$V$ in each term represents the same molecular volume and hence the gases are present in identical molecular concentration. The deviation from this rule is less than 2% in the pressure range studied and at temperatures to 200°. The deviation seems to increase with increasing pressure and decrease with increasing temperature.

The authors take pleasure in acknowledging the friendly coöperation of the staff of the Fixed Nitrogen Research Laboratory in the solving of the many problems of this investigation. Especially are we indebted to W. E. Deming for mathematical study of the solubility of hydrogen in steel, and to W. H. Edwards and J. R. Dilley who assisted in the designing of the high pressure equipment and to the expert technicians who were instrumental in its building.

## Summary

*The compressibility isotherms of nitrogen, hydrogen and a 3:1 mixture* of these gases have been determined through a pressure range of 1000 atmospheres and a temperature range of 400°.

The additive volume rule in the case of these gases apparently holds within the limits of experimental error at a temperature of 300°. At lower temperatures there is decided deviation.

The additive pressure rule is discussed in its various forms and is shown to hold to within 2% if defined as follows. "The pressure exerted by one constituent in a gaseous mixture equals the product of its mole fraction and the pressure it would exert as a pure gas at a molecular concentration equal to the molecular concentration of the mixture."

Some suggestions for the practical use of the experimental data are presented.

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# THE EQUILIBRIUM OF NITROGEN AND HYDROGEN WITH AMMONIA IN A CORONA DISCHARGE

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The synthesis and decomposition of ammonia under the action of electric discharges were early observed.[1] Equilibrium studies were first reported by Berthelot[2] who found that 3% of ammonia by volume resulted under the action of the silent discharge. From studies of reaction rate,

[1] (a) Deville, *Compt. rend.*, **60**, 317 (1865); (b) Chabrier, *ibid.*, **75**, 484 (1872); (c) Thenard, *ibid.*, **76**, 983 (1873); (d) Donkin, *Proc. Roy. Soc.* (*London*), **21**, 281 (1873); (e) de Hemptinne, *Z. physik Chem.*, **22**, 358 (1897).

[2] Berthelot, *Bull. soc. chim.*, [2] **26**, 101 (1876).

Pohl[3] calculated that 1.2 to 1.4% of ammonia resulted at equilibrium in a Siemens ozonizer. Davies[4] found the equilibrium concentration of ammonia in a Siemens tube to be 2.88%, which varied but little with current strength and potential. According to Davies these results are in agreement with those of Falckenberg.[5] In discharges at low pressures (0.7–2.5 mm.)[6] decomposition has been found to be practically complete. Briner and Mettler[7] observed the formation of 3 to 4% of ammonia from its elements under the influence of the electric spark.

The present research shows that under the experimental conditions and at atmospheric pressure and temperature, 4.1% of ammonia by volume results from the action of the 60-cycle corona discharge between a wire and a coaxial cylinder. As a basis for comparing the action of the corona with purely thermal effects, the temperature at which this concentration of ammonia would result if the equilibrium were purely thermal was calculated and found to be 270°. A higher temperature, above 2500°, which also may correspond to the same equilibrium concentration will be discussed.

## Experimental Methods

Equilibrium was approached from both sides, starting in one case with pure ammonia and in the other with a 3:1 ratio by volume of hydrogen and nitrogen. Equilibrium was regarded as established when the pressure remained constant for several hours of discharge, and when experiments with widely differing periods of discharge showed the same final gas composition.

The ammonia used in the experiments was taken from a tank containing liquid ammonia. Samples of the gas when analyzed by noting the decrease in volume from absorption in 10 cc. of 83% sulfuric acid contained in a Hempel pipet and confined over mercury, averaged 99.7% of ammonia by volume.

The discharge tube is shown in Fig. 1. It was composed entirely of Pyrex glass with the exception of the wire and the pressure regulating device. The latter consisted of mercury contained in a leveling bulb connected with the lower end of the discharge tube by rubber tubing. The high potential electrode, a platinum wire, C, 0.51 mm. in diameter (B. and S. gage No. 24), was carefully centered and sealed while under tension. The tube through which the wire was centered consisted of two sections, each surrounded by a condenser jacket. Dilute sulfuric acid was circulated through the jackets by means of an air lift. The acid served as the grounded external electrode and as a cooling medium. The discharge tube was 1.2 cm. in internal diameter, 1 mm. in wall thickness and, in all, 65 cm. in length. The maximum volume including that of the enlarged end at the bottom was 70 cc.; the volume of the actual discharge space was 47 cc.

[3] Pohl, *Ann. Physik*, **21**, 879 (1906).

[4] Davies, *Z. physik. Chem.*, **64**, 657 (1908).

[5] Falckenberg, *Dissertation*, Berlin, **1906**.

[6] Hutchison and Hinshelwood, *Proc. Roy. Soc.* (*London*), **117A**, 133 (1927).

[7] Briner and Mettler, *Compt. rend.*, **144**, 694 (1907); *J. chim. phys.*, **6**, 137 (1908).

Preliminary experiments showed that when starting with ammonia the final gas volume was approximately double the initial. For experiments on the decomposition of ammonia, therefore, an initial volume of about 25 cc. of ammonia (half the volume of the discharge space) was transferred to the discharge tube from an all-glass gas holder through the tube A by displacement of mercury. To avoid possible gas leakage, the pressure was maintained approximately at atmospheric during the rapid volume change resulting from the action of the corona on the ammonia. This was effected by means of the mercury leveling bulb. To prevent short-circuiting through the mercury to the lower section of the grounded electrode, the discharge was maintained only in the upper section (the acid having been removed from the lower jacket) until the volume increased sufficiently to use both.

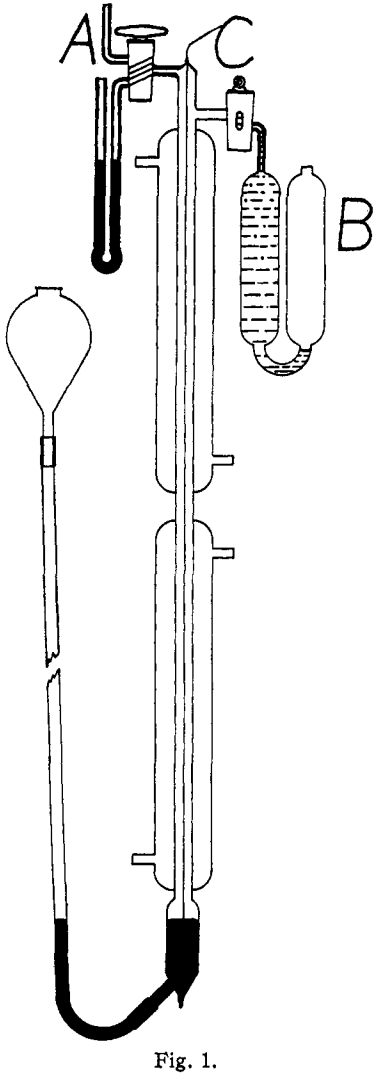

Fig. 1.

In experiments on the formation of ammonia from the elements, the nitrogen–hydrogen mixture in the ratio of exactly 1:3 by volume was prepared from ammonia in the discharge tube itself. The procedure was identical with that above, the ammonia being decomposed by the action of the discharge until the pressure remained constant. The undecomposed ammonia was then removed by absorption in concentrated sulfuric acid in the pipet B. The acid had previously been freed from air and saturated with nitrogen and hydrogen.

The electrical energy was supplied by a 60-cycle, 110-volt line. The high voltage was obtained with a 20,000-volt, 2.5 KVA., Type T-3 Thordarson transformer. The circuit included a voltmeter in the primary and a thermionic milliammeter in the secondary circuit. During the final hour of each experiment, electrical factors, temperature and pressure were carefully maintained at constant values.

The equilibrium mixture was analyzed for ammonia by absorbing a 40cc. sample in 0.01 *N* hydrochloric acid and titrating the excess acid with 0.01 *N* potassium hydroxide, using methyl red as the indicator.

## Results

After numerous preliminary experiments and modifications in the apparatus to give the simplest conditions of operation and of measurement, consistent equilibrium results were obtained. The results of the final series of experiments are given in Table I.

TABLE I

AMMONIA EQUILIBRIUM IN A 60-CYCLE CORONA DISCHARGE

Temp., 28.5°C.; pressure, 733 mm.; sec. current, 4.2 milli-amp.; sec. voltage, 13,400 v.

| Initial gas | Time of discharge, hours | $NH_3$ by volume, % |
|---|---|---|
| $N_2 + 3H_2$ | 15.5 | 4.0 |
| | 11.7 | 4.0 |
| | | Mean 4.0 |
| $NH_3$ | 30.7 | 4.4 |
| | 21.6 | 4.0 |
| | 22.8 | 4.2 |
| | | Mean 4.2 |
| | Equilibrium concentration | 4.1 |

## Discussion

The results show that the corona discharge yields an equilibrium mixture containing a higher concentration of ammonia than has yet been reported for any other type of electric discharge. According to the equation $3H_2 + N_2 = 2NH_3$, 71.9% of hydrogen and 24.0% of nitrogen are in equilibrium with 4.1% of ammonia. The equilibrium constant, $K_p$, is given by the equation

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

where $p$ is the partial pressure of the respective components. Since the partial pressure is equal to the product of the concentration, $c$, and the total pressure, $P$, the equation becomes

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

Substituting the experimental data

$$K_p = \frac{(0.041)}{(0.719)^{3/2} \times (0.24)^{1/2}} \times \frac{760}{733} = 0.142$$

To compare these results with those obtained from the analogous thermal decomposition, that is, to note the temperature to which it would be necessary to heat ammonia to effect the same degree of decomposition, requires the use of the Van't Hoff equation

$$\frac{d(\ln K_p)}{dT} = \frac{\Delta H}{RT^2}$$

and a knowledge of the variation of the heat of reaction, $\Delta H$, with temperature. The completed equation is[8]

$$\text{Log}_{10} K_p = \frac{2074.8}{T} - 2.494 \log_{10} T - 0.1256 \times 10^{-3} T + 0.186 \times 10^{-6} T^2 + 2.099$$

Substituting the value 0.142 for $K_p$ and solving, $T$ is found to be 543. The corona equilibrium for ammonia thus corresponds to a theoretical

[8] See Larson and Dodge, THIS JOURNAL, 45, 2927 (1923).

thermal equilibrium at 543°K. or 270°C. The thermal decomposition and formation of ammonia at this temperature are so slow that it is impossible to attain equilibrium even with the use of the best catalysts.

That there is possibly a second temperature, above 2500°, at which 4.1% of ammonia would result at equilibrium is suggested by the experiments of Maxted.[9] While an increase in temperature is usually considered to result in a decrease in the ammonia concentration at equilibrium, Maxted found that above 1000° an increase in temperature results in an increase of ammonia at equilibrium. On the basis of his experimental temperature–concentration curve, a value of 4.1% for ammonia would require a temperature above 2500°. This is of interest in the interpretation of the above results since Wendt and Farnsworth[10] found that the equilibrium of carbon dioxide with carbon monoxide and oxygen in a similar corona discharge corresponds to a thermal equilibrium at 2300°.

The decomposition and formation of ammonia in the corona take place, therefore, as if all the gases were heated to a temperature of 270° in the presence of an effective catalyst; or, possibly, as if all the gases were heated to a temperature above 2500°. The attainment of such temperatures in the discharge tube, in which the average temperature was less than 30°, is precluded. Hence the mechanism of the corona discharge appears to be that of activating various molecular species in such a way as to increase enormously the reaction velocities, to change the ratio of decomposition and formation and to produce a shift in equilibrium corresponding to that at elevated temperatures.

## Summary

The equilibrium of ammonia with a 3:1 ratio of nitrogen and hydrogen resulting from the action of a 60-cycle corona discharge between a platinum wire and a coaxial cylindrical glass electrode is such that at a pressure of 733 mm. of mercury and a temperature of 28.5°, 4.1% of ammonia by volume results under the conditions of the experiments. The temperature at which the same equilibrium concentrations would result thermally was calculated and found to be 270° and, possibly, a temperature above 2500°.

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[9] Maxted, *J. Soc. Chem. Ind.*, **37**, 105T, 232T (1918); *J. Chem. Soc.*, 113, 168, 386 (1918). See also criticism by Moldenhauer, *Chem.-Ztg.*, **48**, 73 (1924).

[10] Wendt and Farnsworth, THIS JOURNAL, **47**, 2494 (1925).