# JOHN  HUGHES DAVIES. THE EFFECT OF THE SILENT ELECTRICAL DISCHARGE ON THE AMMONIA SYSTEM*

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## The Reversibility of the Hydrogen-Nitrogen-Ammonia System

The Haber-Bosch process for the manufacture of ammonia from its elements was a triumph of German science and technology.  The commercial production of ammonia by this process began in 1913 (1).  Because of its industrial and economic importance, this introduction has tended to overshadow the numerous studies on the basic reaction:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad (1)$$

As early as 1785 Claude Louis Berthollet (1748-1822) studied the decomposition of ammonia by electric sparking.  He found that 0.725 by volume of hydrogen and 0.275 by volume of nitrogen were produced.  Several other workers confirmed this effect of sparking but noted that some $NH_3$ always remains.  The partial formation of $NH_3$ when mixtures of $H_2$ and $N_2$ were subjected to various forms of electrical discharge was also observed.  In other words, the system is reversible (2).

## The Silent Electrical Discharge

As is obvious from the widespread use of power lines, air—a typical gas—acts electrically as an insulator.  If an electromotive force (emf) is applied to a pair of metallic conductors that are separated by a small gap, the flow of current is essentially zero.  However, if the emf is progressively increased to very high levels (thousands of volts) and the gap is viewed in the dark, a faint glow, associated with a tiny current flow, becomes visible.  This is the region of the *silent electrical discharge.*  The glow becomes much stronger and brushlike when the emf is further increased.  Eventually, at some critical higher emf, the system enters the highly visible arc or spark region, where the current becomes much larger.  This region is easily attained by the use of an induction coil or static electricity generator, but it is difficult to employ quantitatively.  The more controllable silent discharge region is preferable for investigative purposes.  The discharge is most conveniently produced from an alternating current source, the voltage of which can be readily stepped up as high as desired by use of a suitable transformer.

## Effect of the Silent Discharge on the Formation and Decomposition of Ammonia

Several mid-19th century workers investigated the formation and decomposition of ammonia, brought about by the silent electrical discharge.  The investigations continued after the turn of the century (3).  Despite the several decades of study, it appears that the validity of the law of mass action under such discharge was still an open question.  John Hughes Davies, born in Merthyr Tydfil, Wales, carried out experiments aimed at settling the question while at the University of Leipzig.

Davies began his studies on the ammonia system at University College, Cardiff (now Cardiff University). His research director was Edgar Philip Perman (1866-), who had joined the faculty in 1892. Perman was strongly interested in the direct synthesis of ammonia (4) and, with Davies, studied some of its physical constants (5).

Davies was also the joint author of studies on the determination of molecular weight (6) and of vapor pressure (7). When he arrived in Leipzig, he was therefore a skilled experimenter, had firsthand experience with the ammonia system, and was well acquainted with relevant literature. It is therefore not surprising that he was able to carry out his extensive examination of the effect of the silent discharge on the ammonia system in the short period between Easter, 1907, and Whitsun, 1908 (8).



*Figure 1* *Apparatus used by Davies*

Davies arrived in Leipzig at a time of significant change. Wilhelm Ostwald (1853-1932) had retired from the University in 1906. His successor as professor of physical chemistry was Max Le Blanc (1865-1943), who had been one of Ostwald's assistants from 1890 to 1896. Le Blanc then became director of electrochemistry at the firm of Farbenwerken Hoechst until 1901, when he joined the faculty of the Technische Hochschule in Karlsruhe (9). He returned to Leipzig in 1906, this time as successor to Ostwald, and remained there until his retirement in 1933. Le Blanc directed the work carried out by Davies (8, 10). Davies was fully aware of a recent study that covered, at least from the experimental point of view, much of the area that he proposed to attack. This study was by Robert Pohl (1884-) at the University of Berlin (11). Davies pointed out that, although Pohl recognized the dependence of the decomposition of ammonia on various physical factors, the study was to see whether Faraday's law applied in the silent discharge reaction. Pohl's experiments showed that, under

these conditions, this law was invalid. The principal concern of Davies was the validity, or otherwise, of the law of mass action under similar conditions.

The experimental arrangement used by Davies, shown in Fig. 1, is similar to that used by Pohl. Davies stated that the reaction vessel was a Siemens ozonizer tube. However, it seems obvious from Fig.1 that the tube was of the so-called Brodie form, shown schematically in Fig. 2. The shading indicates mercury and dilute $H_2SO_4$, which act as the actual electrodes for the electrical discharge. Several tubes were used, so that, in the narrow annular space, the volume of gas varied between 20 to 30 ml and the path length through the gas between approximately 1 and 2 mm. This narrow space can be evacuated to permit the introduction of the gas, and suitable stopcocks control the various functions. The three-way stopcock D permits the isolation of the major portion of the system, evacuation, or release of the vacuum by entry at N of air, dried by the system N, Z. Bulb Q contains either nitrogen or hydrogen, which passes through drying system P, O before use. The gentle heating (even by hand!) of normally refrigerated solid AgCl (2NH$_3$), contained in vessel G, generates ammonia. This is dried by passage through the system Y, X, which is cooled by an ice-salt mixture. In
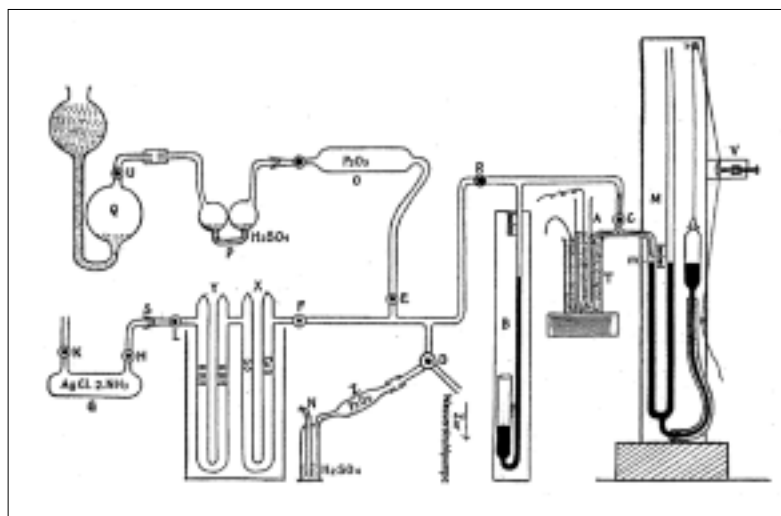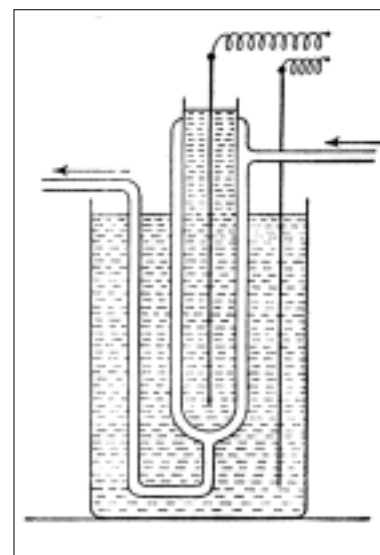


*Figure 2* *Ozonizer tube*

experiments where the gas pressure is kept constant, the mercury level in the left-hand limb of Manometer M is maintained at mark *m*. The capillary connection between A and M keeps the dead space small. Manometer B is used to control the filling of the ozonizer tube with the desired gas.

High-voltage alternating current is applied to the ionizer tube by wires that dip into the liquids, as indicated. The heights of these liquid electrodes govern the volume of gas subjected to the discharge. The glass surfaces are rendered nonconducting by a coating of shellac. The approximately 140-V output of a rotary dc-to-ac converter could be stepped up to as high as 10,000 V by a transformer. The applied voltage is measured by a precision voltmeter, connected through a mercury switch and a high resistor. The voltage drop across a smaller resistor, placed in the lead to the inner contact, is measured by a quadrant electrometer. This permits the estimation of the current passing through the gas. This current is actually the sum of the current that passes through the gas and the *Aufladungsstrom* (charging current) of the tube. The latter current, determined at several voltages after evacuation of the tube, is deducted from the total current. When the volume of gas is kept constant, any reaction that occurs can be indicated by change in pressure, measured by manometer M.



*Figure 3  Decomposition constants at fixed current levels.*

Pohl had observed and Davies confirmed that the gases must be dry. Ammonia ($NH_3$), stored as $AgCl(2NH_3)$, is released as required by warming. Nitrogen and hydrogen, stored in glass flasks, are with-

drawn as needed. To prepare a $N_2$-$H_2$ mixture in stoichiometric proportions corresponding to $NH_3$, ammonia was strongly heated over iron or nickel. The residual $NH_3$ was absorbed by dilute sulfuric acid. Davies justified his working at ambient temperature by showing that the rate of decomposition of ammonia is comparatively insensitive to temperature.

Because the nitrogen-hydrogen-ammonia system is reversible, the decomposition of $NH_3$ was limited to not more than 10% to minimize the influence of the reverse reaction. The general method was to keep the volume of gas constant and to assess the extent of decomposition from the change in pressure. Before each experiment the reaction tube was thoroughly dried by repeated evacuation and entry of dry air, while being heated to 300° to 400°. After cooling and introduction of ammonia, the mercury level in the left limb of manometer M was brought to mark **m**. Then the level of mercury in the right limb of M ( the initial pressure of $NH_3$, $A_0$ ) was noted. Alternating current of known strength was then switched on and the successive timed readings of M (*total* pressures at times *t*, *A*) were taken.

In order to calculate the decomposition constant of the reaction, the pressures $A_t$ of *ammonia* at times *t* are needed. When two molecules of ammonia decompose, they give four molecules of products. Accordingly, At = $2A_0 - A$ and with this information, the values of $K_1$ and of $K_2$, the respective constants for a unimolecular and for a bimolecular reaction, can be calculated. Figure 3 is a table, reproduced from Davies's paper, which gives results for two current strengths. The results show that the constants are highly dependent upon the current strength and that the values of $K_2$ change considerably with time. On the other hand, the values of $K_1$ shift
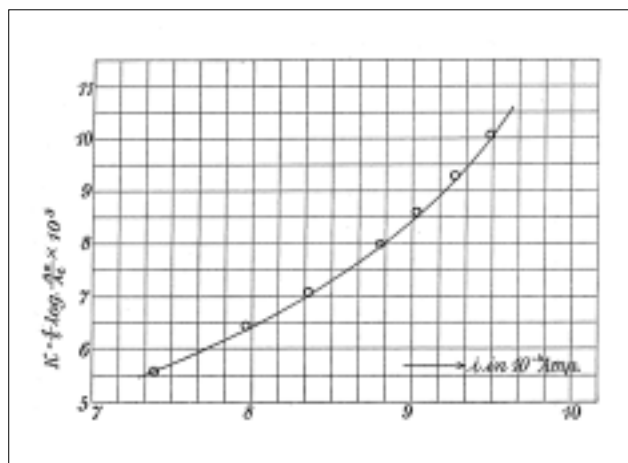


*Figure 4  Relationship between decomposition constant and current strength*
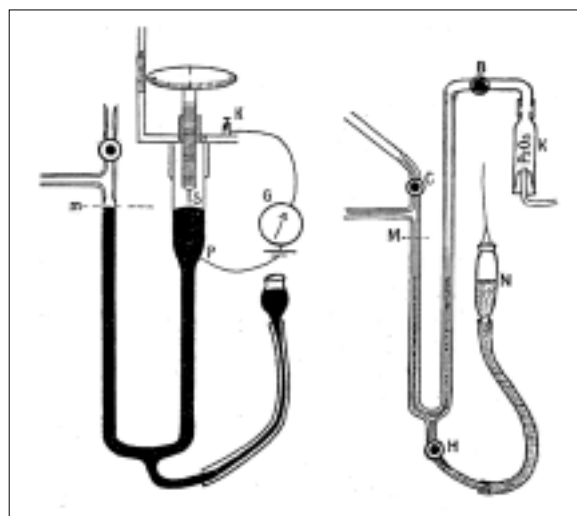
*Figure 5* *High-sensitivity manometers*

only slightly.  Thus the evaluation of $K_1$ should be a reasonable criterion for comparison in subsequent experiments.  The effect of current strength on the value of $K_1$ was investigated more fully, with the results graphed as indicated in Fig. 4.  Davies described this curve as being approximately linear, so that $K_1$ can be regarded as being proportional to the current strength.

To examine the effect of pressure of ammonia on the "constant," $K_1$, two sets of experiments were performed, one at a constant current of 1.3 mA, the other at a constant voltage of 7216.  From his findings, Davies concluded that the results of subsequent experiments should be comparable if constant current is used, but not if voltage is the chosen fixed quantity.

Because the ultimate aim of the investigation was to check the validity of the law of mass action, an obvious approach was to study the decomposition of ammonia after mixing it with one of its decomposition products.  The system used by Davies allowed such mixtures to be made for subjection to the silent discharge.  His results showed that $K_1$ decreases as the $H_2 : NH_3$ ratio is increased.  On the other hand, an increase in the $N_2 : NH_3$ ratio brings about an increase in the value of $K_1$.  If the excess of nitrogen is large, the constant can be much larger than for ammonia itself.  Davies noted that, with excess hydrogen, the luminescence was yellowish.  In the presence of an excess of nitrogen a very strong violet color appeared.

The reversibility of the ammonia system implies that equilibrium could be reached either by the decomposition of ammonia or by its formation from its elements.  In his experiments on the formation of ammonia, Davies found that the pressure changes were too

small to be measured by a conventional mercury manometer.  For most of these experiments he used the high-sensitivity mercury manometer shown on the left of Fig. 5.  With the fine adjustment provided for the height of the leveling bulb of the manometer, pressure changes could then be read to approximately 0.05 mm.  The alternative manometer on the right was of conventional form, but filled with an oil of specific gravity 0.895.  The lower end of the screw of the micrometer reading device of the manometer carries a platinum spike S.  A battery in series with galvanometer G causes the latter to deflect when the tip of the spike just touches the mercury surface.

The experiments were carried out at constant volume, i.e., the level of mercury in the left-hand limb of the manometer was kept at mark **m**.  Because pressure changes were small, the equilibration of temperature was particularly important.  For the equilibrium study with a stoichiometric mixture of nitrogen and hydrogen, the pressure was read and the constant current was turned on.  The process was continued until the pressure showed no further change.  Three determinations were made, with initial pressures in the range 757.7 to 764.0 mm Hg.  The ammonia so formed ranged from 2.83 to 2.88%.  Using the same reaction tube, Davies approached the state of equilibrium by decomposing ammonia.  He found 2.87% of ammonia in the final mixture.

The results of similar studies involving a wide range of $N_2 : H_2$ ratios are tabulated in Fig. 6.  Clearly, a mixture with the stoichiometric $N_2 : H_2$ ratio of 1:3 gave the highest equilibrium amount of ammonia.  Despite the wide range of mixtures, the change in voltage (and hence in energy input, since the current is constant) did not exceed 20%.  However, the widely varying values in column 4 show that the law of mass action does *not* hold for the system under silent discharge.  Davies commented that very little was known of the process taking place in the tube and, for the present, the matter should be left with the statement of the invalidity of the law of mass action.

Davies examined the rate of formation of ammonia from stoichiometric mixtures.  In all cases the initial pressure was 760 mm when timed runs were made at a constant current of three different levels.  The results, depicted graphically in Fig. 7, show that ammonia is formed most rapidly in the early stages of the runs. This conclusion was confirmed by a run lasting only one minute, with observations at 5-second intervals.

The final set of experiments involved mixtures in which the $N_2 : H_2$ ratio lay between 1 : 7 and 4 : 1.  The

| Initial pressure mm Hg | N$_2$ : H$_2$ ratio in the mixture | NH$_3$ formed mm Hg | $\dfrac{[N_2][H_2]^3}{[NH_3]^2}$ | Potential Volt |
|---|---|---|---|---|
| 740 | 1 : 20 | 14.04 | 457 x 10$^4$ | 8528 |
| 740 | 1 : 12 | 16.05 | 544 | 8592 |
| 740 | 1 : 5 | 19.53 | 603 | 8674 |
| 760 | 1 : 3 | 21.08 | 636 | 8774 |
| 740 | 2 : 5 | 19.50 | 653 | 8838 |
| 740 | 2 : 3 | 16.02 | 837 | 8928 |
| 740 | 7 : 6 | 12.08 | 892 | 8976 |
| 740 | 9 : 1 | 1.48 | 1085 | 9184 |
| 740 | 10 : 1 | 1.26 | 1180 | 992 |

*Figure 6* *Equilibrium studies with differing nitrogen:hydrogen ratios.*

constant current runs were terminated at 6 minutes.  The rate of formation, [NH$_3$] / time, was 0.88 with a gas ratio of 1 : 7, but fell to 0.45 when the gas ratio was 4 : 1.

Davies concluded that he had shown the decomposition of ammonia by the silent electrical discharge to be essentially a reaction of the first order.  The decomposition constant, approximately a linear function of the current strength, has a temperature coefficient much smaller than those of chemical reactions in general.  Approximately 3% of ammonia remains when equilibrium is reached.  The same percentage is obtained in formation experiments with a stoichiometric mixture of nitrogen and hydrogen.  However, the percentage of ammonia formed is smaller in nonstoichiometric mixtures and the results *do* not fit the requirements of the law of mass action.

The decomposition velocity is decreased by an excess of hydrogen and increased by an excess of nitrogen.  These effects are reversed in formation experiments.  The luminescence associated with the discharge is normally pale but becomes vividly violet when nitrogen is in excess.  Davies speculated that this light might be the cause of the accelerating effect of nitrogen on the rate of decomposition of ammonia.  The effect of light on various other chemical reactions was well known; and a photochemical reaction often has a small temperature coefficient, like that found in the ammonia experiments.

Davies was granted his Ph.D. in 1908 for these studies, which apparently he did not pursue further.  In fact, an author search in the decennial indexes of *Chemical Abstracts* for the period 1907 to 1936 revealed only two entries for "J. H. Davies."  Both concerned methods for welding.  In a less extensive survey of *Chemisches Zentralblatt*, no further entry that could be attributed to John Hughes Davies was found.  Although he may have continued to undertake research, it appears that he did not publish the results.

Davies returned to the United Kingdom.  When he became a member of the Chemical Society in 1910, he stated that he was Vice President of St. Peter's College in Peterborough  His name is listed in the Society's Register of 1936 but is absent in the next Register, not pub-
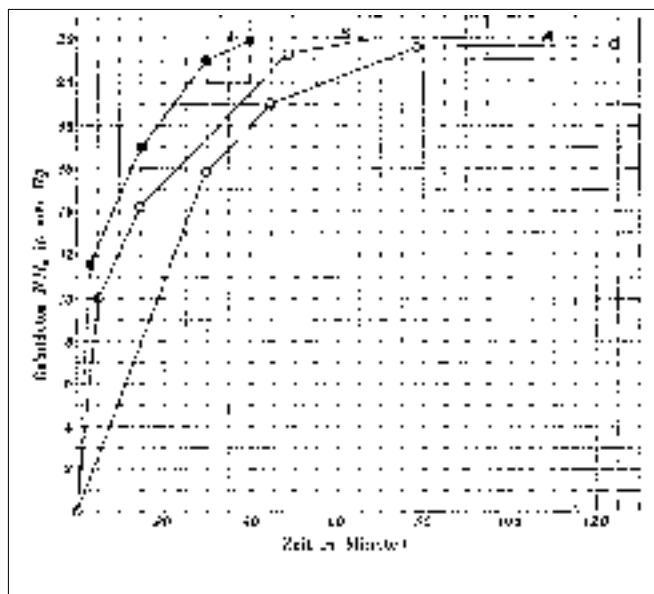


*Figure 7*  *Rate of formation of ammonia in a stoichiometric mixture. Current, mA:-*
*curve A, 0.84;  curve B, 1.54;  curve C, 1.80.*

lished until 1948.  The University of Cardiff could provide no information concerning Davies.

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†      Deceased.

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Dexter Awardee John T. Stock, Professor Emeritus of Chemistry, University of Connecticut, Storrs, died February 6, 2005.

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