THE REDUCING ACTION OF HYDROGEN.

III.—The Reduction of Molybdic and Vanadic Acids.

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IN the course of his classical research on vanadium and its compounds, Roscoe (*Journ. Chem. Soc.*, 1868, **31**, 322) called attention to the fact that vanadium pentoxide in sulphuric acid solutions is reduced by zinc to the dioxide (V_2O_2), but by magnesium to the trioxide (V_2O_3) only. This very interesting and important observation does not appear to have attracted much attention until Glasmann (*Ber.*, 1905, **38**, 600) proposed to base upon it an oxydymetric method for the estimation of molybdic and vanadic acids when present together, he having found (*Ibid.*, 604) that molybdenum trioxide was completely reduced to the sesquioxide by magnesium in sulphuric and hydrochloric acid solutions. It should be mentioned that the reduction of molybdic acid had already been made the subject of research by Von der Pfordten (*Ber.*, 1882, **15**, 1925), who showed that with zinc in sulphuric acid solutions reduction takes place to a lower point even than the sesquioxide, into which, however, this lower oxide instantly passes on admitting air into the flask. Considered in the light of our work on the production of arseniuretted hydrogen from the oxides of arsenic by the action of hydrogen obtained from various sources, these results appeared to us to possess more than merely analytical significance, and we therefore decided to repeat and to extend these observations.

In all the reduction experiments described in this communication small flasks were employed, fitted with corks carrying tap-funnels for the introduction of the necessary acid, and pieces of tubing drawn out to fine jets for the escape of the hydrogen. At the end of the reduction period the contents of the flask were rapidly filtered through glass wool in an atmosphere of hydrogen, and immediately titrated with $\frac{N}{20}$ potassium permanganate.

REDUCTION OF MOLYBDENUM TRIOXIDE.—The purity of the molybdenum trioxide used in these experiments was determined by reducing known weights to the dioxide by ignition in a current of hydrogen. The first experiments were made for the purpose of ascertaining whether complete reduction to the sesquioxide in solutions containing sulphuric or hydrochloric acid could be effected by magnesium as well as by zinc, and such was found to be the case. The purest obtainable magnesium in the form of rods was used, and it was noticed that during the reduction a brownish-coloured deposit formed on the surface of the metal as soon as the acid added had become partly neutralised, which protected the metal from further action. This substance, which probably consisted of the hydrated sesquioxide, was readily soluble on the addition of more acid; but this, of course, gave rise to a very rapid disengagement of gas, and so rendered the action a difficult one to control. Reduction experiments were next made with zinc alone, and with zinc coated with nickel, silver, cadmium, and platinum. In all cases

complete reduction to the sesquioxide occurred; but it was observed that there were marked differences in the rate of change, the platinum-coated zinc acting more slowly and with greater difficulty than the zinc alone, and the cadmium-coated zinc being the most efficient of all. The general order of colour change was as follows: pale blue, dark blue, green, brownish-green, reddish-brown, and finally deep brown; but with different metals the colours were not always quite the same, although the above order was always roughly observed. With zinc and zinc-cadmium the blue colour was very transient, and the solution quickly became brown; but with the platinum-coated zinc the blue colour was more persistent, and the complete reduction was slower. This difference is best shown by the following experiments: In all cases 0.1 gram of molybdenum trioxide was taken, and the reduction carried out in solution containing sulphuric acid. In view of our numerous experiments on the reduction of the oxides of arsenic, using various metals, it was felt that it would suffice for our present purpose to work with zinc coated with cadmium on the one hand and with platinum on the other, as representing very nearly the two extremes. With the latter, the solution at the end of eight minutes had a deep blue colour, and after filtering required 10 c.c. $\frac{N}{20}$ permanganate, whilst with the cadmium-coated metal the solution at the end of the same time was brown, and required 36.6 c.c. of permanganate, the volume of permanganate corresponding with complete reduction being 41.7 c.c. The exact amount of reduction taking place in a given time with the platinum-zinc depends on the nature of the coating; when this is thick a tendency to flake off is noticeable, and the reduction proceeds in consequence more rapidly. Similar results were obtained using 0.05 gram MoO_3 . Thus, with the zinc-cadmium 20.8 c.c. of permanganate were required at the end of seven minutes, which corresponds with complete reduction, and 20.0 c.c. at the end of five minutes; whilst with the zinc-platinum three readings at the end of five minutes were 10.0 c.c., 14.5 c.c., and 10.5 c.c. respectively.

VANADIC ACID.—Pure recrystallised ammonium vanadate was taken, a solution containing 0.5 per cent. V_2O_5 being used for the reduction experiments. Roscoe's observation as to the difference between zinc and magnesium as reducing agents was practically confirmed, the final colour of the solution when using the latter metal being blue or green, and never assuming the pale violet colour which indicates reduction to the dioxide. The amount of permanganate solution required for oxidation was usually in fair agreement with reduction to the trioxide, even when the action was allowed to proceed for as long as five hours, but in a few experiments a little more than the theoretical quantity of permanganate was required. Experiments were next made with zinc alone, and with zinc coated with cadmium and with platinum. With zinc alone, using 10 c.c. of the vanadate solution ($= 0.05$ gram V_2O_5), the following volumes of the permanganate solution were required at the end of the times indicated. It should be added that sufficient of the metal was taken to provide for the evolution of hydrogen throughout the whole experiment, and filtration was carried out in an atmosphere of hydrogen.

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ZINC.

Duration of Experiment.						Volume of $\frac{N}{20}$ Permanganate.
8 minutes	(greenish-blue)	...	...	...	...	26.3 c.c.
5 "	" " "	...	...	...	...	26.5 c.c.
5 "	" " "	...	...	...	...	27.0 c.c.
15 "	" " "	...	...	...	...	28.5 c.c.
30 "	(lavender)	...	...	...	...	30.4 c.c.
60 "	" "	...	...	...	...	30.8 c.c.

Reduction to V_2O_3 was therefore nearly complete at the end of half an hour, the volume of permanganate corresponding with complete reduction being 32.7 c.c.

ZINC COATED WITH CADMIUM.

Duration of Experiment.						Volume of $\frac{N}{20}$ Permanganate.
8 minutes	(nearly colourless)	...	...	...	...	27.6 c.c.
8 "	(lavender)	...	...	...	...	29.4 "
8 "	" "	...	...	...	...	29.5 "
5 "	" "	...	...	...	...	29.3 "

It will be seen that here again reduction to V_2O_3 is nearly reached, but that the action is, if anything, rather more rapid than with the zinc alone.

Experiments were next made with zinc coated carefully with platinum, the same quantity of vanadate solution being taken :

Duration of Experiment.						Volume of $\frac{N}{20}$ Permanganate.
5 minutes	(brownish-green)	...	...	...	...	20.2 c.c.
5 "	" " "	...	...	...	...	22.3 "
8 "	" " "	...	...	...	...	21.9 "
30 "	" " "	...	...	...	...	25.9 "
60 "	" " "	...	...	...	...	27.5 "

These results show that the hydrogen evolved from the platinum-coated zinc has sufficient reducing activity to carry the reduction below the stage of V_2O_3 , but that the action is much slower than with the zinc-cadmium.

As there was considerable difficulty in preventing the separation of the platinum from the zinc in experiments lasting so long as one hour, it was thought that more striking results would be obtained by using zinc alloyed with small quantities of platinum. In the first series an alloy was used containing 0.4 per cent. platinum. The following results were obtained :

Duration of Experiment.						Volume of $\frac{N}{20}$ Permanganate.
30 minutes	...	...	...	...	...	22.8 c.c.
2 hours	...	...	...	...	...	24.6 "
4 "	...	...	...	...	...	24.0 "

Two other alloys were then prepared, each made to contain as nearly as possible 0.4 per cent. platinum. These are referred to below as "No. 2" and "No. 3" respectively :

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ALLOY No. 2.

Duration of Experiment.						Volume of $\frac{N}{20}$ Permanganate.
2 hours (greenish-blue)	...	...	...	...	...	22.6 c.c.
3 " " "	...	...	...	...	...	22.2 "
4 " " "	...	...	...	...	...	22.6 "
5 " " "	...	...	...	...	...	24.2 "

ALLOY No. 3.

Duration of Experiment.						Volume of $\frac{N}{20}$ Permanganate.
30 minutes	...	...	...	...	...	23.0 c.c.
30 " "	...	...	...	...	...	24.0 "
45 " "	...	...	...	...	...	26.7 "

This alloy was then regranulated from a graphite crucible, and this gave the following results:

Duration of Experiment.						Volume of $\frac{N}{20}$ Permanganate.
2 hours	...	...	...	...	...	23.0 c.c.
4 " "	...	...	...	...	...	23.5 "

The result of merely regranulating No. 3 alloy is interesting, the reducing efficiency of the hydrogen obtained from it being very much inferior to that of the hydrogen from the original alloy. These differences are doubtless due to the fact that it is difficult to prepare a homogeneous alloy of zinc and platinum, and that in some cases a much larger proportion of the hydrogen is evolved from the zinc surface than in others. A sample of highly insensitive zinc containing iron was next tried, and at the end of thirty minutes the volume of permanganate required was 25.7 c.c. (after correcting for the iron), which shows its inferiority to the purer metal or to the zinc coated with cadmium.

These experiments having confirmed our results for the reduction of the oxides of arsenic, and having afforded further evidence of the general correctness of our views as to the relation between "supertension" and reducing activity, we thought it would be interesting to carry out some electrolytic experiments. 0.2 gram ammonium vanadate was used in the electrolytic cell in each case, and six experiments were made of which the following are briefly the conditions:

1. Cathode of pure zinc. Cathode area, 20 cm². Current, 1 ampère. Time, two hours. 46.5 c.c. $\frac{N}{10}$ permanganate solution required.

2. Cathode of pure zinc. Cathode area, 20 cm². Current, 2 ampères. Time, two hours. 48.2 c.c. $\frac{N}{10}$ permanganate solution required.

3. The conditions were the same as in 2, but a cathode of zinc and cadmium was used. 48.2 c.c. $\frac{N}{10}$ permanganate solution required. The volume of $\frac{N}{10}$ permanganate solution corresponding with the reduction of the whole of the V₂O₅ used to V₂O₃ is 50.9 c.c., so that the reduction in each case approached the stage of V₂O₃.

These experiments are of course open to the objection that the cathodes used were soluble during the experiment, and in the following lead was therefore employed.

4. Conditions same as in 2, but the cathode consisted of pure lead. 44.5 c.c. $\frac{N}{10}$ permanganate solution required.

5. In this experiment the conditions were the same as in 1, but the cathode consisted of platinised platinum which had been previously used as a cathode with dilute sulphuric acid as the electrolyte. 26.5 c.c. $\frac{N}{10}$ permanganate solution required.

6. In this experiment the conditions were the same as in 2, using the same cathode as in 5. 28.0 c.c. $\frac{N}{10}$ permanganate solution required. It will be seen, therefore, that when using a platinised platinum cathode the reduction does not under the conditions of the experiments proceed even as far as V_2O_3 , whilst with zinc, cadmium, or lead it approaches the lowest point possible—viz., V_2O_2 .

We hope to experiment similarly with other reducible substances, and to communicate our results to the Society in due course.

DISCUSSION.

Dr. J. T. HEWITT said that, in the electrolytic cell, from the very circumstances of the case, the arsenate ions, instead of tending to approach the cathode, must wander towards the anode. Possibly this might account for the failure to reduce the arsenate electrolytically.

Mr. SEYLER said it was interesting to notice that the authors had been unable to completely reduce the vanadic acid. That might perhaps account for some difficulties which he had met with in trying to estimate vanadium in steel. He asked whether the authors had entered into, or knew of any work on, the physical aspect of the question, in the direction of determining the potential at which the gas was given off.

Mr. E. HINKS asked whether the authors considered the platinum or cadmium deposited on the zinc to be in the state of alloy; in other words, whether the deposited metals were, in effect, in the same state as the alloyed ones.

Mr. CHAPMAN said that the possibility naturally suggested itself that the hydrogen arsenate ions might tend to wander in the way mentioned by Dr. Hewitt, and they had dealt with this point somewhat fully in their last paper. But while to some extent that might account for the difference as regards reduction between arsenates and arsenites, it did not account for it completely. Some quantity of arsenic acid was still in sufficiently prolonged contact with the cathode for its reduction if it were capable of being reduced. In the experiments with vanadic acid, which had been carried out as carefully as was possible in an ordinary analytical operation, the degree of reduction was always a little short of what it would be if the V_2O_2 stage were completely reached, though whether that was due to the fact that slight oxidation could not be prevented, or whether it might not be due to decomposition of the water by the V_2O_2 , they were not prepared to say. The question of the potential at which the gas was given off was one which Mr. Law and he had often discussed, but they were not aware that anybody had shown the exact relationship between this and the chemical activity. Broadly speaking, it was clear that a certain amount of energy was necessary for the reduction of any particular oxide, and in certain cases the hydrogen possessed sufficient energy to effect the change, while in other cases it did

not. Roscoe's observation afforded an interesting example of what might be called the limiting amount of energy. In the case of vanadic acid the hydrogen evolved from magnesium at a low supertension had sufficient energy to effect part of the reduction, but not the whole, whereas in the case of molybdic acid that amount of energy was sufficient to carry the reduction right down. With regard to Mr. Hinks' question, the results obtained with a homogeneous alloy were, as far as their experiments were concerned, the same as those with a uniform and adherent deposit. That, at any rate as far as reduction was concerned, was what they had observed, and was, he thought, probably what was to be expected.

Mr. LAW said that, beyond the bare facts of the experiments, they did not wish to theorise very much. The subject was one on which much speculation was possible, but without further knowledge it was impossible to proceed with certainty further than they had indicated. Their results could never be more than very roughly quantitative, because they were dealing with alloys or couples which were changing during the whole course of the experiments. In the case, for instance, of an alloy of platinum and zinc, the zinc dissolved and gradually exposed more and more of the platinum. The actual relationship between the chemical action and the potential had never been accurately determined. They had constructed some rough mathematical formulæ in their last paper, but these were more or less of an empirical nature, and did not bring out the relationship in absolute units. Tafel had attempted to work out the problem mathematically, but without success, and he (the speaker) had also been unsuccessful in his attempts at a mathematical solution, because of the continual change that went on. They hoped, however, by gradually accumulating results, to get a better idea of the subject, which might enable them to generalise on the whole of the facts at some future time.