CCCXIV.—*The Order of Removal of Metals from Amalgams.*

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IT was shown by Russell, Evans, and Rowell (J., 1926, 1872) that the order in which metals are removed by oxidising solutions from mercury in which they are dissolved or suspended is zinc, cadmium, manganese, thallium, tin, lead, copper, chromium, iron, bismuth, cobalt, mercury, and nickel. The reasons for the abnormal positions occupied by manganese, chromium, iron, cobalt, and nickel were discussed. Russell and Rowell (*ibid.*, p. 1881), in the course of other work, extended these results to molybdenum and tungsten : working with amalgams of these metals of very low concentrations only, they found that both metals lie close to mercury, molybdenum being on the less reactive, and tungsten on the more reactive side. Since this work, Jackson, Russell, and Merrill (preceding papers) have prepared more concentrated (up to 10%) amalgams of these metals, and by using them the present author has been able to fix the positions of these metals more accurately. He finds that molybdenum in mercury is definitely on its reactive side and lies between iron and cobalt; on the other hand, tungsten is definitely on the less reactive side and is removed from amalgams after nickel. During this work it was found that the position assigned to bismuth was in error : it lies, not between iron and cobalt, but between lead and copper. The corrected order is therefore zinc, cadmium, manganese, thallium, tin, lead, bismuth, copper, chromium, iron, molybdenum, cobalt, mercury, nickel, and tungsten.

EXPERIMENTAL.

The Position of Molybdenum.—Amalgams containing 1% of the metals iron, molybdenum, cobalt, and nickel were prepared by electrolysing known concentrations of solutions of their salts and using mercury as cathode. Those of iron, cobalt, and nickel were prepared by the usual methods, and that of molybdenum by the method of Merrill and Russell (this vol., p. 2389). From these were prepared mixed amalgams of iron, nickel, or cobalt with molybdenum in approximately atomic proportions. When the first of these was shaken with a solution of $N/10$-potassium permanganate or $N/10$-ferric sulphate in $2N$-sulphuric acid, the analysis of the resulting solution showed that the iron had been responsible for practically the whole of the reduction effected. When the amalgam of molybdenum and nickel was similarly treated, it was found that the whole of the reduction was effected by the molybdenum; and in the case of the cobalt–molybdenum amalgam, 70% and 66% of the reduction were effected by the molybdenum when potassium permanganate and ferric sulphate respectively were used. From this result and from earlier results with mixed amalgams of zinc and cadmium, cadmium and tin, and tin and lead, it was inferred that molybdenum, although it is definitely removed before cobalt, lies very close to it in the order of their removal from mercury.

A 1% amalgam of molybdenum, in contradistinction to a 1% amalgam of cobalt, was found to reduce permanganate or ferric sulphate quantitatively, *i.e.*, the quantity of molybdenum oxidised is equivalent to the reagent reduced. Cobalt, in these circumstances, is known from the earlier work to be accompanied by mercury. This is additional proof that molybdenum lies further from mercury than cobalt. With amalgams of molybdenum weaker than 1%, however, some mercury was found to accompany the molybdenum when reduction was effected, more mercury taking part in the reduction of a given volume of permanganate the weaker the amalgam in molybdenum. In this respect molybdenum resembles cobalt; in comparative experiments with amalgams of similar atomic percentages of molybdenum and cobalt, however, more mercury was found always to accompany the cobalt than the molybdenum.

From these results it is clear that the order of removal from mercury is iron, molybdenum, cobalt, and mercury; also that molybdenum and cobalt lie close together.

The Position of Tungsten.—A 5% tungsten amalgam, prepared by the method of Jackson, Russell, and Merrill (*loc. cit.*), was shaken with an acidified solution of $N/10$-potassium permanganate until the latter was decolorised. The resulting solution, on analysis, was found to contain an amount of mercury equivalent to the permanganate reduced, but no tungsten detectable by the blue colour characteristic of tungsten solutions when they are shaken with zinc or zinc amalgam. Similar results were obtained with alkaline permanganate and acidified dichromate as oxidising agents. Acidified permanganate was then decolorised by a 1% nickel amalgam, and the resulting solution analysed. The atomic ratio of mercury to nickel taking part in the reduction was found to be approximately 4, and a 2% nickel amalgam gave a similar result. These experiments suggested that nickel lies closer to mercury in its behaviour towards permanganate than does tungsten. This suggestion was confirmed by preparing an amalgam containing equal atomic proportions (approx. 0·5%) of nickel and tungsten, shaking it with permanganate until the latter was decolorised, and analysing the resulting solution. It was found that 72% of the atoms going into solution were mercury and the remainder nickel; tungsten took no part in the reduction. An identical result was obtained when silver was substituted for tungsten. Tungsten and silver are therefore removed from mercury after mercury and nickel, and nickel is nearer to mercury in its behaviour towards permanganate than it is to tungsten or silver. It was not possible by these methods to decide the relative positions of tungsten and silver.

The discrepancy between these results for molybdenum and tungsten and those obtained earlier has been traced to the concentrations of the amalgams and to the methods used for detecting these metals. Russell and Rowell (*loc. cit.*) worked principally with amalgams of these metals containing only about 10^{-3} g. of metal in 100 g. of mercury, and had to rely for their detection, not, as in the present work, on the ordinary gravimetric and volumetric methods of analysis, but on their catalytic effect on the reaction $2H \longrightarrow H_2$ initiated by action of zinc upon acids. This effect is shown by concentrations of these metals below those detectable by ordinary methods, and is not proportional to the quantity of metal present. Now, as has been mentioned above, the less concentrated a molybdenum amalgam is, the more does mercury assist the molybdenum in reducing permanganate. A weak amalgam of molybdenum, in consequence, would appear not to be further weakened when shaken with permanganate provided there is sufficient to give the catalytic effect used to detect the presence of the molybdenum, and work at this range of concentration would lead to the conclusion that molybdenum is more noble than mercury. At a still smaller concentration, nearly the whole of the molybdenum would appear suddenly to be removed by the permanganate owing to the disappearance of the very small quantity necessary to give the catalytic effect, and any one working at this range of concentration would conclude that molybdenum was less noble than mercury. Similar results have been obtained with tungsten amalgams: very small quantities of tungsten (below concentrations detectable by ordinary methods) are easily removed from mercury by permanganate, a result which might suggest that tungsten is on the reactive side of mercury, whereas when concentrated amalgams are employed, as has been shown above, the experiments lead to the opposite conclusion. These observations explain why Russell and Rowell were misled.

The Position of Bismuth.—A 1% amalgam of bismuth, prepared by dissolving the metal in 200 g. of mercury, was found to reduce copper sulphate in sulphuric acid solution to copper. This suggested that the former observation that bismuth is removed from mercury after copper is erroneous. Amalgams of bismuth were mixed with those of equal atomic concentrations of tin, lead, and copper and shaken with acidified solutions of potassium permanganate, ferric sulphate, uranyl sulphate, and other oxidising agents. The analyses of the resulting solutions showed clearly that bismuth is removed from mercury after lead and before copper.

Summary.

The order of removal of molybdenum, tungsten, and bismuth from mercury by oxidising agents has been redetermined with respect to other metals whose positions are known from earlier work. The complete order of those metals investigated is Zn, Cd, Mn, Tl, Sn, Pb, Bi, Cu, Cr, Fe, Mo, Co, Hg, Ni, and W. Molybdenum and cobalt lie close together in this order, and so do mercury and nickel.

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