ACTION OF AMMONIUM PERSULPHATE ON METALS

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The analogy between chemical and electrochemical reactions has been studied in considerable detail in this[1] and other laboratories, and many data have been collected. Many reactions commonly considered and spoken of as purely chemical are in reality electrochemical. Still there is no sharp line of demarcation. Frequently, reactions are induced by galvanic action, set up by bringing together in a corrosive medium and in the presence of the compound with which a certain reaction is desired, two metals of differing electro-properties so that an electric couple is formed. The zinc-copper couple of Gladstone and Tribe may be cited as an example of such a case. This is producing chemical action by a concealed, electrochemical reaction. We can go a step farther and induce an electrochemical phenomenon in a purely chemical way—we can liberate ions which generally are set free only by electrolysis.[2]

When sulphate ions, SO_4, are discharged electrolytically against a metallic anode they do one of three things—in cases where the anode is soluble they dissolve the anode quantitatively forming sulphates; if the anode is insoluble and the current density low oxygen is set free; or if the current density is high and also the concentration of sulphate the sulphate ions combine to form the divalent, persulphate ion, S_2O_8.

If we decompose the persulphate in the presence of an insoluble anode (or in the absence of any anode, which amounts to the same thing) we should expect the evolution of oxygen, and that we get. This may be shown by mixing, in a gas evolution bottle, concentrated sulphuric acid with a saturated solution of ammonium persulphate, containing an excess of persulphate crystals and a small amount of man-

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[1] Bancroft: Trans. Am. Electrochem. Soc., 8, 33 (1905).

[2] Bancroft: Ibid., 8, 43 (1905).

ganous sulphate to act as catalytic agent and accelerate the reaction. An active evolution of oxygen ensues, a fact which may be demonstrated by bringing a glowing splint to the opening of the bottle. Since the addition of the sulphuric acid to the solution causes such a rise in temperature, a thin glass bottle is the safest to use.

Again, if this liberation of sulphate ions is analogous to that produced by the electrolysis of a sulphate solution we should expect a soluble metal to be attacked, thus acting as an anode, and quantitative solution to take place.

To test this point a series of determinations were made in this laboratory of the solubility of pure, metallic copper, as the ideal anode, in a dilute, aqueous solution of ammonium persulphate, the consumption of persulphate being in each case also determined. The object of this paper is to present the results of these determinations. The method of procedure was simple and was as follows: A copper strip was bent into a spiral so that a large surface could be exposed in a small space. After having been cleaned and weighed it was placed in a beaker containing a solution of ammonium persulphate (10 cc of a standard solution .containing 0.0829 gram per cubic centimeter being added to 100 cc of water). This solution was stirred vigorously for an hour by a glass stirring rod attached to the axis of a small "Ajax" motor. At the end of the hour the strip was removed, washed, dried and weighed, and the loss in weight was noted. To the solution was then added a weighed amount of ferrous ammonium sulphate, 10 cc of concentrated sulphuric acid and 100 cc of boiling water.[1] It was then titrated rapidly with standard $KMnO_4$ solution. The excess of ferrous iron was calculated. Subtracting this value from the total iron added, gave the amount employed in reducing the unused persulphate. This in its turn, subtracted from the total amount of persulphate, gave the weight of that which had reacted with the copper. From this last value was calculated the equivalent weight of

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[1] Friend: Jour. Chem. Soc., **85**, 1533 (1904).

copper. A comparison was then made between the calculated and observed values. The following table gives the data on copper:

	Total per-sulphate	Excess per-sulphate	Persulphate used	Cu. equiv.	Actual loss
I	0.8293	0.0990	0.730	0.2035	0.2050
2	0.8293	0.0258	0.8035	0.2240	0.2279
3	0.8293	0.0477	0.7817	0.2179	0.2185

The amount of persulphate which was not employed in dissolving the copper is indicated in the table by "excess" per-sulphate. The amount reduced by the copper is recorded under the head, "Persulphate Used." This weight of copper dissolved is equivalent to the action of a current of about 0.18 ampere for the same length of time.

It is seen that a varying excess of copper over that called for by the calculation is recorded. This excess loss could not be attributed to error in the analytical work as all deter-minations of persulphate in the standardization of solutions were easily duplicated. The possibility of the solubility of copper in $(NH_4)_2SO_4$ in the presence of oxygen being sug-gested, a blank run with copper in neutral ammonium sul-phate was made, with the result that it was seen that an average of 0.0025 gram was dissolved per hour in the ammo-nium sulfate. This would bring the results for copper easily within the limits of experimental error. The addition of ammonium hydroxide to the ammonium persulphate, it may be remarked, accelerates the rate of solution of the copper.

Sulphate ions discharged electrolytically against a nickel anode normally dissolve nickel but slightly. Instead, oxygen is evolved. The presence of chlorides in the solution, it has been shown, causes corrosion and the formation of black nickelic oxide. Nickel plates in ammonium persulphate, on the other hand, do dissolve to the sulphate. The results of two typical runs are given in the subjoined table:

	Total per-sulphate	Excess per-sulphate	Persulphate used	Ni equiv.	Actual loss
1	0.8293	0.2419	0.5874	0.1510	0.1326
2	0.8293	0.3510	0.4783	0.1230	0.1047

It will be observed that the solution of the nickel in the persulphate is not quite quantitative, there being a difference of about 13 percent between the actual loss due to the corrosion and the calculated nickel equivalent of the reduced per-sulphate. A slight evolution of oxygen may have occurred, but was not noticed. The nickel salt produced by the corrosion may act catalytically, as does manganese sulphate, to accelerate the decomposition of the persulphate. However, this point was not investigated, but attention was turned rather to the determination of the cause of the surprisingly large solubility of the nickel in the ammonium persulphate. Chlorides were sought for as a possible cause, but were found to be absent. As passivity of an anode is generally due to the formation on its surface of films of oxides or hydroxides, and as nickel hydroxide is known to be soluble in ammonium sulphate it was deemed possible that the activity of the nickel anode in the persulphate was due to the presence of ammonium sulphate which dissolved the film of oxide that produced the passivity. Accordingly, to eliminate the ammonium salts the solubility of nickel in sodium persulphate was determined, under conditions of temperature and concentration of solution similar to those which obtained in the like experiment with ammonium persulphate. The slight loss in weight of 0.0005 gram from a surface of about 20 sq. cm. was detected after an hour's stirring. This is in agreement with the electrolytic corrosion of nickel by sulphates, the presence of ammonium salts acting here as they do in the electrolysis to render the anode active—hence the use of the double sulphate of nickel and ammonium in the electrolytic purification and deposition of nickel.

Nickel, like copper, shows a slight solubility in neutral ammonium sulphate, 10–20 mg dissolving in an hour from an exposed surface of 20 sq cm.

Cadmium

Cadmium, it was found, dissolves readily in ammonium persulphate without apparent evolution of gas. The calculated and observed values, however, do not agree. As the error gives the excess to the calculated rather than to the observed value it cannot be explained as was that in the case of the copper, by the solubility of the metal in ammonium sulphate. The source of this discrepancy was not investigated.

Aluminum

Aluminum as anode in the electrolysis of sulphates is but slightly corroded, due to the oxide films and consequent passivity. Furthermore, it tends to intercept the electric current by preventing the discharge of the anions. This phenomenon is made use of in the aluminum current rectifiers. In ammonium persulphate solution only slight corrosion of the aluminum occurs, about 20 mg in one hour from a surface of 40 cm^2 exposed to corrosion; no oxygen is evolved. The analogy then between the corrosion of aluminum in persulphate solution and as anode in sulphate solution seems to be complete.

Iron

Iron anodes are dissolved by sulphate ions, at low current densities, quantitative solution taking place. The valence assumed by the dissolved iron is that of the ferrous condition. In a solution of ammonium sulphate it reacts with the alkaline solution from the cathode region and precipitates as the slightly oxidized, green, ferrous hydroxide. At higher current densities, the rapid corrosion of the iron being prevented, oxygen is set free.

Ammonium persulphate acts on iron similarly and dissolves it to ferrous sulphate, thus upholding our analogy. The excess of ammonium persulphate reacts with the ferrous sulphate and oxidizes it, but only partially, to the ferric state. This is clearly shown by adding to the solution a known excess of ferrous ammonium sulphate and after following the prescribed procedure, titrating with perman-

ganate. The presence of an amount of ferrous iron in excess
of that added is indicated by the titration. The amount of
the excess depends on the extent of the corrosion and on the
temperature. In the case of our own experiments this con-
dition was always shown, in one instance the ferrous iron in
the solution in excess of that added to reduce the persulphate
being equivalent to 0.80 gram of ferrous ammonium sulphate.
The ferric sulphate formed readily hydrolyzes, precipitating
ferric hydroxide. There is also a free evolution of gas which
is not absorbed by alkaline pyrogallol and is also combustible
in air. The origin of this gas must be either (1) from hydrogen
set free by the action of acid in the solution on the iron, or
(2) from hydrogen dissolved in the iron,[1] (3) from the decom-
position of carbides within the iron, evolving gaseous hydro-
carbons, or (4) the breaking down of ferrous sulphate to ferric
sulphate with the liberation of hydrogen, in a manner analo-
gous to the decomposition of chromous salts.

The first explanation seemed quite improbable as abun-
dant ferric hydroxide formed in the solution, indicating a
practically neutral solution in spite of a slight acid reaction
to litmus. Furthermore, a piece of iron was allowed to stand
without stirring in a solution of ammonium persulphate made
alkaline with ammonia; the iron became covered with a
deposit of ferric hydroxide. The evolution of gas was still
noted. This made it seem extremely improbable that the
liberation of gas was due to an acid solution.

If the gas was hydrogen dissolved in the iron then the
same volume should be obtained on making the iron anode in
ammonium sulphate. Accordingly, an iron anode thrust
into an inverted burette with a parchment diaphragm sur-
rounding the burette to prevent the diffusion of the cathode
gases into the anode compartment, was dissolved by electrol-
ysis in a neutral, 1 percent ammonium sulphate solution. A
current density was used which would produce a slight evolu-
tion of oxygen at the anode. The cathode was of platinum.

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[1] Burgess: Trans. Am. Electrochem. Soc., **9**, 197 (1906).

The gases evolved from the anode were collected in the burette and withdrawn for analysis. The results of four such runs are given in the following table:

	Total volume cc	Oxygen	Hydrogen
1	18.0	12.2	5.8
2	32.5	26.2	6.3
3	16.0	12.6	3.4
4	18.0	13.0	5.0

More iron was dissolved in these experiments than was in the corrosion with ammonium persulphate, yet a smaller volume of hydrogen was obtained, so this explanation of the source of all the hydrogen had to be abandoned. The third point, the question of the formation of hydrocarbons, was tested by making an analysis of the gas by combustion in a Winkler-Dennis combustion pipette. The total contraction in volume equaled the volume of gas taken for analysis plus one-half of its own volume—two volumes of gas combined with one of oxygen; this fact, coupled with the absence from the combustion products of carbon dioxide, showed the gas to have been only hydrogen.

If hydrogen is evolved by the transition of ferrous into ferric salts in ammonium persulphate solutions the addition of ferrous salts should accelerate the reaction. Accordingly, two parallel runs were made by placing in 1 percent ammonium persulphate solution in two beakers iron strips in inverted burettes. To one solution was added 2 grams of ferrous sulphate. From the iron in pure persulphate were obtained 14.6 cc gas in 19 hours and from the one to which had been added the ferrous salt 16.0 cc in the same time, showing a slight acceleration produced by the iron in spite of the decreased concentration of the persulphate, due to its partial reduction by the ferrous sulphate. To make the concentration more nearly comparable a third run was made using a more concentrated solution of the persulphate; the ferrous sulphate was added by squirting it, in concentrated solution,

through a tube against the face of the iron strip. A still greater acceleration was recorded in this case, 16.0 cc being evolved in 6 hours, as compared with the same volume evolved in 19 hours as observed in the case of one of the others. This clearly indicated that the acceleration was due to the increase in the concentration of the iron salts and not to that of the persulphate. It is doubtful if, in the last described experiment, there was any actual increase in the concentration of persulphate in the solution immediately surrounding the iron, as the ferrous sulphate was admitted directly against the iron and tended to displace the persulphate solution. While these phenomena were in accord with our theory, when attempts were made to determine what was acting as the catalytic agent to bring about this remarkable decomposition, it was noticed that iron in pure ferric sulphate solution, unstirred, also evolved hydrogen. Litmus showed such a solution to be acid. Alkaline hydroxides precipitated ferric hydroxide, but left the solution still acid. Ferrous sulphate and iron did not react to produce hydrogen; it is clearly impossible by definition for the reduction of ferric iron to be a reaction which evolves hydrogen, and as ferric sulphate hydrolyzes to produce free sulphuric acid, this acid seemed to be the source of the hydrogen. If this were true then the action of the alkaline ammonium persulphate had to be brought into agreement with it, so reversion was made to the persulphate. It has been mentioned above that the iron in the persulphate soon became incrusted with ferric hydroxide, due to the solution of the iron in the persulphate to ferrous sulphate, the oxidation of a part of this to ferric sulphate and the precipitation of the ferric hydroxide by hydrolysis. A further solution of iron within the crust, even in the presence of free alkali in the solution, would lead to the production of ferric sulphate which, hydrolyzing, would leave an acid solution immediately surrounding the iron and would thus give rise to an evolution of hydrogen. Vigorous stirring from the beginning, on the other hand, should produce a film of hydroxide adherent and impermeable to the persulphate—should render the iron

passive. This, it was found, it did. However, on standing in the solution unstirred, this film was broken through in spots, and long threads of hydroxide grew out like roots from the iron. The evidence then seems to be in favor of our first explanation, however improbable it at first appeared. We feel sure that this is the true explanation of the phenomenon.

It may be suggested that the corrosion of iron in the presence of oxygen in many so-called neutral solutions is probably due to the free acid produced by the hydrolysis of ferric salts. The free acid may serve to carry the iron into solution as ferrous salt which is then oxidized. The acid is regenerated by the hydrolysis of, the resulting salt, just as in the commercial reduction of nitrobenzene to aniline by means of iron and hydrochloric acid, the acid is regenerated. While the acid is supposed to act catalytically we know that it enters into the intermediate reactions.

Summary

(1) Sulphate ions are discharged when persulphates are decomposed in aqueous solution. These ions behave analogously to sulphate ions produced electrolytically.

(2) Copper in ammonium persulphate behaves just as does copper when employed as the anode in the electrolysis of sulphates.

(3) Nickel, cadmium and aluminum bear out the analogy between the chemical corrosion in ammonium persulphate and the electrolytic corrosion in ammonium sulphate.

(4) Iron is dissolved by persulphates. A portion of the dissolved iron subsequently appears as ferric sulphate, being oxidized by the persulphates in the solution.

(5) The free acid formed by the hydrolysis of ferric sulphate acts as a catalytic agent in the reaction between iron and water.

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