[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

Metallic Aluminum in Solution in Liquid Ammonia

BY ALBERT D. MCELROY, JACOB KLEINBERG AND ARTHUR W. DAVIDSON

The results of preliminary observations upon the electrolytic behavior of aluminum in liquid ammonia have been reported in an earlier communication from this Laboratory.[1] More detailed investigations, and their results, are described in the present paper.

Experimental

Materials.—A method outlined by Fitzgerald[2] was used for the preparation of anhydrous aluminum iodide. The liquid ammonia used in the experiments was obtained by the condensation of gaseous ammonia from a commercial cylinder into the electrolytic cells. The cathode consisted of a strip of bright platinum, approximately 10 sq. cm. in area, and a rod of aluminum[3] of high purity, 0.63 cm. in diameter and 4 cm. long, served as the anode. The concentration of the electrolyte, aluminum iodide, varied from about 0.1 g. to 0.5 g. in 50 g. of ammonia. Cathode current densities were usually within the range from 0.005 to 0.1 amp. per sq. cm. An inert atmosphere was maintained in the electrolytic cell by continuous passage through it of nitrogen which had been circulated over heated strips of metallic copper to remove oxygen, and then passed through a calcium chloride drying tower.

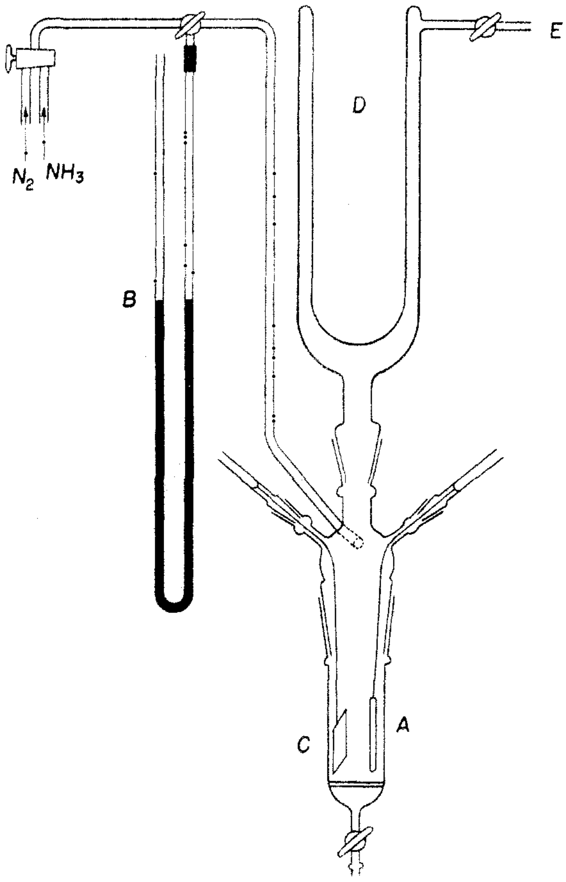

Fig. 1.—Electrolytic cell: A. aluminum anode; C, platinum cathode; B, mercury manometer; D, low temperature condenser, filled with Dry Ice–alcohol mixture; E, gas outlet, through a trap into a jar of water.

Apparatus and Experimental Procedure.—The apparatus for the electrolytic expts. is illustrated in Fig. 1. The entire apparatus was dried before each run by having nitrogen passed through it for four or five hours. The electrolyte was then added and gaseous ammonia was condensed in the cell. By immersion of the cell in a Dry Ice–alcohol-bath, the electrolyses could be carried out at temperatures in the range from −33 to −78°. The condenser D was not used during the conductivity measurements, since the conductivity electrodes were introduced into the electrolytic cell through a ground-glass joint used to connect the condenser to the cell.

In order to collect and measure the gas evolved, electrolyses were carried out at atmospheric pressure and at a temperature of about −50°. Upon completion of the electrolysis, the solution was stirred with a glass-encased magnetic stirrer until the blue color had entirely disappeared. The effluent gases were collected over mercury, ammonia was removed by scrubbing through dilute sulfuric acid solution and hydrogen was determined in the residual gas by combustion with oxygen.

A silver coulometer was included in the electrical circuit so that the quantity of electricity could be correlated with the loss of weight of the anode, and with the amount of gas liberated.

Results and Discussion

The time required for the formation of the intensely blue solutions, and the permanence of the color after the termination of electrolysis, were found to be dependent upon the temperature and the concentration of the electrolyte. When the initial concentration of aluminum iodide was about 0.5 g. in 50 g. of ammonia, a current of 0.1 amp. resulted in the formation of an intensely colored solution in about an hour if the temperature was maintained at −33°, and in about one-half hour at −60°. This time was reduced to 15 minutes at −60° when the concentration of electrolyte was 0.1 g. in 50 g. of ammonia, and the color faded completely in another 15-minute interval. When the electrolysis was continued at the same rate for two hours at the latter conditions of concentration and temperature, the color persisted for an hour or more. However, the solubility of the colored substance appears to decrease sharply as the temperature is lowered, for at −78° a dark blue solid was precipitated during electrolysis, the supernatant liquid remaining colorless. The blue solid remained unchanged in appearance for at least 24 hours at this temperature.

A bulky white precipitate was always formed as the result of electrolysis, even at low temperatures, along with the blue substance. This white solid was found to react vigorously with water

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[1] Davidson, Kleinberg, Bennett and McElroy, THIS JOURNAL, **71**, 377 (1949).

[2] Fitzgerald, *ibid.*, **29**, 1693 (1907).

[3] The aluminum rod, of 99.996% purity, was furnished by the Aluminum Company of America, through the courtesy of Dr. P. V. Faragher.

with the liberation of ammonia, a reaction characteristic of amides. Qualitative tests disclosed that the substance contained also aluminum and iodide ions. Samples of this solid were washed several times with liquid ammonia, permitted to stand for 24 hours at room temperature in an atmosphere of ammonia and nitrogen and analyzed quantitatively for aluminum, iodide and nitrogen. The results agreed very satisfactorily with those corresponding to the formula $Al(NH_2)_3 \cdot Al(NH_2)_2I \cdot 2NH_3$: *Anal.* Calcd.: Al, 18.3; I, 43.0; N, 33.2. Found: Al, 18.5; I, 43.5; N, 31.8. Franklin[4] reported the preparation, by the addition of sodium amide to a liquid ammonia solution of aluminum iodide, of the ammonia-insoluble compound $Al(NH_2)_3 \cdot Al(NH_2)_2I \cdot NH_3$.

Since the conversion of ammonia to amide by solutions of alkali metals is known to be catalyzed by a small amount of iron oxide, tests were performed on the electrolytically produced blue solutions in order to ascertain whether or not a similar catalytic effect could be observed. Iron and iron oxide were used as the catalytic agents.[5] The results of these tests are shown in Table I.

TABLE I

EFFECT OF CATALYSTS

	Time, minutes	
	For blue color to fade	For appearance of color on electrolysis
No catalytic agent	10	5, intense blue
Clean iron nails	5	10, intense blue
Oxide-coated nails	2	30, light blue

It is evident that the addition of iron or iron oxide to the colored solution hastened the fading of the color. Conversely, the electrolytic formation of colored solutions was inhibited by the addition of these agents.

Solutions in which the concentration of aluminum iodide was low, or more concentrated solutions which had previously been electrolyzed for about two hours, showed a striking increase in conductivity coincident with rapid development of intense color. Conductivity maxima occurred at points where the intensity of the color also appeared to have reached a maximum. The maximum conductivities were about two to three times that of the colorless solutions. A corresponding decrease in conductivity took place coincident with the disappearance of color. The observed conductivity changes were in line with what would be expected if the highly mobile ammoniated electron is responsible for the blue color. However, in view of the complexity of the system, these variations in conductivity cannot positively be attributed to the colored substance alone. Part of the increase, for instance, may have been due to an increase in concentration of Al^{+3} ion during electrolysis, and the decrease may have resulted in part from the removal of ions from the electrolyte as constituents of the white precipitate. Hence the only conclusion which can safely be drawn is that conductivity changes, although in the expected direction, were not of sufficient magnitude to constitute conclusive evidence of electron dissolution.

The relation between the quantity of electricity and the weight of aluminum dissolved from the anode indicates that this electrode process consisted solely of the reaction

$$Al = Al^{+3} + 3e^-$$

Appreciable evolution of gas from the colored solutions was observed, even when there was no flow of current. This gas was collected, measured and analyzed according to the procedure outlined previously. The results of three experiments are given in Table II.

TABLE II

RESULTS OF GAS ANALYSIS

	Expt. 1	Expt. 2	Expt. 3
Faradays/2	0.00186	0.00164	0.00208
Moles of gas	.00190	.00167	.00202
Moles of hydrogen	.00188	.00170	.00213

From these results it is evident that the evolved gas was hydrogen, in quantity equal to that calculated on the assumption of cathodic evolution of hydrogen as the primary electrode reaction. If the solution was still colored at the end of the electrolysis, however, the evolution of gas was found never to be complete at that time. This characteristic feature of the gas evolution was investigated further by measurement of the volume of the evolved gas at intervals during and after electrolysis, in order to determine whether or not hydrogen was evolved at a rate corresponding to the measured current intensity. The results of one such experiment in which the blue color faded very slowly, are shown in Fig. 2. Curve B is drawn through points which represent the number of moles of gas actually evolved. Curve A, ob-

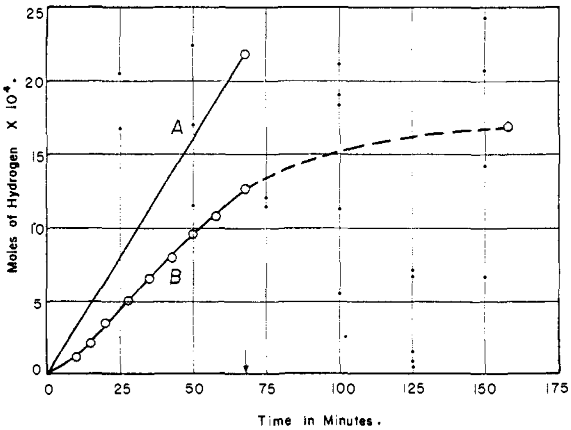

Fig. 2.—Evolution of gas: A, quantity of hydrogen calcd. from current; B, observed quantity of hydrogen evolved. The arrow indicates termination of electrolysis.

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(4) Franklin, THIS JOURNAL, **37**, 847 (1915).

(5) We are indebted to Professor H. A. Laitinen of the University of Illinois for suggesting this expt.

tained by drawing a straight line from the origin to the point determined by measurement of the total quantity of electricity, represents the number of moles of hydrogen which would be expected for cathodic evolution. This straight line, incidentally, coincides satisfactorily with one calculated from the measured current intensity, which was held at a constant value throughout the run.

These data on gas evolution may be interpreted in the following manner. Although the final result of the reduction reaction at the cathode is the liberation of the theoretical amount of hydrogen, the time lag in the evolution indicates that this is not the primary electrode process. Apparently the primary cathode reaction is the formation of a reducing agent which is capable of existing in solution for some time before it eventually reacts with the solvent. Since this time lag is observed only when the colored substance formed at the cathode is persistent, the reducing power of the solution evidently should be attributed to the same component which is responsible for the color.

The distinguishing characteristics of the cathode phenomenon may be summarized: (1) A blue color is formed at the cathode surface, and intensely colored blue solutions are obtained. (2) The rate of disappearance of color increases in the presence of iron or iron oxide. (3) The formation of colored solutions is accompanied by an increase in electrical conductivity. (4) The number of moles of hydrogen evolved from the beginning of electrolysis to complete disappearance of color from the solution is equal to the number of moles calculated on the assumption of cathodic evolution of hydrogen, but the time lag in this process indicates that such evolution is not the primary electrode reaction.

These characteristics may all readily be explained in terms of the theory that the primary cathode process is the dissolution of electrons into the solution. In accordance with this theory, the electrode reactions and subsequent reactions in the solution may be formulated as

Electrode reactions

Anode: $Al = Al^{+3} + 3e^-$

Cathode: $3e^- + 3nNH_3 = 3e(NH_3)_n^-$

Secondary reactions

$$3e(NH_3)_n^- + 3NH_3 = 3NH_2^- + 3/2H_2 + 3nNH_3$$

$$4NH_3 = 2NH_4^+ + 2NH_2^-$$

$$2Al^{+3} + I^- + 5NH_2^- + 2NH_3 = Al(NH_2)_3\cdot Al(NH_2)_2I\cdot 2NH_3$$

The blue solid which is formed at low temperatures may possibly be a solid ammoniate, similar to the previously described ammoniates of calcium, strontium and barium.[6] However, the conditions under which this blue solid is formed are such that the results of any attempts at analysis would be inconclusive.

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Summary

The results of the electrolysis of solutions of aluminum iodide in liquid ammonia may readily be explained on the hypothesis that the blue solutions formed result from a cathode reaction consisting in dissolution of electrons, which are capable of existing in the presence of a considerable concentration of Al^{+3} ion. The blue solute consists, therefore, of ionized metallic aluminum in liquid ammonia. The ammoniated electron reacts with the solvent to form amide ion and liberate hydrogen.

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[6] Biltz and Huttig, *Z. anorg. Chem.*, **114**, 241 (1920).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STATE UNIVERSITY OF IOWA]

Adsorption Equilibria of Liquid Mixtures of Benzene and Methanol with Charcoal

H. H. ROWLEY, R. B. OLNEY[1] AND W. B. INNES[2]

The vapor adsorption study of this system was reported in a previous paper.[3] The present work concerns the liquid adsorption equilibria. The approach used is largely the same as employed in studying the system CCl_4–CH_3OH on charcoal.[4]

Experimental

Materials.—The materials used for all measurements reported here were the same as used for the vapor adsorption study on this system except that the charcoal was powdered and sieved to a size smaller than 30 mesh.

Direct Measurements of Selective Adsorption. The same method used for earlier work[4] without pre-evacuation of charcoal was employed. Concentration change was determined by use of a Pulfrich temperature controlled refractometer.

Data and Discussion

Direct Measurements.—The results of these experiments are plotted in Fig. 1. The agreement of these data with other data reported by Bartell and Sloan[5] for this system (though not

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[1] From a dissertation submitted by R. B. Olney to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the Master of Science Degree, August, 1942.

[2] American Cyanamid Company, Stamford, Conn.

[3] H. H. Rowley, R. B. Olney and W. B. Innes, *J. Phys. & Colloid Chem.*, in press.

[4] W. B. Innes and H. H. Rowley, *J. Phys. Chem.*, **51**, 1173 (1947).

[5] F. E. Bartell and C. K. Sloan, THIS JOURNAL, **51**, 1654 (1929).