NASCENT HYDROGEN.

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Fourteen years ago Thorpe[1] published some very interesting measurements on the reduction of ferric sulfate in acid solutions by magnesium and zinc. It appeared that, for equal reacting weights of magnesium and zinc dissolved, there was three to four times as much ferric sulfate reduced with zinc as with magnesium. This seemed to prove the existence of a specific reducing effect due to the metal attacked ; but Thorpe recognized that the experiments were inconclusive for the following reason. The time necessary to dissolve one reacting weight of magnesium is much less than the time necessary to dissolve one reacting weight of zinc, the surfaces of the metals in contact with the solutions being the same in the two cases. As other experiments showed that increased reaction velocity meant decreased reduction of ferric sulfate, Thorpe decided that the discrepancies between the reducing powers of magnesium and zinc were probably due to the different rates at which these two metals dissolved. While this conclusion may be correct it is no more proved than the preceding one. At the request of Professor Bancroft, I took up the work at the point where it was left by Thorpe with the intention of settling the question whether the nature of the metal acted upon has any effect upon the reducing power of the hydrogen formed. The research developed rather differently than had been expected so that, with the limited time at my disposal, I was unable to reach any satisfactory conclusion on this point though I have obtained some results which bear upon the problem.

In order to eliminate the effect due to the different reaction velocities, it is necessary to have the metals dissolve at the same rate. There are two ways of doing this. Different amounts of surface might be exposed by having one metal in the form of heavy wire and another in thin plates. In this way it would be possible to

[1]Jour. Chem. Soc. **41,** 287 (1882).

have the two metals dissolve at nearly the same rate ; but this would be very cumbrous and inaccurate. The other way, which has been adopted, is to avail oneself of Faraday's Theorem that a given current dissolves equivalent amounts of different metals in the same time provided there are no secondary reactions. As it was impossible to apply this method to magnesium, the metals zinc, cadmium and copper were taken. Ordinary amalgamated zinc was used and also some sticks of very pure zinc from the chemical museum ; the cadmium was the purest stick cadmium of commerce and was obtained from Eimer and Amend. It was not amalgamated. For the copper electrode heavy wire was taken. The method employed was to set up three cells in series in three beaker glasses with zinc, cadmium and copper as anodes and the same quantity of a known solution of ferric sulfate and sulfuric acid in each beaker. The reaction was hastened by connecting the three cells with the dynamo-current supplied to the laboratory. By measuring the loss of weight of the anodes, there could be calculated the total amount of hydrogen which might have been given off, while a determination of the ferrous sulfate formed gave the amount which had been used for reducing purposes. At first mercury was used as the cathode ; but it was found that the results were very irregular. This proved to be due to the transference of the ·metal of the anode to the cathode. As soon as the concentration of the zinc sulfate, for instance, around the cathode reaches a definite value, it becomes possible to precipitate zinc and hydrogen while with copper sulfate, copper only would be precipitated under proper conditions of electromotive force and current-density. The mercury electrodes were accordingly replaced by platinum because a precipitation of zinc, cadmium or copper could be more easily detected under these circumstances. The platinum electrodes were placed in beakers distinct from those containing the anodes so as to avoid the presence of salts of these metals at the cathodes. The results were not satisfactory even then for it was found that the decrease in weight at the anodes was not proportional to the reacting weights of the metals employed and that the percentage of hydrogen oxidized varied with each experiment. Under these circumstances the measurements are not comparable and indeed have no significance, so that I shall not communicate them. Since some secondary reaction was evidently taking place, it was

decided to analyze the liquid round the anode. It was found that the reduction was equal to and in some cases greater than the reduction at the cathode. This made matters clear at once. It was evident that zinc, cadmium and copper reduced ferric sulfate directly. To test this a solution of ferric sulfate was carefully neutralized with sodium hydrate. To different portions of this solution, zinc, cadmium and copper were added. At the end of a few hours the solutions were poured off, acidified and titrated with a permanganate solution. In all three cases very considerable quantities of ferrous iron were found, showing the direct reducing action of the metals. With zinc and cadmium this is not surprising after one knows that it happens. Both these metals stand above iron in the electrochemical series and should precipitate it from solution just as copper does silver. The metallic iron thus formed would react with the ferric sulfate forming the ferrous salt. It is not clear why copper should act in this way nor is it certain that it does. It may be that with all three metals the reaction takes place directly and not in two stages even with zinc and cadmium. For the present the mechanism of the reaction is not important ; but merely the fact that a reaction takes place. This explained the discordant results hitherto obtained. No special pains had been taken to insert the anode exactly the same distance into the liquid each time. As the amount of the direct reduction is proportional, among other things, to the surface of the metal in contact with the solution the results would naturally vary. Any states of stress in the different portions of the cast metal would influence the reaction velocity. Unfortunately this source of error was not discovered until too late in the year to make a series of determinations in which this was avoided.

From some measurements upon the reduction of potassium chlorate by the action of sulfuric acid on zinc, cadmium and copper it seems probable that these metals act directly upon the chlorate part of the salt though this was not definitely established. There is nothing improbable in this. Gladstone and Tribe[1] found that zinc reduces potassium nitrate directly. I give their description of the experiment verbatim. ''A boxwood cell was cut vertically into two equal parts, some pieces of parchment paper were placed between these,

[1] Jour. Chem. Soc. **33**, 144 (1878);

and the divisions of the cell held firmly together by a clamp. A
solution of nitre was placed in each of the divisions, a strip of zinc
being placed in one, a strip of platinum in the other. The strips
were connected together by a metallic wire, and allowed to remain
so for two to four days, the action being a feeble one. The general
result of several experiments was, a little ammonia in each of the
divisions ; free potassium hydrate in the platinum one, none in the
zinc ; and about ten times less nitrate in the platinum than in the zinc
division.)) The reduction of the potassium nitrate and the forma-
tion of caustic potash in the platinum division are due to electrolysis
and nascent hydrogen. The reduction in the zinc division is due to
the direct action of the metal. A piece of the same zinc was found
to reduce potassium nitrate when no platinum was present. Part of
this effect was due to impurities in the zinc setting up local galvanic
action ; but granulated, redistilled zinc behaved in the same way
though the reduction was a good deal less. Some experiments on the
electrolysis of potassium nitrate between zinc and platinum elec-
trodes induced Gladstone and Tribe to reject this explanation,
unwisely as it seems to me. Gladstone and Tribe[1] have also found
that spongy lead reduces potassium nitrate ; and potassium chlorate
when a little sulfuric acid is present. This is in accordance with
the results of Johnson[2] who found that finely divided copper did not
reduce aqueous potassium chlorate. He did not try the effect of
adding acid. More recently Tower[3] has found that zinc acts upon
zinc nitrate though the nature of the reaction was not investigated.
The same result was found by Neumann[4] to be the case with all
metals in solutions of their nitrates. Higley and Davis[5] have con-
cluded from their investigations upon the action of nitric acid on
metals that direct reduction must take place though they did not
establish this point very satisfactorily.

Returning to the reduction of ferric salts in acid solution in the
presence of a metal, usually zinc, it is clear that two reactions go on
simultaneously ; the direct reduction of the ferric salt by the metal and
the indirect reduction due to the action of the acid on the metal. There

[1]Jour. Chem. Soc. **43,** 347 (1883) ; [2]Ibid. **35,** 240 (1879).
[3]Zeit. phys. Chem. **20,** 204 (1896) ; [4]Ibid. **14,** 193 (1894) ;
[5]Am. Chem. Jour. **18,** 587 (1896).

is no reason to assume that the first reaction is not a quantitative one. That the second is not a quantitative one is shown by the fact that hydrogen is evolved experimentally. Any circumstances which increase the amount of the first reaction relatively to that of the second will increase the amount of reduction per unit quantity of metal going into solution. This can be tested by means of Thorpe's data. Increasing the surface of the metal exposed, increasing the concentration of the ferric sulfate and decreasing the amount of free acid are all changes which promote the direct reduction and Thorpe found that the reduction per unit quantity of metal dissolved was increased by each of these three changes. The last two changes not only promote the direct reduction but decrease the indirect reduction, while a change in the surface of the metal accelerates both reactions though not necessarily to the same extent. In accordance with this it was found that increasing the surface of a sheet of zinc three-fold only increased the percentage of hydrogen retained to that assumed to have been evolved some 5%. Increasing the concentration of the ferric sulfate five-fold much more than doubled the percentage of hydrogen oxidized. The effect due to the change in the concentration of the free acid is not as great as one would expect but this may be due to the hydrolysis of the ferric sulfate. On the other hand, the more readily a metal is attacked by acid, the greater will be the indirect reduction and the amount of reduction per equivalent of metal going into solution will be decreased. Experimentally the amount of oxidized hydrogen at 25° is 6.5% with magnesium, 26.7% with zinc, and 40.7% with iron under the conditions of the experiment. Wrapping the metal to be dissolved in a platinum wire forms a galvanic couple, increasing the rate at which the metal is dissolved. This should decrease the amount of effective hydrogen. This is the case with zinc though the effect is not very marked. With magnesium and iron, on the contrary, there is a slight increase in the reduction. It is not clear to what this can be due. It is possible that the platinum might increase the effectiveness of the indirect reduction. The well-known catalytic action of the platinum lends possibility to the hypothesis ; but one would expect this action to manifest itself with zinc. This point, which was left unexplained by Thorpe, needs further investigation. Another curious result found by Thorpe, is that the presence of zinc sulfate increases the

reaction of velocity and decreases the amount of reduction. A given weight of zinc will dissolve more rapidly in an acid of given volume concentration if some zinc salt be added to the solution. This result is so unexpected that it seems as if there must be some error in the measurements.

It is impossible to predict the effect of an increase of temperature upon the amount of reduction per equivalent amount of metal dissolved without further measurements. The direct action of the zinc, for instance, upon the ferric sulfate will be increased while the free acid will attack the metal more rapidly. Until there are determinations of the relative changes of these two velocities there are no data upon which to base an opinion. A further complication comes in with the possibility that the percentage amount of indirect reduction may be a function of the temperature. Experimentally Thorpe found that at high temperatures more ferric sulfate was reduced for equivalent quantities of magnesium and zinc than at low temperatures while the contrary is true of iron.

Since there are two reactions taking place simultaneously when an acidulated solution of a ferric salt acts upon zinc, it is evident that the only way to get a clear idea of what is taking place is to separate these reactions so that each can be studied by itself. This can best be done by arranging the system as a two liquid cell, measuring the current and analyzing the solutions round the anode and the cathode. If the effect due to nascent hydrogen is all that is to be studied, the substance to be reduced can be placed round the cathode only and the current calculated from the loss in weight of the anode.

The results of this investigation are :—

1. A solution of ferric salt is reduced directly by zinc and other metals.

2. An acid solution of ferric salt is reduced indirectly by the action of the acid on zinc or other metals.

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