[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE AMMONIA EQUILIBRIUM

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The first determination of the ammonia equilibrium was made by Haber and van Oordt[2] in 1905. In this investigation the reaction was studied at 1000° and 1 atmosphere pressure. In 1907 Haber and Le Rossignol[3] published results of experiments which they had made at 1 atmosphere pressure and at temperatures ranging from 700° to 1000°. About this same time papers by Nernst[4] and Jost[5] appeared in which approximately this same temperature range was covered, but the pressure range was extended to 72 atmospheres. The following year Haber and Le Rossignol[6] studied the ammonia equilibrium at 30 atmospheres, covering a temperature range essentially the same as that of their earlier report. The most recent work on the ammonia equilibrium appeared in 1914–1915 when Haber[7] published a series of papers in which he gave the results of a redetermination of the equilibrium at 30 atmospheres. In the latter experiments an attempt was made to reach temperatures as low as 450° but without success, 561° apparently being the lowest temperature at which equilibrium could be established.

Using results obtained at a pressure of 30 atmospheres and temperatures ranging from 974° to 561° Haber computed the probable equilibrium values for the pressure range of 1 to 200 atmospheres and temperatures as low as 200°. These computations were based on the van't Hoff isochore, the integration of which required a knowledge of the variation with temperature of the heat of formation of ammonia from its elements. This heat of formation Haber determined experimentally.

In computing the equilibrium values for the ammonia reaction, Haber recognized the danger of applying his formula to a wide range of pressures. For the lower pressures it was felt that the effect of the deviations of the compressed gases from the perfect gas law would be negligible. At relatively high temperatures (915°) Jost[5] has shown this to be the case.

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[1] Assisted by L. A. Stengel.

[2] Haber and van Oordt, *Z. anorg. Chem.*, **43**, 111 (1905).

[3] Haber and Le Rossignol, *Ber.*, **40**, 2144 (1907).

[4] Nernst, *Z. Elektrochem.*, **13**, 521 (1907).

[5] Jost, *Z. anorg. Chem.*, **57**, 415 (1908).

[6] Haber and Le Rossignol, *Z. Elektrochem.*, **14**, 181 (1908).

[7] I. Haber, *Z. Elektrochem.*, **20**, 597 (1914). II. Haber, Tamaru and Ponnaz, *ibid.*, **21**, 89 (1915). III. Haber and Maschke, *ibid.*, **21**, 128 (1915). IV. Haber and Tamaru, *ibid.*, **21**, 191 (1915). V. Haber, Tamaru and Oeholm, *ibid.*, **21**, 206 (1915). VI. Haber and Tamaru, *ibid.*, **21**, 228 (1915). VII. Haber and Greenwood, *ibid.*, **21**, 241 (1915).

Just what the effect would be at lower temperatures, say below 500° was, however, not known. Since the ammonia equilibrium had not been determined over a wide range of pressures, and particularly at the low temperatures now possible, it has been considered worth while to make such an investigation. The equilibrium results which have been obtained at 10, 30, 50 and 100 atmospheres' pressure are given in this paper.

Experimental Part

The experimental procedure of this investigation was essentially as follows. A mixture of nitrogen and hydrogen (1:3) at 100 atmospheres was purified and then passed through a catalyst bomb in which any desired percentage of the gas could be converted into ammonia. If an ammonia-free gas was desired, the catalyst bomb was by-passed. When pressures lower than that of the purification train (100 atmospheres) were being investigated, an automatic reducing valve served to effect the reduction of the pressure to the desired value.

The gas now passed through a coiled iron pipe containing the catalyst. The catalyst was prepared by reducing iron oxide containing potassium oxide and aluminum oxide as promoters. (A detailed description of this type of catalyst will be published in a later paper.) A needle valve placed at the exit end of the coiled iron pipe was employed in regulating the flow of gas through the apparatus. This valve was provided with an electric heater which prevented condensation of ammonia at this point. After leaving this valve the gas pressure was reduced to atmospheric and the gas was then passed through a friction tube flowmeter. The equilibrium was approached from both sides, in every case the space velocity being progressively decreased until further reduction in flow produced no change in ammonia conversion.

Preparation and Storage of Gas

The nitrogen-hydrogen mixture was prepared by burning electrolytic hydrogen and air in such proportions that the resulting gas mixture contained approximately 75% by volume of hydrogen. The remaining 25% was essentially a mixture of nitrogen and argon, the latter forming about 0.3% by volume of the total mixture. The flow of the hydrogen and the air was automatically controlled so that a gas of uniform composition was practically insured. The freshly prepared gas mixture was led into a (14 cu. meter) water-sealed gas holder, from which samples were withdrawn and analyzed by the explosion method. After the gas had been analyzed it was compressed into a storage system (200 atmospheres) which held about 113 cu. meters of gas (N.T.P.).

Analyses covering a period of 117 days gave as the average composition of the gas, 76.2% of hydrogen and 23.8% of nitrogen plus inert gas. The maximum deviation for the hydrogen was 2.2%. The volume of gas in the high-pressure storage was about eight times the daily production, so that daily variations in the composition of the freshly prepared gas mixture were largely smoothed out. The average of the daily analyses represented with sufficient accuracy (see discussion of errors) the composition of the gas employed in these equilibrium experiments.

Gas Purification

Purification of the gas was accomplished by first bringing it into contact with copper at 300–400°. Here the oxygen was removed by conversion to water. The gas was then passed over a nickel catalyst maintained at 250–300°, where carbon monoxide combined with hydrogen to form methane and water. The gas was then passed through a water-cooled condenser, a tower containing soda-lime, two towers filled with porous granular alumina and finally a single tower containing fused potassium hydroxide.[8]

The purity of the gas was tested at regular intervals by slowly passing about 15 liters through a glass coil immersed in liquid air. No trace of condensable impurities was ever observed. An additional check on the gas purity was obtained by operating continuously a pilot catalyst whose efficiency would soon drop if a catalyst poison appeared in the gas.

Pressure Control

The pure gas under 100 atmospheres' pressures was reduced to any desired pressure by means of an automatic reducing valve.[9] A pilot gage was placed in the line and served to indicate fluctuations in pressure, while the actual pressure was measured by means of an oil float (deadweight) gage, which had been checked against a similar gage calibrated by the Bureau of Standards. By means of this arrangement the desired pressures could be accurately maintained to within ± 0.034 atmosphere.

Temperature Control

The catalyst was placed in an iron tube (length, 493 cm.; o. d., 1.72 cm.; i. d., 0.95 cm.) wound in an open coil. This coil was placed in a thermostat filled with fused sodium nitrate-potassium nitrate (1–1), the essential details of which are indicated in Fig. 1. The thermostat was made from a section of iron pipe (21 cm. in diameter and 46 cm. in length) with a welded-on bottom. Nichrome ribbon was wound on the outside of this pipe and served to maintain the fused salt mixture at approximately the desired temperature. The close regulation of the temperature was accomplished by means of a second heater (not shown in Fig. 1), immersed in the salt bath. The flow of current through this heater was controlled by means of a platinum resistance thermometer placed in the bath and

[8] Tour, *Chem. Met. Eng.*, **26**, 588 (1922).

[9] Larson and Karrer, *J. Ind. Eng. Chem.*, **14**, 1012 (1922).

connected to a Wheatstone bridge and contact galvanometer. With this arrangement the temperature fluctuations did not exceed ±0.25°.

Alumel-chromel thermocouples were placed at different levels in the thermostat, the locations of two of them being indicated in Fig. 1. These couples were frequently checked either at the boiling point of sulfur[10] or by direct comparison with a platinum-platinumrhodium couple calibrated by the Bureau of Standards. The bath was stirred at such a rate that a further increase did not have any effect on the temperature uniformity.

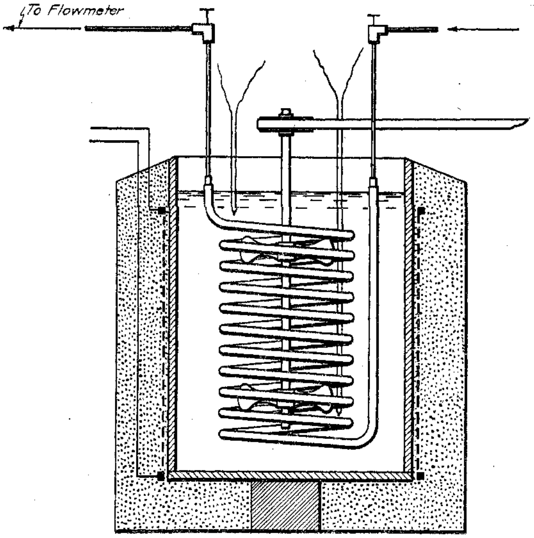

Fig. 1.—Fused salt bath

Analysis of Gas Sample

The ammonia content of the gas was determined by passing the gas through an absorber and collecting the nitrogen-hydrogen residue in a compensating buret.[11] Samples of gas were analyzed under each condition of temperature, pressure and gas flow until three or more consecutive samples taken at intervals of from 5 to 15 minutes showed deviations of less than 1% of their value. The average of these last samples was taken as the value for the ammonia content of the equilibrium gas mixture.

The ammonia was determined in two ways, both of which gave concordant results. In one of these methods the ammonia was absorbed in 4% boric acid solution containing either methyl orange or bromophenol blue (tetrabromo-phenolsulfonephthalein) as indicator, the ammonia being titrated with 0.1 *N* sulfuric acid. In the other method the ammonia was absorbed in 0.1 *N* sulfuric acid with sodium alizarin-sulfonate as indicator, the quantity of acid being slightly less than that required for neutralization of all the ammonia, and the excess of ammonia titrated with additional 0.1 *N* sulfuric acid. The sulfuric acid absorbent with sodium alizarin-sulfonate as indicator was generally used because of the particularly sharp end-point. Less than 0.05 cc. of 0.1 *N* sulfuric acid gave a decided color change. Its disadvantage lies in the necessity of knowing in advance approximately the amount of ammonia in the sample in order to

[10] See U. S. Bur. Standards, *Bull.*, **170** (1921).

[11] Tour, *Chem. Met. Eng.*, **23**, 1104 (1920).

determine approximately the correct amount of acid required for the sample. The efficiency of the absorption was tested by using two absorption bottles in series but no titrable amounts of ammonia were ever found in the second bottle.

Gas Flow

The rate of flow of gas passing through the catalyst coil was measured by dropping the pressure of the gas to atmospheric and passing it through a friction tube flowmeter. The flow was progressively decreased until the ammonia content of the gas leaving the catalyst coil became constant. When this occurred it was assumed that equilibrium had been reached.

With the most active catalyst available, equilibrium is not reached, particularly at the higher pressures, when the space velocity is in excess of 5000, and the temperature is lower than 450°. For example, at 50 atmospheres' pressure and 350° equilibrium was not reached until the space velocity was lowered to 10. With 1 cc. of catalyst for example, this would give only 0.167 cc. of gas per minute, a flow which is difficult to regulate closely. Furthermore, at such a low rate of flow analyzable samples of gas cannot be withdrawn in a reasonable length of time. Under the conditions just specified, it would require 10 hours to remove a 100cc. sample. It was necessary, therefore, to use a relatively large volume of catalyst. Accordingly, about 0.5 liter of catalyst was used (484 cc.); this permitted a gas flow which was easily controllable even at the lowest space velocities

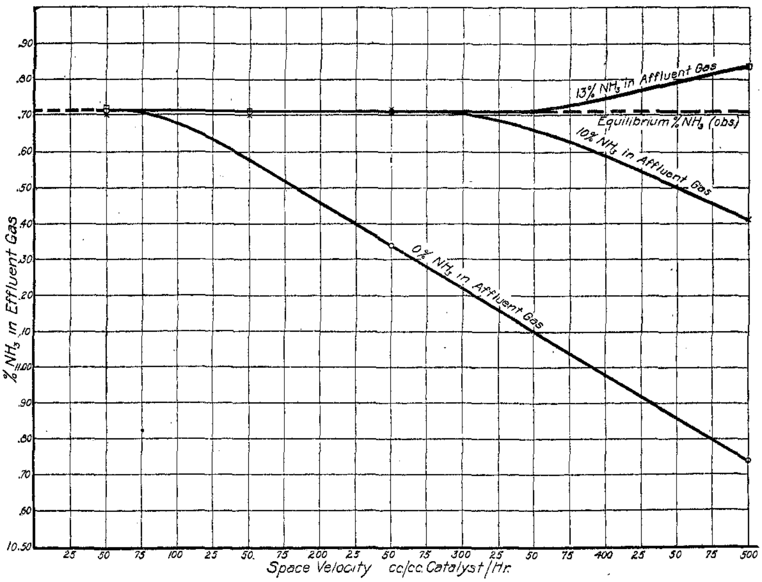

Fig. 2.—Pressure, 50 atm. (abs.) Temperature, 425°. Equilibrium, % NH_3 (obs.) 11.71

employed, and allowed the rapid withdrawal of a sample sufficiently large for analysis.

In order that the experiment might not consume too much time the gas mixture was brought very nearly to the equilibrium condition before it entered the catalyst coil. With this assistance equilibrium was of course more readily attained. Fig. 2 shows the consequences of adding ammonia to the gas when the operating conditions permitted equilibrium to be reached readily on an ammonia-free gas. In this particular case not enough observations were made to determine the shape of the curve; but for our purpose these intermediate points were unnecessary. (The results of other investigations indicate that the space-velocity curves always approach equilibrium in this manner.)

Discussion of Errors

The accuracy of this determination depends on the validity of four assumptions and on the accuracy of five measured values. The assumptions are: (1) that equilibrium is actually attained; (2) that the equilibrium is attained at the measured pressure; (3) that the equilibrium is attained at the point at which the temperature is measured; and (4) that no change in the composition of the gas mixture occurs while the gases are passing from this point to the analytical apparatus.

1. In all cases, concordant results were obtained by approaching the equilibrium from both sides, a proof that equilibrium had actually been attained.

2. The non-existence of a pressure gradient of more than 0.068 atmospheres throughout the reaction coil was proved by measuring the pressure simultaneously at both ends under the limiting conditions of the investigation (that is, between 10 atmospheres' and 100 atmospheres' pressure and with flows ranging from 7 cc. per minute to 7 liters per minute).

3. The temperature was measured in a constant-temperature zone which surrounded approximately the top half of the catalyst coil. Although the temperature of this portion of the catalyst bath was uniform, there might still be an appreciable temperature gradient within the catalyst. In fact, for reactions involving the formation or decomposition of ammonia where large quantities of heat are liberated or absorbed a uniform temperature throughout the entire mass of the catalyst can be only approximated experimentally. By using a tube of relatively small diameter, the difference in temperature between the catalyst and the bath was probably not very great, even in that region where the reaction was most rapid. An inspection of the curves in Fig. 2 shows that when operating on ammonia-free gas, equilibrium was not attained until the flow of gas was decreased to a space velocity of 50. But at a space velocity of 500

we note that the reaction is approximately 90% completed. In other words, while operating at a space velocity low enough to give equilibrium (50 s. v.) 90% of the equilibrium amount of ammonia is formed in the first tenth of the catalyst. Since the catalyst filled the coil completely and the gases entered at the bottom there is no doubt that the equilibrium attained in the catalyst coil corresponds to the temperature of the bath surrounding the upper half of the catalyst coil.

4. In order to comply with the requirements of the fourth assumption a 1.6 mm. copper tube fitted with a steel adapter was pushed down to the catalyst. The copper tube was silver-soldered to the adapter and the adapter was welded to the iron pipe. (See Fig. 3.) In practice, the surface of the fused-salt bath was kept just below this soldered connection. In order to prevent particles of catalytic material being carried into the copper tube, a fine platinum gauze was placed between the catalyst and the copper tube. By passing the gas at a comparatively high linear velocity through a tube which has no catalytic action at these low temperatures, it is believed that there was no change in composition of the gas after it left the catalyst.

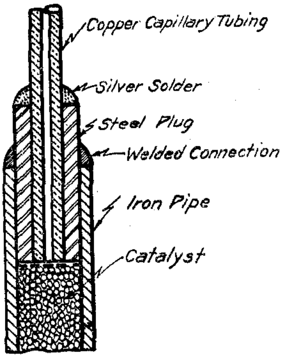

Fig. 3

The five measured values on which the accuracy of the determination depends are (1) the composition of the gas mixture used, (2) the pressure, (3) the measurement of the residual gas volume, (4) the titration of the ammonia absorbed from the equilibrium mixture and (5) the temperature.

1. In calculating the results the average composition of the gas mixture taken was 76.2% of hydrogen, 23.5% of nitrogen, 0.3% of argon. Since a 10% variation in the 3:1 hydrogen-nitrogen ratio produces an error of only 0.2% in the equilibrium constant and less than 1% in the percentage of ammonia at equilibrium, no appreciable error is introduced in employing this average value.

2. The pressure in the reaction coil was measured with an accuracy of 0.034 atmosphere. An error of 0.068 atmosphere at 10 atmospheres would cause only 0.7% error in the equilibrium constant; at the higher pressures the error would, of course, be correspondingly less.

3. The residual gas volume was measured with an accuracy of 0.2% which corresponds to an equal error in the calculation of the percentage of ammonia at equilibrium and an approximately equal error in the equilibrium constant.

4. The error in the standard acid solution was not greater than 0.5%. An error of 0.05 cc. in the titration of samples taken at 10 atmospheres

and 500° would cause a 1% error in the percentage of ammonia (at the lower temperatures and higher pressures the error would be correspondingly less). All the errors of analysis acting in the same direction would give an error of 1.7% in the percentage of ammonia. This corresponds to an approximately equal error in the equilibrium constant.

TABLE I

OBSERVED PERCENTAGE OF AMMONIA AT EQUILIBRIUM

Temp. °C.	Pressure (Atm. abs.) 10	30	50	100
325	10.38	...	...	...
350	7.35	17.80	25.11	...
375	5.25	13.35	19.44	30.95
400	3.85	10.09	15.11	24.91
425	2.80	7.59	11.71	20.23
450	2.04	5.80	9.17	16.35
475	1.61	4.53	7.13	12.98
500	1.20	3.48	5.58	10.40

5. An inspection of Table I, shows that a 1° change in the temperature produces about 1% change in the percentage of ammonia at equilibrium. Since the temperature was measured with an accuracy of 0.5° the errors from this source probably do not exceed 0.5%. This would produce approximately the same percentage error in the equilibrium constant.

From the above considerations it is evident that the maximum error in the equilibrium constant might reach 3%. It is believed that the probable error, however, is very much smaller than this.

Results

The equilibrium percentages of ammonia obtained for the temperatures and pressures studied are given in Table I. In Table II the constant for the expression $K_p = \frac{p_{NH_3}}{p_{N_2}^{1/2} \times p_{H_2}^{3/2}}$ has been calculated for each of the pressure and temperature conditions indicated in Table I.

Thermodynamic Calculations

If experimental data were available showing the volume changes which the nitrogen-hydrogen-ammonia mixture undergoes for various conditions of temperature and pressure, it might be possible with the aid of the van't Hoff equation to formulate a single expression which would satisfy the data given in Table I. By means of such a formula one would then be able to compute the equilibrium percentage of ammonia for any other temperature and pressure. Haber's formula[7](I) has been used for this purpose and is probably quite exact for relatively high temperatures. Jost[5] working at 915° in Nernst's laboratory found that the pressure effect was negligible. Undoubtedly the ammonia is sufficiently "perfect" a gas at this high temperature so that the effect of pressure becomes negligible. At somewhat lower temperatures, however, deviations from the "perfect" gas laws undoubtedly become sufficiently great so that the pressure effect cannot be wholly ignored. The only experimental evidence for this so far presented is that by Greenwood[7](VII) in Haber's laboratory who showed that the equilibrium constants in the neighborhood of 537° did vary with the pressure. Greenwood found, however, that the constant increased as the pressure is decreased, an observation which is quite the opposite of that shown in Table II. It is reasonably certain; however, that equilibrium was not reached in Greenwood's experiments, so not much importance is attached to this apparent disagreement with our result.

TABLE II

OBSERVED EQUILIBRIUM CONSTANT

$$^1/_2N_2 + {}^3/_2H_2 = NH_3$$

$$K_p = \frac{p_{NH_3}}{p_{N_2}^{1/2} \times p_{H_2}^{3/2}}$$

Temp. °C.	Pressure (Atm. abs.) 10	30	50	100
325	0.0401	....	....	....
350	.0266	0.0273	0.0278	....
375	.0181	.0184	.0186	0.0202
400	.0129	.0129	.0130	.0137
425	.00919	.00919	.00932	.00987
450	.00659	.00676	.00690	.00725
475	.00516	.00515	.00513	.00532
500	.00381	.00386	.00388	.00402

Unfortunately, no data are at present available which make possible even a rough calculation of the extent to which the equilibrium constant might be expected to vary with the pressure. Whatever the pressure range covered, nitrogen and hydrogen are probably nearly "perfect" gases even at the lowest temperature studied. Although the temperatures studied by us are somewhat higher than those investigated by Roth,[12] the indications are that even at these temperatures the ammonia is still somewhat more compressible than a "perfect" gas, so that even if the magnitude of the effect cannot be predicted from present data, the effect as observed by us is certainly in the right direction.

For any given constant pressure, however, the van't Hoff equation $\left(\frac{\partial \log K_p}{\partial T}\right)_p = \frac{Q_p}{RT^2}$ may be employed to treat the variation of the equilibrium constant, K_p, with the temperature. To integrate this expression it is first necessary to know how the heat of formation of ammonia from its elements varies with temperature. The integration constant may then be exactly evaluated from a single equilibrium determination, or approximately evaluated by means of Nernst's heat theorem. At present the heat

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[12] Roth, *Ann. Physik.*, [2] **11,** 1 (1880).

of reaction and thermal properties of these gases are not known with sufficient accuracy to make possible the computation of equilibrium data by this method. Consequently, any formula which closely fits the observed data must of necessity be largely empirical.

Taking the best data available, Haber formulated the following expression based upon the reaction isochore, which he held to combine all the results of his equilibrium experiments and thermal determinations

$$\log K_p = \frac{9591}{4.571T} - \frac{4.98}{1.985} \log T - \frac{0.00046}{4.571} T + \frac{0.85 \times 10^{-6}}{4.571} T^2 + 2.10$$

This formula was largely derived from results obtained at 30 atmospheres.[7]

If we use the more recent data for the specific heats of the gases[13] $c_{p_{H_2}} = 6.50 + 0.0009\ T$, $c_{p_{N_2}} = 6.50 + 0.0010\ T$, and $c_{p_{NH_3}} = 8.04 + 0.0007\ T + 5.1 \times 10^{-6}T^2$ and the heat of formation of ammonia at $T = 0$ as 9500,[14] integration of the van't Hoff reaction isochore gives

$$\log K_p = \frac{9500}{4.5787T} - \frac{4.96}{1.9885} \log T - \frac{.000575}{4.5787} T + \frac{0.85 \times 10^{-6}}{4.5787} T^2 + I$$

By choosing proper values for the integration constant and modifying the numerical coefficients we obtained empirical equations which fit our experimental data within the limits of experimental error. The constants and coefficients for the equations are given below. The equation has the general form $\log K_p = \frac{\alpha}{T} + \beta \log T + \gamma T + \delta T^2 + I$.

Pressure Atm.	α	β	γ	$\delta \times 10^7$	I
10	+2074.8	−2.4943	0	+1.856	+1.993
30	+2074.8	−2.4943	-3.4×10^{-5}	+1.856	+2.021
50	+2074.8	−2.4943	-1.256×10^{-4}	+1.856	+2.090
100	+2074.8	−2.4943	-1.256×10^{-4}	+1.856	+2.113

The observed data and those computed from these formulas are collected in Tables III and IV. For purposes of comparison we have included values computed from Haber's formula (see above). The observed results for temperatures above 500° were obtained by plotting Haber's experimental data and selecting from the curve the most probable values for the temperatures indicated.

Because of the interest attached to the Nernst heat theorem we have included in Table III values for 30 atmospheres, computed from his formula.[15]

In the absence of exact thermal data, calculation based on the Nernst heat theorem will, of course, give only an approximate evaluation.

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[13] Lewis and Randall "Thermodynamics," McGraw-Hill Book Co., **1923,** p. 80.

[14] Ref. 13, p. 557.

[15] Nernst, *Z. Elektrochem.*, **16,** 101 (1910). See Also Maurer, *Z. anorg. Chem.*, **108,** 284 (1920).

TABLE III

PERCENTAGE OF AMMONIA AT EQUILIBRIUM

Pressure, 30 Atm. abs.

Temp. °C.	Observed	F.N.R.L.[a] calc.	Haber calc.	Nernst calc.
200	....	67.56	67.57	73.21
250	....	47.22	49.16	54.89
300	....	30.25	31.76	36.15
350	17.80	17.78	18.81	21.22
400	10.09	10.15	10.72	11.67
450	5.80	5.86	6.13	6.36
500	3.48	3.49	3.62	3.62
600	(1.48)	1.39	1.43	1.31
700	(0.70)	0.68	0.66	0.55
800	(.34)	.36	.35	.27
900	(.28)	.22	.21	.14
1000	(.12)	.14	.13	.09

[a] Fixed Nitrogen Research Laboratory.

TABLE IV

PERCENTAGE OF AMMONIA AT EQUILIBRIUM

	10 Atm. abs.			50 Atm. abs.			100 Atm. abs.		
Temp. °C.	Obs.	F.N.R.L. calc.	Haber calc.	Obs.	F.N.R.L. calc.	Haber calc.	Obs.	F.N.R.L. calc.	Haber calc.
200	..	50.66	51.14	...	74.38	73.76	...	81.54	80.61
250	..	28.34	30.57	...	56.33	57.44	...	67.24	67.40
300	..	14.73	16.03	...	39.41	40.39	...	52.04	52.12
350	7.35	7.41	8.04	25.11	25.23	26.03	...	37.35	37.35
400	3.85	3.85	4.12	15.11	15.27	15.86	24.91	25.12	25.13
450	2.04	2.11	2.21	9.17	9.15	9.50	16.35	16.43	16.26
500	1.20	1.21	1.27	5.58	5.56	5.77	10.40	10.61	10.43
600	..	0.49	0.48	...	2.25	2.34	...	4.52	4.47
700	..	0.23	0.22	...	1.05	1.10	...	2.18	2.14
800	..	0.14	0.12	...	0.57	0.59	...	1.19	1.15
900	..	0.08	0.07	...	.33	.34	...	0.70	0.68
1000	..	0.05	0.04	...	.21	.22	...	.45	.44

The results of this paper indicate that the computation of equilibrium values for pressures other than those actually observed cannot be made with any degree of exactness. For the present, at least, computation of

TABLE V

PERCENTAGE OF AMMONIA AT EQUILIBRIUM

(Calculated from Experimental Data of the F.N.R.L.)

	Pressure (Atm. abs.)			
Temp. °C.	10	30	50	100
200	50.66	67.56	74.38	81.54
250	28.34	47.22	56.33	67.24
300	14.73	30.25	39.41	52.04
350	7.41	17.78	25.23	37.35
400	3.85	10.15	15.27	25.12
450	2.11	5.86	9.15	16.43
500	1.21	3.49	5.56	10.61

equilibrium values for much higher pressures than those reported in this paper would, therefore, not be very exact. For any of the pressures studied however, equilibrium values for temperatures lower than those actually observed can probably be computed with considerable accuracy. Such computations have been made for temperatures down to 200°, the results of which are given in Table V.

Molecular Heat of Formation of Ammonia

Theoretically, it should be possible to calculate the heat of the ammonia reaction by means of the van't Hoff equation. By taking equilibrium constants for temperatures very close together and assuming that the temperature coefficient for those temperature intervals can be neglected, integration of the van't Hoff equation gives the heat of formation. Computations based on the constants in Table II have been made, the results of which are given in Table VI. For purposes of comparison we have also included the heat of formation as calculated by Haber from the heat absorbed during the "cracking" of ammonia. Since a 1% error in equilibrium constant makes an error of about 5% in the calculated heat of reaction, this method of determining thermal data cannot be considered very satisfactory. As Haber has pointed out[16] thermal data obtained in this way can serve only as a check on the more direct experimental methods for reaction heats and specific heats. An inspection of Table VI will show that the attempt to formulate an expression for the heat of the reaction from these would be futile.

TABLE VI

MOLECULAR HEAT OF FORMATION OF AMMONIA

$$Q_p = 4.5707 \frac{\log K_{p1} - \log K_{p2}}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

Temperature interval °C.	Haber	F.N.R.L. Calculated from experimental data, Atm. abs. 10	30	50	100
325–350	12,425	12,206	....	....	....
350–375	12,505	12,248	12,636	12,924	....
375–400	12,590	11,779	12,283	12,386	13,373
400–425	12,672	12,712	12,694	12,468	12,311
425–450	12,751	13,340	12,342	12,099	12,376
450–475	12,825	10,558	11,785	12,741	13,339
475–500	12,896	13,903	13,138	12,801	12,888

Summary

1. Equilibrium values for the reaction, $N_2 + 3H_2 \rightleftarrows 2NH_3$, have been determined at 10, 30, 50 and 100 atmospheres' pressure for the temperature range of 325° to 500°.

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[16] Haber, "Thermodynamics of Technical Gas Reactions," Longmans, Green and Co., **1908**, p. 65.

2. Equilibrium constants have been computed for each of the pressure-temperature conditions studied. These "constants" were found to increase with an increase in pressure.

3. By means of empirical formulas the percentage of ammonia at equilibrium has been calculated for a temperature range of 200–1000°, and a pressure range of 10–100 atmospheres.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

VAPOR PRESSURES OF LITHIUM CHLORIDE SOLUTIONS AT 20°

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This paper is a continuation of a series of studies of the vapor pressures of aqueous solutions begun by Frazer and Lovelace[1] using an accurate static method which depends upon the measurement of the difference in pressure between pure solvent and solution contained in bulbs immersed in the same accurately regulated water thermostat by means of a Rayleigh manometer. The error involved in measuring the pressure differences by this method is approximately 0.0006 mm. The measurements were made at 20° and in the concentration range from 0.1 to 1.0 *M*.

Experimental Details

A detailed description of the apparatus used in this work is given by Frazer and Lovelace,[1] and by Lovelace, Frazer and Miller.[2] No change in the apparatus was made except to replace the Gaede pump with a Langmuir pump using a three-stage rotary oil pump as auxiliary.

The solutions of lithium chloride were prepared from a carefully standardized stock solution, the salt for which was purified as follows. A commercial C. P. grade of lithium chloride was dissolved in distilled water, a small amount of ammonium carbonate solution added and the mixture heated and stirred for four hours to precipitate any magnesium, calcium, barium, iron or aluminum possibly present, then filtered. The ammonium carbonate used in the preparation left no residue on sublimation. To the filtered lithium chloride solution, ammonium carbonate solution was added in slight excess and the lithium carbonate filtered off and washed thoroughly with hot water. It was then heated in a platinum dish at a sufficiently high temperature to volatilize any ammonium carbonate possibly present. The salt was then suspended in a small amount of distilled water and pure hydrochloric acid added until the solution was neutral to rosolic acid. Analyses of the solution for lithium and for chlorine checked within 0.04%.

In previous investigations the removal of dissolved air from the solutions has been quite a time-consuming operation. Tests for air in the solution or solvent were made by allowing it to come to equilibrium with a large

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[1] Frazer and Lovelace, THIS JOURNAL, **36**, 2439 (1914).

[2] Lovelace, Frazer and Miller, *ibid.*, **38**, 515 (1916).