CCCI.—Determination of Metals Dissolved in Mercury. Rapid Method of Purifying Mercury.

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The work to be described is dependent on two observations, both of which, we think, are new: (1) that all metals more electropositive than mercury except cobalt go rapidly into solution as sulphates without the accompaniment of mercury when amalgams of them are shaken with potassium permanganate or certain other oxidising agents in dilute sulphuric acid, and (2) that the point at which the last trace of the metal in the mercury has gone into solution is shown by the breaking of the surface of the mercury into bubbles. For the determination of single metals in mercury by the method to be described it is necessary that the reducing power of the metal be 100%, that is to say, that the metal go into solution only in so far as it reduces the permanganate or other oxidising solution. For purifying mercury, on the other hand, rapidity of action between the metals to be removed and the oxidising solution is more necessary than efficiency of reducing power.

We find * that the order in which metals when dissolved in mercury are removed from it by oxidising solutions is not the same as that of the electrode potentials of the metals in the free state. This order in mercury is (proceeding from electropositive to noble metals and including only those with which we have experimented): zinc, manganese, cadmium, thallium, tin, lead, copper, chromium and iron, bismuth, cobalt, mercury, and nickel. It was found by obtaining the metals two at a time in mercury and finding out which went first into solution when ferric sulphate, or potassium permanganate or uranyl sulphate in sulphuric acid was reduced. The order seems quite definite; it appears to be the same whatever oxidising solution be reduced, whether the solution be hot or cold, whether sulphuric or hydrochloric acid be employed, and whatever other metals be present in the amalgam. The order in mercury differs from the order of the electrode potentials of metals in the free state only in the absolute positions of chromium, manganese, iron, cobalt, and nickel (atomic numbers 24 to 28). This is ascribed to passivity (Russell, loc. cit.). The relative order of these elements in both series is the same.

EXPERIMENTAL.

The reducing efficiency of a metal in mercury was investigated as follows : an amalgam containing from 0.2 to 0.4 g. of the metal in 200 g. of mercury was prepared either by direct solution, or by electrolysing solutions of sulphate in sulphuric acid the concentrations of which before and after electrolysis had been determined; the amalgam was shaken in a 300 c.c. stoppered bottle with 80 c.c. of 2N-sulphuric acid and a volume of accurately N/10-potassium permanganate until the pink colour was just discharged; further volumes of permanganate were run into the bottle and the colour discharged until a point was reached such that on further shaking the surface of the mercury became a mass of small bubbles. This point could be accurately judged with experience to about 0.2 or 0.3 c.c. and was taken as the point at which the whole of the metal had left the mercury. The mass of the metal theoretically necessary to oxidise the volume of reduced permanganate was then compared with the known weight contained originally in the mercury.

* This experimental work with discussion will be published elsewhere. In *Nature*, 1925, **115**, 455, one of us (A. S. R.) gave this order slightly differently. By a slip *chromium* read *manganese*. The position of manganese had not then been investigated.

The results obtained for seven metals and potassium permanganate are in the table below.

Gram taken.	Gram found.	% efficiency.	Gram taken.	Gram found.	% efficiency.		
	Zinc.			Lead.	5		
0.210	0.193	91.9	0.100	0.101	101		
0.210	0.192	91·4	0.202	0.200	99		
0.219	0.200	91.3	0.502	0.206	100.5		
0.929	0.865	93·1	0.206	0.206	100		
			0.406	0.410	101		
	Cadmium	•		0			
0·222 0·230 0·263	0·222 0·228 0·261	100 99·1 99·2	0·1115 0·1673	Copper. 0·1115 0·1680	$100 \\ 100 \cdot 4$		
0.281	0.279	99.3		Iron.			
	Tin.		0·1791 0·3658	$0.1722 \\ 0.3515$	96-1 96-1		
0.400	0.400	100		D ' 1			
0.401	0.402	100.2	Bismuth.				
0.403	0.400	99-2	0.302	0.305	100		
0.403	0-401	99-5	0.367	0.365	99.5		

It is seen that the results obtained by this rapid method (an experiment could be easily completed in 5 minutes) are fairly consistent and that each metal tried, with the exception of zinc and iron, is 100% efficient as oxidiser of potassium permanganate. These results contrast remarkably with the reducing efficiencies, and also the rate of oxidation, of some of these metals in the free state as investigated by Thorpe (J., 1882, **41**, 287) and Sugden (J., 1921, **119**, 233).

The results obtained in a similar manner when the metals reduced a N/10-solution of ferric sulphate in 2N-sulphuric acid were approximately 100% for cadmium, tin, lead, copper, and bismuth, as with permanganate. Zinc, however, was now also 100% efficient, the actual values obtained being 100, 100.9, and 100.1. The reducing efficiency of iron was, however, again less than 100%, the values obtained varying from 94 to 97. Ferric sulphate was found to oxidise the metal of the amalgam much more rapidly than permanganate, and shaking had to be carefully done to avoid over-running the end-point and bringing some of the mercury itself into solution.

When uranyl sulphate was reduced, none of the metals showed reducing efficiencies of 100%. Of the seven metals mentioned above, only zinc, cadmium, tin, and lead could be investigated, because these alone were found to reduce uranium quantitatively from the sexavalent to the quadrivalent form. The mean values of their efficiencies decreased in decreasing order of potential, the mean values found being 91, 88, 82, and 74 for zinc, cadmium, tin, and lead, respectively.

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It is obvious that the reducing efficiency of a metal may be investigated in this way only when it is completely removed from the mercury without being accompanied by mercury. It was found that mercury invariably accompanied cobalt and nickel when amalgams of these elements were shaken with oxidising solutions. The number of atoms of cobalt oxidised by the permanganate was found to be greater than that of mercury, and the number of atoms of nickel less. Cobalt appears, therefore, to act like a more electropositive and nickel like a more electronegative metal than mercury. It was found possible by sacrificing some mercury to remove the whole of the cobalt, but not the whole of the nickel from the mercury by shaking with oxidising solutions. These are the only metals which lie in potential between zinc and mercury in the free state which cannot be determined quantitatively by the method described in this paper.

The whole of these results receive a ready explanation with the help of present knowledge of the phenomenon of over-voltage. When a metal dissolved in, and more reactive than, mercury is shaken with sulphuric acid, it goes to some extent into solution and the equivalent amount of ionic hydrogen is discharged at the surface of the mercury. This has been proved to occur whether or not the metal is more electropositive than hydrogen in the potential series (S. W. J. Smith, Phil. Mag., 1909, 17, 834). Two extreme courses are open to this atomic hydrogen : it may wholly combine with the oxidising solution present (in which case the reducing efficiency of the metal is 100%), or it may wholly combine to form molecular hydrogen at the surface of the metal. The former course, it is expected, would be favoured by the presence of ions which are quickly reduced, and by a metal the power of which for catalysing the formation of molecular from atomic hydrogen is small; the latter course would be favoured by the presence of ions that are reduced slowly, and by a metal which catalyses the formation of molecular hydrogen. Of the three solutions tried, ferric sulphate was found by a series of comparative tests to be reduced most quickly, and uranyl sulphate most slowly, by amalgams of each of the metals investigated. Of these metals, mercury has the highest, and iron the lowest, hydrogen over-voltage, and, if this phenomenon be interpreted as the inability of the metal to catalyse the reaction $2H \rightarrow H_{2}$, it follows that, of the metals under discussion, mercury does this most slowly and iron most quickly.

The experiments described above may now be explained. When potassium permanganate is reduced in acid solution, only the very reactive zinc can generate more hydrogen (or more reactive hydrogen) than can be retained at the surface of the metal until it

reacts with the permanganate. When ferric sulphate is reduced, the increased rate of reaction between it and the atomic hydrogen is sufficient to prevent any formation of molecular hydrogen; zinc is consequently, like the other metals, 100% efficient as a reducer. When uranyl sulphate is reduced, the slower rate of reaction between it and atomic hydrogen explains the smaller reducing efficiency of zinc. Comparative tests which we have made on the rate of reduction of uranyl sulphate in acid solution by amalgams of different metals, show that as the metal becomes more and more electronegative the rate at which it reduces uranyl sulphate relative to that at which it reduces permanganate decreases rapidly. Zinc, for example, reduces permanganate about 20% more rapidly than the less reactive lead under similar conditions; it reduces uranyl sulphate, however, about ten times more rapidly. These observations explain the low efficiencies of metals and their decrease with decrease in electrode potential when they reduce uranyl sulphate.

Since iron falls in the potential series of metals in mercury between copper and bismuth, it is to be expected from the results above that it would show a 100% reducing efficiency both with potassium permanganate and with ferric sulphate. The lower values found cannot be explained by supposing that the iron, which appears to be in the passive state in mercury, has become active, because there is no other evidence that iron when reducing permanganate or ferric sulphate becomes active, and further, zinc, which is 100% efficient as a reducer of ferric sulphate, is more electropositive than active iron. The explanation of the low values is that iron is the only metal in the amalgams investigated which so catalyses the reaction $2H \longrightarrow H_2$ that not all of the atomic hydrogen is used in reducing the oxidising solution. This is confirmed by the results of experiments on the reducing efficiency of zinc on permanganate in amalgams containing one other metal.

We find that cadmium, tin, and lead do not lower the reducing efficiency of zinc, that iron lowers it a little, and that tungsten, molybdenum, and platinum, which have very small hydrogen over-voltages, reduce it considerably. These experiments will be detailed in a separate communication. The following experiments lead more simply to the same result: (1) When a c.c. of N/10permanganate are shaken in sulphuric acid solution with iron amalgam the permanganate is first reduced and the resulting ferric sulphate is then quantitatively reduced by more iron to the ferrous condition. When this solution is titrated with the same permanganate, it requires theoretically a/2 c.c., if iron has a reducing efficiency of 100%. Experimentally it requires usually from 0.2 to 0.5 c.c. in excess of this amount, showing that some of the iron

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present in the amalgam has gone into solution without performing any reduction of either the permanganate or the ferric solutions present. (2) When a c.c. of N/10-ferric sulphate are shaken in sulphuric acid solution with iron amalgam a solution of ferrous sulphate results. This solution should theoretically require 3a/2 c.c. of N/10-permanganate when titrated. Experimentally it requires from 0.2 to 0.5 c.c. in excess of this amount for the reason explained above. (3) When the same volume of the solution in (2) is shaken with a tin- instead of an iron-amalgam, ferrous sulphate and stannous sulphate but no stannic sulphate are found to form. This solution should theoretically require 2a c.c. of N/10-permanganate, since stannous sulphate and ferrous sulphate are formed in equivalent amounts. Experimentally this value is found, which shows that tin is 100% efficient in these circumstances.

From this survey it follows that, of the metals considered, iron alone cannot be directly determined in mercury by measuring the volume of potassium permanganate or ferric sulphate reduced by the metal. Owing to the rapidity of the reaction between the metal and the ferric sulphate and consequent danger of over-running the end-point, it is better to use potassium permanganate in presence of 2N-sulphuric acid as oxidiser except when zinc is being determined. Iron may be determined easily and quantitatively by the following modification of the method. The iron amalgam is shaken with the permanganate until the end-point is obviously passed. The reduced solution is transferred to a bottle and shaken for one minute with 1% zinc amalgam. Mercury salts are thereby reduced to the metal, which dissolves in the amalgam, and iron salts are wholly reduced to the ferrous state. The liquid is then decanted from the amalgam, which is washed by decantation with two volumes of 50 c.c. of water containing dilute sulphuric acid and the whole titrated with N/10-permanganate.

The method described above should be a rapid and useful alternative to several more accurate but tedious processes. Three readily suggest themselves and we have carried out a few experiments on each: (1) the determination of the solubilities of metals in mercury, (2) the determination of tin and lead in solder, (3) the determination of metals electrolytically using a cathode of mercury.

Determination of Solubilities of Tin and Iron in Mercury at 15° .— To 800 g. of mercury were added 15 g. of pure tin. The solid phase was obviously present. The mixture was kept for an hour at 15° and then pressed through chamois leather three times to remove the whole of the solid phase. The amalgam was shaken with acidified permanganate in the usual way until the end-point was reached; the whole of the tin was then in solution in the

stannic form, since tin amalgam was found not to reduce stannic sulphate in measurable amount. The mass of tin in the known weight of the amalgam was then calculated from the volume and strength of the permanganate. The percentage of tin in solution in mercury at 15° was found in this way in two experiments to be 0.61 and 0.60.

A similar experiment was carried out with iron. This metal was obtained in solution by electrolysing a normal solution of ferrous sulphate containing sulphuric acid with a current of 3 amperes with a mercury cathode until the solid phase was obviously present. The solid phase was removed at 15° as with tin. Owing to the very small solubility of iron in mercury, as well as to its not being 100% efficient, the permanganate was used merely to remove the iron quantitatively from the mercury. The solution containing the iron was then treated as mentioned above and titrated with permanganate. In three experiments the solubility of iron in mercury at 15° was found to be 0.00138, 0.00140, and 0.00140%. Richards and Garrod Thomas (Z. physikal. Chem., 1910, 56, 758) found by other methods the value 0.00134 at 20°.

Determination of Tin and Lead in Solder.-The conditions necessary for success in these determinations are (a) that the alloy dissolves without difficulty in warm mercury, (b) that it has two constituents only, each of which is 100% efficient in reducing the oxidising solution used, and (c) that the equivalents of the metals be as widely different as possible. Solder fulfils these conditions well. A table was compiled showing the quantities of decinormal permanganate theoretically required by a gram of solder (containing lead and tin only) of varying tin composition when it is oxidised to stannic and lead sulphates. It showed that a difference in percentage composition of tin or lead of 0.1 corresponded to 0.24 c.c. of N/10-potassium permanganate. Since the end-point in our method can be judged with practice to about 0.2 to 0.3 c.c. of permanganate, the error of a single determination need not exceed 0·1. In practice, however, this accuracy was not always attained. In the table below, the percentage compositions of three solders obtained by the new method are compared with those determined gravimetrically.

	Percen	tages det	ermined	by new m	ethod.	Average values.	% determined gravimetrically.
Sn Dh	46-4	46.3	46.5	46.3	46.4	46.4	46.4
r D Sn	36·4	03.1 36.3	55.5 36.1	93.1	99.0	23.0 36.3	23.0 36-1
Pb	63·6	63.7	63.9			63.7	63.9
Sn Pb	50·7 49·3	49·8 50·2	50·0 50·0			50·2 49·8	50·5 49·5

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It is seen that in the three cases the agreement is fair. A determination by the new method which includes the time taken to weigh the solder may be made in 15 minutes. We usually weighed out about 0.2 g. and this required about 60 c.c. of N/10-permanganate. As is to be expected from its position in the potential series, tin in the solder oxidises the permanganate before lead. This is inferred because the discoloured solution is at first clear. Later the white precipitate of lead sulphate makes its appearance. The precipitate does not obscure the end-point.

Modification of E. F. Smith's Method of Determining Metals with a Mercury Cathode .-- The following metals have been found by Smith and others to be rapidly and quantitatively precipitated from solution with the use of a rotating anode and a mercury cathode: bismuth, cadmium, chromium, cobalt, copper, gold, iron, lead, manganese, mercury, nickel, silver, tin, and zinc (E. F. Smith, "Electroanalysis," 6th edition, 1919). These metals are determined by Smith's method as the difference in the weight of pure mercury before electrolysis and that of the amalgam after. With our method neither the pure mercury nor the amalgam need be weighed, so that the errors involved, especially in the second of these weighings, are avoided. On the other hand, the error of determination is greater with our method (about 0.5%) than with Smith's method when properly carried out (0.1 to 0.2%). Moreover, our method is confined to the determination of bismuth. cadmium, copper, iron, lead, manganese, tin, and zinc. The other metals named above, except chromium and cobalt, cannot be determined because they are more electronegative than mercury. Chromium cannot be determined by our method because instead of forming chromium sulphate, as is to be expected, in presence of an oxidising agent, it leaves the mercury in a finely divided state and becomes oxidised to chromous oxide. The case of cobalt has already been considered.

Rapid Method of Purifying Mercury.

A rapid method of purifying mercury from other metals may be founded on the quantitative determinations described above and is indeed obvious. It cannot be used for removing nickel or metals more electronegative than mercury, and cobalt presents some difficulty. The remaining metals more electropositive than mercury, even when in the passive state, may be removed quickly, completely, and without any loss of mercury.

If the amalgam is a concentrated one, it should be pressed twice through chamois leather to withdraw the whole of the metals in the solid phase. This lowers the concentrations of cadmium,

indium, thallium, lead, zinc, and tin to approximately 3, 2, 2, 1, 1, and 0.5%, respectively, and leaves those of copper and iron less than 0.003% (Richards and Wilson, Z. physikal. Chem., 1910, 56, 729; Richards and Garrod Thomas, ibid., p. 758). The amalgam may then be placed in a stout reagent bottle and shaken vigorously with a mixture of equal volumes of 9N-sulphuric acid and saturated aqueous solution of potassium permanganate till it becomes discoloured. More of the oxidising solution is then added and the shaking continued till bubbles of mercury appear on the surface. The amalgam is then washed from impurities by a stream of water, and the removal of the last traces of the impure metal completed by shaking with N/10-permanganate acidified with 2N-sulphuric acid till the end-point, at which the mercury when shaken becomes a mass of small bubbles, is reached. The mercury should then be again washed by a stream of running water, shaken with 2N-sulphuric acid to destroy the bubbles, and pressed through chamois leather.

If N/10-potassium permanganate in sulphuric acid solution be used instead of the more concentrated solution the rate at which the metallic impurities are removed is slower. For small concentrations of impurities, however, this rate is not unduly slow (the removal of 0.2 g. of zinc, for example, would require about 2 minutes' shaking), and whenever the reduced solution is intended to be subsequently analysed this rate is recommended because it ensures that the end-point is not over-stepped. When the amalgam is shaken with a concentrated solution of ferric sulphate in sulphuric acid or with a mixture of this solution with permanganate, the rate at which the impurities are removed is very greatly increased. This is due to the observed fact that ferric sulphate is reduced much more rapidly than permanganate, and the greater the concentration of the ferric sulphate the more rapid is the reduction. Ferric sulphate thus catalyses the reduction of potassium permanganate and other oxidising solutions by amalgams because the former after reduction to ferrous sulphate reacts almost instantaneously with the latter and the ferric sulphate regenerated is then reduced by more of the metal of the amalgam. Using a normal solution of ferric sulphate in 2N-sulphuric acid, we were able, by vigorous shaking, to remove 1 g. of lead from 200 g. of amalgam in 10 seconds, and 7 g. of zinc in $\frac{1}{2}$ minute. With a concentrated solution of permanganate in 6N-sulphuric acid and 20 c.c. of N/10ferric sulphate we removed completely, by shaking in a large reagent bottle, 14 g. of a mixture of zinc, cadmium, tin, lead, solder, and bismuth from 480 g. of pure mercury, to which it had been added, without the loss of any mercury except a little removed

mechanically in washing. This fact is of interest because in the literature on the purification of mercury it is stated that when an amalgam is passed through, or shaken with, the oxidising solutions in general use, either the mercury is not completely freed from the more electropositive metals or, if it is, a considerable proportion of mercury accompanies the other metals into solution (Harries, Z. angew. Chem., 1921, 34, 359; Harries and Evers, *ibid.*, p. 541; Hulett and Minchin, *Physical Rev.*, 1905, 21, 396).

Summary.

1. The order in which metals are removed from mercury by oxidising solutions has been determined, and is given but not discussed.

2. The reducing efficiency of amalgams of zinc, cadmium, tin, lead, copper, iron, and bismuth has been determined in solutions of ferric sulphate, potassium permanganate, and uranyl sulphate containing dilute sulphuric acid. The results are interpreted in terms of the hydrogen over-voltages of these metals.

3. The results are applied to rapid, approximate methods of determining (a) the solubilities of metals in mercury, (b) tin and lead in solder, (c) metals deposited by electrolysis with a rotating anode and a mercury cathode.

4. A rapid method of purifying mercury from more electropositive metals by shaking the amalgam with an oxidising agent is described. It removes such metals completely without necessarily the loss of mercury. The rate at which this purification is done may be regulated.

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