Summary

The photochemical decomposition of acetone has been studied, using two different pressure ranges, and the decomposition products have been analyzed. The method of analysis is described. More hydrogen is produced by decomposition in the Schumann region than when light in the near ultraviolet is used. The low pressure reaction differs considerably from the one at high pressures, both in rate and in products formed.

PROVIDENCE, R. I. RECEIVED SEPTEMBER 7, 1934

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Kinetics of the Decomposition of Ammonium Amalgam

BY ALDEN J. DEYRUP[1]

The decompositions of ammonium and the substituted ammoniums offer a possibility of comparison of reaction kinetics in such widely different solvents as liquid metals and non-metals. Of reactions in mercury solution the decomposition of ammonium is most accessible to interpretation because properties of ammonium amalgam have been already investigated. The similarity to amalgams of the alkali metals has been shown with respect to electrode potential,[2] molal freezing point depression,[3] and photoelectric effect.[4] The products of the decomposition are well established[5]

$$NH_4 \longrightarrow NH_3 + {}^1/_2H_2$$

The reverse reaction is negligible. The free energy change of the process

$$NH_3\ (\text{g., 1 atm.}) + {}^1/_2H_2\ (\text{g., 1 atm.}) \longrightarrow NH_4\ (\text{1 molal soln. in mercury})$$

may be calculated from the e. m. f. of the aqueous cell

$$\text{Pt, } H_2\ (\text{g., 1 atm.}) \mid NH_4^+\text{, 1 m.; } \overset{NH_3\ (\text{g., 1 atm.})}{\overset{\upharpoonleft\downharpoonright}{NH_3}} \mid NH_4\text{, (1 molal solution in mercury)}$$

The electrode potential of ammonium amalgam is not known exactly but is approximately the same as that of sodium amalgam.[2] Hence only a provisional value can be calculated for the free energy change, $\Delta F^\circ = 30$ Cal.[6]

Experimental Method and Preparation of Materials

Ammonium amalgams were prepared by electrolyzing an aqueous solution of ammonium acetate saturated with ammonia gas between mercury electrodes at about −38° Ammonium acetate was prepared from freshly distilled acetic acid and ammonia gas. Mercury was purified by distillation in a current of air under reduced pressure. The cathode was kept partially frozen and was stirred during the electrolysis. Electrical connection was made by iron wires dipping into the mercury but not in contact with the electrolyte. The kinetic effect of iron dissolved, if any, was found to be negligible by a series of experiments in which connections to cathode and anode were made by mercury-filled siphons. Ammonium amalgams after preparation were filtered rapidly and kept frozen at −78°, at which temperature no decomposition is detectable.

A method for analysis of ammonium amalgams (and other alkali metal amalgams) is based on the reduction of iodate ion to iodide in neutral solution

$$6H_2O + IO_3^- + 6NH_4 = 6NH_4^+ + I^- + 3H_2O + 6OH^-$$

followed by acidulation, distillation of the liberated iodine and titration with thiosulfate. A sample was shaken with a 0.5 molar solution of iodide-free lithium iodate in 60% ethyl alcohol (free from aldehyde) at about the freezing point of mercury. The solution was separated from the mercury, since iodic acid oxidizes mercury, and rinsed into an all-glass still. Excess acetic acid was added and the liberated iodine was distilled into potassium iodide solution in a receiver cooled to about 0° and protected by a trap containing potassium iodide solution to prevent possible loss of iodine. Acetic acid was used in the distillation because strong acids cause a gradual reduction of iodate ion by the ethyl alcohol which had been used to lower the freezing point of the iodate solution. Blanks were made on all reagents used. The following experiments were made to establish the accuracy of the method and the rapidity and completeness of the initial reduction of iodate ion by ammonium amalgam. A solution of sodium in mercury was analyzed by this method and also acidimetrically using B. of S. potassium hydrogen phthalate as primary standard. The respective mean results by the two methods were 0.0646 and 0.0648 molal. To determine the completeness and rapidity of the reduction of iodate ion use was made of a test depending on the minimum concentration of alkali metal amalgam which will give a clearly discernible hydrogen evolution with dilute acid. This minimum concentration was found, by dilution of a sodium solution with mercury, to be about 0.0002 molal. When

---

(1) National Research Fellow in Chemistry.

(2) G. McP. Smith, THIS JOURNAL, **29**, 844 (1907).

(3) Rich and Travers, *J. Chem. Soc.*, **89**, 872 (1906).

(4) Sander and Nitsche, *Z. Elektrochem.*, **34**, 244 (1928).

(5) J. W. Mellor, "Inorganic and Theoretical Chemistry," Longmans, Green and Co., Vol. IV, p. 1005.

(6) The formation of ammonium amalgam from mercury, ammonia, and atomic hydrogen appears, however, to be thermodynamically possible.

sodium or ammonium amalgam was shaken gently with aqueous alcoholic lithium iodate solution at about −38° the concentration of alkali metal was reduced to less than this minimum in less than one minute. Since the heterogeneous reaction starts with a small slope (Fig. 2) the error introduced by decomposition of ammonium during the analytical reaction is negligible.

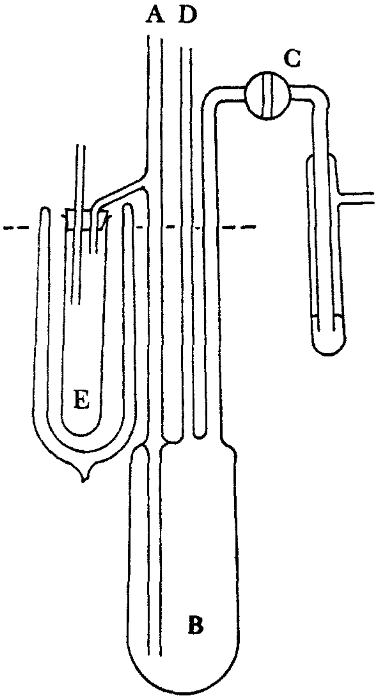

Fig. 1.

In Fig. 1 is shown the apparatus in which the rates of decomposition of ammonium amalgams were determined in an inert atmosphere. The apparatus was swept out with a nitrogen-hydrogen mixture (about 95% nitrogen) which had been passed successively over copper powder at a dull red heat, soda lime, calcium chloride and phosphorus pentoxide. A frozen ammonium amalgam was melted and introduced through tube A into the decomposition bulb B. The solution was stirred at intervals by passing a current of gas through tube A. At definite time intervals samples were removed by closing the stopcock C and applying pressure through D, forcing a sample of the solution over into the sample tube E, in which it was rapidly frozen by a bath of dry ice and chloroform in the small Dewar flask. The uncertainty in the time interval, including the initial time of temperature equalization, is probably about ±1.0 min. The whole apparatus was immersed to the level indicated by the dotted line in a thermostat bath maintained at ±0.1°. Temperatures were determined with an alcohol-filled thermometer which was calibrated with a copper resistance thermometer.

Solutions of ammonium containing known concentrations of lithium or sodium were prepared by breaking weighed bulbs of lithium or sodium amalgam in known weights of ammonium amalgam in an inert atmosphere and then freezing the solution. A series of these bulbs was prepared by filling *in vacuo* with an alkali metal solution and sealing off. The concentration of alkali metal in a series of bulbs was obtained by breaking one under excess lithium iodate solution and determining the iodide ion by the method already described.

Freezing point determinations were made on ammonium and alkali metal amalgams under nitrogen in a modified Beckmann apparatus. Samples of solution in equilibrium with solid mercury were siphoned off and frozen in a nitrogen atmosphere and later analyzed by the iodate method. Temperatures were determined by means of a copper resistance thermometer.

Experimental Results

In Table I are given some representative data for the decomposition of pure ammonium solutions at −20 and −30°, where a is the initial molal concentration, n the number of measurements, and d the average deviation of the velocity constant k_2. The data for −20° are plotted in Fig. 2. An equation for the rate of decomposition

$$dx/dt = k_2(a - x)^{1/2}x \qquad (1)$$

was obtained empirically from graphically determined values of dx/dt. The constancy of k_2 is probably within experimental error. It is evident, however, that the equation cannot be correct at small values of x because if so infinite time would be required for partial reaction.[7]

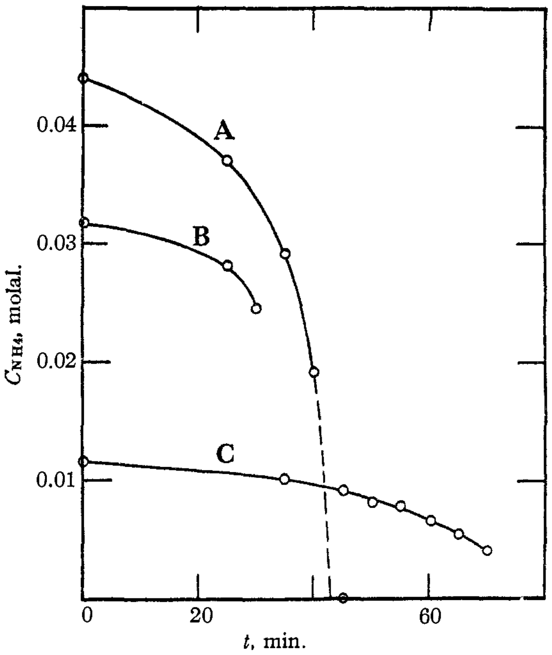

Fig. 2.—Decomposition of pure ammonium amalgams at −20°.

---

[7] While equation (1) cannot be directly integrated, the rate cannot be greater than if the term $(a - x)^{1/2}$ were replaced by $a^{1/2}$, in which case $t = \int_0^x dx/a^{1/2}x = \infty$.

Equation (1) is apparently that of an autocatalytic reaction. This was confirmed by an experiment in which a freshly melted solution of ammonium was divided into two equal parts. One part was kept at 0° for thirty minutes to decompose it completely and then the two were mixed at −20°. The initial rate was found approximately equal to $k_2\ a^{1/2}\ a$, where a was the initial concentration at the time of mixing.

TABLE I

DECOMPOSITION OF PURE AMMONIUM SOLUTIONS

a	n	$k_2 \times 10^3$	d
		−30°	
0.0146	3	4.4	0.3
.0198	3	3.6	.3
.0208	5	3.5	.2
.0324	2	3.4	.3
		Av. $3.7 \times 10^{-3}\ m^{1.5}$ sec.$^{-1}$	
		−20°	
0.0438	3	9.5	0.7
.0316	2	10.5	1.3
.0115	7	9.3	0.7
		Av. $9.7 \times 10^{-3}\ m^{1.5}$ sec.$^{-1}$	

The following experiments were undertaken to determine the nature of the autocatalysis. It was suspected that the autocatalyst was destroyed by complete freezing of the solution since the amounts of decomposition were different during preparation of the ammonium amalgams, all of which were frozen after preparation, for each experiment in Table I. This was verified by freezing a half decomposed solution, then melting and determining the rate of decomposition (Table I, −30°, second experiment). To determine whether the autocatalyst was a substance dissolved in the mercury solution, freezing point determinations were made on freshly melted solutions, partially decomposed solutions and completely decomposed solutions. The molal freezing point depressions for the first two types of solution were the same, 51°, within experimental error. The freezing points of two completely decomposed ammonium solutions of initial concentration 0.015 and 0.010 molal differed by less than 0.002° from the freezing point of pure mercury. If anything that does not reduce iodate ion is present in the solution, its concentration must therefore be less than about 0.00004 molal. It is concluded therefore that the autocatalyst is the final gaseous or liquid product and that the reaction is heterogeneous, taking place at the surface between the bubbles and the mercury solution. The destruction of the autocatalysis by freezing is probably due to reduction of surface of the bubbles by aggregation through the somewhat porous mass of mercury crystals. Considerable gas evolution on freezing was noticed in some cases. Some sample tubes containing completely decomposed ammonium solutions of fairly high concentration liberated so much gas on freezing that the stoppers were blown out violently.

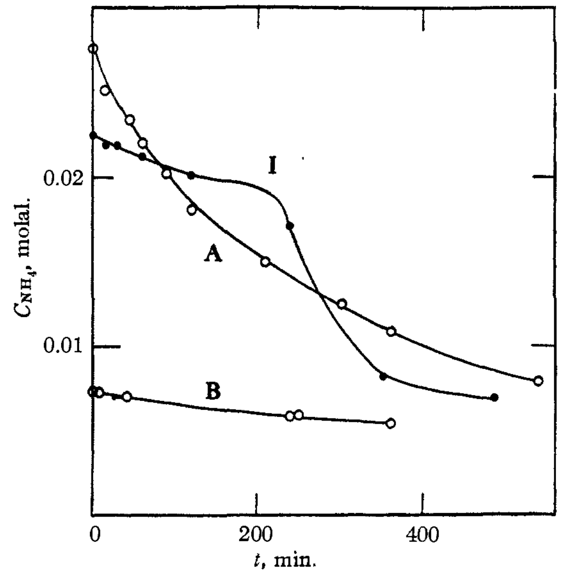

Fig. 3.—Decomposition of ammonium amalgams containing lithium: I, −10°, C_{Li} = 0.0010; A, 0°, C_{Li} = 0.0049; B, 0°, C_{Li} = 0.0067.

In the presence of lithium the decomposition of ammonium is very much slower and follows a different differential equation. Between concentrations of lithium from about 0.0007 to 0.002 molal the rate of decomposition is apparently complex (*e. g.*, Curve I, Fig. 3). During an initial period dx/dt decreases; it then increases rapidly, and finally decreases.

At concentrations of lithium higher than about 0.005 molal the reaction again follows a simple differential equation (Fig. 3). It is a second order reaction and independent of the lithium concentration (up to about 0.01 molal; the effect of larger concentrations of lithium could not be obtained precisely since the concentration of ammonium in these solutions was obtained by difference). In Table II are given data from which the velocity of decomposition was calculated at 0, +10 and +20° in the presence of lithium. The velocity constants (k_1, Table II, column 4) were obtained from the integrated form of the equation

$$dx/dt = k_1(a - x)^2$$

TABLE II

DECOMPOSITION OF AMMONIUM SOLUTIONS CONTAINING LITHIUM

C_{Li}	a	n	$k_1 \times 10^3$	d
		0°		
0.0049	0.0276	8	2.54	0.11
.0067	.0073	3	2.35	.15
			Av. 2.45 × 10^{-3} m^2 sec.$^{-1}$	
		+10°		
0.0115	0.0258	1	10.3	..
.0058	.0186	2	10.6	0.2
			Av. 10.5 × 10^{-3} m^2 sec.$^{-1}$	
		+20°		
0.0119	0.0133	3	48	5
.0123	.0121	3	64	3
			Av. 56 × 10^{-3} m^2 sec.$^{-1}$	

The reaction is homogeneous, since addition of a decomposed solution did not alter the velocity constant.

The energy of activation obtained from the slope of a plot of log k_1 against $1/T$ was 22,400 cal.

A solution of ammonium (0.01 molal) containing sodium (0.0012 molal) decomposed completely in less than five minutes at 0°, from which it is concluded that the inhibitory effect, if any, of sodium on the heterogeneous reaction is very much less than that of lithium.

Discussion of Results

The simultaneous homogeneous and heterogeneous decompositions of ammonium appear to be experimentally separable. A third process, the aggregation and settling of bubbles, has little or no effect on the first two under the conditions here encountered. This swelling to a pasty mass accompanied by gas evolution has sometimes been confused with the actual decomposition of ammonium and has led to discordant and erroneous qualitative estimates of the rate of decomposition.[5] Under certain conditions complete decomposition takes place before appreciable gas evolution or decrease in density occurs.

Calculation shows that the homogeneous reaction is negligible in pure ammonium solutions except during the first few minutes, and hence the method of obtaining k_2 above needs no correction for the homogeneous reaction. The change in the rate equation caused by the addition of lithium, together with the fact that doubling the concentration of lithium produces no effect on k_1, indicate that lithium inhibits the heterogeneous reaction without affecting the homogeneous reaction.

The Homogeneous Reaction.—The molecular state of ammonium in solution has not been established fully. The most probable hypothesis is that it is completely dissociated into an ammonium ion and an electron, both more or less solvated, rather than that an uncharged molecule NH_4 exists, which is improbable from considerations of molecular structure. Facts supporting the former hypothesis are the insolubility (or instability) of ammonium and its homologs in solvents that do not dissolve electrons, and the equality of the electrode potentials of the tetrasubstituted ammoniums in liquid ammonia.[8]

The kinetic data in mercury can be explained equally well on either hypothesis, as can also the fact that the molal freezing point depression is approximately equal to that calculated for an undissociated molecule. A decision between the hypotheses cannot be made from these data because the free electron concentration in mercury is so high as to be practically unaltered by addition of more free electrons.[9] On the first of the above hypotheses the second order reaction can be explained as resulting from an effective collision between two ammonium ions and two electrons

$$2NH_4^+ + 2e \longrightarrow 2NH_3 + H_2$$

A second order equation results from the high and constant concentration of electrons in mercury. If the same mechanism is predominant in liquid ammonia solutions a fourth order reaction rate law would be expected. This might account for the result of Schlubach[10] that although solutions of tetraethylammonium in liquid ammonia are fairly stable at −78° they cannot be concentrated by evaporation of ammonia at reduced pressure and temperature.

The Heterogeneous Reaction.—In a decomposing ammonium solution the total area of interface between the products and the mercury solution might be expected to depend on the number, average radius, and size distribution of the bubbles. Assuming the gas laws to hold, the ratio of total area A to mass m of n spherical bubbles of radius r is

$$A/m = \frac{4\pi r^2 n}{4/3\pi r^3 n(P + 2\gamma/r)M/RT} \qquad (2)$$

---

[8] Forbes and Norton, THIS JOURNAL, **48**, 2278 (1926).

[9] Wagner, *Z. physik. Chem.*, **15B**, 347 (1932).

[10] Schlubach, *Ber.*, **53**, 1689 (1920); Schlubach and Ballauf, *ibid.*, **54**, 2825 (1921).

where P is the external pressure and γ is the surface tension. When the surface tension pressure $2\gamma/r$ is small compared with the external pressure P the area of a given mass depends on the one-third power of the number of bubbles. In the case of an actual suspension of bubbles, where the radii are not equal, A/m depends both on the number and size distribution of bubbles. When, however, $2\gamma/r$ is large compared with P equation (2) reduces to

$$A/m = 3RT/2\gamma M = 3 \times 10^7 \text{ sq. cm./g. (for H}_2\text{)} \quad (3)$$

It is possible to obtain experimentally an upper limit for the average radius of the bubbles in a completely decomposed ammonium amalgam by determining the initial volume of the amalgam v and the final volume of gas liberated at 1 atm., V. For example, a completely decomposed ammonium amalgam at 0° had a volume $v = 10.403$ cc. It contained a volume $v_{\text{Hg}} = 10.336$ cc. of mercury, calculated from the mass and density of mercury. The final volume of gas liberated at 1 atm. was $V = 8.7$ cc.[11] Assuming the volume of gas to be inversely proportional to the pressure, the average radius r was obtained from the equation

$$V/(v - v_{\text{Hg}}) = (1 + 2\gamma/r) \text{ atm. /1 atm.}$$
$$2\gamma/r = 130 \text{ atm.}; \; r = 8 \times 10^{-6} \text{ cm.}$$

This calculation gives only an approximate upper limit to the average radius. As a closer approximation V should be multiplied by one-third ($2\gamma/r = 43$ atm.; $r = 2 \times 10^{-5}$ cm.) since at this high pressure the ammonia must be liquid (NH_3:H_2 = 2:1). Further, the interfacial tension between liquid ammonia and liquid mercury should be substituted for the surface tension of mercury, γ. The solubility of hydrogen in liquid ammonia[10] can be neglected safely up to considerably higher pressures. In spite of the approximateness of the calculation, the following conclusions may safely be drawn: The bubbles must be composed of spherical shells of liquid ammonia containing gaseous hydrogen and surrounded by liquid mercury. The ratio of total surface to total mass of hydrogen is of the order of 10^7 sq. cm./g., and is independent of the number, size distribution, and rate of aggregation of bubbles by collision (equation (3)). Since the rate of a heterogeneous reaction may be expected to be directly proportional to the area this would account for the simple proportionality of dx/dt to x in the empirical rate equation (1).

The rate of decomposition of ammonium at the interface between mercury and liquid ammonia (equation (1)) bears a formal similarity to the equation of Brönsted and Kane[12] for the reaction of sodium amalgam with acids:

$$dx/dt = Kc^{1/2}$$

where the constant K is given for a surface of constant area. The equation of Brönsted and Kane has been shown[13] to be derivable from the empirical equation relating current I and overvoltage ΔE established by the work of Bowden for large overvoltages.[14]

$$I/A = ke^{0.5F\Delta E/RT} \quad (4)$$

A possible mechanism therefore for the heterogeneous decomposition would be the reaction of ammonium amalgam with ammonium ions produced by the self-ionization of liquid ammonia

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$
$$c_{NH_4^+} \times c_{NH_2^-} = K_{\text{diss.}} \quad (5)$$

In this case dx/dt is proportional to I and ΔE is the e. m. f. of the cell in liquid ammonia

$$NH_{4(\text{Hg})} \mid NH_4^+ \mid H_2, \text{ Pt}$$

Since $c_{NH_4^+}$ is constant (equation (5))

$$\Delta E = E_0 + RT/F \ln c_{NH_4}/p_{H_2}^{1/2} \quad (6)$$

As an approximation, strictly correct only when all radii are equal

$$p_{H_2}^{1/2} = (2\gamma/r)^{1/2} = \text{const.}/x^{1/4} \quad (7)$$

Substituting (3), (6) and (7) in the overvoltage equation (4) and setting dx/dt proportional to I we obtain

$$dx/dt = \text{const. } (a - x)^{1/2}x^{9/8} \quad (8)$$

Summarizing: on the assumptions that pv is constant over a pressure increase of ten-fold, that the heterogeneous reaction is an electrode reaction obeying the empirical law of overvoltage on a metal surface of low catalytic activity, and that the overvoltage is equal to the electromotive force of ammonium amalgam against a hydrogen electrode in pure liquid ammonia, we obtain equation (8) which is not distinguishable within experimental error from the empirical equation (1).

The inhibition of the heterogeneous reaction by lithium can be explained on this basis. The electrode reaction for ammonium does not alter the ammonium ion concentration in the liquid ammonia shell

---

[11] The decomposition was complete but less than 1% of the gas had been liberated when the initial volume was determined in a combined dilatometer and eudiometer.

[12] Brönsted and Kane, THIS JOURNAL, **53**, 3624 (1931).

[13] Frumkin, *Z. physik. Chem.*, **160A**, 116 (1932).

[14] For references see Hammett, *Trans. Faraday Soc.*, **29**, 770 (1933).

$$NH_{4(Hg)} + (NH_4^+ + NH_2^-) \longrightarrow NH_4^+ + {}^1/_2H_2 + NH_3 + (NH_2^-)$$

On the other hand, a similar reaction with lithium increases the amide concentration and so (equation (5)) decreases the concentration of ammonium ion

$$Li_{(Hg)} + (NH_4^+ + NH_2^-) \longrightarrow Li^+ + {}^1/_2H_2 + NH_3 + (NH_2^-)$$

While an exact calculation cannot be made for the relation between electrode potential of an alkali metal and the concentration at which complete inhibition of the heterogeneous reaction takes place, it can generally be predicted that metals having electrode potentials considerably greater than ammonium will inhibit the reaction, while those with lower electrode potentials will not. This is in agreement with the fact that inhibition, if any, by sodium is very much less than that by lithium, whose amalgams have electrode potentials about 0.2 volt higher than sodium amalgams of equal concentration. An alternative explanation, based on the formation of a stable compound from lithium and ammonium, is ruled out by the fact that the heterogeneous reaction is slowed down considerably although not completely inhibited by a concentration of lithium as small as 0.0005 molal, or one-fortieth of the ammonium concentration.

In agreement with the electrode reaction hypothesis of the heterogeneous reaction, it was found that an ammonium amalgam (100 g., c_{NH_4} = 0.01 molal) reacted rapidly with a solution of ammonium chloride in liquid ammonia. In this case the surface (about 25 sq. cm.) was less than the surface of bubbles ($10^2 - 10^4$ sq. cm.), but the ammonium ion concentration in liquid ammonia (0.01 molar) was very much greater than in pure liquid ammonia.

The author wishes to thank Professor Farrington Daniels for many valuable suggestions.

Summary

1. The decomposition of ammonium amalgam at -20 and $-30°$ follows the rate law $dx/dt = k_2(a - x)^{1/2}x$.

2. The decomposition in pure solutions is mainly heterogeneous, taking place at the surface of the bubbles of reaction products.

3. The bubbles of reaction products have an average radius less than 10^{-4} cm., and consist of spherical shells of liquid ammonia enclosing gaseous hydrogen.

4. The rate of decomposition, as well as other evidence, is in accord with the hypothesis that the heterogeneous reaction is an electrode reaction obeying the laws of overvoltage.

5. In the presence of relatively small concentrations of lithium (>0.005 molal) the heterogeneous reaction is completely inhibited.

6. The homogeneous decomposition measured at 0, +10 and +20° follows a second order rate law: $dx/dt = k_1(a - x)^2$.

7. The second order equation may be explained by effective collisions between two ammonium ions and two electrons.

8. The energy of activation of the homogeneous reaction is 22,400 cal.

MADISON, WIS. RECEIVED SEPTEMBER 10, 1934