and magnesium chloride, and for potassium bromate and potassium nitrate. It is slightly less for barium bromate than for barium nitrate, and for thallous sulfate than for silver sulfate. Thallous and silver sulfates are somewhat less ionized than lead nitrate, and all three are much less ionized than nearly all other uni-bivalent salts. In fact below 0.05 normal their degrees of ionization are less than for the two uni-trivalent salts, lanthanum nitrate and potassium citrate, investigated by Noyes and Johnston.[1] The ionization is even less in the case of lead chloride and is still less in the case of cadmium chloride. It is evident that a number of salts[2] such as those of silver, thallium, lead and cadmium, are less ionized than typical salts of the same valence product type[3] and thus occupy an intermediate position between typical strong electrolytes, and weak electrolytes, such as mercuric chloride.

In conclusion the author wishes to express his indebtedness to Professor A. A. Noyes and Professor W. C. Bray, of this laboratory, for assistance in connection with the experimental work and the preparation of this article for publication.

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CONTRIBUTIONS TO THE ELECTROCHEMISTRY OF HYDRONITRIC ACID AND ITS SALTS. I. THE CORROSION OF SOME METALS IN SODIUM TRINITRIDE SOLUTION.

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Introduction.

While hydronitric acid has received its full quota of attention from investigators in both inorganic and organic chemistry, and a large mass of experimental data concerning this interesting new addition to the family of inorganic acids has been accumulated, its study from the electrochemical point of attack has been for the most part neglected.

It is the purpose of the research, one chapter of which is here reported, to investigate the behavior of the nitride ion (1) on being discharged against a soluble anode; (2) on being discharged against an insoluble anode; (3) on being acted upon in the anode region by discharged anions, or anode products (electrochemical oxidation); and (4) on being acted upon in the cathode region by discharged cations, or cathode products (electrochemical reduction). Also, the determination of some of the electrochemical constants of hydronitric acid and its compounds is anticipated. In all of this work special attention will be paid to a comparison of the behavior of the nitride ion with that of other ions, in order that its true position in the family of anions may be shown.

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[1] THIS JOURNAL, 31, 1002 (1909).

[2] Cf. Abbott and Bray, THIS JOURNAL, 31, 753 (1909).

[3] Noyes and Johnston, *Loc. cit.*, 1003.

The anion from hydronitric acid and its salts, the trinitrides, would be called the *trinitride* ion. However, as there is no other series of water-soluble nitrides capable of forming anions containing nitrogen alone, no confusion can arise if this name be abbreviated to *nitride* ion. So, in this paper, the N_3^- ion will be so designated. Dennis and Browne[1] have applied the name *nitrine* to the hypothetical polymer, $(N_3)_2$, to connote the predicted analogy of that substance with the free halogens. Likewise, the name, nitride ion, connotes the analogy of this ion with the ions from the halogenides, the cyanides and with other oxygen-free anions.

The existence of analogies between the nitride and chloride ions[2] has been frequently intimated. Evidences gathered from the corrosion by the nitride ion, and its oxidation and reduction electrochemically, will be brought to bear on this interesting comparison.

Historical.—Ostwald[3] applied conductivity methods to the determination of the degree of ionization of hydronitric acid in aqueous solution, in order to determin its relative strength as an acid. West[4] repeated Ostwald's work, and Hantzsch[5] performed experiments of like nature. Hittorf[6] electrolyzed ammonium trinitride in aqueous solution, obtaining hydrogen and nitrogen as the respective cathode and anode products. Ammonia remained in solution. He determined some of the electrochemical constants of this compound from which he derived its heat of combination. Peratoner and Oddo,[7] in the belief that the nitride ion would discharge as a polymeride, which would prove to be identical with argon, electrolyzed solutions of hydronitric acid and of sodium trinitride.

Szarvasy[8] made a study of the electrochemistry of various hydrides of nitrogen. He electrolyzed solutions of hydronitric acid and sodium trinitride under various conditions of concentration and of current density, and measured the electrode products. He found but a slight variation from the ration of 1 : 3 between the hydrogen evolved at the cathode and the nitrogen at the anode. In some solutions traces of ammonia were obtained after electrolysis.

Browne and Lundell[9] electrolyzed a solution of potassium trinitride in liquid hydronitric acid at —80°. This daring investigation showed

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[1] THIS JOURNAL, 26, 577 (1904).

[2] Dennis and Browne, *Loc. cit.*, see page 607; Dennstedt and Göhlich, *Chem.-Ztg.*, 21, 876; Curtius, *Ber.*, 23, 3023, also *vide infra*.

[3] Curtius and Rodenhausen, *J. prakt. Chem.*, [2] 43, 207 (1891).

[4] *J. Chem. Soc.*, 77, 705 (1900).

[5] *Ber.*, 32, 3066 (1899).

[6] *J. Phys. Chem.*, 10, 593 (1892).

[7] *Gazz. chim. ital.*, 25, II, 13 (1895); *Chem. Centr.*, 1895, II, 864.

[8] *J. Chem. Soc.*, 77, 603 (1900).

[9] THIS JOURNAL, 31, 435 (1909).

that while liquid hydronitric acid is a non-conductor itself, like water, liquid ammonia, liquid hydrochloric acid and anhydrous hydrazine, it is an ionizing solvent. The electrolysis of potassium trinitride in the liquid hydronitric acid yielded hydrogen and nitrogen as the respective cathode and anode products, and in the approximate ratio of 1 : 3, corresponding to the ratio of hydrogen and nitrogen in hydronitric acid. The behavior of potassium trinitride in this solution is strictly analogous to that of potassium hydroxide in water solution. In some cases the ratio of 1 : 3 was not obtained, a lower ratio being observed. Appreciable amounts of ammonia were obtained, indicating a reduction at the cathode. And the accumulation in the electrolytic cell of some unstable compound, producing violent explosions, led to the supposition of the possible formation there of the polymer of nitrogen.

Experimental.

In this description of the electrochemical corrosion of metals in sodium trinitride solution, the experiments will be taken up in the order of the electrochemical nature of the metals studied, although this is not their chronological order.

General Procedure.—In the paragraphs immediately following, such statements will be made as apply in general to all the experiments alike. Where the conditions of electrolysis cannot be covered by such a general statement, they will be described under the individual experiment.

Two series of corrosions were made in the case of each metal, in unstirred and in stirred solution. All other conditions, with a few exceptions, were kept approximately constant. The electrolytic bath was a 2 per cent. solution of NaN_3. The salt was obtained from **Raschig** and was used without recrystallization. The temperature of the electrolytic bath was room temperature, except where it became warm through the action going on within it.

In those experiments where corrosions were studied in unstirred solution, beakers of 350 cc. capacity were employed. Across their tops rested the electrode holder, consisting merely of a block of wood of a convenient size, containing two parallel slits, 3.2 cm. apart. Into the slits were inserted the electrodes. As such supports were employed in every case, the electrodes were always the same distance apart. This factor, therefore, was a constant one.

As the electrodes were not always of uniform size, no general statement can be made covering their dimensions. Where the broad sheet electrodes were in use, their proximity (3.2 cm.) to each other and to the cell walls made it probable that not more than one-third of their outer surfaces was electrochemically active. On the other hand, where the anodes had the form of strips of metal, or of cylindrical sticks, it is very probable that the electrolytic action took place with fair uniformity over their surfaces.

All other factors which are known to influence current density[1] will be described in the account of the individual experiments.

Where the corrosions were performed in stirred solutions, the latter were contained in beakers of 250 cc. capacity.

In these experiments the agitation of the electrolytic bath was effected in most instances by rotating the anode. Thus, corrosions were studied under conditions of stationary and rotated anodes.

A rotating device was employed which admitted of the electrolysis of five cells in series, each with a rotating anode (or cathode). The electrode to be .rotated was fastened by means of a clutch to a pulley, the axis of which was vertical. The five pulleys were actuated by means of belts working over a second set of pulleys mounted on a common axis. The latter was placed horizontally and was rotated by an electric motor.

Electrical connection was made with the metal of the first pulleys and, through it, with the electrode attached thereto; a wire to which could be joined the opposed electrode connected with the metal of the next pulley, and so on. There was additional wiring so arranged that, by means of two-way switches, the electric current could be shunted around any cell or cells, without interrupting the experiment.

As all the parallel pulleys of the machine were of the same size and were operated by belts from a common shaft, the speed of rotation of the anodes, or of the agitation of the electrolytic bath in cases where the anode was not rotated, but the solution was stirred by the rotation within it of some other body, was the same in all five cells. For any one series, then, that factor also was a constant. While the speed of rotation was the same in all five cells at any one moment, it varied from time to time, due to the fluctuations of the current operating the motor. The speed averaged about four revolutions a second, a rate which was sufficient to keep the entire solution within the cell actively whirling.

For cathodes in the stirred solutions, a thin platinum wire was always used. This was immersed to such a depth that the length of its active area equaled that of the anode. As the cathode paralleled the anode, a uniform current density on the latter was assured.

The anodes were carefully cleaned in proper reagents and were dried and weighed. After they had been subjected to the corrosion they were again cleaned as thoroughly as was possible with running water and soft cloths, and were again dried and weighed. In some instances it was not possible by the means employed to free them absolutely from the precipitate formed on their surfaces. To facilitate drying, the electrodes were washed finally in absolute alcohol. Except where the presence of explosive compounds was suspected, the alcohol was burned off; otherwise, it was allowed to evaporate spontaneously.

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[1] Turrentine, *J. Physic. Chem.*, 14, 152 (1900).

Efficiency[1] was calculated on the basis of values obtained from a copper coulometer. The latter was filled with a solution of copper sulfate, acidulated with nitric acid and containing alcohol.[2] The electrodes were stationary copper plates which presented so large an active surface (46 cm^2.) to the electrolytic action that a satisfactory cathode deposit was invariably obtained. The usual method of washing coulometer electrodes was followed, after which they were allowed to come to constant weight in desiccators.

Calculations were based on cathode values.

Magnesium. Unstirred Solutions.—Magnesium anodes were prepared from cylindrical sticks of metal, by splitting. This yielded anodes hemicylindrical in shape and 1 cm. in width on their flat surface.

The anodes were immersed in the electrolytic bath to a depth of 7.5 cm., exposing a surface of 19 cm^2. The cathodes were platinum wires. Two cells were run in series.

During the electrolysis, which was prolonged 1 hr., the solution became filled with a white flocculent precipitate of magnesium hydroxide, or of basic magnesium trinitride.[3] The anodes were loosely coated with the white precipitate. They became roughened and pitted so that it was difficult to remove the last of this precipitate. There was a vigorous evolution of gas from the anodes, which did not cease abruptly with the interruption of the current, but continued at a decreasing rate for several minutes.

The anode losses and efficiencies as determined in four experiments are expressed by these figures: (Expt. 1) 0.2488 g.; efficiency 186.6 per cent. (Expt. 2) 0.0086 g.; efficiency 171.4 per cent.; theory for Expts. 1 and 2 on basis Cu: Mg 0.1333 g. (Expt. 3) 0.2374 g.; efficiency 176.3 per cent. (Expt. 4) 0.2394 g.; efficiency 177.7 per cent.; theory 0.1347 g. (Expt. 5) 0.1957 g.; efficiency 160.4 per cent. (Expt. 6) 0.1798 g.; efficiency 160 per cent.; theory 0.1220 g. (Expt. 7) 0.1917 g.; efficiency 170 per cent. (Expt. 8) 0.1872 g.; efficiency 166.6 per cent.; theory 0.1123 g.

Experiments 1–4, inclusive, were performed in cells of one compartment, as described. Experiments 5–8, inclusive, were carried out under the conditions subsequently to be described. As the conditions controlling current efficiency were approximately the same as those which obtained in experiments 1–4, the values from all eight experiments are reported together.

These figures show that the anode efficiencies approach 200 per cent. Superficially, an evolution of gas at the anode would merely mean imperfect corrosion efficiency, a discharge of some nitride ions instead of the formation of magnesium ions. In view of the fact that an efficiency approaching 200 per cent. was being obtained, this supposition of an imperfect corrosion scarcely looked plausible.

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[1] That is, the amount of corrosion compared with that required by Faraday's law.

[2] Oettel, *Z. Elektrochem.*, 1, 57 (1894).

[3] Curtius and Rissom, *J. prakt. Chem.*, 58, 362.

It has been shown[1] that when magnesium is made anode in sodium sulfate solution, hydrogen is evolved from the anode. In agreement with this, it was supposed that the gas evolved from the magnesium anode in sodium trinitride solution was likewise hydrogen. An experiment was planned, therefore, with a view to the determination of the nature of the anode gases.

The magnesium anodes used in the preceding experiment were thrust through the side arm of coulometer tubes. These were glass tubes, the main length of which, about 50 cc. in capacity, was calibrated. This bore at one end a stopcock, surmounted by a capillary, and at the other end an enlargement, 3.5 cm. internal diameter. The enlarged portion bore the side-arm and was open at the bottom. This constituted the anode compartment. Over the side-arm was slipped a section of rubber tubing which fitted around the protruding end of the magnesium anode and made an air-tight joint. The open end of the tube was then immersed in a crystallizing dish containing a solution of the electrolyte and was surrounded by a parchment diaphragm, extending entirely to the bottom of the cell. This effectually prevented the cathode gases from wandering into the anode compartment. The solution was then drawn up into the coulometer tube until it had entirely displaced the air therein. The cathode was a thin platinum wire.

The electrolysis was prolonged for 1 hr. with a current of 0.3 amp. The current density was variable and was slightly higher than in the preceding experiments.

At the end of the hour the collected gases were drawn off into Hempel burets and were measured. The electrodes were removed and cleaned and their loss in weight was noted. The collected gases were then subjected to analysis for oxygen and hydrogen. The former was measured by absorption over alkaline pyrogallol and the latter, by combustion in the presence of an excess of oxygen in a Hempel-Dennis gas pipet. The loss in volume was taken as representing the volume of hydrogen, plus its equivalent volume of oxygen. Two-thirds of the loss in volume then was taken as hydrogen. Nitrogen was determined by difference.

Four such experiments were performed under practically the same conditions of electrolysis. The results obtained are given in Table I:

TABLE I.

Expt. No.	T. V. Cc.	O_2. Cc.	O_2. Per cent.	H_2. Cc.	H_2. Per cent.	N_2. Cc.	N_2. Per cent.
5................	18.2	0.4	2.1	5.4	29.6	12.4	68.3
6................	17.0	0.5	2.9	4.6	27.0	11.9	70.1
7................	16.8	0.6	3.5	4.6	27.3	11.6	69.2
8................	17.7	0.6	3.2	5.4	30.5	11.7	66.3

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[1] Turrentine, *J. Physic. Chem.*, 12, 448 (1908); *Trans. Am. Electrochem. Soc.*, 13, 289 (1908).

In the first series (Expts. 5 and 6) the anode was removed first in Expt. 6, and in the second series (Expts. 7 and 8) in Expt. 7. It has been mentioned that the evolution of gas from the anode continued after the electrolysis had ceased. So, in those experiments (Expts. 5 and 8), where the anodes were left in the solution for a longer time, there was obtained a slightly greater volume of gas. In these instances also there was a larger percentage of hydrogen present. In order to determin the nature of the gas evolved in the manner just mentioned, portions of it were collected and were analyzed.

The evolution after the first few minutes became very slow, so that at the end of 19 hours only 3 cc. had accumulated. On analyzing this volume of gas there was no absorption in alkaline pyrogallol; on combustion, the loss in volume was 4.5 cc., corresponding to 3.0 cc. H_2, the original volume. Attention is called to the fact that the volume of hydrogen evolved by the anode standing for 19 hours in the solution is less than that volume evolved in 1 hour during the electrolysis.

Discussion of Results.—In the light of Faraday's law, the foregoing results from the corrosion of magnesium anodes in sodium trinitride solution show that the electrochemical equivalent of magnesium is twice as great as what we should expect from the usual chemical behavior of that element. The valence manifested here is one instead of two. In no other way are we able to explain satisfactorily the high corrosion efficiency observed.

While magnesium in all of its known salts exhibits bivalence, there are reactions recorded where the metal appears in a hypothetical, unstable, univalent condition. Beetz,[1] on the basis of a suboxide of magnesium, explains certain phenomena observed when he electrolyzed an aqueous solution of magnesium sulfate with magnesium anode. A black substance formed on the anode which gradually reacted with the water to form hydrogen and a precipitate of magnesium hydroxide. Beetz made a series of quantitative measurements of the hydrogen evolved and of the magnesium dissolved from the positive pole and found in every case that the two were equivalent.

Christomanos,[2] on cooling suddenly a flame from burning magnesium, obtained a gray powder, which from its analysis appeared to have the formula Mg_8O_5. Baborovsky[3] regarded the compound obtained by Christomanos as identical with that obtained by Beetz. Luther and Schilow[4] hypothesized a univalent condition of magnesium to explain

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[1] *Phil. Mag.*, 32, 269 (1866); *Pogg. Ann.*, 127, 45; Cf. also Elsasser, *Ber.*, 9, 1818 (1876); 11, 587 (1878).

[2] *Ber.*, 36, 2076 (1903).

[3] *Ibid.*, 36, 2719 (1903).

[4] *Z. physik. Chem.*, 46, 803 (1903).

the reaction which takes place between magnesium, iodine and methyl alcohol whereby hydrogen is evolved.[1] Their supposition of an intermediate reaction in which is formed a *magnesious* iodide is represented by the equation:

$$Mg + \tfrac{1}{2} I_2 = MgI$$

$$MgI + CH_3OH = MgIOCH_3 + \tfrac{1}{2} H_2.$$

In a previous research[2] involving the action of magnesium when made anode in sodium sulfate solution, it was observed that there ensued a vigorous evolution of hydrogen at the anode, continuing for several minutes after the electrolysis had ceased, and that in the anode region a copious precipitate of magnesium hydroxide formed. These phenomena were explained by the supposition that the magnesium went into solution as unstable magnesious sulfate and there reacted with the solvent, water, to form magnesic compounds and hydrogen. This reaction may be represented by the equation:

$$Mg_2SO_4 + 2H_2O = MgSO_4 + Mg(OH)_2 + H_2.$$

This hypothesis accounted for all the observations in a perfectly satisfactory manner.

To explain the excessive current efficiency at the anode when magnesium is made anode in sodium trinitride solution we must suppose, likewise, the occurrence of univalent magnesium. The magnesious trinitride, then, formed at the anode should react with the solvent and evolve hydrogen, in a manner analogous to the reaction of magnesious sulfate. As we have seen from the analysis of the anode gases, only a small amount of hydrogen is evolved, not enough to correspond to the amount of magnesium dissolved in the univalent form. The hydrogen, or its equivalent in reducing power, must be consumed in some reduction.

The only reducible substance present, besides water, is the nitride ion. Szarvasy[3] obtained ammonia as a product of the electrochemical reduction of the nitride ion, or of the hydronitric acid molecule. Curtius and Rissom[4] observed the formation of ammonia when metallic tin and zinc dissolved in hydronitric acid, and Curtius and Darapsky[5] noted a similar reaction when antimony and arsenic dissolved in that acid. Cook[6] reduced hydronitric acid chemically to ammonia and hydrazine by means of such reducing agents as sodium amalgam, zinc and hydrochloric (or sulfuric) acid, sodium sulfide and ferrous hydroxide. Ammonia was

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[1] "Data on the Chemical Role of Catalytic Agents," *J. Russ. Physic. Chem. Soc.*, **35**, 399; *Chem. Centr.*, 711, 277 (1903).

[2] Turrentine, *Loc. cit.*

[3] *J. Chem. Soc.*, **77**, 603 (1900).

[4] *J. pr. Chem.*, [2] 58, 292.

[5] *Ibid.*, [2] 61, 408 (1900).

[6] *Proc. Chem. Soc.*, **19**, 213 (1903).

the chief product. Hydrazine was found present only where it was protected from further reduction by forming some insoluble compounds, which removed it from the sphere of reaction. The reaction proposed by Cook may be represented by the equation:

$$HN_3 + 3H_2 = NH_3 + N_2H_4.$$

This investigator showed likewise that hydrazine could be reduced to ammonia, thus in a way substantiating his theory. The reduction of hydrazine to ammonia has been observed by other investigators.[1]

Dennis and Doan[2] reduced thallium trinitride to ammonia by heating the salt in a stream of hydrogen; and Dennis and Isham[3] obtained ammonium chloride and nitrogen from the interaction of gaseous hydrochloric and hydronitric acids. Curtius and Rissom[4] obtained the same products when the two acids were allowed to react in aqueous solution.

If the magnesious compound reacted as a reducing agent toward the nitride ion we should have the formation of ammonia, or of ammonia and hydrazine. Such a reaction could be represented thus:

$$(1) \quad 12\,MgN_3 + 14H_2O = 5MgN_6 + 7Mg(OH)_2 + 2NH_3 + 2N_2H_4$$

This equation is based on that proposed by Cook.

Or, one of the nitrogens of the magnesious trinitride may be reduced to ammonia and the other two liberated as molecular nitrogen. Equation (2) expresses such a reaction:

$$(2) \quad 4MgN_3 + 6H_2O = MgN_6 + 3Mg(OH)_2 + 2NH_3 + 2N_2.$$

This equation is of especial interest because by means of it we are able to account for the large evolution of nitrogen from the anode. It has been noted[5] that one of the nitrogens of hydronitric acid acts differently from the other two.

The anode evolution of nitrogen is explicable on the assumption that some N_3^- ions are discharged. This would mean a low corrosion efficiency, and would be the logical explanation, if an efficiency of less than 100 per cent. had been obtained.

If the corrosion efficiency were based on univalent magnesium the efficiency would be less than 100 per cent. In Expt. 5 the theoretical anode loss at the anode would be 2 × 0.1220 = 0.244 g. The observed value being 0.1957 g., there is a deficiency of 0.0483 g. Mg. Under the condition of temperature and atmospheric pressure obtaining at the time of the experiment, this weight of magnesium would be equivalent

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[1] In the summer of 1907, in attempts made by the writer to prepare sodium hydrazide by the interaction of metallic sodium and imperfectly dehydrated hydrazine, the formation of ammonia resulted.

[2] THIS JOURNAL, 18, 970.

[3] *Ibid.*, 29, 18 (1907).

[4] *Loc. cit.*

[5] Dennis and Isham, *Loc. cit.*

to 80 cc. N_2 (Mg : N_3); observed, 14.3 cc. N_2. This represents the maximum amount of nitrogen that could be evolved in this manner.

It is conceivable that the reduction might result in ammonia quantitatively, either directly, or through hydrazine as an intermediate product, as indicated in equation (3):

$$(3) \qquad 16MgN_3 + 18H_2O = 9Mg(OH)_2 + 7MgN_6 + 6NH_3.$$

Or, again, reactions as indicated in equations (1) and (2) might take place simultaneously, producing all three substances, ammonia, hydrazine and nitrogen, as reduction products. This reaction may be represented as follows:

$$(4) \quad 8MgN_3 + 10H_2O = 3MgN_6 + 5Mg(OH)_2 + 2NH_3 + N_2H_4 + N_2.$$

In agreement with these hypotheses, the solution in which the corrosions had been performed should have contained ammonia or hydrazine, or both. Accordingly, portions of these solutions were subjected to a quantitative analysis for ammonia by distillation from an alkaline solution. Two such analyses gave identical results. The amount of ammonia present in the total volume of solution (700 cc.) was found to be 0.118 g.

The residue left in the distillation flask was tested for hydrazine with Fehling's solution. Reductions were obtained repeatedly, indicating the presence of the N_2H_4 radical.[1] The distillate, after it had been titrated, was tested likewise with Fehling's solution. No reduction of the test solution was obtained.

These results, while merely qualitative when applied to the question under study, give strong support to our theory accounting for the anomalous behavior of magnesium anodes in sodium trinitride solution. They indicate that the reduction which takes place here, leading to the formation of ammonia, hydrazine and nitrogen, is of the order represented by equation (4). They are also in agreement with the chemical reduction of hydronitric acid as accomplished by Curtius and by Cook.[2]

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[1] The reaction with Fehling's solution, of course, is not characteristic of hydrazine alone.. In this test it is necessary to suppose the absence of other reducing agents. However, considering the conditions under which the experiments were performed and in the light of the work of other investigators, we believe that we are justified in stating that hydrazine was here present.

[2] One other explanation suggests itself. In examining the action of ammonium persulfate on metals (Turrentine, *J. Physic. Chem.*, 11, 623 (1907)), the author observed that iron dissolved to ferrous sulfate and evolved hydrogen. The ferrous sulfate was oxidized by the persulfate present to ferric sulfate, which hydrolyzed and produced a precipitate of ferric hydroxide. Although, in the beginning, the solution was stoichiometrically neutral, after ferric hydroxide had been formed it reacted acid to litmus paper. It appeared, then, that the evolution of hydrogen from the iron in ammonium persulfate solution might be due to the reaction of the free acid on the iron. Likewise, iron immersed in a solution of ferric sulfate also evolved hydrogen. The solution showed acidity when tested with litmus. Alkaline hydroxides added to this solution precipitated ferric hydroxide, but left the solution still acid.

A similar evolution of hydrogen was noted also when iron was made anode in ammonium sulfate solution, and a current was passed of such strength as to afford a current density at the anode high enough to cause oxygen to be evolved.

While it is difficult to harmonize the theory advanced with this last phenomenon, yet the mass of evidence points to the reaction of the acid, formed as indicated, on the iron.

In sodium trinitride solution, hydrolysis increases the concentration of the hydroxyl ion and produces alkalinity. However, in the case of magnesium, the coating of precipitated magnesium compound on the anode makes the solution actually in contact with the anode quite independent of the main solution. Its state of acidity or neutrality is not influenced by that of the main solution. If, then, the hydrolysis of the magnesium trinitride liberated sufficient hydronitric acid to bring the concentration of the latter to a point where it would dissolve magnesium, we should expect an evolution of hydrogen were the corrosion taking place *chemically*. The hydronitric acid then would be acting as a catalytic agent in the reaction between magnesium and water. The hydrogen evolved would be free to reduce a trinitride present in its vicinity. This case would be different from that of iron, however, in the particular that here at most only one-half of the hydronitric acid is liberated (assuming that magnesium trinitride, like zinc trinitride, hydrolyzes to the basic trinitride), and would constantly decrease next to the electrode. While these reactions could take place were the corrosion chemical, it is hardly conceivable that they would take place with electrolysis, that free hydrogen could be evolved by a weak acid in dilute solution at an anode where new ions are being formed. The hydrogen liberated by the hypothetical magnesious compound reacting with water, to be sure, takes place in the anode region, but not in absolute contact with the anode as must the reaction between the anode and an acid. While the latter reaction may take place chemically or hydrogen may be evolved potentially, the electrochemical tendency at the anode is to produce new cations, and not to liberate them, and to prevent the discharge of hydrogen. This is tacitly acknowledged whenever we use a copper coulometer filled with an acid solution. While we recognize the solubility, chemically, of the electrodes in the acid of the electrolytic bath, we rely on the electrochemical action at the anode (and cathode) to prevent the chemical action. The weak point in this explanation is that it can be applied only in those cases where hydrolysis occurs; aluminium trinitride hydrolyzes completely, zinc trinitride, to the basic trinitride, and magnesium trinitride, perhaps slightly.

In the foregoing discussion no mention has been made of the possibility of explaining change in valence on the basis of linkage,[1] a possibility which should be considered in assigning valencies to elements existing in combination. Such considerations, however, scarcely apply when the effective valence of an element, based on Faraday's law and the electrochemical equivalents, that valence which manifests itself in electrochemical corrosions, is being dealt with.

Aluminium. Unstirred Solution.—Aluminium anodes were prepared from thin sheet aluminium. Two anodes were employed whose dimensions were respectively 5.5 by 5 cm. and 6.0 by 6.0 cm. Their distance from the cathodes and from the walls of the cell was such that about one-third of the area of their back surfaces was regarded in computing current density. The cathodes were aluminium plates similar to the anodes.

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[1] Turrentine, *J. Physic. Chem.*, 12, 448 (1908), see p. 454.

In some of the experiments the electrolysis was continued for two hours, while in others, for one hour. The strength of the current employed varied from 0.10 to 0.21 amp. No general statement therefore can be made which will cover all the conditions of current density.

There was an evolution of gas from the anode from the beginning of the electrolysis. A white gelatinous precipitate, presumably $Al(OH)_3$, accumulated in the solution.

The anodes, while much roughened, remained comparatively clean and free from precipitate.

The anode losses recorded are given in the following table:

TABLE II.

Expt. No.	Time. Hrs.	Current density.	Anode loss. Gram.	Theory. Gram.	Efficiency. Per cent.
13	2	0.004	0.1033	0.0895	115.0
14	2	0.004	0.1031	0.0895	115.0
15	2	0.003	0.0858	0.0720	119.0
16	2	0.003	0.0861	0.0720	119.0
17	2	0.004	0.1128	0.1949	117.0
18	2	0.004	0.1221	0.1949	128.5
19	2	0.004	0.1175	0.1044	117.3
20	2	0.004	0.1173	0.1044	118.7
21	1	0.03	0.0871	0.0632	138.2
22	1	0.03	0.0863	0.0632	137.0
23	1	0.03	0.0912	0.0713	127.9
24	1	0.03	0.0870	0.0713	122.0

Discussion of Results.—The high current efficiency observed made it appear probable that the aluminium was dissolving at the anode at a valence lower than three and was then reducing the water present, becoming again the trivalent aluminium and evolving hydrogen. This supposition was based on the behavior of aluminium as observed when it is made anode in sodium chloride solution; under these conditions hydrogen is evolved from the anode.[1]

To ascertain the character of the gases evolved from the anode of aluminium, experiments were performed with enclosed anode as was done in the case of magnesium and in an electrolytic cell of the same construction as has already been described.

The anodes were cut from aluminium foil and had the shape of a flat spoon. The diameter of the disc-shaped bowl of the spoon was 3.0 cm. and was something less than that of the coulometer tube forming the anode compartment, while the handle part was sufficiently narrow (0.5 cm.) and long to be thrust through the side arm of the tube. A disc-shaped anode was thus obtained which made possible a fairly uniform current density on its lower face when held in the tube horizontally. A rubber stopper closed the outer end of the side arm. The narrow portion of the

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[1] Turrentine, *J. Physic. Chem.*, 12, 448 (1908).

anode projected out of the side arm past the stopper, but it was sufficiently thin and flexible to admit of the stopper's being inserted firmly and in such a manner as to make an air-tight joint. The outer end was joined to the source of the electric current by means of a split connector. Two such cells were joined in series with each other and with a copper coulometer. The anodes were weighed before and after the electrolysis and their corrosion noted. The time duration of the experiment was 1 hr. The current strength was 0.21 amp. The entire lower face of the disc-shaped portion of the anode and about 1 cm. of the narrow portion, equaling a total area of about 7.5 cm^2., constituted the active surface of the anode. With a current of the strength mentioned, a current density was obtained of about 0.03 amp. per cm^2. The results obtained are given below in tabular form:

TABLE III.

Expt. No.	Vol. gas. Cc.	O_2. Cc.	O_2. Per cent.	H_2. Cc.	H_2. Per cent.	N_2. Cc.	N_2. Per cent.
21	18.0	1.7	9.4	0.5	2.5	15.8	88.1
22	18.6	1.7	9.1	0.7	3.7	17.2	87.2
23	17.0	1.0	5.8	..	..	..	..
24	18.0	0.9	5.0	0.2	1.1	16.9	95.9

These results show that the gas evolved from an aluminium anode in sodium trinitride solution is essentially nitrogen. Small amounts of oxygen were found invariably, the presence of which can scarcely be ascribed to experimental error. Likewise, traces of hydrogen were indicated, though the values obtained for hydrogen approached the limits of accuracy of the analytical method employed.

It is established that as far as the evolved gases are concerned, the action of this metal in sodium trinitride is not similar to that in sodium chloride solution. It is not easy, however, to account for the excessive anode efficiency of aluminium except by supposing the corrosion of aluminium at a valence lower than its normal valence.

The evolution of hydrogen from an aluminium anode in sodium chloride solution has been accounted for by the theory that the metal goes into solution electrochemically as uni-, or bivalent aluminium (more probably as the bivalent aluminium, thus carrying out its analogy with iron), which is unstable, and then reacts with water, evolving hydrogen. Such a reaction could be expressed by the equation:

$$6AlCl_2 + 6H_2O = 4AlCl_3 + 2Al(OH)_3 + 3H_2.$$

The rôle of aluminium as a "carrier" in chlorination processes likewise calls for the supposition of an unstable aluminous compound. Norden[1] produces evidence from mineralogical and other sources to substantiate the occurrence of such a form of aluminium. The evolution of nitrogen at the anode, instead of hydrogen, is explainable on the assumption that

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[1] *Z. Elektrochem.*, 6, 159 (1899–1900).

the hydrogen, or its equivalent in aluminous ions, is oxidized by the nitride ion.

This reaction would be strictly analogous to those already illustrated by equations under the discussion of the action of magnesium as anode in sodium trinitride solution. However, in the case of aluminium, the solutions in which the electrolyses had been performed were not analyzed for ammonia and hydrazine, so no new corroboration of the theory can be obtained from that source.

In Stirred Solution.—In the determination of the corrosion of aluminium in stirred solution four measurements were made. As only sheet aluminium anodes were available, the anode was not rotated as was done in the like experiment with magnesium; instead, the solution was stirred vigorously by means of glass rods, attached to the rotating axes of the rotating device already described. The size of the cells made it necessary to place the anodes against the walls of the cells. So, only one face of the anodes was active. The electrolysis was continued for 1 hr. with a current of 0.20 amp. This gave an average current density of 0.006 amp. per cm^2. Gas was evolved from the anode, but no precipitate was formed as in previous experiments.

On weighing the anodes only a slight and varying change of weight was observed; so slight was the change in weight that it was concluded that under the conditions observed in these experiments aluminium becomes passive in sodium trinitride solution.

An examination of the solution in which the corrosion of aluminium anodes had been conducted showed the presence of a soluble aluminium compound. Portions of this solution were evaporated to the point where crystallization appeared. The resulting crystals proved to be only sodium trinitride. The mother liquor was found to contain aluminium in a form from which it could be precipitated by acid as $Al(OH)_3$. Without further experimentation it was concluded that this compound was an aluminate of sodium, formed by the action of the free sodium hydroxide produced during the electrolysis on the aluminium hydroxide present. Curtius[1] observed that the Al^{+++} ion was precipitated as hydroxide by sodium trinitride. The only compound of aluminium that could be present, then, would be one of the type of an aluminate.

In the succeeding experiments, with the exception of those dealing with silver, the formation of a metallic deposit on the cathode may be attributed to the deposition of metallic ions from a compound of the type of an aluminate. This would probably form where the metallic hydroxides are soluble in sodium hydroxide. The latter was always present, through hydrolysis and electrolysis.

Zinc. Unstirred Solution.—The anodes employed were rectangular zinc

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[1] *Loc. cit.*

plates 5 × 10 cm. in dimension. In each case they were immersed to a depth of 7 cm., affording an area exposed to electrolytic action of about 45 cm^2. This includes one-third of the area of their obverse sides. The cathodes were similar plates situated in a parallel position. This should have afforded a uniform current density on the face of the anode. The results obtained are given in the following table:

TABLE IV.

Expt. No.	Time. Hrs.	Current density amps/cm^2.	Anode loss. Gram.	Theory. Gram.	Efficiency. Per cent.	Current. Amps.
29	2	0.003	0.5609	0.3212	174.5	0.15
30	2	0.003	0.6232	0.3212	191.1	0.15
31	2	0.002	0.4100	0.2553	160.5	0.10
32	2	0.002	0.4270	0.2553	167.2	0.10
33	1	0.004	0.5205	0.3348	150.9	0.20
34	1	0.004	0.5264	0.3348	152.6	0.20
35	1	0.004	0.6699	0.6348	183.6	0.25
36	1	0.004	0.7221	0.6348	197.9	0.25
39	55/60	0.04	0.4613	0.2695	171.1	0.28
40	55/60	0.04	0.4583	0.2695	170.5	0.28
41	40/60	0.04	0.3136	0.1841	170.3	0.28
42	40/60	0.04	0.3140	0.1841	170.5	0.28

In Expts. 29–36, inclusive, plate electrodes were employed. In the other four, the anodes were cylindrical sticks of zinc, about 0.5 cm. in diameter. In these four experiments the anodes were exposed to the electrolytic action for about 4 cm. of their length. Their position was such that a uniform current density could not be obtained. The figures for these experiments in the foregoing table, then, represent the mean current density. The theory was calculated on the basis Cu : Zn. There was an evolution of gas from the anode which would tend to show that the corrosion was not quantitative or that some electrode reaction was taking place whereby gas was evolved. The solution became clouded with a white precipitate of zinc hydroxide or of basic zinc trinitride.[1] Most of the precipitate adhered to the anode, forming thereon a thick crust. This was grayish-white in color. A qualitative examination of the anode precipitate revealed the presence of the N_3 radical therein. This would make it appear that this compound is the basic trinitride obtained by Curtius. The anode precipitate was washed repeatedly with distilled water; the wash water continued to give distinct tests for the N_3^- and the Zn^{++} ions, the former in neutral or slightly acid solutions with silver nitrate and the latter with ammonium sulfide. Also, when this precipitate was dissolved in dilute sulfuric acid, effervescence occurred. The evolved gas, by suitable tests, was found to be, in part at least, vapor of hydronitric acid. A precipitate likewise appeared at the cathode of a white gelatinous consistency, which was dislodged by the evolution of

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[1] Curtius, *Loc. cit.*

gas. A loosely adherent, gray-colored precipitate also formed there, which was taken to be metallic zinc.

In order to determin the character of the gases evolved from the anode, electrolyses were conducted with the anode enclosed in a coulometer tube. The apparatus employed was the same as that which was used in the similar experiment with magnesium anodes. A cylindrical, stick anode was thrust through the side-arm of the coulometer tube and was secured by a section of rubber tubing slipped over the end of the side-arm. Two such electrolyses were performed with an oxy-hydrogen gas coulometer in series. The coulometer was of the modified type[1] with adjustable electrodes and leveling bulb, and contained dilute sulfuric acid.

A current whose strength was 0.2–3 amp. was passed for a length of time sufficient to give a convenient volume of gas for analysis. As about 4 cm. of the electrodes were exposed, this current strength gave a minimum density at the anode of 0.03–4 amp. per cm^2. At the completion of the experiment, 42 cc. of gas had been evolved in the coulometer and 10 cc. and 11 cc., respectively, in the anode compartments of the other two cells. As the corrosion efficiency of the zinc in these experiments was not determined, these results are of no value except to show the relative amounts of the gases evolved.

The accumulated gases from the anode compartments were analyzed in the usual way for oxygen and hydrogen. There was no absorption in alkaline pyrogallol nor a loss in volume on combustion. The gas, then, was pure nitrogen.

Four other electrolyses were conducted with a copper coulometer in series. The anode gases were measured and analyzed and the anode corrosion efficiencies were noted. These are presented in Table V.

TABLE V.

Expt. No.	Anode loss.	Theory Zn.	Efficiency. Per cent.	Gas evolved. Cc.
37	0.3448	0.1841	...	44.8
38	0.3168	..	...	40.8
39	0.4613	0.2695	171.1	55.6
40	0.4583	0.2695	170.5	53.6
41	0.3136	0.1841	170.3	40.3
42	0.3140	0.1841	170.5	40.0

Discussion of Results.—These results show that zinc dissolves electrochemically in sodium trinitride solution more nearly as the univalent zinc than as the bivalent form. From analogy with the preceding metals, and from our knowledge of zinc compounds, where the zinc invariably occurs as the bivalent form, if zincous compounds form at the

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[1] Turrentine, *J. Physic. Chem.*, 13, 349 (1909); *Trans. Am. Electrochem. Soc.*, 15, 515 (1909).

anode they probably become at once zincic. This must be accompanied by a reduction. Applying to zinc the hypotheses advanced to account for the anomalous behavior of magnesium and aluminium, we are led to expect the formation of some reduction products of the nitride ion. If the nitrogen evolved at the anode came from the discharge of N_3^- ions, just as when in a sulfate solution, on incomplete corrosion, oxygen is evolved, then we should be able to calculate from the results set forth in Table V how much nitrogen should have been evolved. In Expt. 38 there was an observed anode loss of 0.4613 g. zinc. If there had been a quantitative corrosion as univalent zinc the anode loss would have been 0.5390 g. The deficiency on this basis was 0.0777 g. zinc. The N_3^- ions discharged should give an amount of nitrogen equivalent to this weight of zinc, which would be 0.052 g. N_2; at 27° and 740 mm. pressure (the conditions of temperature and pressure under which the measurements were made) this weight of nitrogen would occupy a volume of 47.2 cc. The observed volume was 55.6 cc.

The calculated value of 47.2 cc. represents the maximum amount of nitrogen that could be evolved through the discharge of the N_3^- ions. Furthermore, it is hardly to be supposed that there is a quantitative corrosion as the unstable univalent zinc. How much zinc dissolves as univalent and how much as bivalent is of course unknown and is indeterminate. As there is obtained experimentally a volume of nitrogen in excess of the maximum calculated, there must be some evolved by a secondary reaction taking place at the anode. Such a reaction has been illustrated in preceding paragraphs. Calculations were made to determin how much ammonia would have been formed from the reduction of hydronitric acid by the amount of univalent zinc produced in the various electrolyses with zinc anodes, computing all the zinc dissolved as univalent zinc. This amount was found to be 0.19 g. The solutions in which these electrolyses had been conducted were mixed and 100 cc. portions were taken for analysis for ammonia. The total volume was 700 cc. On the bases of the results obtained in two analyses, it was found that the total amount of ammonia present was equal to 0.13 g. All tests for hydrazine made on this solution with Fehling's solution gave negative results.

In Stirred Solution.—The anodes used in the experiments about to be described were cylindrical sticks of zinc. They were exposed to the electrolytic action for a depth of 6 cm. Being 0.5 cm. in diameter, they afforded an active area of about 9.5 cm^2. each. The anodes were rotated.

The electrolysis was continued for one hour with a current whose strength was 0.25 amp. This afforded a current density of 0.026 amp. per sq. cm. The anodes became encrusted with a coating of precipitate which was fairly adherent. Five cells were electrolyzed in series with a copper coulometer. On the cathode value of the latter the theoretical loss was 0.3381 g. The observed losses and efficiencies were as follows: (Expt. 43) 0.5994 g.; efficiency 177.3 per cent. (Expt. 44) 0.6200 g.; efficiency 183.3 per cent. (Expt. 45) 0.5888 g.; efficiency 174.2 per cent. (Expt. 46) 0.6004 g.; efficiency 177.6 per cent. (Expt. 47) 0.5750 g.; efficiency 170 per cent.

Iron. Unstirred Solution.—Rectangular sheet iron anodes 10 × 5 cm. were used in these corrosions. They were immersed to a depth of 7.5 cm. Cathodes similar to the anodes were placed in a parallel position and 3.5 cm. distant. The electrolyses were continued for a period of 2 hrs. with a current of 0.1–0.15 amp., affording an anode current density of 0.002–0.003 amp. per sq. cm.

In the beginning of the electrolyses the solutions became blood-red in color, due to the formation of ferric trinitride. However, as the experiments were continued, this color was superseded by the greenish color of impure ferrous hydroxide. Gas was evolved from the anode in every case. The cathode was coated with a greenish precipitate of, presumably, ferrous hydroxide. The anodes in two cases were covered with a uniform coating, firmly adhering, jet black in color. This turned dark red on drying in the air. The third anode on its removal from the solution was coated with a glossy, dark red coating.

On replacing an anode in the solution without first removing the coating just described, it was found that the iron had become passive.

The theoretical values were calculated on the basis of both bivalent and trivalent iron. These were found to be: 0.2743 g. as Fe^{++} and 0.1831 g. as Fe^{+++}. The observed values are: (Expt. 48) loss 0.1745 g.; efficiency 63.6 per cent. as Fe^{++}; 95.3 per cent. as Fe^{+++}. (Expt. 49) loss 0.1998 g.; efficiency 72.8 per cent. as Fe^{++}; 109.1 per cent. as Fe^{+++}. The theoretical values calculated are: 0.2743 g. as Fe^{++} and 0.1831 g. as Fe^{+++}. (Expt. 50) loss 0.0045 g.; efficiency 2.0 per cent. as Fe^{++}; 3.1 per cent. as Fe^{+++}; theory 0.2178 g. as Fe^{++}; 0.1449 g. as Fe^{+++}. The low value in Expt. 50 is explained on the supposition that the anode soon became passive. The deep red coating found on it was probably ferric oxide.

Stirred Solution.—Stick electrodes were employed whose cross section was a square, 0.6 cm. on an edge. One end was machined so that it could be inserted into the clutch on the rotating device. They were covered by the solution to a depth of 7 cm., thus exposing an area of 16.8 sq. cm. to the electrolytic action. The anodes were rotated. Five cells were joined in a series with each other and with a copper coulometer. The electrolyzing current, of 0.175 amp. strength, was passed for 1 hr. There was no change in the appearance of the solution nor in that of the anodes. The loss in weight observed in each case was (Expt. 51) 0.0001 g.; (Expt. 52) 0.0001 g.; (Expt. 53) 0.0002 g.; (Expt. 54) 0.0004 g.; (Expt. 55) 0.002 g. These results show that iron, like aluminium, becomes passive when made anode in a stirred solution of sodium trinitride.

Nickel. Unstirred Solution.—Sodium trinitride solution was electrolyzed between electrodes of sheet nickel, the dimensions of which were 5 × 10 cm. The electrodes were 3.5 cm. apart and were parallel and opposite to each other. The dimensions of the portion exposed to the electrolytic action was 5 cm. × 7 cm. Including one-third of the back of the electrodes, the active area would be about 47 sq. cm. A current of 0.1–0.15 amp. strength was passed for 2 hrs. This would afford a current density at the anode of 0.002–0.003 amp. per sq. cm. Gas was evolved from the anode. There was no alteration in the appearance of the anode nor in that of the solution. The cathode, however, became coated with a brilliant black deposit, resembling that which is obtained on a nickel cathode when a solution is electrolyzed which contains both nickel and arsenic. On the back of the cathode where the deposit was thin and of a varying thickness, iridescent effects were produced. The anode losses recorded were as follows: (Expt. 56) 0.0050 g.; efficiency 2.0 per cent. (Expt. 57) 0.0045 g.; theory on basis

Cu: Ni 0.2928 g. (Expt. 58) 0.0198 g.; efficiency 8 per cent. (Expt. 59) 0.0016 g.; theory 0.2348 g.

These figures show that nickel anodes in sodium trinitride, as in numerous other solutions, become passive. To see if a change in temperature could decrease in any degree the passivity of the nickel anode, a series of corrosions were run in hot NaN_3 solution. The solution was kept at its boiling point during the experiments. The current employed gave a density at the anode of about twice that which obtained in the preceding experiments with nickel. The time was 1 hr. The anode losses were: (Expt. 60) 0.0003 g. and (Expt. 61) 0.0074 g.; theory, 0.4055 g. These figures indicate that the passivity of the nickel is even more marked in hot than in cold solution, and signally fail to uphold the analogy in this particular between the nitride and chloride ions.

In Stirred Solution.—The nickel anodes employed in the five experiments here described were cylindrical in shape and were 0.5 cm. in diameter. They were immersed to a depth of 6 cm., thus exposing to the electrolytic action of the current an area of about 10 sq. cm. Six cells, together with a copper coulometer, were joined in series. The anodes were rotated. The electrolysis was continued for an hour with a current whose strength was 0.225 amp. The current density at the anode was 0.02 amp. per sq. cm. There was no precipitate produced in the solution nor was there an apparent alteration in the anode. The anode losses recorded were: (Expt. 62) 0.0006 g.; (Expt. 63) 0.0006 g.; (Expt. 64) 0.0010 g.; (Expt. 65) 0.0004 g.; (Expt. 66) 0.0006 g.; theory 0.2537 g.

Tin. Unstirred Solution.—The anodes employed in Expts. 67–72, inclusive, were made from block-tin sheets. They were 5 cm. wide and extended into the solution to a depth of 9 cm. The backs of the anodes touched the sides of the beaker, so in computing current density only their faces were considered. The active area, then, was 45 sq. cm. Those used in Expts. 73 and 74 were rectangular strips of block tin 0.5 × 1 cm. in cross section and were immersed to a depth of 8 cm. As the cathode was 3.2 cm. distant from the anode, and the latter was about 2 cm. from the cell walls, it is probable that the current density was about the same on all faces. The active area, then, was about 25 sq. cm. In the first six experiments the current density was approximately 0.0006 amp. per cm^2.; in the last two, it was 0.012 amp. per sq. cm. The cathodes in each case were copper plates of about 35 sq. cm. active area. The corrosions were prolonged for 1 hr. with a current whose strength was 0.3 amp. There was a constant evolution of gas, presumably nitrogen, from the anode. The anodes acquired a black coating, partially removable with a wet cloth, which was iridescent on the black where it was thin and of a variable thickness. A gray deposit, but slightly adherent, resembling metallic tin, formed on the cathode. The results obtained were as follows: (Expt. 67) anode loss 0.0863 g.; efficiency 13 per cent. (Expt. 68) anode loss 0.0954 g.; efficiency 14.3 per cent.; theory on basis Cu: Sn 0.6647 g. (Expt. 69) anode loss 0.0241 g.; efficiency 29 per cent. (Expt. 70) anode loss 0.0536 g.; efficiency 6.5 per cent.; theory 0.8319 g. (Expt. 71) anode loss 0.0471 g.; efficiency 5.7 per cent. (Expt. 72) anode loss 0.0298 g.; efficiency 3.6 per cent.; theory 0.8243 g. (Expt. 73) anode loss 0.0360 g.; efficiency 5.4 per cent.; theory 0.6647 g. (Expt. 74) anode loss 0.0910 g.; efficiency 10.9 per cent.; theory 0.8219 g.

The anode deposit was not analyzed. While it may have been a nitrogen compound of tin, at first it was regarded rather as a film of finely divided tin, produced through the slight disintegration of the anode.

Stirred Solution.—Cylindrical anodes of block tin were employed whose average diameter was about 0.5 cm. Being immersed in the electrolytic bath to a depth of 7 cm., they afforded an active surface of 11 sq. cm. The anodes were rotated. Five cells were electrolyzed in series with each other and with a copper coulometer. A current of 0.15–2 amp. was passed for 1 hr. The current density at the anode was 0.013–8 amp. per sq. cm.

In every instance the anodes were covered with a black deposit as was observed in the electrolyses in unstirred solution. The losses at the anode were comparatively slight, in only one instance giving an efficiency as high as 5.7 per cent. (Expt. 77). The losses observed were as follows: (Expt. 75) 0.0078 g.; (Expt. 77) 0.0236 g.; (Expt. 78) 0.0126 g.; theory 0.4095 g. In Expt. 76 there was a gain in weight at the anode of 0.0313 g. and in Expt. 79 of 0.0050 g. The gain in weight instead of a loss observed in two experiments would indicate that the anode deposit was a nitrogen compound of tin instead of a coating of finely divided metal.

Lead. Unstirred Solution.—Two anodes of sheet lead were exposed to the electrolytic action of the electric current for 2 hrs. They were 3 cm. in width and were immersed to a depth of 7 cm. This gave an active surface, including one-third of the obverse side, of about 28 sq. cm. The cathode was a copper plate 3.2 cm. distant and in a parallel position. The strength of the current employed was 0.1–0.15 amp. and gave a current density at the anode of 0.0045 amp. per sq. cm. Gas was evolved at the anode. While there was no precipitate found in the electrolytic bath, there was an accumulation in the bottom of the cell of a solution of a distinct yellow tint and evidently of a greater specific gravity than the rest of the bath.

At the end of the experiments a loosely adherent deposit, of a reddish brown color, had formed on the anodes. This resembled lead peroxide. On examination, however, it was found to dissolve readily in dilute nitric acid, with effervescence, and in sulfuric acid more slowly, also with effervescence. These facts would show that this compound was not an oxide but rather a trinitride, or other nitride, of lead.

The cathode became covered with a thin, but a uniform and adherent deposit of lead (by inspection).

The anode losses observed were slight; they were: (Expt. 80) 0.0142 g. (1.3 per cent. efficiency); theory on basis Cu: Pb 1.068 g. (Expt. 81) 0.0429 g. (5.07 per cent. efficiency); theory 0.8452 g.

Stirred Solution.—The anodes here employed were rectangular pieces of sheet lead 0.2 cm. in thickness; one end was cut down to fit the clutches whereby they were attached to the rotator. They were 0.7 cm. in width and extended into the solution to a depth of 6.5 cm. This afforded an active area of 11.5 sq. cm.

The anodes were rotated. The electrolyzing current had a strength of 0.22 amp. The current density at the anode, then, was about 0.02 amp. per sq. cm. The duration of time was 1 hr.

As in the previous experiments with lead, the anodes were lightly coated with the reddish brown deposit. In every number but one of this series of experiments there was a gain in weight of the anode, instead of a loss. The results observed were: (Expt. 82) anode gain 0.0012 g.; (Expt. 83) anode gain 0.0016 g.; (Expt. 84) anode gain 0.0004 g.; (Expt. 85) 0.0004 g.; (Expt. 86) anode loss 0.0001 g.; theoretical loss on basis Cu: Pb 0.922 g.

These results uphold our supposition that the anode deposit is a nitrogen compound of lead, and tend to show that, with rotating anode, there is a deposition of nitrogen on the anode, probably as the nitride ion in combination with lead, instead of a solution of lead.

Cadmium. Unstirred Solution.—Cadmium anodes were constructed of rectangular strips of metal whose cross section was 1 × 0.5 cm. For a depth of 8 cm. they were covered by the electrolytic bath, thus exposing an active area of 25 sq. cm. The shape of the anodes and their position relative to the cathode and the cell walls make it probable that the current density at the anode was fairly uniform throughout the exposed surface. With a current of 0.3 amp. in strength, the anode current density was about 0.012 amp. per sq. cm. For cathode, a copper plate was employed. The electrolysis was continued for 1 hr.

There was a vigorous evolution of gas from the anode. A voluminous, white precipitate formed which, without analysis, was taken to be cadmium hydroxide. Curtius has prepared the normal trinitride of cadmium, soluble in water. A subsequent examination of the solution used in the electrolysis showed the absence of the Cd^{++} ion, from which it must be concluded that the cadmium dissolved from the anode had been precipitated quantitatively by the sodium hydroxide formed at the cathode. The anodes when removed from the cell were quite free from adhering precipitates and revealed a striking crystallin structure, invisible before their corrosion.

The observed losses and anode efficiencies were: (Expt. 87) 0.6467 g.; theory on basis Cu : Cd 0.6611 g.; efficiency 97.8 per cent. (Expt. 88) 0.8008 g.; theory 0.7753 g.; efficiency 105.2 per cent. (Expt. 89) 0.7989 g.; theory 0.7776 g.; efficiency 102.7 per cent.

It is surprizing that, with an efficiency of 100 per cent. at the anode, there should be in addition a vigorous evolution of gas. This was observed also where the corrosion exceeded 100 per cent. While a slight excess over 100 per cent. at the anode could be overlooked, or laid to faulty experimentation, the excessive anode efficiency and the simultaneous evolution of gas make it necessary to apply to this anomaly the same explanation that has been applied to the case of magnesium, aluminium and zinc, where the same phenomena are observed. In accordance with this theory, then, cadmium corrodes as both cadmous and cadmic trinitrides. The former is very probably unstable. In breaking down to the bivalent form it may react with water and evolve hydrogen, or it may act as a reducing agent toward the nitride ion. Morse and Jones,[1] by heating with metallic cadmium the respective halides of cadmium, prepared a substance which had the composition typified by the formula Cd_4Cl_7, probably a mixture of cadmous and cadmic compounds. This exhibited strong reducing properties, reducing Hg^{++} to Hg^{+} and metallic mercury; a reaction with water produced well defined cadmous hydroxide.

This element, occupying a position in the periodic system between mercury, which forms two series of stable salts, and zinc, which forms only one, exhibits the transitional properties of the two. We should expect to find in zinc, and, perhaps, even in magnesium, latent tendencies to exhibit two valencies.

The examination of the anode gases and of the electrolytic bath for reduction products of hydronitric acid was neglected.

Stirred Solution.—The anodes used in these experiments were similar in shape to those employed in the like experiments with tin. Their area immersed in the sodium trinitride solution was 10 cm^2. The anodes were rotated. Five cells, in series with a copper coulometer, were electrolyzed for 1 hr. with a current 0.25 amp. in strength. The current density at the anode was 0.025 amp. per sq. cm.

The solution became filled as before with a voluminous white precipitate. The anodes again were etched so as to bring out in a most striking manner their crystallin structure.

The anode losses and efficiencies were: (Expt. 90) 0.5380 g.; efficiency 102.1 per cent. (Expt. 91) 0.5397 g.; efficiency 102.4 per cent. (Expt. 92) 0.5440 g.; efficiency 103.2 per cent. (Expt. 93) 0.5470 g.; efficiency 103.8 per cent. (Expt. 94) 0.5455 g.; efficiency 103.5 per cent.; theory 0.5269 g.

Copper. Unstirred Solution.—In these experiments rectangular copper plates served

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[1] *Am. Chem. J.*, 12, 488 (1890).

as anodes. The area of the portion submerged in the sodium trinitride solution was 30–35 sq. cm. on a face. The cathodes were similar in shape and size to the anodes and were similarly placed. The electrolysis which was continued for 2 hrs. was effected by a current of 0.1–0.15 amp. The current density computed on the basis of the area of the face, plus one-third of the back, of the anode was about 0.002 amp. per sq. cm.

In the beginning of each experiment the corrosion seemed to be quantitative, as there was no visible evolution of gas from the anode. A voluminous yellow precipitate formed. This would indicate the presence of cuprous compounds, yielding cuprous hydroxide, a fact which can not be compromized with the results obtained by Curtius showing that in the interaction of copper and hydronitric acid only the difficultly soluble, brown-yellow, cupric trinitride is obtained.[1] Early in the electrolysis there invariably appeared on the anode a closely-adhering, black precipitate, and simultaneously an evolution of gas began. From this point the corrosion was no longer quantitative. For this reason the results obtained are of little interest. A subsequent examination of the black precipitate showed that it could be dissolved from the anode readily in dilute nitric acid, with effervescence, and in dilute hydrochloric acid. When dissolved in the latter, the odor of hydronitric acid was observed (CuN_6?). Attempts to remove the precipitate mechanically from the anode, the latter being held under cold running water the while, resulted in an explosion which was accompanied by a deafening report, and was of sufficient violence to inflict injuries on the operator. Curtius regards the cupric trinitride as one of the most unstable of the trinitrides. He remarks that it is explosive when incompletely dehydrated, but does not record that it may explode also when immersed in water. No efforts were made to identify this black compound.

The anode losses and efficiencies observed were: (Expt. 95) 0.1534 g.; efficiency 39.8 per cent. (Expt. 96) 0.1334 g.; efficiency 34.3 per cent.; theory 0.3879 g. (Expt. 97) 0.0854 g.; efficiency 27.7 per cent. (Expt. 98) 0.0052 g.; efficiency 1.6 per cent. (Expt. 99) explosion. (Expt. 100) 0.1585 g.; efficiency 64.4 per cent.; theory 0.2475 g.

The electrolytic bath, on the subsidence of the precipitates, was of a yellow color. On standing it assumed a dark brown color along its surface where it was in contact with the air.

Stirred Solution.—Cylindrical anodes were employed in these experiments. They were immersed to such a depth that an area of about 12 sq. cm. was exposed to the electrolytic action. The anodes were rotated.

Five cells were connected in series and a current of 0.2 amp. was passed (Expt. 101–105 inclusive). The current density at the anode was 0.016 amp. per sq. cm.

A precipitate, of a distinct blue color, formed in every case. This is exactly what one would expect under these conditions, as, even if a cuprous compound were formed, it would be oxidized to the cupric form by the oxygen of the air with which the stirring of the solution intimately mixed it. A black precipitate adhering to the anode again appeared. After the electrolysis had continued for 15 minutes an explosion occurred in one cell, shattering the beaker containing the solution. On continuing the electrolysis again, by closing the appropriate switch and thus throwing out of circuit the demolished cell, after 5 minutes a second explosion occurred. On continuing the electrolysis further an explosion occurred about every 5 minutes until all the cells had been demolished. The jarring caused by the rotating device was sufficient to cause the compound of copper to explode, even though the compound was bathed in water solution.

Silver.—Having in mind the analogy that has been referred to as existing between the nitride and halogen ions, and also the insolubility of the

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[1] The reaction between copper and hydronitric acid is now being studied in the Wesleyan laboratory and will be reported in an early communication.

silver salt of hydronitric acid, it was deemed possible that the N_3^- ion could be deposited electrochemically on a silver anode in a manner similar to that in which Smith and his collaborators[1] have deposited those other ions quantitatively which form insoluble salts with silver.

The analogy between the N_3^- and, for example, the Cl^- ions, is based on the following considerations: (1) The similarity in properties between the silver and the mercurous salts of the N_3^- and the Cl^- ions. (2) Curtius[2] has compared the solubilities of the halogen salts of the metals of the alkali, and of the alkaline earth group with those of the trinitrides of these elements. In the series, Na, K, Rb, Cs, NH_3 and Tl, the comparison places the N_3^- ion between Cl^- and Br^-, and in the series Ba, Ca, Sr and Li, between Cl^- and F^-. (3) The *ionic* weight of the N_3^- ion falls between those of the F^- and Cl^- ions, and more nearly approaches that of the latter. (4) The relative position of nitrogen and the halogens in the periodic table would lead one to conclude that an anion in which nitrogen existed alone would possess properties analogous to those of the halogen ions.[3] Curtius[4] prepared carbonyl trinitride, $CO(N_3)_2$, an analog of carbonyl chloride.

The Precipitation of the Nitride Ion on a Silver Anode.—The anode used in these experiments was a platinum electrode, silver-plated. It was disc-shaped, perforated, and was supported by a stem of platinum wire, attached to the center of the disc. By means of the stem, the anode was fastened to the vertical shaft of a small electric motor. The area of the anode, counting both faces, was about 20 sq. cm. The cathode was a thin platinum wire immersed in the solution to a depth of about 3 cm.

Accurately measured volumes of a standard solution of sodium trinitride (1 cc. = 0.0004 g. NaN_3) were diluted to a convenient volume, (about 150 cc.) with distilled water. The amounts of sodium trinitride taken were sufficient to give a convenient weight of silver trinitride.

With anode rotating, a current of about 0.02 amp. was passed until the precipitate formed on the anode began to darken. The anode was then removed, and was washed, dried and weighed.

In every instance the increase in weight at the anode was slight (0.7–2.0 mg.) below the theoretical increase calculated from the amount of N_3^- ion present. The anode precipitate was not very adherent, but was dislodged to a slight extent and caused a cloudiness in the solution. When the anode was immersed for an instant in dilute (*N*) nitric acid, the precipitate dissolved therefrom with effervescence and the loss in weight

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[1] Hildebrand, THIS JOURNAL, 39, 447; E. F. Smith, "Electro-Analysis," 4th ed., p. 297, *et seq.*

[2] Curtius and Rissom, *J. prakt. Chem.*, 58, 306.

[3] Cf. also Dennis and Browne, THIS JOURNAL, 26, 607 (1904); Dennstedt and Göhlich, *Chem.-Ztg.*, 21, 876.

[4] *Ber.*, 27, 2684.

was in some cases as much as 0.023 g. This fact is mentioned to show that while the actual gain in weight at the anode was slight, the amount of silver trinitride formed there was considerable. This could only mean that some silver was removed from the anode during the electrolysis. Another test applied to this precipitate showed it to be a trinitride. An examination of the solution showed that traces of N_3^- ions were still present. As was anticipated, the OH^- ion had supplanted the N_3^- ion on the impoverishment of the latter and, by causing oxygen to be evolved at the anode, had oxidized the silver to the oxide, as shown by the darkening in color of the anode deposit. This complication was avoidable by the use of the Hildebrand cell[1] or by substitution a solution of hydronitric acid for that of the sodium salt. The latter was preferred. Accordingly, then, a very dilute solution of hydronitric acid[2] was electrolyzed in the manner just described.

In these experiments a dark gray precipitate was observed on the needle-shaped cathode. A microchemical examination of this substance showed it to be *metallic silver*. The solution was rendered cloudy by the presence of a precipitate. This latter was filtered out; on examination, it was found to be a mixture of silver trinitride and metallic silver.

In one experiment where the motor stopped and the anode became stationary, the cathode deposit "treed" until it came into contact with the anode. Dilute solutions, it will be remembered, favor the phenomenon of "treeing." The hydronitric acid invariably was found to be decomposed completely by the end of the second half hour of electrolysis. On discovering the probable presence of a soluble compound of silver, as was strongly indicated by the formation of a cathode deposit of silver, attempts to precipitate the N_3^- ions quantitatively on a silver anode were abandoned until a time when this phenomenon could be explained and avoided. Instead, corrosions were determined as with previous metals.

Corrosion of Silver Anodes in Hydronitric Acid Solution.—The silver anodes were strips of silver foil, 1.3 cm. in width. They projected into the solution to a depth of 6.0 cm., affording an active surface of about 8 sq. cm., on a face. The anode was suspended against the sides of the beaker. Only the face, then, was exposed to the action of the current. The cathode was the silver-plated, rotating, platinum electrode used in the previous experiments. This was rotated and the solution was stirred thereby. The electrolytic bath was a very dilute solution of hydronitric acid (1 cc. 0.0003 g. NH_3, approx.).

The current in the beginning of Expts. 106 and 107 was 0.1 amp. in strength, but as the electrolysis continued, and the concentration of the hydronitric acid decreased, the current diminished. The anode density was about 0.016 amp. per sq. cm. In Expts. 108–111, inclusive, the current strength varied between 0.045 and 0.015 amp.

Efficiencies were based on values obtained from a copper coulometer electrolyzed in series with the test cell.

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[1] Hildebrand, *Loc. cit.*

[2] The exact strength of this solution electrolyzed is not known as only the amount of the hydronitric acid present was made note of, and not the concentration.

A slimy white precipitate of silver trinitride formed on the anode and was dislodged by the agitation of the electrolytic bath. This disclosed a dark gray precipitate beneath of a different consistency, which was more firmly adherent to the anode but which could be removed on gently rubbing.

In every instance there was a deposit on the cathode. In preparing the cathode to be weighed, however, most of this precipitate was unavoidably removed. As the cathode gains recorded, for that reason, do not show the weight of the deposit on the cathode, they will be omitted here.

The anode losses and efficiencies observed are given in Table VI.

TABLE VI.

Expt. No.	Time duration. Min.	Anode loss. Gram.	Theory. Gram.	Efficiency. Per cent.
106	..	0.0307	0.0282	108.8
107	..	0.0460	0.0363	127.7
108	67	0.0479	0.0440	108.8
109	30	0.0380	0.0306	124.5
110	30	0.0745	0.0764	95.5
111	30	0.0512	0.0420	121.5

The hypothesis of an occurrence of silver of a valence lower than that normally displayed, offered in explanation of the excessive anode efficiency observed here, has abundant substantiation from the work of others with this element. The occurrence of the sub-halogen compounds of silver has been established by photochemistry. From a solution of silver fluoride, silver subfluoride, or argentous fluoride, is deposited on the anode. Also, in a concentrated solution of silver fluoride, metallic silver forms argentous fluoride. In the presence of an excess of water, the argentous fluoride breaks down again to the argentic, with the precipitation of metallic silver and the evolution of heat.[1] The occurrence of an oxide of silver where the silver possesses a valence lower than one is much mooted. Conspicuous among those who have published results in support of its occurrence are Wöhler,[2] Von Bibra,[3] Cavillier,[4] and Guntz,[5] while its occurrence is attacked by a number of investigators, conspicuous among whom are Bailey and Fowler,[6] Newberry,[7] and Lewis.[8]

The case of silver, however, is markedly different from those studied which lie at the other end of the electrochemical series. While in the case of magnesium, zinc and aluminium, from electrochemical considerations we should expect a strong reduction when the metal undergoes the change from a lower to a higher valence, in that of silver we should look for

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[1] Guntz, *Compt. rend.*, 110, 1337 (1890).

[2] *Ann.*, 30, 1 (1839).

[3] *J. prakt. Chem.*, 120, 39 (1875).

[4] *J. pharm.*, 1830.

[5] *Compt. rend.*, 138, 996 (1899).

[6] *J. Chem. Soc.*, 51, 416 (1887).

[7] *Am. Chem. J.*, 8, 196 (1886).

[8] THIS JOURNAL, 28, 139 (1906).

merely the precipitation of metallic silver, unless, indeed, there were some substance present easily reduced. The equation expressing such a reaction could be written: $Ag_2N_3 = AgN_3 + Ag$.

The presence of the dark gray precipitate observed under the precipitate of silver trinitride, in close proximity to the metal of the anode and markedly distinct from the silver trinitride, suggests the possibility of this being the metallic silver produced by the breaking down of the hypothetical subtrinitride. This finely divided precipitate would be acted on electrochemically and converted into trinitride again, so that we should always have a deposit of silver trinitride covering the deposit of silver.

The presence of metallic silver in the precipitate filtered from the solution was explicable as coming either from the supposed anodic formation thereof, or (more probably) from the pulverulent cathode deposit. The presence of a soluble compound of silver in a solution containing the N_3^- ion can be explained in several ways, but the explanations are so completely without substantiation by experimentation that they are withheld until the phenomenon can be investigated further.

In Sodium Trinitride Solution.—When the two per cent. sodium trinitride solution was substituted for the dilute solution of hydronitric acid, the anode loss was very much less marked. The same apparatus as just described was employed. The electrolyzing current had a strength of 0.15–9 amp. At the end of approximately one-half hour runs, the loss was respectively 0.0013 g. and 0.0003 g.; theory, 0.03 g. These results indicate that the unexpected behavior of silver as anode is a function of very dilute solutions.

Summary.

The results presented in this paper may be summarized as follows:

1. Among the ten metals studied, magnesium, aluminium, zinc and cadmium, in 3 per cent. NaN_3 solution, and silver in very dilute hydronitric acid solution, give anode efficiencies exceeding 100 per cent. of the corrosion predicted by Faraday's law.

2. To account for the excessive anode efficiency the assumption is made that these metals dissolve electrochemically, partially at least, at a valence lower than that usually ascribed to them, forming compounds which are readily oxidized.

3. In support of this hypothesis, reduction products of the N_3^- ion, such as ammonia, hydrazine and nitrogen, are formed in the anode region, indicating the production there of some reducing agent.

4. A new reduction of hydronitric acid is supposed which involves the formation of free nitrogen in addition to ammonia, or ammonia and hydrazine, as the reduction products.

5. The metals, nickel and lead, become passive in unstirred solution, while aluminium, iron, nickel, tin, lead and silver become passive, or practically so, in stirred solution.

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