

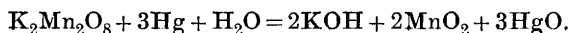
CLIX.—*Some Reducing Actions of Mercury.*

By DAVID BORAR.

It is stated by Kirchman (*Arch. Pharm.*, 1872, **200**, 203) that mercury is oxidised when agitated with a solution of potassium permanganate, mercurous oxide being formed if the solution is cold, and mercuric oxide if the solution is hot. At the suggestion of Dr. E. P. Perman I have investigated the action of mercury on potassium permanganate and on a number of other substances.

In all the experiments the solutions were agitated with mercury in a stoppered bottle, and at the ordinary room temperature unless otherwise stated. The mercury used was purified by the ordinary methods, and no doubt contained traces of other metals.

Potassium Permanganate.—No action takes place between dry potassium permanganate and mercury. In the presence of water, however, reduction of the permanganate takes place readily. With excess of mercury the reduction is complete, and the amount of potassium hydroxide formed from a known amount of permanganate was determined by titration with standard acid. Experiments were also made in which permanganate was in excess, and the amount required to oxidise a given weight of mercury was determined. The results of these experiments show that all the potassium in the permanganate is converted into potassium hydroxide, part of which seems to form adsorption compounds or unstable manganites with the manganese dioxide formed. As a mean of three experiments it was found that 1 gram of mercury reduces 0.519 gram of permanganate. These results indicate that the reaction between mercury and potassium permanganate takes place in accordance with the equation :



Potassium Dichromate.—Mercury does not reduce neutral solutions of potassium dichromate to any extent measurable by ordinary analytical methods. In the presence of hydrochloric acid, however, reduction takes place readily. Experiments were made in which excess of mercury was used, and others in which excess of dichromate was taken. The former showed that the dichromate was completely reduced to chromium chloride, and the latter that the amount of dichromate reduced by a given weight of mercury was constant providing that too large a quantity of hydrochloric acid was not taken. It was found as a mean of five experiments that 1 gram of mercury reduces 0.2452 gram of dichromate. The precipitate obtained in the various experiments was tested for mercurous chromate and mercuric chloride, neither of which could be detected, and the precipitate was found to consist of mercurous chloride only. From the equation:



1 gram of mercury reduces 0.2456 gram of dichromate. The number found by experiment is in good agreement with this number. Hence the equation given probably represents the reaction which takes place.

Ferric Salts.—A solution of ferric chloride in water is readily reduced by mercury. Iron alum in the presence of hydrochloric acid is also reduced, but without the addition of hydrochloric acid reduction does not take place to any extent. Using mercury as reducing agent and titrating with standard dichromate in the usual way, the amount of iron in iron alum is found to be 11.61 per cent. The theoretical number is 11.59 per cent.

The amount of iron in hæmatite was determined by using mercury as reducing agent, and again using stannous chloride as reducing agent. The amount found was 91.30 per cent. by the first, and 91.16 per cent. by the second method.

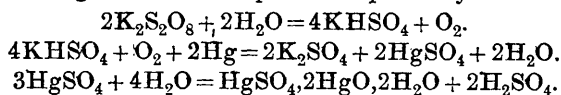
Reduction takes place rapidly, especially if the solution is heated to 60–70°. The precipitate of mercurous chloride which forms during the process settles down rapidly from the hot solution, leaving the liquid clear. The presence, however, of comparatively large quantities of mercurous chloride does not affect the titrations appreciably.

The results obtained show that mercury may well be employed as a reducing agent for ferric compounds in the estimation of iron, and this method is less troublesome than the usual methods.

Potassium Persulphate.—On shaking a cold solution of potassium persulphate with mercury a slight, black precipitate was first formed, and then a white precipitate, which slowly changed to a lemon-yellow colour on keeping. The solution became acid, and

1416 BORAR: SOME REDUCING ACTIONS OF MERCURY.

potassium sulphate remained in solution. In a hot solution, however, the yellow precipitate was formed almost immediately. This precipitate was insoluble in water, but soluble in dilute sulphuric acid. It decomposed on heating into mercury, oxygen, and sulphur dioxide. Mercuric sulphate readily gives the yellow basic sulphate with water, whereas mercurous sulphate does not, even on boiling. Hence the changes which take place are probably as follows:



Copper Sulphate.—A fairly good yield of cuprous chloride was obtained by shaking mercury with copper sulphate solution and excess of hydrochloric acid.

Nitrobenzene.—Mercury in the presence of hydrochloric acid was found to reduce nitrobenzene to aniline, but only to a small extent, even on heating.

The action of mercury was also tried on potassium nitrate in neutral and in acid solution, but no change could be detected. Solutions of potassium chlorate and sodium peroxide also had no action on mercury.

After the work of which this paper gives a brief account had been completed, my attention was called to a paper by Carnegie (Trans., 1888, **53**, 471) on the reduction of ferric salts by finely divided metals. Carnegie found that many metals, amongst them mercury, will reduce solutions of ferric salts, but does not point out that mercury can be used conveniently and possibly with advantage in the estimation of iron in ferric compounds. Previous work on the action of potassium permanganate on mercury, for example, that by Giles (*Chem. News*, 1867, **15**, 204), does not appear to have been carried out quantitatively.

In conclusion, my best thanks are due to Dr. E. P. Perman for many helpful suggestions and advice.

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