

the formation of lead bromide from its elements, an independent value for the entropy of bromine is found, $S_{298} = 18.6 \pm 1.0$ cal. per degree.

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A MASS ACTION EQUATION FOR COMPRESSED GASES, WITH APPLICATION TO THE HABER EQUILIBRIUM DATA

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Recently the following equation was derived¹ for the fugacity (f_e) of a gas in a mixture, from the assumptions that at sufficiently low pressures the equilibrium pressure of a gas in a mixture (or its "partial pressure") approaches the mole fraction—total pressure product and the fugacity approaches the pressure.

$$RT \ln f_e = \int_{p^\times}^p (\partial v / \partial n_1 - v_1 / n_1) dp + RT \ln f_p + RT \ln x_1 \quad (1)$$

Here f_p is the fugacity of the pure gas at the total pressure of the mixture, x_1 is the mole fraction, $\partial v / \partial n_1$ is the partial molal volume of the gas in the mixture, and v_1 / n_1 is the molal volume of pure gas, the molal and partial molal volumes being measured at the same pressure (p). The integration is at constant temperature and composition and is carried from a very low pressure p^\times up to the total pressure of the mixture. Utilizing the definition of fugacity and adding and subtracting the term $\int_{p^\times}^p (RT/p) dp$, we obtain

$$RT \ln f_p = \int_{p^\times}^p (v_1 / n_1) dp + RT \ln p^\times = \int_{p^\times}^p (v_1 / n_1 - RT/p) dp + RT \ln p \quad (2)$$

Substituting in Equation 1 and simplifying, we have

$$\ln f_e = (1/RT) \int_0^p (\partial v / \partial n_1 - RT/p) dp + \ln p x_1 \quad (3)$$

To find the mass action expression, let ν_1 denote the stoichiometrical coefficient of Substance 1 in a chemical equation, these coefficients being taken negative for disappearing species, and let K_p and K_f be the usual mass action expressions in terms of "partial pressures" ($p x_1$) and fugacities, respectively. Summation for all the species gives us

$$\sum \nu_1 \ln f_e = \ln K_f = \ln K_p + (1/RT) \sum \nu_1 \int_0^p (\partial v / \partial n_1 - RT/p) dp \quad (4)$$

Equation 4 is a general mass action expression for pressure and concentration effects at constant temperature, since K_f must be a function of the temperature alone. The integration is subject to the same conditions as before, the constant compositions being equilibrium compositions.

¹ Gillespie, THIS JOURNAL, 47, 305 (1925).

We lack data for evaluating the partial molal volumes and can use Equation 4 only after simplifying assumptions. The simplest such assumption is that the partial molal volume does not vary with the composition. Equation 4 shows that in this case, and not in general otherwise, the ordinary K_p is constant with varying concentrations at constant T and p . In this case the partial molal volume must be equal to the molal volume of pure gas at the same temperature and pressure, since pure gas is a special case of particular composition. Therefore Equation 1 reduces to the fugacity rule given by Lewis and Randall² and Equation 4 reduces to

$$\log K_p = \log K_f + (1/2.3 RT)\Sigma\nu_1 \int_0^p (RT/p - v_1/n_1) dp \quad (5)$$

Equation 5 may be derived directly from the rule of Lewis and Randall. This rule requires therefore that K_p be a function of the temperature and pressure only, and this, no matter what may be the equations of state for the individual pure gases.

We may introduce another simplifying assumption, that $RT/p - v_1/n_1$ is constant during the integration, equal to its limiting value at low pressures $(A_1/RT) - \beta_1$, which is to be calculated from the Keyes equation. This gives us

$$\log K_p = \log K_f + (\Sigma\nu_1 A_1)/(2.3 R^2) \cdot p/T^2 - (\Sigma\nu_1 \beta_1)/(2.3 R) \cdot p/T \quad (6)$$

Applications to the Haber Equilibrium

Equation 6 has been applied to all the K_p data given by Larson and Dodge³ and Equation 5 has been applied to as many isotherms as seemed necessary to check the second simplifying assumption. The constants considered (until very recently) as best in the Keyes equation

$$p = RT/(v - \beta 10^{-\alpha/v}) - A/(v + l)^2 \quad (7)$$

are given in Table I, in units of cc. per mole, atmospheres and centigrade degrees absolute ($T = t + 273.13$).

TABLE I
CONSTANTS OF THE KEYES EQUATION OF STATE

| Constant | A | l | β | α |
|-----------------|-------------------------|--------|---------|----------|
| NH ₃ | 8.5408.10 ⁶ | 33.93 | 135.7 | 68.24 |
| N ₂ | 1.2747.10 ⁶ | 8.277 | 43.082 | 8.723 |
| H ₂ | 0.15883.10 ⁶ | -2.384 | 19.385 | 2.539 |

R was taken as 82.058 cc. — atm./mole. An accurate value was taken for the natural log 10. The ammonia constants are lately determined

² This rule is $f_s = f_p x_1$. The equivalence of this rule and of the rule of additive volumes at any one temperature was shown in Ref. 1. It may be well to point out here that the part of the conclusions given in Ref. 1 dealing with heat content is based on a faulty proof which was added in a final revision of the manuscript and does not affect any other section of the discussion. A note of correction appeared in THIS JOURNAL in December, 1925.

³ Larson and Dodge, THIS JOURNAL, 45, 2918 (1923). The values for 300 atmospheres are given by Larson, *ibid.*, 46, 367 (1924).

by Beattie and Lawrence,⁴ the nitrogen constants are given by Smith and Taylor,⁵ and the hydrogen constants are those preferred by Keyes, Townsend and Young.⁶

In these various references the volume unit is the cc. per gram.

K_p is written for the reaction producing 1 mole of ammonia. Log K_p was obtained from the empirical equation recently given⁷ by putting $p = 0$. Equation 6 becomes then numerically

$$\log K_p = 2679.35/(t + 273.10) - 5.8833 + 494.38 p/T^2 - 0.4503 p/T \quad (8)$$

The results are given in Table II, together with those of the check calculations from Equation 5. In applying Equation 5 the complete Keyes equation was used for the integrals. It was observed that the slopes of the curves: $RT/p - v_1/n_1 = f(p)$ do not approach zero at low pressures⁸ except at a unique temperature, which is for the van der Waals equation one-half the Boyle-point temperature. Nevertheless the variation is not too great. It is greatest from a percentage standpoint for ammonia but the area for ammonia is curiously not so important as that for nitrogen and especially for hydrogen.

The individual areas were compared with the corresponding areas computed with constant ordinate and it was found that the agreement between Equations 5 and 8 did not depend on compensation of errors to any significant degree.

At the Boyle-point the ordinate $RT/p - v_1/n_1$ is zero at zero pressure. For a gas near the Boyle-point, the value of the ordinate varies much with the pressure (in this case passing through a minimum at about 100 atm.), but the ordinate remains small and the area is not so important if more nearly perfect gases are also involved in the reaction. For such gases, which are at temperatures above the Boyle-point, the ordinate becomes greater at higher temperatures, but also more constant.

It appears probable that Equation 6 will in general be a fairly good approximation of Equation 5, except in the case that one of the gases is at temperatures rather far *below* its Boyle-point.

⁴ Lawrence, *Thesis, Massachusetts Inst. Techn.*, 1924.

⁵ Smith and Taylor, *THIS JOURNAL*, 45, 2107 (1923).

⁶ Keyes, Townsend and Young, *J. Math. Phys. Massachusetts Inst. Techn.*, 1, 243 (1922).

⁷ (a) Gillespie, *ibid.*, 4, 84 (1925). (b) The equation is: $\log K_p = (2679.35 + 1.1184 p)/(t + 273.10) - (5.8833 + 0.001232 p)$.

⁸ Diagrams from the Keyes or van der Waals equation do not resemble in this respect Fig. 2, p. 195 of Lewis and Randall's "Thermodynamics," (McGraw-Hill Book Co., New York, 1923) and no sudden changes of slope have been seen. The tangent at $p = 0$ is given for the Keyes equation by $\partial/\partial p(RT/p - v) = A^2/(RT)^3 - 2A(\beta + l)/(RT)^2 + 2.3 \alpha\beta/RT$. This expression was confirmed by the plots. By putting $\alpha = l = 0$ and $\beta = b$, we get the expression for the van der Waals equation. The approximate integration may be in general improved by use of this expression with due caution as to maxima or minima.

TABLE II
 K_p CALCULATED AND OBSERVED AT VARIOUS PRESSURES AND TEMPERATURES (CENTI-
 GRADE)

| | Temperature | 325° | 350° | 375° | 400° | 425° | 450° | 475° | 500° |
|----------|-------------|--------|--------|--------|--------|---------|---------|---------|---------|
| 10 atm. | { Eq. 8 | 0.0401 | 0.0264 | 0.0180 | 0.0126 | 0.00909 | 0.00669 | 0.00502 | 0.00384 |
| | { Obs. | .0401 | .0266 | .0181 | .0129 | .00919 | .00659 | .00516 | .00381 |
| | { Eq. 5 | ... | .0264 | .0180 | ... | ... | .00669 | ... | .00384 |
| 30 atm. | { Eq. 8 | ... | .0271 | .0184 | .0129 | .00924 | .00679 | .00509 | .00389 |
| | { Obs. | ... | .0273 | .0184 | .0129 | .00919 | .00676 | .00515 | .00386 |
| | { Eq. 5 | ... | .0271 | .0184 | ... | ... | .00678 | ... | .00389 |
| 50 atm. | { Eq. 8 | ... | .0278 | .0188 | .0131 | .00940 | .00689 | .00516 | .00393 |
| | { Obs. | ... | .0278 | .0186 | .0130 | .00932 | .00690 | .00513 | .00388 |
| | { Eq. 5 | ... | .0277 | .0188 | ... | ... | .00688 | ... | .00393 |
| 100 atm. | { Eq. 8 | ... | ... | .0199 | .0138 | .00981 | .00715 | .00533 | .00404 |
| | { Obs. | ... | ... | .0202 | .0137 | .00987 | .00725 | .00532 | .00402 |
| | { Eq. 5 | ... | ... | .0197 | ... | ... | .00711 | ... | .00403 |
| 300 atm. | { Eq. 8 | ... | ... | ... | ... | ... | .00830 | .00606 | .00453 |
| | { Obs. | ... | ... | ... | ... | ... | .00884 | .00674 | .00498 |
| | { Eq. 5 | ... | ... | ... | ... | ... | .00829 | ... | .00452 |

Table II shows an excellent agreement between the observed data and the figures calculated from the approximate Equation 8 up to and including 100 atmospheres. A single error as large as 2.8% occurs, and this at 475°, 10 atmospheres where experimental error is responsible. Elsewhere there are one or two errors of 1.5%, at 375° and 100 atmospheres, and at 450°, 100 atmospheres. The results of the more exact Equation 5 support in general the agreement, the worst errors being at 100 atmospheres; 2.3% at 375° and 2.0% at 450°. The agreement is good, though a comparison of the values, especially with the aid of the empirical equation, makes it evident that at the higher pressures the errors become consistently greater as the temperature decreases.⁹ One concludes that the equations and hence the Lewis and Randall fugacity rule are verified excellently up to 50 atmospheres and well at 100.

Equation 6 was further tested by making reasonable variations in the Keyes constants. For instance, changing only those for ammonia and making use of A and β values from Keyes and Brownlee¹⁰ for ammonia, the coefficients of p/T^2 and p/T become 591.00 and -0.5955 , respectively. Making use of the best values for ammonia and nitrogen but using values for hydrogen derived by Keyes, Townsend and Young⁶ from Onnes' data alone, the coefficients of p/T^2 and p/T become 492.62 and -0.4362 , respectively. Although the new sets of coefficients differ considerably, they represent the data through 100 atmospheres just as well as do those from the best constants when put in Equation 6. When A and b were calculated by van der Waals' theory from critical data no agreement was

⁹ On recalculating precisely K_p from the percentage of ammonia, I find in this corner of the field small differences up to 0.8% of K_p in the direction to increase this trend.

¹⁰ Keyes and Brownlee, "Thermodynamic Properties of Ammonia," John Wiley and Sons, New York, 1916.

found, the calculated pressure effects being considerably greater than the observed effects. All this is as it should be if the agreement reported is not accidental.

Table II shows that at 300 atmospheres we find deviations of 6 to 10%. A certain discrepancy was expected since empirical study has shown an experimental discrepancy between the high- and the low-pressure data.^{7a} We cannot apply the equations to still higher pressures because here the calculated pressures for ammonia begin to decrease with diminution of volume. This happens at 450° and 361 atmospheres.

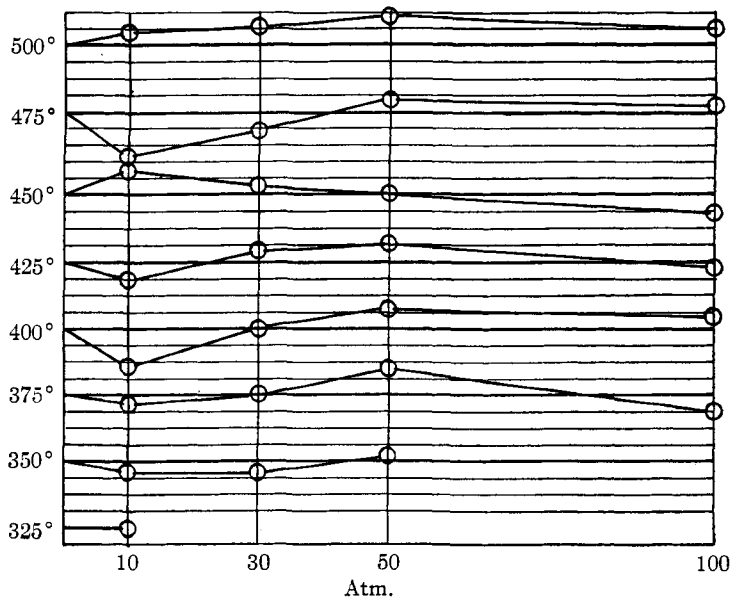


Fig. 1.—Deviations, in percentages of calculated from observed K_p values, as functions of the pressure at different temperatures. Base lines of zero deviation are in heavy lines opposite the temperatures. One scale division = 1%.

Recently the work of Smith and Taylor on nitrogen has been recalculated and the following values have been given me by Professor Keyes: $A = 1.2651 \cdot 10^6$ and $\beta = 46.429$. These values together with the corresponding values for ammonia and hydrogen from Table I, give the numbers 494.69 and -0.4414 for the coefficients of p/T^2 and p/T , respectively, in Equation 6. Equation 6 with these numbers in it satisfies the data probably a little better than before, as a certain trend in the deviations has nearly or quite disappeared. Fig. 1 shows the deviations, in percentages, of the calculated from the observed values of K_p . Fig. 1 illustrates well the principal result of this paper, if it is remembered that the irregularities in the deviations are entirely due to the data, since the equation furnishes

smooth results. The greatest deviation is 2.7% at 10 atm., 475°; the next is 1.8% at 50 atm., 500°. Larson and Dodge stated that their maximal error might reach 3%, though the probable error should be much smaller. Up to 100 atmospheres, therefore, the representation appears to be within the experimental error. At 300 atmospheres, and at 450°, 475° and 500°, the deviations are 5, 9, and 8%, all negative.

Any of the equations will furnish K_p values at pressures lower than 10 atmospheres much within the experimental error, which is greater because of the sensitivity of K_p to errors of analysis at low pressures.

Summary

1. A general mass action expression (A) is derived for compressed gases at constant temperature.

2. By assuming that the partial molal volumes can be replaced by the molal volumes a simpler equation (B) is obtained, which can also be derived from the Lewis and Randall fugacity rule.

3. The equation was further simplified to the approximate relation (C):

$$\log K_p = \log K_f + (\sum \nu_i A_i) / (2.3 R^2) \cdot p / T^2 - (\sum \nu_i \beta_i) / (2.3 R) \cdot p / T \quad (C)$$

where K_f is the value of K_p for $p = 0$, and A and β are constants in the Keyes equation of state.

4. Using the Keyes equation of state as the means for extrapolating existing $p - v - t$ data to the region in question, Equations (B) and (C) were applied to the Haber equilibrium data obtained by the Fixed Nitrogen Research Laboratory and were found to represent the data within the experimental error to and including 100 atmospheres.

5. These results furnish an excellent verification of the fugacity rule proposed by Lewis and Randall, which rule has not hitherto been subjected to any very exacting experimental test.

6. These results lead thermodynamically to the expectation that for the Haber equilibrium K_p will not vary greatly with composition at constant temperature and pressure up to about 100 atmospheres.

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