

Pressure dependence of the equilibrium constant of ammonia

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The pressure dependence of the equilibrium constant of a slightly imperfect gas is calculated. At sufficiently high temperatures, the constants occurring in the formula for the equilibrium constant can be expressed in terms of the van der Waals constants. The latter can be obtained from the second virial coefficients.

Numerical results for ammonia give good agreement between the theory and experiments.

1. INTRODUCTION

Experimental results of the equilibrium constants of gaseous mixtures are usually represented as integrals of the van't Hoff equation. The constants in this integral are then adjusted so as to represent the equilibrium constant over a fair range of temperatures and pressures.

However, the van't Hoff equation is correct only in the limiting case of zero pressure, owing to the fact that for non-vanishing pressure the heat content produced by the reaction depends explicitly on the concentration. It seems therefore worth while to consider the theory of the pressure dependence of the equilibrium constant for a particular example, although at present a calculation of more than the first order term—corresponding to the second virial coefficient—seems to be impracticable.

In a recent paper (Fuchs 1941) the general theory of a mixture of imperfect gases has been developed and the general equations determining chemical equilibrium have been derived. For the purposes of the present paper, however, the far simpler theory of slightly imperfect gases is sufficient. Those readers who are more interested in the connexion with the general theory, will easily establish the relation with the paper just quoted.

2. CHEMICAL EQUILIBRIUM OF SLIGHTLY IMPERFECT GASES

I use in the following the notation of Fowler and Guggenheim (1939). The free energy of a mixture of slightly imperfect gases is given by (cf. Fowler and Guggenheim, p. 265, equ. (704.3))

$$A = kT \left[\sum_A N_A \left(\ln \frac{N_A}{\phi_A V} - 1 \right) + \sum_{AB} \frac{N_A N_B}{V} B_{AB}(T) \right]. \quad (2.1)$$

Here N_A is the number of molecules of type A ; B_{AB} are essentially the generalized second virial coefficients

$$B_{AB}(T) = \frac{1}{2} \int_0^\infty (1 - e^{-\epsilon_{AB}(r)/kT}) 4\pi r^2 dr, \quad (2.2)$$

and ϕ_A is given by (cf. Fowler and Guggenheim, p. 257, equ. (701.8))

$$\phi_A = \frac{(2\pi m_A kT)^{3/2}}{h^3} j_A(T). \quad (2.3)$$

Here the first factor arises from that part of the partition function due to the integration over the momentum coordinates and the second factor $j_A(T)$ is the internal partition function of the molecule.

Consider now a chemical reaction given by the equation

$$\sum_A \nu_A(A) = 0. \quad (2.4)$$

Here (A) represents a molecule of type A and ν_A are the number of molecules taking part in the reaction.

Consider next a variation of the number N_A of molecules of type A due to the reaction. From (2.4) follows that the variations δN_A satisfy the relations

$$\frac{\delta N_A}{\nu_A} = \frac{\delta N_B}{\nu_B}. \quad (2.5)$$

Chemical equilibrium is established, if the variation of the free energy vanishes, i.e.

$$\sum_A \frac{\partial A}{\partial N_A} \delta N_A = 0 \quad (2.6)$$

with (2.5) follows
$$\sum_A \nu_A \frac{\partial A}{\partial N_A} = \sum_A \nu_A \mu_A = 0. \quad (2.7)$$

Here $\mu_A = \partial A / \partial N_A$ is the chemical potential of the molecules of type A in the mixture. It can be obtained from the free energy (2.1) (cf. also Fowler and Guggenheim, equ. (704.5)) with the result

$$\sum_A \nu_A \ln \frac{N_A}{\phi_A V} + 2 \sum_{A,B} \nu_A \frac{N_B}{V} B_{AB} = 0. \quad (2.8)$$

I now form the expression

$$\ln K_p = \sum_A \nu_A \left(\ln \frac{N_A}{N} + \ln P \right), \quad N = \sum_A N_A, \quad (2.9)$$

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which is connected with the equilibrium constant K by the equation

$$K = K_p P^{-\nu}, \quad \nu = \sum_A \nu_A. \quad (2.10)$$

Now, the pressure P is given by (cf. Fowler and Guggenheim, equ. (704.4))

$$P = \frac{kTN}{V} \left(1 + \sum_{A,B} \frac{N_A N_B}{NV} B_{AB} \right). \quad (2.11)$$

With the help of (2.11) and (2.8) we find for K_p

$$\ln K_p = \sum_A \nu_A \ln(\phi_A kT) - 2 \sum_{A,B} \nu_A \frac{N_B}{V} B_{AB} + \nu \ln \left(1 + \sum_{A,B} \frac{N_A N_B}{NV} B_{AB} \right). \quad (2.12)$$

If the volume V is now eliminated by means of (2.11), one must neglect the second order terms, since they give only terms of the third order in (2.12). Similarly in the expansion of the logarithm only the first term need be taken into account. Thus

$$\ln K_p = \sum_A \nu_A \ln(\phi_A kT) + \frac{P}{kT} \sum_{A,B} B_{AB} \left\{ \nu \frac{N_A N_B}{N^2} - 2 \frac{\nu_A N_B}{N} \right\}. \quad (2.13)$$

The first term $\ln K_p^o = \sum_A \nu_A \ln(\phi_A kT)$ (2.14)

is independent of the pressure. I further introduce the mole fractions $c_A = N_A/N$. Then (2.13) takes the form

$$\ln K_p = \ln K_p^o + \frac{P}{kT} \sum_{A,B} (\nu c_A c_B - 2\nu_A c_B) B_{AB}. \quad (2.15)$$

At sufficiently high temperatures the B_{AB} can be expressed in terms of the van der Waals constants. Considering the molecules as rigid spheres of radii ρ_A and an interaction $\epsilon_{AB}(r)$, if they do not overlap, it follows that

$$B_{AB} = \frac{1}{2} \left\{ \frac{4\pi}{3} (\rho_A + \rho_B)^3 - \frac{\alpha_{AB}}{kT} \right\}, \quad \alpha_{AB} = - \int_{\rho_A + \rho_B}^{\infty} \epsilon_{AB}(r) 4\pi r^2 dr. \quad (2.16)$$

The constants in this equation are related to the van der Waals constants a_A , b_A of the pure gases as follows

$$2a_A = N\alpha_{AA}, \quad 2b_A = \frac{4\pi}{3} N(2\rho_A)^3, \quad (2.17)$$

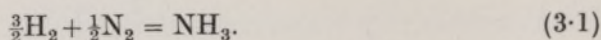
(2.15) may then be written in the form

$$\ln K_p = \ln K_p^o + \frac{P}{kT} \sum_{A,B} \left\{ \frac{1}{2} \nu c_A c_B - \nu_A c_B \right\} \left\{ \frac{4\pi}{3} (\rho_A + \rho_B)^3 - \frac{\alpha_{AB}}{kT} \right\}. \quad (2.18)$$

3. PRESSURE DEPENDENCE OF THE EQUILIBRIUM CONSTANT OF AMMONIA

In conclusion let us consider the chemical equilibrium for a specified substance. I choose ammonia for this purpose, since the chemical equilibrium of this gas has been investigated over a wide range of pressures. This was done by Larson and Dodge (1923) and Larson (1924).

The chemical equation for ammonia is



Thus we have $\nu_1 = \frac{3}{2}$, $\nu_2 = \frac{1}{2}$, $\nu_3 = -1$, $\nu = 1$. (3.2)

Furthermore, starting with pure ammonia, the mole fractions for complete dissociation are $\frac{3}{4}$ and $\frac{1}{4}$.

If x is the mole fraction of ammonia in the mixture, it follows that

$$c_1 = \frac{3}{4}(1-x), \quad c_2 = \frac{1}{4}(1-x), \quad c_3 = x. \quad (3.3)$$

K_p defined by (2.9) is now

$$\ln K_p = \frac{3}{2} \ln 3 - 2 \ln 4 + \ln \frac{(1-x)^2 P}{x}. \quad (3.4)$$

On the other hand, from (2.15)

$$\ln K_p = \ln K_p^o - \frac{P}{kT} [D_0 + D_1 x + D_2 x^2], \quad (3.5)$$

$$\left. \begin{aligned} D_0 &= \frac{1}{16} \{27B_{11} + 18B_{12} + 3B_{22} - 24B_{13} - 8B_{23}\}, \\ D_1 &= \frac{1}{8} \{24B_{13} + 8B_{23} - 9B_{11} - 6B_{12} - B_{22} - 16B_{33}\}, \\ D_2 &= \frac{1}{16} \{16B_{33} + 24B_{13} + 8B_{23} - 9B_{11} - 6B_{12} - B_{22}\}. \end{aligned} \right\} \quad (3.6)$$

I am here interested chiefly in the pressure dependence of K_p . I shall therefore assume for K_p^o the experimental values of Larson and Dodge (1923). The comparison with the theory in this limit has in fact already been made by Larson and Dodge, who analysed their experimental values with the help of van't Hoff's equation. But, as pointed out in the introduction, there is no justification for using van't Hoff's equation except in the limit $P \rightarrow 0$. It is therefore not astonishing that Larson and Dodge had to adjust the constants in the experimental expressions for the heat content produced by the reaction so as to obtain agreement with experiment, and that these adjusted constants turned out to depend on the pressure.

The van der Waals constants can be estimated from the second virial coefficients in the equation of state (cf. Landolt-Boernstein, 1935). In the temperature intervals used for this purpose the virial coefficients are linear in the reciprocal temperature so that the approximation (2.16) is justified.

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The temperature interval in which we shall apply these values is at even higher temperatures. The values obtained are collected in the first three columns of table 1.

The 'mixed' van der Waals constants α_{ij} cannot be obtained in this way, except by a thorough analysis of the influence of the chemical reaction on the virial coefficients. However, we can obtain a good approximation in the following way.

London (1930) has shown the close connexion between the polarizability and the van der Waals forces, the latter being proportional to the square of the polarizability. It is plausible to assume that α_{ij} is proportional to the product of the polarizabilities of the two substances. In fact, corresponding to London's estimate of the van der Waals forces for two molecules of the same type (see equation (13) of his paper), we find easily

$$\frac{3\alpha\alpha'}{4r^6} \sqrt{(V_a V'_a)} \leq -\epsilon(r) \leq \frac{3\alpha\alpha'}{4r^6} \sqrt{(V_j V'_j)}$$

where α, α' are the polarizabilities, V_a, V'_a the excitation energies and V_j, V'_j the ionization energies. London found furthermore that the actual values of the van der Waals forces are always very near the same place in the interval given by the above estimate. I therefore assume

$$\epsilon_{AB}(r) = \sqrt{\{\epsilon_{AA}(r)\epsilon_{BB}(r)\}}.$$

As the dependence on r is the same for all ϵ_{AB} , it follows that

$$\alpha_{ij} = \sqrt{(\alpha_{ii}\alpha_{jj})}. \quad (3.7)$$

In the case of NH_3 there is a complication, as this molecule has a dipole moment. Apart from the dispersion effect, also the induction and direction effect will give contributions to the van der Waals forces. The latter however is important only at low temperatures; the induction effect has been calculated by London (1930) and he has shown that it is only 10% of the dispersion effect (see table 4 of his paper). Therefore it will not influence equation (3.7) appreciably.

The 'mixed' b values on the other hand can be obtained easily by assuming additivity of the radii as in (2.16).

The results are collected in the table 1.

TABLE 1. VAN DER WAALS'S CONSTANTS

	H_2	N_2	NH_3	$\text{H}_2\text{-N}_2$	$\text{H}_2\text{-NH}_3$	$\text{N}_2\text{-NH}_3$	units
a/R^3	12.15	227	354	52.4	65.6	284	degree ² /atm.
b/R	0.223	0.685	0.408	0.410	0.306	0.535	degree/atm.

With the help of this table the B_{ij} can be calculated as given by (2.16), (2.17). Substitution in (3.5) yields

$$\ln K_p = \ln K_p^o - \frac{P}{T} \left[\frac{119}{T} + 0.431 + x \left(\frac{309}{T} - 0.390 \right) + x^2 \left(\frac{554}{T} - 0.621 \right) \right]. \quad (3.8)$$

Here P is to be measured in atmospheres.

Equating (3.4) and (3.8) we obtain an equation for x . The results are best illustrated by plotting the logarithm of the equilibrium constant K_p as a function of the pressure. This is done in figure 1. The curves represent the

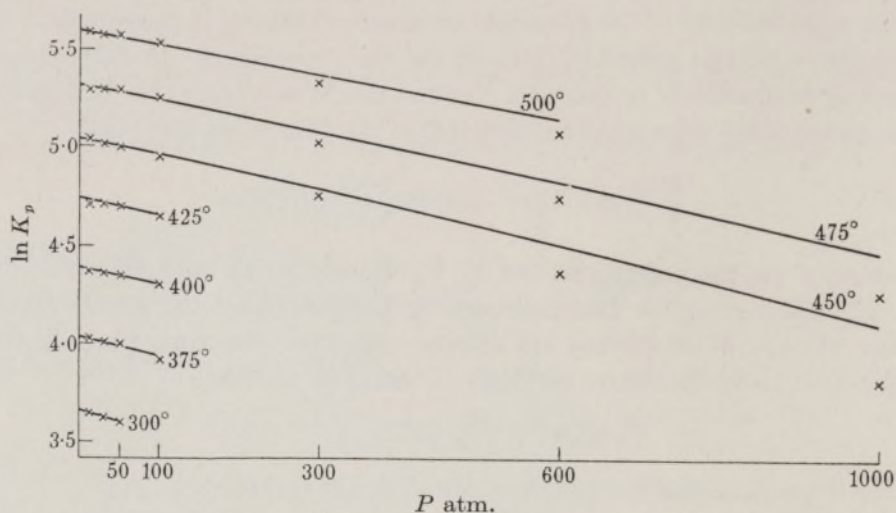


FIGURE 1. The equilibrium constant K_p as a function of the pressure for various temperatures. The curves represent the calculated values. The crosses indicate the experimental values of Larson and Dodge.

theoretical values for various temperatures, the crosses represent the experimental values of Larson and Dodge (1923) and Larson (1924). It will be seen that the slope of the curves for small pressures gives very good agreement between the theoretical and experimental values. For higher pressures, however, deviations occur, which must be due to the higher virial coefficients.

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