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

THE AMMONIA EQUILIBRIUM AT HIGH PRESSURES

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In an earlier paper[2] the equilibrium values for the reaction, $^1/_2\ N_2 + {}^3/_2\ H_2 \rightleftharpoons NH_3$, were given for a pressure range of 10–100 atmospheres and a temperature range of 325–500°. Empirical formulas were given which represented the variation of the equilibrium constant with the temperature. By means of these formulas the temperature range for each pressure studied was extended to 200° and 1000°. Unfortunately, there was not sufficient regularity in the variation of the equilibrium constant with the pressure to make extrapolation to the higher pressures trustworthy.

The only direct determination of the ammonia equilibrium at relatively high pressures is that by Claude.[3] He was not very certain, however, that equilibrium conditions had been really established. The results of some preliminary work in this Laboratory indicate that the real equilibrium values are somewhat higher than those obtained by Claude. It was thought worth while, therefore, to extend the pressure range employed in our earlier investigation to the hyperpressures employed by Claude. The results of these measurements are given in this paper.

Experimental Part

The experimental procedure was essentially the same as that followed in the previous work. 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 gas mixture was first compressed to 100 atmospheres by means of a compressor of standard make. The higher pressures were attained by compressing the gas over water in a steel cylinder (length 56 cm., i.d. 7.6 cm., o.d. 26.5 cm.), water being forced into this cylinder by means of an hydraulic pump. The final pressure was measured by means of a piston type (dead-weight) gage.

The gas was given a preliminary purification at 100 atmospheres by passing it in succession through a copper deoxidizer, a nickel catalyst, soda lime, granular aluminum oxide, and fused potassium hydroxide. Final purification of the high-pressure gas was accomplished by passing the gas mixture through an ammonia catalyst whose temperature was approximately 500°. A relatively small quantity of the ammonia formed was

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[1] Experimental work by L. A. Stengel and C. H. Young. Editorial assistance by R. L. Dodge.

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

[3] Claude, *Compt. rend.*, **169**, 1039 (1919).

permitted to condense in a cooling coil. This liquid ammonia was withdrawn from time to time and effectively removed the small traces of carbon dioxide and water vapor which were introduced by the hydraulic compressor. If any appreciable quantity of ammonia had been removed by this method of purification the partial pressure of the inert gases present would of course have been proportionately increased. It is conceivable that this might lower the partial pressures of the nitrogen-hydrogen mixture to such an extent that there would be an actual lowering of the percentage of ammonia produced. Since it was possible to obtain equilibrium at the higher temperatures where the reaction was relatively rapid without the use of this additional purification, the effect of this purifier was readily made apparent. Comparison tests showed that the amount of ammonia removed by the purifier did not change the equilibrium percentage of ammonia observed.

The reaction bomb consisted of a steel tube (length 430 cm., o. d. 2.5 cm., i. d. 0.8 cm.) wound in an open coil. This was placed in a thermostat filled with a fused 1:1 mixture of sodium nitrate and potassium nitrate. The thermostat was equipped with stirrers, thermocouples, electric heaters, etc., as described in the earlier paper. An expansion valve, by means of which the high-pressure gas mixture was reduced to atmospheric pressure, was placed just above the fused salt bath. The connections up to and including the expansion valve were kept above the critical temperature of ammonia. The catalyst employed was a reduced iron oxide containing potassium oxide and aluminum oxide as promoters. The apparent volume of the catalyst was 167 cc. The rate of flow of the gas passing through the catalyst coil was determined by measuring the volume of the gas leaving the expansion valve. The flow of the gas was progressively decreased until the ammonia content of the gas became constant. When this occurred it was assumed that equilibrium conditions had been established. The ammonia content of this gas was determined by passing the gas through an absorber and collecting the nitrogen-hydrogen residue in a compensating buret.[4] The ammonia was absorbed in 0.5 *N* sulfuric acid with sodium alizarin sulfonate as an indicator.

Discussion of Errors

In the earlier paper it was pointed out that the accuracy of the equilibrium 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 equilibrium is attained at the measured pressure; (3) that 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 gases are passing from this point to the analytical apparatus.

1. In our earlier experiments[2] the equilibrium was approached from the high-ammonia side as well as from the low-ammonia side. Essentially the same constant value was obtained by both methods. In these experiments, therefore, it was considered sufficient to approach equilibrium from the low-ammonia side.

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

2. The pressure gradient in the tube was found to be less than 0.5 atmosphere, which is within the limit of accuracy of the experiment.

3. Since the tube was of relatively small diameter the difference in temperature between the catalyst and the bath in which the tube was immersed was probably not very great. The temperature gradient of that portion of the bath within which the final establishment of the equilibrium took place (approximately the upper half of the catalyst tube) was kept constant to within ±0.25°.

4. As in our earlier experiment, the exit end of the catalyst tube was fitted with an inner tube of copper. Since copper is without action at these low temperatures it is believed that there was no change in composition of the gas after it left the catalyst.

The accuracy of the equilibrium determinations depends on the accuracy of five measured values, namely, the composition of the gas mixture used, the pressure, the residual gas volume, the titration of the ammonia, and the temperature. The maximum error in the equilibrium constant resulting from errors in these measured values was not more than 2%. From the concordance of independent determinations it is believed that the probable error was very much less.

Results

The equilibrium percentages of ammonia obtained for the temperatures and pressures studied are given in Table I.

TABLE I

OBSERVED PERCENTAGES OF AMMONIA AT EQUILIBRIUM

Temp., °C.	Pressure (atm. abs.) 300	600	1000
450	35.5	53.6	69.4
475	31.0	47.5	63.5
500	26.2	42.1	..[a]

[a] The catalyst coil burst and the work was discontinued before results under these conditions were obtained.

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.

TABLE II

EQUILIBRIUM CONSTANT

$$\tfrac{1}{2} N_2 + \tfrac{3}{2} H_2 = NH_3$$

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

Temp. °C.	Pressure (atm. abs.) 300	600	1000
450	0.00884	0.01294	0.02328
475	.00674	.00895	.01493
500	.00498	.00651	...

Discussion of Results

The results confirm those of the earlier paper in showing a marked variation of the equilibrium constant with the pressure. These results are further evidence that the computation of the equilibrium values for pressures other than those actually observed cannot be made with any exactness until more is known about the temperature-pressure-volume relationships of the gas mixtures in question.

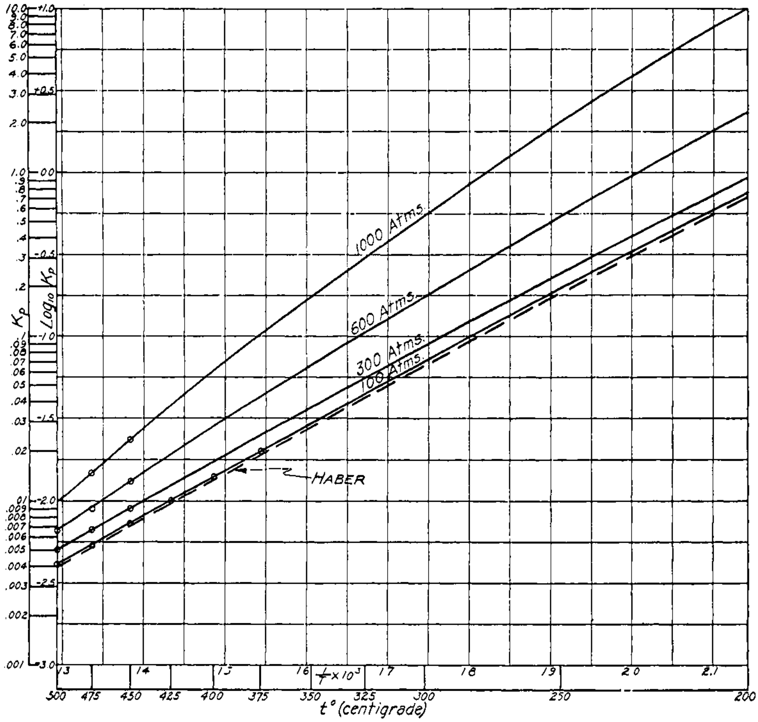

Fig. 1.

Empirical equations of the form of the integrated van't Hoff reaction isochor have been constructed for each of the pressures studied and represent the experimental data within the limits of accuracy of the experiment. The coefficients and constants of these equations are given below. The equation has the general form,

$$\text{Log } K_p = \frac{\alpha}{T} + \beta \log T + \gamma T + \delta T^2 + C$$

Press. atm.	α	β	γ	δ	C
300	+2074.8	−2.4943	-1.256×10^{-4}	$+1.8564 \times 10^{-7}$	+2.206
600	+2074.8	−2.4943	-1.0856×10^{-3}	$+1.8564 \times 10^{-7}$	+3.059
1000	+2074.8	−2.4943	-2.6833×10^{-3}	$+1.8564 \times 10^{-7}$	+4.473

Calculation of the equilibrium constants for lower temperatures by means of these formulas can probably be made with considerable accuracy. The results of such calculation are represented graphically in Fig. 1, the dotted line being the equation given by Lewis and Randall,[5] as derived from the best available data on the specific heats and heats of reaction of the gases and the equilibrium constants as determined by Haber[6] at 30 atmospheres' pressure and temperatures from 561° to 974°. The percentages of ammonia at equilibrium as calculated from these formulas are given in Table III and shown graphically in Fig. 2.

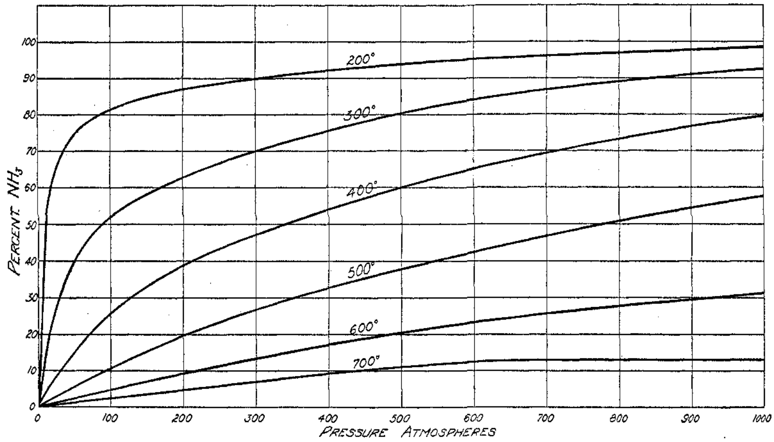

Fig. 2.

TABLE III

PERCENTAGE OF AMMONIA AT EQUILIBRIUM

(Calculated from experimental data obtained at the F.N.R.L.[a])

Temp. °C.	Pressure (atm. abs.)						
	10	30	50	100	300	600	1000
200	50.66	67.56	74.38	81.54	89.94	95.37	98.29
250	28.34	47.22	56.33	67.24	81.38	90.66	96.17
300	14.73	30.25	39.41	52.04	70.96	84.21	92.55
350	7.41	17.78	25.23	37.35	59.12	75.62	87.46
400	3.85	10.15	15.27	25.12	47.00	65.20	79.82
450	2.11	5.86	9.15	16.43	35.82	53.71	69.69
500	1.21	3.49	5.56	10.61	26.44	42.15	57.47
550	0.76	2.18	3.45	6.82	19.13	31.63	41.16
600	.49	1.39	2.25	4.52	13.77	23.10	31.43
650	.33	0.96	1.53	3.11	9.92	16.02	20.70
700	.23	.68	1.05	2.18	7.28	12.60	12.87

[a] Fixed Nitrogen Research Laboratory.

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[5] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923,** p. 80. $\log K_p = \frac{2074.8}{T} - 2.4943 \log T - 0.00012558T + 0.18564 \times 10^{-6}T^2 + 2.099.$

[6] Haber, *Z. Elektrochem.,* **20,** 597 (1914).

For the sake of completeness the values for the pressures 10, 30, 50 and 100 atmospheres as calculated in the earlier paper are included.

Summary

1. Equilibrium values for the reaction $^1/_2\,N_2 + {}^3/_2\,H_2 = NH_3$ have been determined at 300, 600 and 1000 atmospheres' pressure and at temperatures of 450°, 475° and 500°.

2. Equilibrium constants have been computed for each of the pressure-temperature conditions studied. These constants become larger as the pressure is increased and confirm in this regard the results previously obtained at pressures from 10 to 100 atmospheres.

3. By means of empirical formulas the percentage of ammonia at equilibrium has been calculated for a temperature range of 200–700° and a pressure range of 10–1000 atmospheres.

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[Contribution from the Jefferson Physical Laboratory of Harvard University]

THE EXCITATION, REFLECTION, AND UTILIZATION IN CRYSTAL-STRUCTURE ANALYSES OF CHARACTERISTIC SECONDARY X-RAYS

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During the development of a new method of crystal-structure analysis by X-rays, it was discovered that the X-rays characteristic of and excited in the chemical elements in a crystal are reflected by the crystal itself. It was further demonstrated that the reflection takes place both in accordance with the Bragg law, $n\lambda = 2d \sin \Theta$, and also in an anomalous fashion. Some examples of these phenomena, together with a description of the ionization spectrometer utilized in these experiments and of the various steps in the method of analyzing crystals, have already been presented.[2] From the spectra characteristic of the constituent elements it has been possible to determine accurately the spatial distribution of the atoms in potassium iodide, cesium iodide, potassium tri-iodide, cesium tri-iodide, and cesium dibromo-iodide. Thus even cesium and iodine atoms were clearly differentiated, although they are so nearly contiguous in the periodic table and have so nearly the same reflecting power.

It is the purpose of the present paper to present new precision measurements on characteristic spectra, as follows: the iodine K series spectrum from the 100 planes of potassium iodide through five orders; the iodine K series spectrum from the 0001 planes of iodoform, through three orders

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[2] Clark and Duane, *Proc. Nat. Acad. Sci.*, **8**, 90 (1922); **9**, 117, 126, 131 (1923); *J. Opt. Soc. Am.*, **7**, 455 (1923); *Science*, **58**, 398 (1923).