composes into titanium metal and titanium tetrabromide, very slowly at 500° but rapidly at 650°.

Both the di- and tribromide react with hydrogen bromide to produce the tetrabromide. Titanium metal reacts with hydrogen bromide to produce a greater proportion of non-volatile bromides ($TiBr_2$ and $TiBr_3$) to the tetrabromide at 300° than at 450°.

At 300° titanium metal suspended in titanium tetrabromide brings about partial reduction to the tribromide. Silver and mercury reduce titanium tetrabromide, dissolved in benzene, to titanium tribromide; in the case of the latter metal the reduction is practically quantitative.

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THE THERMODYNAMIC TREATMENT OF CHEMICAL EQUILIBRIA IN SYSTEMS COMPOSED OF REAL GASES. III. MASS ACTION EFFECTS. THE OPTIMUM HYDROGEN: NITROGEN RATIO FOR AMMONIA FORMATION IN THE HABER EQUILIBRIUM

BY LOUIS J. GILLESPIE AND JAMES A. BEATTIE

Although the mass action law has often been applied to experimental studies of gaseous equilibrium, there is little or no direct evidence of its inadequacy for gases. This is doubtless due to the fact that most studies have been made at low pressures, and sometimes also at high temperatures, conditions which favor the applicability of the ideal gas laws to real gases.

A recent exception has been furnished by the data on the Haber equilibrium obtained by Larson and Dodge and by Larson.[1] Here it has been found that K_p, the mass action function in terms of ideal gas partial pressures, is not constant at constant temperature, as required by the theory of ideal gases, but increases definitely with the pressure. As already pointed out[2] we must therefore believe that K_p will vary if the concentrations are varied at constant temperature and pressure—in other words, that K_p is not strictly constant with respect to any change of condition whatever.

The contributions of previous investigators to the theory have been discussed at length in Part I of the present series[3] of three papers. Here we shall repeat only the previous results of present interest.

[1] Larson and Dodge, THIS JOURNAL, **45**, 2918 (1923); Larson, *ibid.*, **46**, 367 (1924).

[2] Gillespie, *ibid.*, **47**, 305 (1925).

[3] Gillespie and Beattie, *Phys. Rev.*, **36**, 743 (1930); Part II, *Phys. Rev.*, **36**, 1008 (1930). In this part the heat of reaction was calculated at various temperatures and pressures, and the entropy and energy constants of ammonia were found.

In brief, a general mass action equation has been derived[4] by assuming that certain properties[4,5] of ideal gases hold also for real gases at very low pressures. By assuming further that the equation of state of a gas mixture may be obtained by means of a "linear combination of constants" and that the Beattie–Bridgeman equation of state[6] is to be used for the separate gases a mass action equation has been derived[7] in which all the integrations have been carried out, in terms of the volume of the mixture.

Subject to the same assumptions and to some simplifying assumptions, which should be valid at pressures not too high, the following approximate mass action equation has been derived[8]

$$\ln K_p = \ln K_p^* - \left\{ \Sigma\nu_i [B_{0i} - A_{0i}/RT - C_i/T^3] + \Sigma\nu_i [(A_{0i}^{1/2} - \Sigma x_i A_{0i}^{1/2})^2/RT] \right\} p/RT \quad (1)$$

K_p^* is the limiting value of K_p when the gaseous mixture is maintained in equilibrium and its pressure reduced to zero. It is determined by the temperature alone for a given chemical equation.

An approximate equation similar to Equation 1, but without the constant c, has been obtained by Keyes[9a] from the kinetic considerations leading to the Keyes equation of state.[9b]

The chemical equation for the Haber equilibrium is

$$1/2 N_2 + 3/2 H_2 = NH_3 \quad (2)$$

From the definition of K_p we have

$$\log K_p = \log x - 1/2 \log x_N - 3/2 \log x_H - \log p \quad (3)$$

where x, x_N and x_H are the mole fractions of ammonia, nitrogen and hydrogen, respectively, in the equilibrium mixture, and p is its pressure.

Equation 1 gives us for the Haber equilibrium, after substituting numerical values[3] for the equation of state constants A_{0i}, B_{0i} and C_i

$$\log (K_p/K_p^*) = p[0.1191849/T + 25122730/T^4 + 38.76816\Sigma(x_i A_{0i}^{1/2})/T^2 + 64.49429(\Sigma x_i A_{0i}^{1/2})^2/T^2] \quad (4)$$

where the values of $A_{0i}^{1/2}$ for ammonia, nitrogen, hydrogen and argon are 1.546932, 1.159526, 0.4444097 and 1.136090 liter-(atmosphere)$^{1/2}$ per mole, respectively, and log refers to the base 10.

In Part I of the present series, Equation 4 was applied to the existing data of Haber,[10] of Larson and Dodge, and of Larson, and was found to represent the effect of pressure on the yield of ammonia within the experimental error at all temperatures.

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

[5] Beattie, *Phys. Rev.*, **36**, 132 (1930).

[6] Beattie and Bridgeman, *Proc. Am. Acad. Arts Sci.*, **63**, 229 (1928); THIS JOURNAL, **50**, 3133 (1928).

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

[8] Gillespie, *ibid.*, **34**, 1605 (1929).

[9] (a) Keyes, THIS JOURNAL, **49**, 1393 (1927); (b) *Am. Soc. Refrig. Eng. J.*, **1**, 9 (1914); *Proc. Nat. Acad. Sci.*, **3**, 323 (1917).

[10] Haber, *Z. Elektrochem.*, **21**, 89 (1915).

The temperature variation was expressed by the equation

$$\log K_p^* = -2.691122 \log T - 5.519265 \cdot 10^{-5}T + 1.848863 \cdot 10^{-7}T^2 + 2001.6/T + 2.6899 \quad (5)$$

of which the last two constants, and these only, were arbitrary and chosen to fit the whole body of data.

Theory

Equation 5 rests on the assumptions that the specific heats of the gases at extremely low pressures may be expressed over the necessary temperature interval as functions of the temperature in series, and that the temperature variation of K_p is the same for real gases at extremely low pressures as for ideal gases.[11]   There would be no point here in questioning the validity of these assumptions.   The use to which we put Equations 4 and 5 in this paper depends, however, on the validity of Equation 1 or 4.

We believe that we are in a very good position to calculate the effects of varying composition in the Haber equilibrium by the use of the numerical equation 4 in connection with Equation 5, which serves to eliminate $\log K_p^*$ from Equation 4, for the following reasons: (1) the general assumptions underlying the mass action equations discussed above are supported abundantly by experimental evidence other than that relating to the Haber equilibrium, as has been discussed in Part I.   (2) The agreement of the approximate equation (1) or (4) with the Haber equilibrium data indicates that the simplifying assumptions which have been used to obtain them are not too severe.   (3) The composition terms in $\Sigma(x_i A_{0i}^{1/2})$ occurring in Equation 1 or 4 must be supposed approximately correct, since a mass action equation, which may be considered to be based on the Lewis and Randall rule[12] of fugacities, and which differs from Equation 1 principally by the omission of these composition terms, has been applied to the Haber equilibrium data and found to fail badly at 300 atmospheres to represent the pressure variation of K_p, though the representation at lower pressures was good.[4]

A mass action question of unique interest is the following: At what mole ratio, hydrogen:nitrogen, will there be at given temperature and pressure the largest mole fraction of ammonia in the equilibrium mixture?

When the function K_p is constant at constant temperature and pressure, as is the case not only for ideal gases but also for the case that the Lewis and Randall rule is exact,[4] the optimum ratio is exactly three (provided neither reactant is contaminated with an inert gas), as may readily be shown mathematically by equating to zero the derivative of $\log K_p$ with respect to the ratio $H_2:N_2$.   But according to Equation 1 or 4, or indeed according

[11] For a very simple choice of necessary assumptions for the discussion of thermodynamic equilibrium in real gases, see Beattie, Ref. 5.

[12] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

to any equations which are not based on the ideal gas laws and which differ from the Lewis and Randall rule,[4] K_p varies with composition at constant temperature and pressure, and naturally a value different from three will be expected for the optimum ratio, as already suggested.[13]

By examination of the derivative of the mole fraction of ammonia at equilibrium, below always denoted by x, with respect to r_e, the equilibrium value of the ratio $H_2:N_2$. the following equation is found for the optimum value of r_e when no argon is present in the reactant gases.

$$r_e = 3 - \frac{2}{M} (A_{0N}^{1/2} - A_{0H}^{1/2}) \frac{r_e}{(1 + r_e)} (1 - x) [38.768 + 128.99\Sigma(x_i A_{0i}^{1/2})] \frac{p}{T^2} \quad (6)$$

Here A_{0N} and A_{0H} are the cohesive pressure A_0 constants in the Beattie–Bridgeman equation of state for nitrogen and hydrogen, respectively. The summation $\Sigma(x_i A_{0i}^{1/2})$ is obtained by adding the terms $x_1 A_{01}^{1/2} + x_2 A_{02}^{1/2} + \ldots$, etc., taking the square roots of the cohesive pressure constants, and x_1, x_2, etc., the mole fractions, for all gases present in the equilibrium mixture. M is the modulus of logarithms, $0.43429 \ldots$, p is the pressure in atmospheres (normal) and T is the absolute temperature ($t^\circ + 273.13$).

At zero pressure $r_e = 3$. At other pressures the sign of the correction depends on the term $(A_{0N}^{1/2} - A_{0H}^{1/2})$, which is $+0.7151163$. Hence the optimum ratio lies at less than 3 for all pressures not zero within which the simplifying assumptions used in deriving Equation 1 are valid.

Although r_e appears on both sides of Equation 6, this does not cause any serious difficulty, as the quantity to be subtracted from 3 is small, and hence the use of an approximate value of r_e on the right-hand side of the equation will lead to a good value. More serious is the fact that x and $\Sigma(x_i A_{0i}^{1/2})$ must be consistent with Equation 4. Hence several trials are necessary to arrive at good numerical values of x and r_e. We have used Equation 6 only for checking the results of other computations.

It appeared somewhat more interesting to calculate the best initial value of the ratio $H_2:N_2$, which initial ratio we shall designate by r, in a reactant mixture of hydrogen and nitrogen when the nitrogen contains c mole per cent. of argon.

If in such a reactant mixture containing originally no ammonia there is formation of ammonia subject to Equation 2, then the mole fractions of the various gases at any time, for instance at equilibrium, will be related to each other and to r and c by Equations 7

$$\left.\begin{array}{ll} x_{NH_3} = x & x_N = \dfrac{(1 + x)}{(1 + c + r)} - \dfrac{x}{2} \\[2mm] x_{Ar} = \dfrac{c(1 + x)}{(1 + c + r)} & x_H = \dfrac{r(1 + x)}{(1 + c + r)} - 3\dfrac{x}{2} \end{array}\right\} \quad (7)$$

These relations (7) will be applied only to the mole fractions at equilibrium. From Equations 4, 5 and 7, log K_p, x_N, x_H and x_{Ar} may be eliminated,

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

giving an equation between r, x, c, p and T, containing $\log K_p^*$ which is a function of the temperature. From this equation the derivative dx/dr at constant c, p and T may be found and put equal to zero. This gives finally the following equation for the value of the initial ratio r for which x is a maximum at given values of c, p and T.

$$r = 3(1 + c) - \frac{3cx(1 + c + r)}{2(1 + x)} - \frac{2}{M}\left[A_{0N}^{1/2} - A_{0H}^{1/2}(1 + c) + A_{0Ar}^{1/2}c\right] \times$$
$$\frac{(1 + c + r)}{(1 + x)} x_N x_H \left[38.768 + 128.99\Sigma(x_i A_{0i}^{1/2})\right]\frac{p}{T^2} \qquad (8)$$

For ideal gases the A_0 constants are zero, the last term of Equation 8 vanishes, and we have

$$r = 3 + 3c\frac{1 - x - 0.5cx}{1 + x + 1.5cx} \qquad (9)$$

Thus even for ideal gases the best initial ratio is not three when nitrogen cannot be added without adding argon; although of all equilibrium mixtures containing the same mole fraction of argon, the one whose ratio $H_2:N_2$ is three contains the largest percentage of ammonia.

For any chosen values of c, p and T, Equation 8 may be solved for values of r and x which are also consistent with the mass action and stoichiometric requirements as expressed in Equations 3, 4, 5 and 7. For this purpose an equation may be found of the form $F = 0$, by elimination of $\log K_p$ and $\log K_p^*$ from Equation 4 by use of Equations 3 and 5. For any chosen value of r, a value of x may then be found by trial which will make the function F reduce to zero. Elimination of the mole fractions x_N, x_H and x_{Ar} is best made after calculation of their numerical values from Equations 7.

The Present Calculations

We have made calculations for the temperature $500°$, a series of pressures, and an original mole fraction of argon in the nitrogen, $c = 0.012$. This is about the value of c when nitrogen is made from air and the argon not removed. The function to be reduced to zero is not so formidable as might be expected from the above, once T, p and c have been assigned numerical values, and the numbers have been collected and combined. Thus at 1000 atmospheres the equation we had to solve was

$$F = 0.7985342 + 0.06485898\Sigma(x_i A_{0i}^{1/2}) + 0.10789870\left[\Sigma(x_i A_{0i}^{1/2})\right]^2 +$$
$$\frac{1}{2}\log x_N + \frac{3}{2}\log x_H - \log x = 0 \qquad (10)$$

subject to the relations (7).

At each pressure the optimum value of r was calculated by Equation 8, using approximate values of the mole fractions, and then an equation such as (10) was solved for x at values of r adjacent to this approximate optimum value. Finally Equation 8 was used to confirm or to locate more precisely the optimum value. The final ratio r_e was also computed from the equation

$$r_e = 3(1 + c) - \frac{2}{M} [A_{0N}^{1/2} - A_{0H}^{1/2}(1 + c) + A_{0Ar}^{1/2}c] \frac{(1 + c + r_e)}{(1 - x - 0.5cx)} x_N x_H \times$$
$$[38.768 + 128.99\Sigma(x_i A_{0i}^{1/2})] \frac{p}{T^2} \qquad (11)$$

The optimum values of r, the initial ratio $H_2:N_2$, and of r_e, the ratio at equilibrium, are given in Table I. In Table II are given the percentages of ammonia in the equilibrium mixtures at the optimum value of r and also for $r = 3$. In Table III are given the optimum ratios, and in Table IV the percentages, for the case that no argon is present.

We have thought it of interest to calculate also the percentages at the initial ratios 2 and 4, and also to compare them with the yields that would be expected from the ordinary simple mass action law at the initial ratios 2 and 4 from the percentages for $r = 3$ as given by our improved mass action law. Argon was assumed to be absent.

The yields expected from the ordinary mass action law were obtained by solution of the equation

$$F' = \log p + \log K_p + 1/2 \log x_N + 3/2 \log x_H - \log x = 0 \qquad (12)$$

subject of course to the relations (7), when $\log K_p$ is the correct value of $\log K_p$ found from Equations 4, 5 and 7 for $c = 0$ for the given temperature and pressure.

TABLE I

OPTIMUM RATIOS, INITIAL r AND FINAL r_e OF $H_2:N_2$, WHEN ARGON ACCOMPANIES THE NITROGEN ($c = 0.012$) AT VARIOUS PRESSURES AND AT 500°

p (atm.)	0	100	300	600	1000
r opt	3.036	2.99	2.94	2.91	2.92
r_e opt	3.036	2.99	2.90	2.79	2.72

TABLE II

MOLE PERCENTAGES OF AMMONIA IN EQUILIBRIUM MIXTURES AT VARIOUS PRESSURES AND AT 500° AT OPTIMUM RATIO $H_2:N_2$ AND AT THE RATIO 3, WHEN ARGON ACCOMPANIES THE NITROGEN

p (atm.)	0	100	300	600	1000
r opt	0	10.453	25.653	42.083	58.195
$r = 3$	0	10.453	25.649	42.066	58.163

TABLE III

OPTIMUM RATIOS, INITIAL r and FINAL r_e AT VARIOUS PRESSURES AND AT 500° WHEN ARGON IS ABSENT

p (atm.)	0	100	300	600	1000
r opt	3	2.96	2.92	2.90	2.91
r_e opt	3	2.95	2.87	2.76	2.68

TABLE IV

MOLE PERCENTAGES OF AMMONIA IN EQUILIBRIUM MIXTURES AT VARIOUS PRESSURES AND AT 500° AT OPTIMUM RATIO $H_2:N_2$ AND AT THE RATIO 3, WHEN ARGON IS ABSENT

p (atm.)	0	100	300	600	1000
r opt	0	10.516	25.809	42.343	58.562
$r = 3$	0	10.516	25.802	42.320	58.523

Table V gives a tabulation of the results of these computations as well as the final ratios r_e.

TABLE V

THE YIELD OF AMMONIA AT VARIOUS PRESSURES AND AT 500° AND AT INITIAL RATIOS $H_2: N_2$ OF 2, 3 AND 4 BY THE IMPROVED MASS ACTION EQUATION, AND THE YIELD AT RATIOS OF 2 AND 4, AS CALCULATED FROM THE YIELD AT 3 BY THE ORDINARY MASS ACTION LAW

	Improved equation			Ordinary mass law	
r	2	3	4	2	4
p	Calculated mole per cent. of ammonia in the equilibrium mixture				
100	10.137	10.516	10.304	10.111	10.321
300	24.690	25.802	24.994	24.529	25.122
600	39.962	42.320	40.174	39.585	40.591
1000	54.020	58.523	53.578	53.551	54.430
	Values of r_e the final ratios $H_2: N_2$				
100	1.840	3	4.305	1.840	4.305
300	1.577	3	5.000	1.581	5.008
600	1.251	3	6.527	1.260	6.594
1000	0.890	3	10.822	0.903	11.414

Discussion of the Results

Whether argon is present in the usual quantities or absent, the optimum initial value of the ratio $H_2:N_2$ passes through a minimum at about 600 atmospheres, at which it is only about 3% less than the value 3; but both the minimum and the smallness of the effect are due to the considerable change in the value of the ratio as a consequence of the extensive formation of ammonia at the higher pressures. The optimum value of the ratio at equilibrium passes through no minimum and reaches a value over 10% less than 3 at 1000 atmospheres.

Although reasons were given above for supposing that the approximate equation used for the calculation should give good results, it would not necessarily follow that pressure derivatives of functions such as the optimum ratio would be furnished correctly, as the terms neglected in deriving the approximate equation would affect the pressure derivatives. Nevertheless in calculations of the Joule–Thomson effect,[14] similar approximations were made and yet a correct slope was obtained of the curve for the inversion temperature vs. pressure.

Whether argon is present or not, the maximum mole percentage of ammonia formed at the optimum ratio exceeds the mole percentage formed at $r = 3$ by less than 0.07% of this mole percentage even at 1000 atmospheres. Hence the optimum ratio may safely be taken as 3 for practical purposes, though in point of theory it must be regarded as less.

This practical coincidence of the improved mass action law with the ordinary mass action law is, of course, due to the fact that the value of any

[14] Beattie, *Phys. Rev.*, **35**, 643 (1930).

function cannot change rapidly in the neighborhood of its maximum. From Table V it can be seen that if the ordinary mass action law be used to calculate the mole percentage of ammonia when $r = 2$ or 4, from the value given for $r = 3$, it will be found to produce errors which are 0.87 and 1.59% of the correct percentages, respectively, at 1000 atmospheres. Though the pressure here is high, the variation of composition is rather small.

Comparison of Tables II and IV shows that the yield at any pressure is better in the absence of argon. At 1000 atmospheres the improvement is about 0.63% of the yield.

Theoretically, the optimum mixture from nitrogen which contains argon may be improved by adding pure nitrogen. The best initial ratio depends but very slightly on the argon content, being the same for mixtures containing a constant initial mole fraction of argon equal to 0.003 as the figures listed in Table III for zero mole fraction of argon; but the effect on the yield of adding pure nitrogen in this way is small.

Summary

By means of an improved mass action equation, which had previously been found to represent the combined effects of variations of temperature and pressure together with such concomitant variations of composition as necessarily occurred in the displacement of equilibrium, calculations have been made of the effects on the yield of ammonia produced by systematic variation of the ratio of hydrogen to nitrogen. For the temperature 500° and for the pressures 100, 300, 600 and 1000 atmospheres, the optimum values of this ratio, both the initial values and the values at equilibrium, were found for pure hydrogen and nitrogen, as well as for pure hydrogen and atmospheric nitrogen from which the argon has not been removed.

Except at low pressures, the optimum value of the ratio is less than 3. The optimum value of the initial ratio falls to 2.90 at 600 atmospheres, and that of the final ratio at equilibrium to 2.68 at 1000 atmospheres, when no argon is present. The corresponding figures are 2.91 and 2.72 when atmospheric nitrogen is used.

The percentage of ammonia at the optimum ratio exceeds that at the ratio 3 by less than 0.1% of the percentage at 3 in any case.

The presence of argon is deleterious at any pressure. At 1000 atmospheres the yield when pure nitrogen is used is about 0.6% (of its value) greater than when atmospheric nitrogen is used.

For the case of pure nitrogen, the yields of ammonia were also calculated at the values 2, 3 and 4 at each pressure and at 500°. For comparison, the ordinary mass action law was used to calculate the yield of ammonia at each pressure and at the initial values 2 and 4 from the yield at the value 3, with errors which reached at 1000 atmospheres 1.5% of the yield at 3.

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