The Chemical Equilibrium of the Ammonia Synthesis Reaction at High Temperatures and Extreme Pressures

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Chemical equilibrium in this reaction has been determined experimentally by a static or nonflow method at temperatures of 400° and 450°C. and at pressures of 1,000 to 3,500 atm. Equilibrium was approached from both sides and the two reacting gases were always in the stoichiometric ratio. The results are presented both as mole percentage of ammonia in the equilibrium mixture and as the equilibrium constant K_p. The constant, K_p, which is a function of pressure, was calculated from K_{p°, its value at $p = 0$, by five different methods and from them the corresponding mole percentages of ammonia were derived for comparison with the experimental results. All such calculations involve assumptions of varying degrees of validity, and no calculated value can be considered accurate. However two of the calculation methods give values which agree reasonably well with the experimental values.

The purpose of the present work is to extend the range of pressures for which the chemical equilibrium between ammonia and its elements is known. The chemical equilibrium was determined experimentally for mixtures containing hydrogen and nitrogen, in a mole ratio of three to one, with ammonia at pressures from 1,000 to 3,500 atm. in the temperature range of 400° to 450°C. These temperatures were chosen as being close to industrial ammonia-synthesis conditions. Comparison will also be made between these values and those which were calculated by several of the methods now available for predicting the effect of pressure on chemical equilibrium.

In 1923 Larson and Dodge (*14*) reported the determination of the chemical equilibrium of the ammonia reaction in the pressure range from 10 to 100 atm. at temperatures from 375° to 500°C. In 1924 Larson (*13*) extended these experimental data to 1,000 atm. at 450° and 475°C. A continuous method was used wherein a purified 3:1 hydrogen-nitrogen mixture was passed through a tubular high-pressure reactor filled with a doubly promoted iron catalyst. The flow rate was progressively decreased until successive samples taken at the reactor outlet assumed identical ammonia content. Up to 100 atm., equilibrium was also approached from the ammonia side.

In 1935 Basset (*1*) reported the synthesis of ammonia at a very high pressure without a catalyst and in the presence of impurities such as carbon monoxide and hydrogen sulfide. At 850°C. and 4,350 atm. the 3:1 hydrogen-nitrogen mixture was said to have reacted at a rate of 10 g. of ammonia produced/(hr.)(cc.) of reaction chamber to form a product containing 94 mole % of ammonia. Basset did not determine the chemical equilibrium, but his work is pertinent because it is the only previous investigation of the ammonia reaction materially above 1,000 atm.

The equilibrium constant at zero pressure, K_{p°, can be calculated from the known thermal data on the system and then the effect of pressure can, in principle, be calculated from well-known relations of which the following is typical:

$$\ln \frac{K_p}{K_{p^\circ}} = -\frac{1}{RT}\left\{\sum_i \left[\nu_i \int_0^p \left(\bar{V}_i - \frac{RT}{p}\right) dp\right]\right\}$$

The integral within the square brackets is the logarithm of the activity coefficient of any component i and could be evaluated if pvT data on the ternary mixture were available from zero pressure up to the given equilibrium pressure at the temperature in question. Such data are completely lacking at the present time, and for the calculation various assumptions must be made; for example, one can assume an ideal solution or the validity of various equations of state, evaluating the constants for the mixture from those for the pure components by various common rules. The authors have made many calculations of this kind, but every different assumption leads to a different result and there is no way to decide which one is best. Under these circumstances it is necessary to resort either to direct measurement of the equilibrium constant at the elevated pressure or to obtaining experimentally the pvT data. The first method was chosen.

METHOD OF EQUILIBRIUM MEASUREMENT

There are three methods of determining equilibrium. In the continuous, or flow, method composition and temperature vary with position in the reactor but are invariant with time. The pressure remains constant with time and, if frictional pressure losses and differences in elevation are neglected, with position.

In the batch method, composition, temperature, and pressure approach constant values with time. With elevation differences neglected and time granted for mixing, these properties are invariant with position in the reactor.

The intermittent method resembles the batch method until sampling begins; then, however, the pressure loss is compensated after every sampling by admission of reactants. Consequently, the pressure fluctuates around a constant value with time while the samples are taken. This makes composition and temperature practically constant with time and, owing to insufficient time for mixing, variant with position.

The crucial items of equipment required in the three methods are somewhat different and are worth a brief discussion. The continuous method requires a 4,000-atm. continuous gas compressor followed by purification train. The reactor should be long and of relatively large internal volume in order to obtain an appreciable volumetric flow rate at the low space velocities required to reach equilibrium.

The batch method requires a continuous gas compressor for 500 to 1,000 atm. and either a mercury-sealed 4,000-atm. water pump or a pump for lower pressures with a gas-pressure intensifier or a liquid-pressure intensifier with a mercury seal. The method of analysis should be accurate for small gas samples, and the reactor should have a large internal volume so that the pressure drop after the taking of several samples will be negligibly low.

The intermittent method requires a continuous gas compressor for 500 to 1,000 atm., a gas-pressure intensifier or a mercury-sealed liquid-pressure intensifier,

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a pump, and sensitive product analysis like the batch method. A relatively large reservoir for reactants at 4,000 atm. and room temperature and a smaller reactor of long, tubular shape to prevent rapid mixing are needed.

Although *pure* reactants can be purchased, the larger quantities required by the continuous method dictate the use of a purification train on relatively impure gases. In all three procedures considerable time should be allowed before sampling at a new condition of pressure and temperature, because of the solubility of the reactants in steel at high pressures.

The equipment used in these experiments was designed for catalyst treatment by the flow method, followed by equilibrium determinations by means of batch or intermittent methods as desired.

APPARATUS

As shown in Figure 1, reactants were brought to equilibrium in the catalyst-filled inner tube of the pressure chamber immersed in molten salt in *A*. Pressure was obtained by (1) filling one leg of the U tube *B* with gaseous reactants at medium pressure (300 to 1,000 atm.) from *E* or with liquid ammonia from *L*; (2) compressing through a mercury seal with water pumped to 300 to 1,000 atm. by *D* and intensified in *C* to a maximum of 4,000 atm.; and (3) making connection to the reactor in *A*. Reactor pressure was measured with a calibrated strain gauge (*H* and *I*) and Bourdon gauge 2. Temperature was measured with thermocouples with hot junctions immersed in *A*. Samples taken through valve 13 at the outlet of the reactor were analyzed by directly titrating ammonia absorbed in boric acid solution in 10 and measuring the residual hydrogen and nitrogen in a burette (not shown).

Hydrogen and nitrogen were supplied by the research laboratory of the Linde Air Products Co. and were stated to have the following compositions (dry basis):

Hydrogen		Nitrogen	
H_2	99.9813%	N_2	99.9918%
CO_2	7 p.p.m.	CO_2, CO, HC's	1 p.p.m.
CO	2 p.p.m.	H_2	3 p.p.m.
O_2	14 p.p.m.	He	4 p.p.m.
CH_4	14 p.p.m.	O_2	9 p.p.m.
N_2	150 p.p.m.	Ne	15 p.p.m
H_2O	10 grains/1,000 cu. ft. (257 p.p.m.)	A	50 p.p.m.
		H_2O	3 grains/1,000 cu. ft. (77 p.p.m.)

A mixture was made up in *K* which analyzed 74.78% hydrogen. Ammonia in *L* was stated by the manufacturer to be 99.98% pure. Water and hydrocarbons were removed from the elemental gases in purifier *G*, a small 15,000 lb./sq. in. vessel filled with "gas-adsorbent" charcoal and soda lime. Water-pumped nitrogen in *J* was used to flush out the equipment. Mixtures up to 1,000 atm. were made up in the storage vessel *F* (diameter ratio 2:1, internal volume 1 cu. ft.) by use of a five-stage, 15,000 lb./sq. in. compressor *E* or batchwise by means of a Triplex water pump *D*.

The 60,000 lb./sq. in. intensifier *C*, made by the American Instrument Co., compressed the system by 22 cc. with each stroke. The mercury-piston pump *B*, designed and built at this laboratory, con-

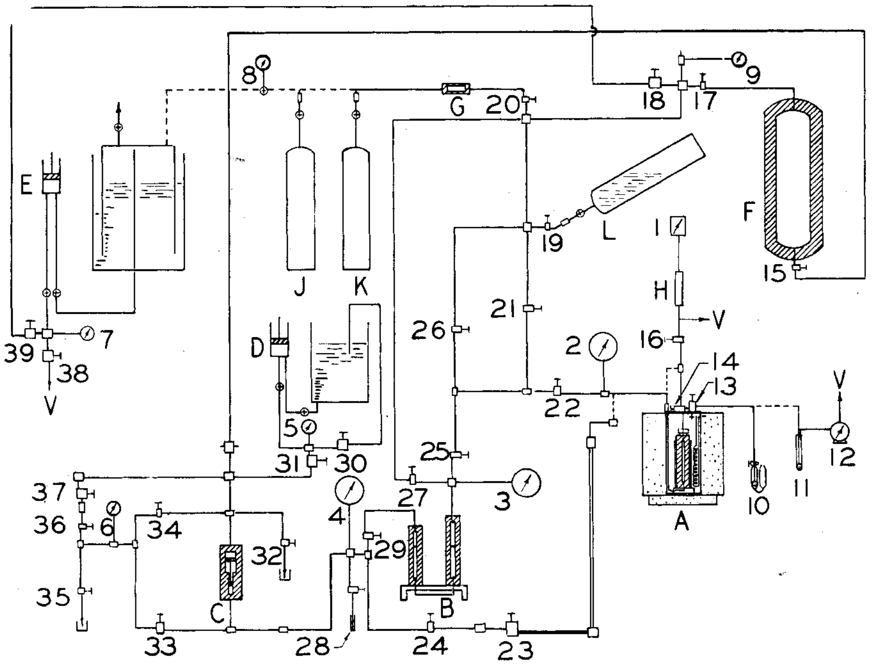

Fig. 1. Diagram of apparatus.

A, thermostat-reactor assembly; *B*, mercury-piston pump assembly; *C*, intensifier; *D*, 1,000 atmosphere liquid pump; *E*, 1,000 atmosphere gas compressor; *F*, 1,000 atmosphere gas-storage vessel; *G*, 1,000 atmosphere drier; *H*, strain gauge pressure cell; *I*, strain gauge indicator; *J*, commercial gas cylinder containing pure nitrogen; *K*, commercial gas cylinder containing pure 3:1 hydrogen-nitrogen mixture; *L*, commercial cylinder containing pure liquid ammonia; *V*, vent to the atmosphere; 2, 100,000 lb./sq. in., pressure gauge (Bourdon type); 3, 100,000 lb./sq. in. gauge; 4, 100,000 lb./sq. in. gauge; 5, 20,000 lb./sq. in. gauge; 6, 20,000 lb./sq. in. gauge; 7, 30,000 lb./sq. in. gauge; 8, reducing pressure gauge; 9, 20,000 lb./sq. in. gauge; 10, sampling pipette; 11, ammonia absorption tube; 12, wet-test meter; 13, 16, 21, 22, 24-29, 60,000 lb./sq. in. Aminco valves, through-type for 1/4 in. tubing; 14, 60,000 lb./sq. in. Aminco valve, three-way type for 1/4 in. tubing; 15, 17, 19, 20, 32, 34, 35, 36, 39, 25,000 lb./sq. in. Aminco valves, through-type, for 1/4 in. tubing; 18, 30, 31, 37, 38, 25,000 lb./sq. in. Aminco valves, through-type, for 9/16 in. tubing; 23, 60,000 lb./sq. in. Aminco valve, through-type, for 9/16 in. tubing; 33, 100,000 lb./sq. in. Aminco valve.

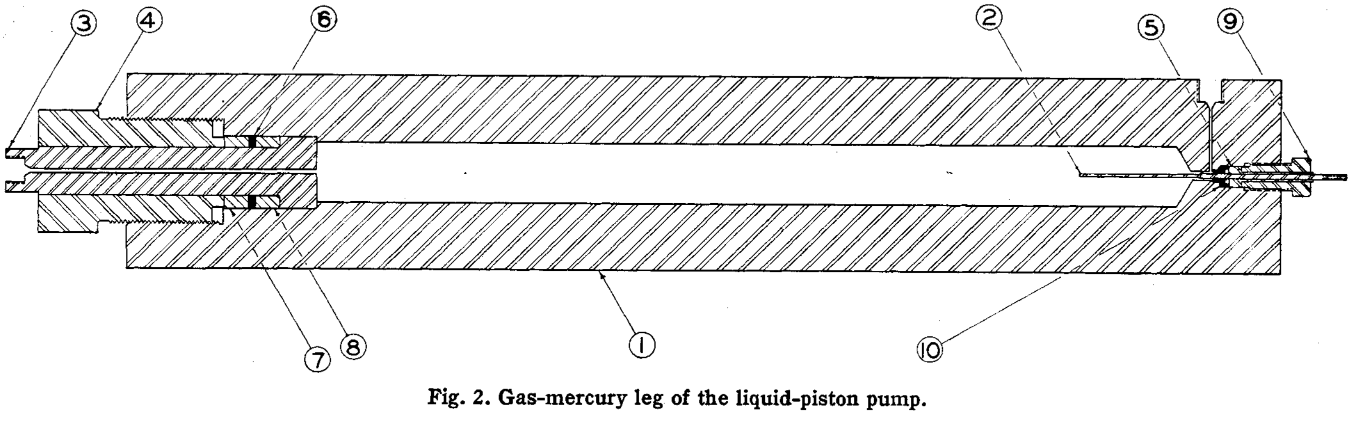

Fig. 2. Gas-mercury leg of the liquid-piston pump.

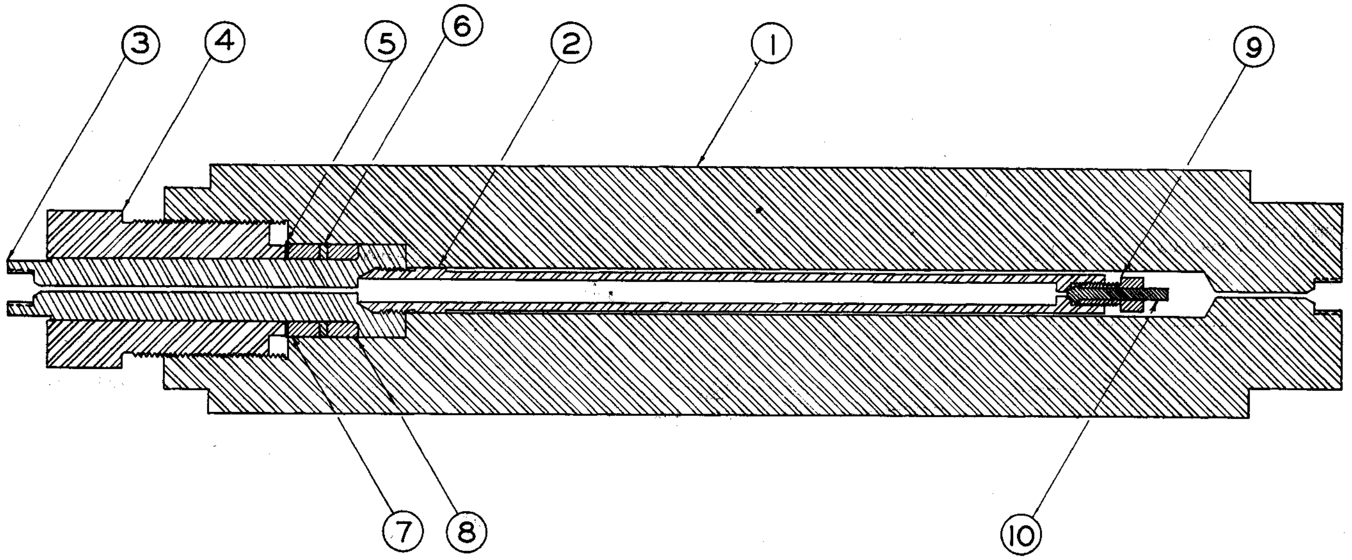

Fig. 3. Reactor assembly.

sisted of a U tube formed by two pressure vessels connected with ¼ × 1/16 in. Cr-Mo steel tubing, a 100,000 lb./sq. in. Bourdon gauge 3, and 60,000 lb./sq. in valves 25, 27, and 29. The gas-mercury leg of *B* is shown in Figure 2. Parts 5 and 10 were made of wood fiber, 6 of neoprene rubber, 2 of Rezistal 416 steel, and 1, 3, 4, 7, 8, and 9 of S.A.E. 4140 steel. The water-mercury leg of *B* was similar in construction except that a floating, conical check valve, instead of the alarm electrode 2, controlled mercury surges. During exploratory experiments a "temporary" liquid-piston pump, consisting of a 10-ft. length of 9/16 × 3/16 in. Cr-Mo steel tubing following valve 23 in Figure 1, and a lens-ring closure vessel, modified for 45,000 lb./sq. in., inside a tubular electric furnace (not shown), were used.

The reactor-thermostat assembly *A* consisted of a high-pressure vessel in a stand with valve-controlled passages for reactants, products, and pressure measurement. The reactor was immersed in an insulated H.T.S.* salt bath heated with two controlled 1 kva. immersion heaters. The reactor and the bath could each be moved vertically with pulleys. Valves 14 and 13 were kept at 150° to 250°C.

During preliminary experiments the reactor evolved through four designs and constructions. The strongest and simplest reactor comprised a solid-bottom, 5:1 diameter-ratio cylinder constructed of a 5% chromium steel of 90,000 lb./sq. in. yield point, closed by a lens ring and a threaded head nut, the latter with a small passage for gas flow. This material was recommended by Midvale Steel Co. (*18*) for use with hydrogen at high stresses up to 400°C., and the vessel was autofrettaged after assembly. To permit continuous catalyst reduction *in situ* a passage was bored in the cylinder bottom. These passages were connected with tubing by means of standard cone-and-seat couplings.

After unfavorable experiences with lens rings, a reactor with an unsupported-area closure was assembled and used for the 450°C. equilibrium determinations (Figure 3). The main body 1, packing retainers 7 and 8, head nut 4, and mushroom piston 3 were made of Rezistal 416 steel. These parts were machined and then heat-treated and tempered to a hardness corresponding to a yield strength of 185,000 lb./sq. in. Adjacent cylindrical surfaces of parts 7, 8, 3, and 1 were ground and polished. The hard tool-steel ring 5 served to prevent cold-welding. The packing ring 6 was made of annealed copper. The Rezistal 416 steel inner tube 2 was tempered at 593°C. to a yield strength of 100,000 lb./sq. in. Together with 3 it constituted a separate reactor when taken out of the assembly. With plug 10 removed, or replaced by a connector, continuous reactions could be conducted in the assembly or separately.

The reactor body 1 (Figure 3) failed in service and the lens-ring reactor body, referred to above (which, bored out to a 3:1 diameter ratio and provided with an unsupported-area closure, had been used as the mercury-water leg in *B*, Figure 1), took its place. The reactor which failed had been subjected to 52,000 lb./sq. in. internal pressure at 400°C. for 12 hr., followed by gradual heating to 450°C. After 5 hr. at 450°C. and 53,200 lb./sq. in., samples were taken and the pressure dropped to 50,000 lb./sq. in. At some time within the next 7 hr. the reactor failed, probably because it was stressed in the intergranular corrosion range, variously stated to be 454° to 593°C. and 482° to 593°C. (*6*, *17*).

Pressure was measured by a metal-resistance, a.c.-excited, Wheatstone's bridge-type, strain-gauge system including a 50,000 lb./sq. in. pressure cell *H* (Figure 1), connected to the reactor through a mercury seal; SR-4, type R strain gauges, made by Baldwin Southwark Division, mounted on the outside of the cell; and a Nultronic indicator made by Foxboro Company, containing power source, capacitive and resistive balancing, and a phase-sensitive electronic discriminator. Bourdon-tube gauge 2 made by U. S. Gauge Company was rated for 100,000 lb./sq. in. for use with gases. Both gauges were calibrated with a free-piston gauge constructed according to designs by Keyes (*11*) and modified to triple its range to 3,000 atm. (*4*, *5*).

Samples for analysis were admitted through valve 13 into absorber 10, partly filled with a boric acid solution previously saturated with 3:1 hydrogen-nitrogen mixture. The absorber was then connected to a Burrell gas-analysis apparatus, the unabsorbed gases were drawn into a 100-ml., water-jacketed burette, and their volume, saturated with water vapor, was measured at atmospheric pressure. The barometric pressure was corrected for temperature and gravity. The ammonia solution was washed into a volumetric flask, and a measured portion was titrated with standardized $0.01255N$ HCl from calibrated 50-ml. burettes the indicator being disodium 4, 4′-bis(*m*-tolyltriazeno)-stilbene disulfonate, which was synthesized after a method by Taras (*21*). This substance gave a sharper end point than other indicators at the low ammonia and acid concentrations involved.

METHOD

The experimental work consisted of the equilibrium determinations preceded by the preparation of a suitable active-catalyst bed, development of a satisfactory reactor closure, and autofrettage of high-pressure vessels.

Catalyst Reduction

The reactor was filled with the catalyst, an 8- to 14-mesh iron oxide promoted with aluminum oxide and potassium oxide; the temperature was raised to 450°C. in *A* (Figure 1) and 150 atm. was exerted by the admission of hydrogen and nitrogen in a ratio of three to one. The gases were purged and replaced repeatedly, but since only traces of ammonia were formed, batch-method reduction was abandoned.

The inner tube 2 (Figure 3) was filled with catalyst and arranged as a separate continuous reactor in a tubular electric furnace. A standard reduction treatment with 3:1 hydrogen-nitrogen to 450°C. was found to be insufficient; consequently, additional reduction to 525°C. at high space velocities was carried out with a resultant improvement in the conversion. Flow rates were measured with a wet-test meter 12, and ammonia was absorbed in a series of test tubes (Figure 1). Unsatisfactory results

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*40% $NaNO_2$, 7% $NaNO_3$, 53% KNO_3 by weight.

after assembly of the reactor and immersion in the salt bath were ascribed to poisoning of the catalyst by (1) hydrocarbons in the graphite paste on the threads of the inner tube and (2) air, inadvertently introduced during the assembly. To avoid these difficulties the above-mentioned reduction treatment was repeated with the inner tube fully installed and with molybdenum sulfide powder on the threads. Equilibrium was subsequently attained at 450°C., but at lower temperatures the catalyst was not sufficiently active. A more active catalyst was then obtained from the duPont Company, and after reduction at up to 500°C. at high space velocity (as suggested by a representative of this company) the catalyst gave satisfactory equilibrium results at 400°C.

Tests of Lens-ring Closures

Several types of lens rings were tested under various conditions of pressure, temperature, and fluid medium in order to determine their suitability as dependable closures for the high-pressure vessels used in the equilibrium determinations. Various rings made of tool steel, hardened so that the ring was harder than the seat, were tested with both liquid and gas pressure. Whereas liquids did not leak at pressures up to 50,000 lb./sq. in., gases leaked at lower pressures and especially when the vessel was heated to approach actual operating conditions. Lens rings softer than the seats, made of copper and of soft steel, were also tested with similar results. It was concluded that lens rings were not successful under conditions of local plastic flow such as at very high pressure and room temperature and at moderately high pressure and high temperature.

Autofrettage

Both reactors were autofrettaged by pumping in a glycerin-water mixture and holding at a pressure of 60,000 lb./sq. in. for 1 hr., followed by heat-treatment at 350°C. The stresses in a cylinder under internal pressure are not uniform across the wall. Hydraulic autofrettage, a method of distributing working stresses more uniformly, consists of exerting sufficient pressure to stress the inside layers nonelastically and then relieving the pressure. A heat-treatment at about 300° to 400°C. follows to reestablish approximately the original yield points in compression and in tension (*16*). Residual stresses, from compressive at the bore to tensile at the surface of the cylinder, remain permanently. Thus, with a yield point of 70,000 lb./sq. in. and a residual bore stress of −65,000 lb./sq. in., an elastic reduced stress of 135,000 lb./sq. in. can be developed at the bore (*22*), whereas before autofrettage the maximum reduced stress attainable at the bore was 70,000 lb./sq. in. If it is assumed that the yield point is known, well defined, and exactly reestablished after heat-treatment, outside-diameter measurements on cylindrical pressure vessels while under a known inside pressure and after pressure release and heat-treatment provide a test of various theories of elastic failure (*12, 19*). The reduced ideal or equivalent stress is a function which is dependent on the three principal stresses and has different forms in each theory of elastic failure.

Without a detailed description of procedure and calculations, it will briefly be stated that tests on the inner tube (part 2, Figure 3) through measurement of the exterior diameter while the tube was under internal pressure and after release of pressure and heat-treatment showed that the strain-energy theory predicts the results best. Comparison was made with the maximum-stress, maximum-strain, shear-stress, Mohr, and inner friction theories (*12, 19*). Tests on other cylinders showed that the exterior expansions were too small to favor any particular theory. These measurements were useful, nevertheless, as a check on the quality of the vessels.

Equilibrium Determinations

The most essential steps during a run in which equilibrium was approached from the side of excess ammonia were as follows: (1) the mercury-piston pump was filled with liquid ammonia (2) the ammonia was repeatedly compressed and admitted to the reactor until the desired pressure was obtained therein and (3) after a period of time samples were taken from the reactor at brief intervals and analyzed. The reaction time allowed was determined from check runs at lower pressures where data were available. If successive samples checked closely, equilibrium was considered to have been reached; otherwise the pressure was reestablished and more time allowed.

To establish further proof that equilibrium had been attained, the authors approached it from the other side. This was done at the lowest pressures and temperatures of the range covered in this paper in order to determine an ample reaction period for conditions of greater reaction rate. The method used to obtain a gas mixture in the reactor higher in content of the elements than called for by the equilibrium was to attain equilibrium at a lower pressure and then pump in ammonia to raise the pressure. This is satisfactory, because less ammonia had to be added to raise the pressure than to reach a chemical-equilibrium composition at the new pressure. This can be readily checked by suitable calculations. A description of actual procedure during some of the equilibrium determinations will be presented based on the symbols given in Figure 1.

At 450°C. with the Reactor in Figure 3. The reactor assembly was installed in the thermostat *A*, the catalyst was reduced, pump *B* was partly filled with pure mercury, the system was flushed with nitrogen and evacuated, and liquid ammonia was admitted to pump *B* through valve 25. Pump *D* was started, and after being adjusted to 15,000 lb./sq. in. in *B* and *A* by means of valves 35 and 30, valve 33 was closed and 34 opened, so that intensifier *C* was brought into play. The piston was returned by closing 34 and opening 32 and 33. Pressure from *B* to *A* was transferred with 29 closed, and pressure in *B* was released when not needed. After two piston strokes in *C* and adjustment of the zero point of strain gauge *I*, the reactor pressure was 29,500 lb./sq. in. according to *I* and Bourdon gauge 2. Of the three thermocouples immersed in the salt in *A*, one registered 450°C., another 449.6°C., with a close check from the third. After a reaction period of 12 hr. pressure and temperature had not changed. After the sampling leads had been vented through valve 13 until the pressure reached 29,000 lb./sq. in., absorber 10 was manually attached to the outlet of 13, which was opened slightly by means of a valve handle 1 ft. long. The first sample contained 91.6 mole % NH_3; second and third consecutive samples contained 90.1 and 89.6 mole % NH_3 respectively.

The method of interpreting these results merits discussion. A dead space, reduced to a minimum by insertion of a wire into the 1/16-in. I.D. sampling lines, existed between the reaction zone and the sampling point. This space had to be vented before sampling. Insufficient venting was preferred in order to avoid excessive pressure drop; therefore, the first sample was sometimes partly unrepresentative of reactor conditions. Owing to the slow reaction rate, established during check runs at lower pressures, and the especially slow net reaction rate near equilibrium, changes in composition due to moderate pressure drops during venting and sampling were considered negligible. With these considerations applied to the run above, the first sample composition was rejected as being unrepresentative of reactor conditions, but the second and third samples checked reasonably closely; therefore, their average, 89.8 mole % NH_3, was taken as the equilibrium content at 29,500 lb./sq. in., the pressure before venting.

The pressure was then lowered to 24,600 lb./sq. in. At this pressure the amount of venting was estimated more successfully, as indicated by a check to within 0.1 mole % NH_3 between the first two samples. At 14,700 lb./sq. in., the second and third samples contained 70.4 and 70.6 mole % NH_3 as compared with 69.4% obtained by Larson (*13*).

In order to make the majority of runs at 400°C. before subjecting the reactor to more severe conditions at higher temperatures, the authors attempted to reach equilibrium at 400°C. and 14,700 lb./sq. in. In accordance with the previously demonstrated sluggishness of the catalyst at 400°C. and lower pressures this attempt remained unsuccessful. Consequently, the pressure was raised to 52,000 lb./sq. in. in the reactor by the same procedure as before, and the temperature was then brought to 450°C. Strain cell *H* having failed at 50,000 lb./sq. in., pressure measurements from here on were confined to the Bourdon gauge 2, shown to be accurate by repeated calibra-

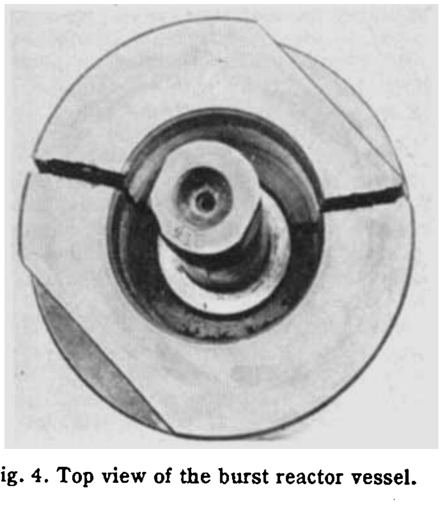

Fig. 4. Top view of the burst reactor vessel.

tions. The temperature increase had raised the pressure to 53,200 lb./sq. in. After 5 hr. of reaction the pressure was 52,000 lb./sq. in., and two samples were taken which checked to within less than 0.1 mole % NH_3. Subsequently the reactor failed at 52,000 lb./sq. in. and 450°C., the contents being ejected with considerable force through two opposite longitudinal cracks narrowing downward from the top to about 4 in. from the bottom of the reactor. (*See* Figures 4 and 5 for two views of the burst reactor.)

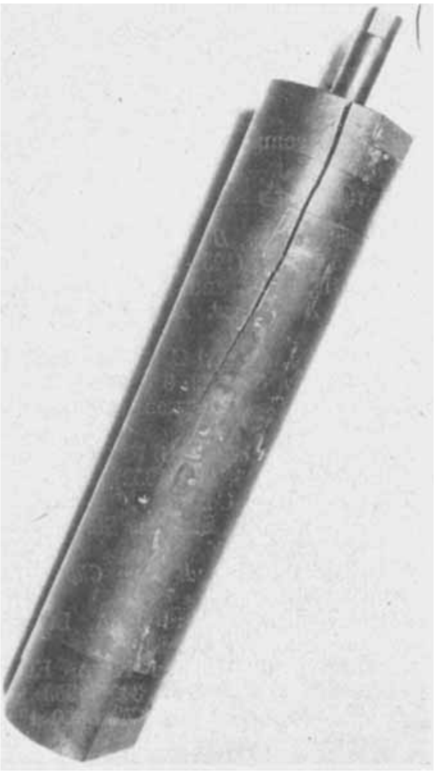

Fig. 5. Side view of burst reactor vessel.

At 400°C. With the new reactor and catalyst mentioned before, ammonia was pumped into *A*, and a pressure of 14,700 lb./sq. in. and a temperature of 400°C. were maintained constant for 4 hr. After the apparatus had been vented down to 14,500 lb./sq. in., first and second samples taken at a 10-min. interval, contained 80.0 and 79.8 mole % NH_3 respectively. After sampling, the pressure had dropped to only 14,400 lb./sq. in., the relatively low drop being due to the larger internal volume of the new reactor. By the procedure explained above, the equilibrium was approached from the side richer in the elements, with first and second samples after 4 hr. of reaction containing 79.8 and 80.3 mole % NH_3 respectively. The equilibrium content reported by Larson (*13*) as an extrapolation of his determinations at 450° and 475°C. and 14,700 lb./sq. in. (made by approaching equilibrium from the side of the elements only) was 79.8 mole % NH_3. Equilibrium attainment in 4 hr. was thus established at 1,000 atm.

After a satisfactory check run at 3,800 lb./sq. in. the pressure was raised to 1,500 atm., and then to 2,000 atm., equilibrium being again approached from the side of the elements. In a fresh start the equilibrium was then approached from the ammonia side by pumping up to 2,500 atm. After 3 hr. of reaction time samples were taken, which checked exactly. The pressure was then raised to 54,000 lb./sq. in., where the loss of pressure through the coupling at the submerged inlet of the reactor was appreciable. At 52,000 lb./sq. in. the sampling line was vented to 51,000 lb./sq. in., and a sample containing 97.7 mole % NH_3 was obtained. A second sample was not taken, because the pressure commenced to fall rapidly.

EXPERIMENTAL RESULTS

The experimental results as mole percentage of ammonia at chemical equilibrium in a mixture with 3 moles of hydrogen to 1 mole of nitrogen are shown in Table 1 and Figures 6 and 7 as a function of pressure at the two temperatures 400° and 450°C. In Table 2 values of the equilibrium constant, K_p, are presented.

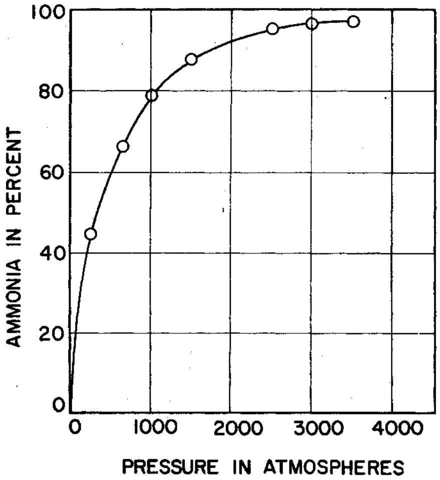

Fig. 6. Mole percent of ammonia at equilibrium as a function of pressure at 400°C.

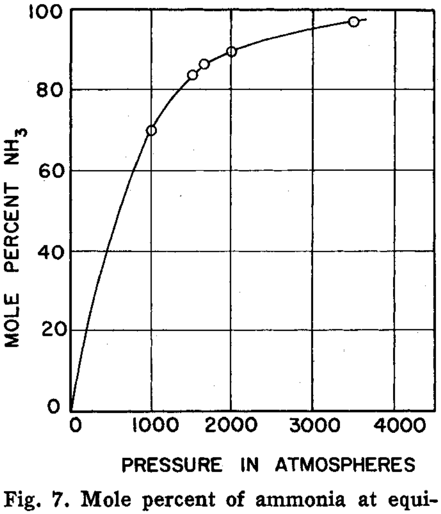

Fig. 7. Mole percent of ammonia at equilibrium as a function of pressure at 450°C.

TABLE 1. EQUILIBRIUM CONTENT OF AMMONIA AT PRESSURES OF 1,000 TO 3,500 ATM. AT 400° AND 450°C.

Run	Pressure, atm.	Temperature, °C.	Mole % NH_3
1.*	1,000	450	70.51
2.*	1,500	450	84.07
3.*	1,650	450	86.89
4.*	2,000	450	89.83
5.*	3,500	450	97.18
6.*	260	400	46.17
7.*	650	400	67.11
8.†	1,000	400	79.88
9.*	1,000	400	80.04
10.†	1,500	400	88.54
11.†	2,000	400	93.07
12.*	2,500	400	96.12
13.†	3,000	400	97.18
14.†	3,500	400	97.73

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*Equilibrium approach from ammonia side.

†Equilibrium approach from hydrogen, nitrogen side.

TABLE 2. EFFECT OF PRESSURE ON THE EQUILIBRIUM CONSTANT FOR THE REACTION $\frac{1}{2}N_2 + 3/2H_2 = NH_3$

Temperature, °C.	Pressure, atm.	$K_p = \frac{(x_{NH_3})p^{-1}}{(x_{N_2})^{1/2}(x_{H_2})^{3/2}}$
450	1,000	0.02496
450	1,500	0.06962
450	1,650	0.09404
450	2,000	0.1337
450	3,500	1.0751
400	1,000	0.06136
400	1,500	0.1384
400	2,000	0.2977
400	2,500	0.7864
400	3,000	1.2543
400	3,500	1.6283

Experimental Error

The following sources of error existed in the equilibrium determinations: (1) measurement of reactant and product composition, (2) fluctuation of temperature and pressure during a run, (3) difference between sample and reaction-space composition, and (4) difference between reaction-space and equilibrium composition.

The reactants, whether the elements or ammonia, were very pure, and therefore the effect of inerts on the equilibrium was negligible. The product composition was affected by various errors in the burettes, barometer, thermometers, standard solution, and volumetric flasks. The maximum total relative error added up to 0.23%. The temperature in the reactor may have been in error by ±1°C. because of temperature gradients in the salt bath and a 0.1°C. error in the reading of the potentiometer. Fluctuations in temperature were ±0.5°C. during the average run. Errors in pressure measurement were ±100 lb./sq. in. for the Bourdon gauge 2 (Figure 1), and ±20 lb./sq. in. for the strain gauge (*H*, *I*, Figure 1). Corresponding pressure fluctuations were ±80 lb./sq. in. at the highest pressures.

The catalyst was kept inside the inner tube 2 (Figure 3) by a screen and since the reaction temperatures were as low as permissible for reasonable rate even with a catalyst, it can be assumed that no further reaction occurred after a sample left the catalyst bed. Pressure in the reactor was uniform, because even at the highest densities the maximum effect of gravity was only 0.5 lb./sq. in. Uniform temperature in the reaction space was insured by the long time allowed for reaching equilibrium and by the large relative heat capacity of the salt bath. Synthesis and decomposition of ammonia at 1,000 atm. to the same ammonia content proved that equilibrium was reached at this pressure, and at higher pressures the reaction rate was probably greater. The method of venting and sampling involved an estimated error of ±100 lb./sq. in. in the equilibrium pressure.

TABLE 3. COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF THE EQUILIBRIUM CONSTANT, K_p, AND THE PERCENTAGE OF AMMONIA AT EQUILIBRIUM AT 450°C.

Method of calculation	K_p 1,000 atm.	K_p 3,000 atm.	% NH_3 at equilibrium 1,000 atm.	% NH_3 at equilibrium 3,000 atm.
1	0.00675	0.00675	51.5	67.9
2	0.01537	0.03214	64.2	83.6
3	....	....	66.8	86.9
4	0.0239	0.600	70.0	96.0
5	....	....	70.6	91.1
Exp.	0.02496	0.484	70.51	95.5

The total error arising from these various causes is believed to result in an uncertainty in the equilibrium ammonia content of not more than ±0.35% and probably less in most cases. On the other hand there is always the possibility of unknown errors creeping in. In work of this kind it is difficult to ensure that equilibrium was actually attained in spite of one's best efforts. Another possible source of hidden error is in the sampling of the equilibrium mixture. In the determination of a composition, error is more likely to reside in the lack of a representative sample than in any other source. All that can be said is that the authors were cognizant of these sources of error and have tried to take precautions to minimize them.

RESULTS

From Tables 1 and 2 it can be seen that the effect of pressure and temperature on the equilibrium is numerically brought out far more by K_p than by the ammonia content. The rate of change of K_p with pressure decreases at high pressures. These observations are in accord with the concept that at very high pressures the molecules themselves begin to be compressed. It is unlikely, therefore, that conversion to ammonia greater than about 99.5% occurs before pressures of about 20,000 atm. are reached. A comparison of the experimental values with some values calculated by various methods is given in Table 3.

The methods referred to by number in the table are as follows:

1. Ideal gas. K_a calculated from the equation given by Harrison and Kobe (*9*), who recently reviewed the thermodynamics of this reaction. $K_a = K_p$ when gases are assumed to be ideal.

2. Assumption of ideal gaseous solution combined with estimation of the fugacities of the pure gases from a generalized chart (f/p vs. P_R and T_R) (*19a*). The following values were used:

Gas	T_R	P_R, 1,000 atm.	P_R, 3,000 atm.	f/p, 1,000 atm.	f/p, 3,000 atm.
H_2	17.5	48.0	144	1.35	2.32
N_2	5.73	29.8	89	1.63	3.95
NH_3	1.78	9.0	27	0.88	1.48

The values for N_2 and H_2 at 3,000 atm. involve a very uncertain extrapolation. The values for H_2 are based on the use of pseudocritical values obtained by adding 8 to the critical pressure in atmospheres and the critical temperature in degrees Kelvin.

3. Use of the Redlich-Kwong equation of state (*20*) with the constants for the individual gases determined from the critical pressure and temperature and the use of linear combination to obtain the constants for the equilibrium mixture. For H_2 a pseudocritical pressure and temperature were used.

4. Use of the equation of Gillespie and Beattie (*8*). This equation is based on a simplified form of the Beattie-Bridgeman equation of state which is explicit in the volume. The equation-of-state constants are those given by Beattie and Bridgeman (*2*) and by Beattie and Lawrence (*3*).

5. Use of Joffe's method (*10*) for the calculation of the fugacity of a gas in a mixture.

Considering the assumptions involved and the uncertainties involved in reading some of the generalized charts, the agreement of methods 4 and 5 among themselves and with the experimental values is surprisingly good.

NOTATION

K_a = equilibrium constant in terms of activities
K_p = equilibrium constant in terms of partial pressures
K_{p° = limiting value of K_p at $p = 0$ and equal to K_a
R = gas constant
p = total pressure
T = absolute temperature
$\overline{V}_i$ = partial molal volume
ν = stoichiometric number
$\sum$ = summation

Subscript

i = any component

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