary mixtures. Molecular simplicity and freedom from the possibility of chemical action in binary mixtures are indeed most important in attempting to determine the equation-of-state constants in mixtures as functions of the constants of the equations of state of the pure components of the binary mixtures.

The present measurements represent a repetition of work already carried out for methane some years ago.[2] However, in the interval, the apparatus has been much improved in many particulars, not the least of which is an increase in the size of the methane container or piezometer. Thus the present container has a maximum volume of about 13.337 cc. at 0°, whereas the earlier had a volume of 7.657 cc. In principle, however, the method remains the same as that in use for this class of work for a number of years.

The earlier work gives smaller pressures for corresponding volumes and temperatures, although above 30 cc. per g. the differences are practically insignificant. At about 10 cc. per g., however, the differences are larger than would have been anticipated in spite of the small size of the piezometer employed in the earlier survey. Thus at 0° the

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[1] The importance of the dielectric constant in relation to the cohesive pressure constant A has been made clear by Debye [*Physik. Z.*, **21**, 178 (1920)]. A recent paper by Keyes and Marshall [THIS JOURNAL, **49**, 156 (1927)] shows that for substances of the simple character referred to, the ratio of the equation-of-state constants A and β (in per mole units) is approximately proportional to the Lorentz constant P_0 in the dielectric equation $V(D - 1)/(D + 2) = P_0$, where V is the molecular volume and D the dielectric constant.

[2] Keyes, Smith and Joubert, *J. Math. Phys. Mass. Inst. Techn.*, **1**, 191 (1922).