CCXLVIII.—*The Order of Removal of Manganese, Chromium, Iron, Cobalt, and Nickel from Amalgams.*

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In a previous paper (J., 1925, **127**, 2221), it was stated without evidence being given that the order in which metals are removed from mercury, in which they are dissolved or suspended, by oxidising solutions is not the same as that of the electrode potentials of the metals when in the free state; that the difference concerns the absolute positions of chromium, manganese, iron, cobalt, and nickel, and that the relative order of these elements is the same in both series. This paper is concerned with the experimental work in support of these statements, and a discussion of the results.

EXPERIMENTAL.

An amalgam of each metal, approximately 1% in concentration, was prepared either by direct solution of a known weight of the metal in the mercury, or by electrolysis of a known concentration of the chloride or the sulphate of the metal in acid solution, using mercury as cathode. By the former method, amalgams of zinc, cadmium, thallium, tin, lead, and bismuth were prepared, and by the latter method, amalgams of manganese, chromium, iron, cobalt, nickel, and copper. Manganese amalgam alone was found difficult to prepare. The method used for obtaining the other amalgams, namely, electrolysis of a solution of the sulphate in $4N$-sulphuric acid, failed for manganese. The electrolysis of manganese chloride

solution, to which a few drops of hydrochloric acid had been added, was successful in preparing the amalgam, although it was not quantitative. Finally, we found that manganese could be driven quantitatively into the mercury by electrolysing a solution of manganese chloride (125 c.c.), to which 6 drops of concentrated hydrochloric acid and 5 c.c. of alcohol had been added, with N.D.$_{100}$ 3—5 amp. at 10 volts for 24 hours, alcohol being added from time to time in order to replace the loss by evaporation.

The amalgams so prepared were comparatively stable with the exception of those of chromium, iron, and manganese, which gradually oxidised in the air. This oxidation was prevented by dissolving a few milligrams of zinc in each, or, in the case of iron, by keeping the amalgam under concentrated sulphuric acid. The fact that a trace of zinc prevented the oxidation by air of the manganese in the amalgam suggested that, in an amalgam, manganese is oxidised after zinc, and this anomalous result was later confirmed.

In order to determine the order in which metals, dissolved in mercury, come out of solution when they reduce an oxidising agent, portions of the amalgams were mixed two at a time and the mixture was shaken with a solution of $N/10$-potassium permanganate or ferric sulphate or uranyl nitrate in $2N$-sulphuric acid, and the resulting solution analysed qualitatively. The various metals were detected by the usual qualitative tests.

It was found that one metal when reducing a particular oxidising agent preceded another quite definitely in all cases and was brought to a fraction of its original concentration in the amalgam before the second metal made itself evident as a reducer, and, in many cases, the first metal could be completely removed while the second was still present. The following results were obtained using permanganate in $2N$-sulphuric acid as oxidising agent. Zinc precedes all the metals tried : then in order come cadmium, manganese, thallium, tin, lead, copper, chromium, iron, bismuth, cobalt, and nickel. In none of the many combinations tried were any anomalies found, the order of precedence being invariably maintained. With the exception of cobalt and nickel, all the metals investigated are quantitatively removed from the amalgam without any mercury going into solution, as was shown previously (loc. cit.). When cobalt is removed, a little mercury accompanies it, but much less in amount, it was found by analysis, than corresponds with the cobalt removed. On the other hand, nickel, although it was removed simultaneously with the mercury, was found to be less in amount than corresponded with the mercury. These results indicate that cobalt, mercury, and nickel are removed from an amalgam in that order.

When ferric sulphate in $2N$-sulphuric acid was used as oxidising agent the metals suffered removal in exactly the same order, for the many combinations tried, as with permanganate, with one exception. With permanganate, tin definitely precedes lead; with ferric sulphate, tin and lead come out simultaneously. This is no doubt, connected with the fact that the electrode potentials of these two metals are very similar.

With uranyl sulphate in $2N$-sulphuric acid as oxidising agent, the metals investigated were confined to those which reduce this reagent partly or quantitatively. These are, in the order in which they are removed, zinc, cadmium, manganese, thallium, tin, and lead, and this order agrees with that given by the other oxidising agents.

Two experiments in illustration of the results given above will now be described.

Zinc and Iron.—200 G. of amalgam containing approximately 0·5 g. of zinc and 2·0 g. of iron were shaken with different volumes of $N/10$-ferric sulphate in $2N$-sulphuric acid, and the reduced solution was titrated with $N/10$-permanganate. So long as zinc only effects the reduction the volumes of ferric sulphate and permanganate should be identical; when iron alone effects the reduction the volume of permanganate required should be 1·5 times that of the ferric sulphate taken, since one atom of iron in being oxidised to the ferrous state reduces two ions from the ferric to the ferrous state. 28·0, 28·0, 21·1, 21·5, 11·5, and 10·7 C.c. of $N/10$-ferric sulphate were successively reduced and 28·1, 28·1, 21·0, 22·5, 14·1, and 14·8 c.c., respectively, of $N/10$-permanganate were required for titration. It is seen from these results that the iron begins to effect reduction after zinc equivalent to between 77·1 and 98·6 c.c. of $N/10$-ferric sulphate has been oxidised, *i.e.*, between 0·25 and 0·32 g. of zinc, or, in this case, between 50 and 64% of the amount taken. After that the iron takes an increasing share in the reduction. It is a conclusion from this experiment that a liquid zinc amalgam, containing a small quantity of iron as impurity, when used for reduction requires no correction, such as is necessary with ordinary zinc, for the iron present.

Copper and Iron.—In all experiments with these metals the amalgam contained originally 1 g. of each. The amalgam was shaken with permanganate, ferric sulphate, or uranyl sulphate in presence of sulphuric and hydrochloric acids, with and without ferrous ions originally present, both at the ordinary temperature and at 80°, to ascertain whether any combination of these conditions could affect the order in which these two metals were oxidised. The results were invariably the same : copper was found to do approxi-

mately the whole of the reduction at first; after about 20% of it had been used up, iron began to take a small but definite part in the reduction, which gradually increased until it became predominant. In no case was iron oxidised before copper.

Action of Amalgams on Various Oxidising Solutions.

A series of oxidising solutions was arranged in the order corresponding with increasing difficulty of reduction, and the action upon them was investigated of amalgams of zinc, cadmium, manganese, thallium, tin, lead, copper, iron, and bismuth in presence of $2N$-sulphuric acid. These experiments were carried out as far as possible under identical conditions : 200 g. of 1% amalgams were used; vigorous shaking was carried out for 1 miniute; the solutions to be reduced were approximately $N/10$ with respect to the ion to be reduced and $2N$ with respect to sulphuric acid; the reductions were effected in presence of air; and the subsequent oxidations were carried out with $N/10$-permanganate. The results are given in the table below; horizontally are arranged the oxidising solutions in decreasing order of ease of reduction, vertically the amalgams in the order (see above), in which they are removed from mercury by permanganate. The letter Q signifies that the reduction is quantitative, P that it is partial, and a dash that it is very slight indeed or absent. Results 5, 7, 9, and 10 for manganese, 5, 7, 9, and 10 for thallium, 5 and 7 for tin, and all but 1 and 2 for iron amalgams are new results. In no case do any of the remainder differ from those published by other workers, notably by Nakazono (*J. Chem. Soc. Japan*, 1921, **42**, 526, 761) and Someya (*Z. anorg. Chem.*, 1924, **138**, 291; 1925, **145**, 168; *Sci. Rep. Tôhoku Imp. Univ.*, 1925, **14**, 47).

Ref. and Serial Numbers. Amalgams.	1. $Mn^{VII}{\rightarrow}Mn^{II}$. 2. $Cr^{VI}{\rightarrow}Cr^{III}$. 3. $V^{V}{\rightarrow}V^{IV}$.	4. $Fe^{III}{\rightarrow}Fe^{II}$.	5. $U^{VI}{\rightarrow}U^{IV}$. 6. $Cu^{II}{\rightarrow}Cu$. 7. $Ti^{IV}{\rightarrow}Ti^{III}$.	8. $Sn^{II}{\rightarrow}Sn$.	9. $V^{IV}{\rightarrow}V^{III}$.	10. $U^{IV}{\rightarrow}U^{III}$.
$Zn \rightarrow Zn^{II}$	Q	Q	Q	Q	Q	P
$Cd \rightarrow Cd^{II}$	Q	Q	Q	Q	P	P
$Mn \rightarrow Mn^{II}$	Q	Q	Q	Q	—	—
$Tl \rightarrow Tl^{I}$	Q	Q	Q	Q	—	—
$Sn \rightarrow Sn^{II}$	Q	Q	Q	—	—	—
$Pb \rightarrow Pb^{II}$	Q	Q	Q	—	—	—
$Cu \rightarrow Cu^{II}$	Q	Q	—	—	—	—
$Fe \rightarrow Fe^{II}$	Q	Q	—	—	—	—
$Bi \rightarrow Bi^{III}$	Q	Q	—	—	—	—
$Hg \rightarrow Hg^{II}$	Q	—	—	—	—	—

It is seen from the table that there are no anomalies of reduction : no amalgam fails to do what a less reactive one can do; no amalgam

succeeds in reducing a solution which, in general, is harder to reduce, after having failed to reduce one which, in general, is more easily reducible. The results in this table may be taken as confirming the order, obtained above, in which metals are removed from mercury by oxidising agents.

Discussion of Results.

The order of the normal potentials of the metals under investigation in the free state is known to be manganese, zinc, chromium, iron, cadmium, thallium, cobalt, nickel, tin, lead, copper, bismuth, and mercury. There is some doubt as to whether copper precedes or succeeds bismuth, but it is agreed that their normal potentials are similar. The order in which the metals are removed from mercury by oxidising agents, found in this research, is zinc, cadmium, manganese, thallium, tin, lead, copper, chromium, iron, bismuth, cobalt, mercury, and nickel. The two orders are seen to differ only in the absolute positions of manganese, chromium, iron, cobalt, and nickel, all of which are displaced in mercury towards the noble metals. The relative order of these five metals is, however, the same in both series, being that given in the last sentence. If, in addition, bismuth should be definitely shown to precede copper in the free state, then the former should be included among these exceptional metals.

The five exceptional metals are the elements of atomic numbers 24 to 28, forming the pre-transition and transition elements of the first long series of the periodic classification. They differ sharply from the remaining metals investigated (which belong to B groups of the periodic classification) in that, whilst possessing electrons which on Bohr's theory are in the 4-quantum orbits, their 3-quantum orbits are incomplete.

There is a correlation pointed out by Bohr and others between the property of possessing inner orbits with an incomplete number of electrons, and other properties of an atom, notably, variable valency, magnetic and catalytic properties, and probably also passivity, although the relation of these properties to each other has not yet been worked out. The five elements under discussion have all been shown to exhibit the phenomenon of passivity (in the free state); they show variable valencies, possess coloured ions, and exhibit to a high degree, for light elements, magnetic and catalytic properties. There is thus a *prima facie* case for the view that passivity is a fundamental property of the atom connected in some way with the orbits of its electrons and not due (or, if so, only secondarily) to the existence of a protective film of oxide or of atoms of oxygen, as is commonly thought.

There can be no objection to our saying that these five metals when obtained in mercury are in the passive state, since the term passive implies merely that an active metal is behaving as though it were a relatively nobler metal. (Whether or not the passivity is ascribed to the formation of an intermetallic compound, a matter still to be investigated, will not affect what is said below, since we believe that the experimental fact that the potential of such a compound lies generally between the potentials of its constituents is due to an alteration in the electronic orbits.) Zinc, thallium, and other metals of the B groups of the periodic classification behave in mercury as they do in the free state as regards their powers of reducing oxidising solutions, and the normal potentials of these metals in the free state and in a saturated amalgam are also very nearly equal. Iron in mercury, on the other hand, behaves like copper; as the table above shows, it cannot effect any reduction which copper cannot effect. It is not certain whether what we mean by " passive " is the same as is commonly implied by the term when applied to these elements. The passive state of these five elements in the free state is indefinite. It varies with the conditions which bring it about; no two workers agree to within 0·2 volt as to the normal potential of any metal in the passive state. This is especially the case with chromium : it may be made so passive as to lie in potential between copper and mercury which agrees with the position we find for it. It may, however, be made as passive as platinum or only as passive as lead (Muthmann and Fraunberger, *Sitzungsber. Bayer. Akad.*, 1904, **34**, 201). Again, passive iron (in the free state) is known to lie on the noble side of both copper and silver, whereas we find that it lies between copper and silver when passive in mercury. On the other hand, the seven elements commonly reported to exhibit passivity in the free state are the five under discussion together with tungsten and molybdenum, which we have also investigated. These seven are the only elements which we have hitherto found to be passive in mercury. The two forms of passivity are thus connected, but the connexion is not discussed here.

Theory of Passivity.

The distribution of electrons in the atoms of the ordinary (active) form of chromium, manganese, iron, cobalt, and nickel, on Bohr's theory, is 2, 8, x-12, 2 in the 1-, 2-, 3-, and 4-quantum orbits, respectively, where x is the atomic number of the element. These metals ionise to form bivalent ions which accordingly have 2, 8, x-12, 0 electrons in the four orbits, respectively. In other words, the bivalent ions correspond in electronic structure with the metals in the active state. Each of these five metals in the active state is

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more reactive than tin and lead. It is to be expected, therefore, that their ions will not easily be reduced to the metallic state, for example, by shaking with zinc. This is borne out experimentally. Iron, passive in mercury, lies on the noble side of copper, as has been shown above, and, when oxidised, becomes the ferrous ion, There is no experimental evidence that the ferrous ion so formed differs from that formed from active iron. Now the ferrous ion does not correspond with passive iron, for, if it did, it should be more easily reduced to the metal when shaken with zinc than the cupric or the stannous ion. Passive iron in consequence cannot have the electronic structures 2, 8, 14, 2 of active iron, or 2, 8, 16, 0, which, on theoretical grounds, would make iron totally incapable of combining with another element. It may have the structures 2, 8, 15, 1, or 2, 8, 13, 3, etc. One electron in the 4-quantum orbit is a more likely disposition than three or another number of electrons, since it is known that there is a stronger tendency in the atoms of these elements to fill up the 3-quantum orbits at the expense of the 4-quantum orbits than vice versa. We think, therefore, that passive iron has the structure 2, 8, 15, 1 and that the four other elements under consideration have similar structures of the form 2, 8, x-11, 1.

Consider now passive iron with the proposed structure 2, 8, 15, 1. Univalent iron is unknown ; there is no ion, therefore, corresponding with the structure 2, 8, 15, 0. In order to form ferrous ion, passive iron must first change to active iron and then expel its two outer electrons. Passive iron is therefore harder to oxidise, *i.e.*, is nobler, than active iron, the energy of oxidation of the former being less than that of the latter by an amount equal to the work required to remove the necessary electron from the 3- to the 4-quantum orbit. Similar considerations apply to the four other elements. Since the elements under discussion are not widely different in chemical activity, and possess similar electronic structures and similar atomic weights, it is likely that the value of this work will be similar in each case. This hypothesis is tested most easily by estimating the difference in the normal potentials of the active and passive states of these elements. The normal potentials of the metals when passive in mercury have not been determined directly, and, indeed, we find great difficulties in such determinations owing to the very small solubilities of these metals in mercury, an account of which will be given in the following paper, but they may be estimated approximately by a consideration of the positions of these passive metals with respect to the metals of known normal potentials. (In what follows, passive refers to passivity in mercury and potentials refer to normal potentials in volts on the hydrogen scale.)

Passive manganese lies between cadmium and thallium; its normal potential therefore lies between -0.42 and -0.32, say -0.37. Passive iron is on the noble side of copper ($+0.35$), has approximately the same reducing properties in $2N$-sulphuric acid as sulphur dioxide with an oxidation-reduction potential of $+0.40$, and is more powerful as a reducing agent than ferrous sulphate in $2N$-sulphuric acid with an oxidation-reduction potential of $+0.51$; its normal potential is therefore close to $+0.4$. Passive chromium lies between copper and passive iron and has, therefore, a normal potential close to $+0.38$. Cobalt and nickel appear to lie close to mercury on its reactive and noble sides respectively. Their potentials may therefore be taken as about $+0.8$. In the table below, these results are compared with the normal potentials of the same metals in the active state.

	Normal potential (volt) in active state.	Normal potential (volt) in passive state.	Difference (volts).
Manganese	-1.0	-0.37	0.63
Chromium	-0.4	$+0.38$	0.78
Iron	-0.43	$+0.4$	0.83
Cobalt	-0.22	$+0.8$	1.02
Nickel	-0.20	$+0.8$	1.00

The table shows that, as is to be expected from the theory advanced, the differences in the normal potentials of the active and passive states of these five elements are of the same order. They apparently increase regularly from the more active to the more noble metals. This relation and the reproducibility of the passive state in mercury seem to us to show that the passive is as definite an electronic state of the atom as the active, and to rule out the view that the passive state is due to the protection of an adhering film. It seems inconceivable that in an amalgam of cadmium, manganese, and thallium, for instance, a film could cover manganese only (since the other two metals behave normally in mercury) and so protect it that no manganese is attacked by acid or oxidising agent until the major part of the cadmium has been removed, and that thereafter the manganese could be attacked to the almost entire exclusion of thallium. There is a further consideration. It will be apparent from the results given in the table above for iron, nickel, and cobalt, that the passive state of these metals is that which corresponds with the ordinary state of the metals of the other two transition groups. This is demonstrated in the table below, which includes, for the sake of a fuller comparison, the approximate values of the potentials of tungsten and molybdenum in mercury found in the work described in the following paper.

Approximate values of $_0E_h$ in volts.

Cr (active).	Fe (active).	Co (active).	Ni (active).
-0.4	-0.4	-0.2	-0.2
Cr (passive).	Fe (passive).	Co (passive).	Ni (passive).
$+0.4$	$+0.4$	$+0.8$	$+0.8$
Mo (passive).	Ru.	Rh.	Pd.
$+0.8$	$ca. +0.9$	$ca. 0.9$	$ca. 0.9$
W (passive).	Os	Ir	Pt
$+0.8$	$ca. +1.0$	$ca. 1.0$	$ca. 1.0$

In view of this result, the passivity of these six metals is as likely to be a fundamental property of their atoms as is the ordinary state of the metals of the palladium and platinum transition groups. It is, of course, a possible, although not a necessary, consequence of this conclusion that these metals could be prepared in the active state. A necessary consequence is that the atom of each of these metals (of the palladium and platinum groups) should have one electron only in the outermost quantum orbit. There is, however, no evidence for or against this conclusion at present. Kramers's work on the spectra of nickel (Kramers and Holst, " The Atom and the Bohr Theory of its Structure," 1923), however, strongly suggests that the nickel atom has ordinarily one electron only in its outermost (4-quantum) orbit. This is consistent with the view put forward here, since it is known that metallic nickel is ordinarily in the passive state in contradistinction to iron and manganese, which are ordinarily in the active state. For example, when a nickel wire is dipped in hydrochloric acid, it behaves as though its normal potential were approximately that of silver, as von Hevesy with radioactive indicators has shown (*Phil. Mag.*, 1912, **23**, 628), a result very similar to our determination of the potential of nickel in mercury given above.

Lambert and Thomson (J., 1910, **97**, 2426; 1912, **101**, 2056; 1915, **107**, 218) made a sample of iron of so pure and uniform a character that it would not rust under conditions which allowed the rapid rusting of ordinary iron by water and oxygen; it also failed to reduce copper sulphate to the metal. When stressed, however, so that the pure iron no longer remained electrically neutral, rusting ensued. The inference from these remarkable observations is that the unreactive is a possible normal state of metallic iron. Our results are consistent with Lambert's work. Iron and the other metals investigated, when obtained in mercury, are entirely free from stress and therefore able to behave like Lambert's pure iron. The observation that his unreactive iron lies on the noble side of copper is also consistent with the position we have found for passive iron in mercury.

Granted that an element may exist in alternative electronic

forms in the metallic state, it is unlikely that it will exist in both states simultaneously when unstressed and mobile in mercury, but why, in the metals investigated, the passive should be preferred to the active configuration, we do not know.

Summary.

(1) The order of removal of zinc, cadmium, thallium, tin, lead, copper, and bismuth from mercury by oxidising agents is that to be expected from the positions of these metals in the normal potential series, whereas that of manganese, chromium, iron, cobalt, and nickel is not according to expectation. The order in mercury is zinc, cadmium, manganese, thallium, tin, lead, copper, chromium, iron, bismuth, cobalt, mercury, and nickel. The absolute positions of manganese, chromium, iron, cobalt, and nickel in mercury are displaced towards the noble elements, but their relative order remains unaltered.

(2) The abnormal behaviour of these elements is ascribed to a type of passivity, an electronic theory of which is put forward. On this theory the active state of these metals is ascribed to the existence of two electrons in the 4-quantum orbit of the atom, and the passive state to one electron in this orbit.

(3) Reducing properties of amalgams of manganese, tin, and iron are described.

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