THE ELECTROLYSIS AND ELECTROLYTIC CONDUCTIVITY OF CERTAIN SUBSTANCES DISSOLVED IN LIQUID AMMONIA

BY HAMILTON P. CADY

The remarkable similarity existing between certain crystalline salts containing water of crystallization and similar salts containing ammonia, has suggested the idea that perhaps water and ammonia might be analogous in some of their other properties. Acting on this suggestion it was thought best to test the dissociative power of liquid ammonia, on dissolved substances.

The only record that could be found of any work bearing directly on this subject, was a statement by Dr. L. Bleekrode,[1] that liquid ammonia was a good conductor of electricity, and that while the current was passing the liquid turned blue, and became colorless again when the current ceased, Weyl,[2] and G. Gore,[3] investigated the action of various substances, dissolved in liquid ammonia, upon each other, but they seem not to have tried the conductivity of such solutions.

The liquid anhydrous ammonia used in the following experiments, was the ordinary commercial ammonia used in the manufacture of ice, and proved to be of sufficient purity for the purpose. The experiments were made in vacuum-jacketed test tubes, which were made in our laboratory by Prof. E. C. Franklin, and answered admirably for the purpose. This may be illustrated by the fact that 15 cc. would not all evaporate inside of three hours, at the ordinary temperature. The test tubes were fitted with a doubly-bored cork stopper, through one of the holes of which the ammonia was led in,

---

[1] Phil. Mag. [5] **5**, 384 (1878).

[2] Pogg. Ann. **121**, 601 ; **123**, 350 (1864).

[3] Proc. Roy. Soc, **20**, 441 (1872),

while the uncondensed gas was allowed to escape through a long glass tube, inserted into the other opening and bent at right angles. This arrangement protected the ammonia from moisture while it was being drawn from the cylinder. During the experiment the ammonia was protected by a calcium chloride tube, filled with soda lime.

The electrodes used in the experiments on electrolysis, were simply platinum plates held in position by glass rods, fused to the leading-in wires. When pure ammonia was submitted to the action of a battery of six storage cells having a potential of 12 Volts, no signs of a current could be detected. Even with a potential of 110 Volts and electrodes 1 cm. apart, and having an area of 25 square cm., only a few hundredths of an ampere passed through. The liquid did not turn blue, but simply boiled vigorously. If however a small quantity of a soluble salt be added to the ammonia the solution becomes an excellent conductor, and in the case of the sodium or potassium salts, the solution turns blue, if the 110 volt current be used, but it becomes colorless again when the current is shut off.

This furnishes an explanation for the difference between these results and those obtained by Dr. Bleekrode, l. c. His ammonia was prepared as follows: «The chlorides of silver and calcium were saturated with the gas; and with them quicklime and sodium were enclosed in the condensation tube, in order, on expelling the gas by heating, to remove the last traces of water. The separated liquid ammonia was several times poured back over the sodium, by inverting the tube, and redistilled». Evidently the ammonia had become contaminated with some of the sodium hydroxide, formed by the action of water on sodium. This makes a solution that conducts readily and the sodium set free at the cathode dissolves, forming a bright blue solution, the color disappearing when the current is shut off. Dr. Bleekrode ascribed the blue coloration to the formation of free ammonium, NH_4, according to the reaction $2NH_3 = NH_4 + NH_2$.

Weyl l. c. describes the formation of ammonium by the action of a solution of sodium upon ammonium chloride or sulphate. He obtained a bright blue liquid that rapidly decomposed into ammonia and hydrogen. Since the solution of sodium in ammonia is also bright blue, it would appear to be difficult to say just when the color was due to sodium and when it was caused by free ammonium. If an excess of ammonium bromide or iodide, both of which are very soluble in ammonia, be added to a solution of sodium in that menstrum, the blue color is instantly destroyed, and at the same time hydrogen is evolved. With ammonium chloride or sulphate the action is the same only slower, as these salts are not very soluble in ammonia.

If an electric current of 110 volts be passed through a solution of an ammonium salt in ammonia, there is a violent evolution of gas, but no signs of a blue coloration. In neither of these experiments could any evidence of a blue coloration that might be ascribed to the presence of free ammonium, be detected.

If a current of varying strength, up to 110 volts be passed through solutions of salts of silver, copper, or barium, the metals are deposited upon the cathode,but there is no sign of a blue color. If sodium be added to a solution of one of these salts the metal is precipitated but no blue color appears until an excess of sodium is present. Weyl, thought that he had obtained a blue solution of ammonium compounds of these metals by the action of sodium solution on their chlorides according to the reaction—

$$N_2H_6Na_2 + 2NH_3 + BaAl_2 = N_2H_6Ba + 2NH_3NaCl.$$

According to Weyl these ammonium compounds easily decompose into ammonia and the metal. Their existence is not confirmed however by the above experiments. The blue color observed by Weyl was due perhaps to the presence of free sodium. In every case he used chlorides of the metals, and these being only slightly soluble the action of the sodium would be relatively slow.

If potassium iodide be dissolved in ammonia and a current of from six to twelve volts be passed through the solution, electrolysis takes place, hydrogen is evolved and a deposit collects on each electrode. On the cathode the deposit is dark gray and reacts violently with water, giving a hissing sound and ammonia and potassium hydroxide are formed. The deposit probably consisted of potassium amide KNH_2, but a sufficient quantity for analysis could not be obtained. If the current be passed in series through the potassium iodide solution and through an apparatus for the generation of electrolytic gas, the ratio of the hydrogen from potassium iodide solution, to the mixed electrolytic gas was not that required by theory, but the volume of hydrogen was always too small. That the gas was hydrogen was proven by exploding it with oxygen.

The deposit on the anode varied from bluish black to olive green. It was insoluble in water but soluble in ether, alcohol and chlroform, and in potassium iodide solution, in each case with the evolution of gas. It explodes violently on heating, by friction and on contact with acids. The same substance was formed in the electrolysis of several other iodides. It was impossible to obtain enough of this compound to use for analysis, but it agrees closely in physical and chemical properties with the compound formed by the action of iodine on liquid ammonia, and which has the composition HN_3I, as noted in a previous article.[1]

Mercuric iodide dissolves easily in ammonia. The solution conducts readily, and the products of electrolysis are mercury and the explosive compound of iodine noted above.

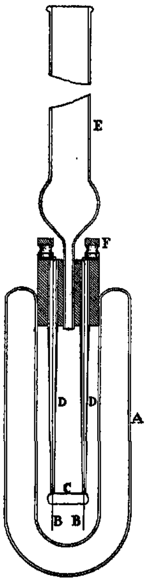

FIG. 1

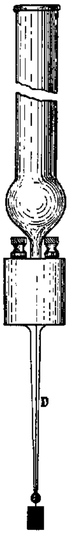

FIG. 2

Silver nitrate is also readily soluble and the solution is a good conductor. Metallic silver is deposited on the cathode.

Lead nitrate is easily soluble and the solution is a moderately good conductor, while metallic lead is deposited.

The behavior of a solution of sodium in ammonia is quite remarkable; the solution is an excellent conductor. There is no deposit on the electrodes; no gas is evolved, and the blue color of the sodium is not altered by the passage of an enormous quantity of electricity. If only a little sodium is present the color becomes more intense around the cathode. There is no polarization current.

In the experiments on conductivity the following apparatus was used :—

«A» is a vacuum jacketed test-tube. It is graduated so that

---

[1] Kan. Univ. Quar. Vol. VI, No. 2, p. 71 (1897).

the volume of the ammonia can be read directly. B B are the electrodes, consisting of a stout platinum foil welded to strong platinum wires and held in position by the glass rod C which is fused on to the wires. The wires that conduct the current are insulated by the slender glass tubes D D, the lower ends of which are fused on to the wires, and the latter are connected with the binding posts F F. E is a calcium chloride tube filled with soda lime. Fig. 2 is a side view of the electrodes and connections.

The results given below are preliminary and are not regarded as possessing any very great accuracy ; they are however close enough to settle the question as to whether or not ammonia possesses the power of dissociating dissolved substances to a degree comparable with water. The chief sources of error that have not been fully overcome, are the impossibility of preventing boiling at the electrodes which increases the apparent resistance and consequently lowers the molecular conductivity ; the difficulty of accurately controlling the dilution on account of the evaporation of the ammonia ; and finally the slight impurity of the ammonia. This latter of course increases the error in the determination of substances that are only slightly dissociated.

The presence of a small amount of water does not seem to have a measurable effect on either the conductivity of ammonia alone or of solutions of substances dissolved therein. The ammonia used had a conductivity of 71×10^{-7}.

Mercuric nitrate is not completely soluble, as a yellow compound resembling basic nitrate separates out, so no determination could be made.

In the case of the sodium solution, no signs of a polarization current could be detected with a sensitive galvanometer, and it will be noticed that the molecular conductivity rises with the concentration, contrary to that of electrolytes. As has been mentioned above no gas is given off when the solution is submitted to electrolysis. The sodium is not affected by the current, nor is there any deposit on the electrodes. In spite of the fact that the sodium is in solution, the solution seems to conduct like a metal and not like an electrolyte.

In this connection it is interesting to note that J. J. Thomson has shown that the vapor of sodium is a conductor, a result that we had also obtained before learning of his researches.

Salt used	Dissolved in ammonia at — 34°		Dissolved in water		
	V	μ	V	μ	
Potassium chloride	Not sufficiently soluble				
Potassium iodide,	80.	169.	100.	116.	at 18°
	100.	178.			
	110.	179.			
Potassium bromide,	100.	169.	128.	117.	at 18°
	120.	179.			
	135.	181.			
Potassium nitrate,	80.	123.	100.	114.	at 18°
	100.	124.			
	120.	131.			
Ammonium chloride,	40.	96.5	55.7	105.	at 18°
	50.	98.5			
	55.	99.			
	61.5	103.			
Ammonium bromide,	40.	124.			
	50.	132.			
	57.5	143.			
	67.5	144.			
Ammonium iodide,	40.	146.			
	50.	155.			
	60.	173.			
Sodium bromide,	140.	154.	128.	115.8	at 25°
	150.	158.			
Sodium iodide,	150.	166.	128.	112.3	at 25°
Silver nitrate,	140.	147.	166.	103.3	at 18°
Mercuric iodide,	150.	102.			
Mercuric cyanide,	130.	39.			
Lead nitrate,	105.	77.			
	130.	88.			
Metallic sodium,[1] 23 being taken as the molecular weight,	4.28	393.			
	3.97	413.			
	3.8	448.			

---

[1] These results are somewhat low, because the ammonia contained some water. This of course would react with the sodium and form sodium hydroxide, which has a much lower conductivity than sodium.

In conclusion it may be said that ammonia seems to possess the power of dissociation of dissolved substances to as great an extent as water, and in most cases the ions seem to travel even faster in it than in water. It would seem, furthermore, that water and ammonia do resemble each other in their power to dissociate dissolved substances, as well as in their ability to unite directly with certain metallic salts.

It is proposed to continue this work with improved apparatus, and it is hoped that greater accuracy may be attained.