

382. *Intermetallic Compounds formed in Mercury. Part V. Compounds in the Zn-Mn, Zn-Co, Zn-Ni, Al-Fe, Sn-Mn, and Sn-Co Systems.*

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THE compounds of tin or zinc with copper or iron, prepared by the usual processes in metallurgy, and investigated by *X*-ray or thermal methods, are, on the whole, richer in tin or zinc than those formed in mercury at the ordinary temperature; *e.g.*, Sn_2Fe , SnFe , and SnFe_2 have been found by *X*-ray or thermal methods (Edwards and Preece, *J. Iron Steel Inst.*, 1931, **124**, 41; Ehret and Westgren, *J. Amer. Chem. Soc.*, 1933, **55**, 1339; Wever and Reinecken, *Z. anorg. Chem.*, 1926, **151**, 349); but SnFe_2 , SnFe_3 , and SnFe_5 are formed in mercury (Russell, Kennedy, Howitt, and Lyons, *J.*, 1932, 2340); the other three types of compound (Sn-Cu , Zn-Cu , and Zn-Fe) show similar differences. In three of these four systems, there are four compounds common to both methods of investigation (*viz.*, SnFe_2 , Sn_5Cu_6 , SnCu_3 , ZnCu).

It is important to get as much evidence as possible as to whether or not the compounds which are formed so readily in mercury at the ordinary temperature, and are capable of being analysed so simply *in situ*, have the same empirical formulæ as those prepared at high temperatures and investigated by *X*-ray and thermal methods. To this end were sought systems in which tin-rich, aluminium-rich, and zinc-rich compounds in mercury were stable and, further, in which mercury itself would not complicate comparisons by combining to form ternary compounds. In the Sn-Cu , Zn-Cu , and Cd-Cu systems, which have been extensively investigated in mercury, ternaries including mercury form more readily than do binaries, and, on the whole, are stabler. These systems, therefore, are not suitable for the purpose in hand although they are interesting because of the large number of ternary compounds they contain.

The systems mentioned in the title have been found suitable at the ordinary temperature, the following being unsuitable: Cd-Fe , Cd-Mn , Cd-Co , Cd-Ni , Pb-Cu , Pb-Fe , Bi-Cu , Bi-Fe , Tl-Cu , and Tl-Fe , because no binary appeared to be formed; and Al-Cu , because only ternary compounds were formed with mercury.

The methods of preparation and analysis were in principle those already described (Russell *et alii*, *J.*, 1932, 841, 852, 857). A compound of zinc, aluminium, or tin with manganese, cobalt, nickel, or iron was first made as rich as possible in the former metal. This was then decomposed with the formation of uncombined zinc, aluminium, or tin and a new compound richer in the second class of metal. After analysis, this was further decomposed until another compound was formed and it was analysed; the process was repeated until no further change in the composition of the binary compound could be brought about. Only in the Al-Fe system did mercury combine with the binary compound at any stage.

In Table I are given for comparison the approximate, empirical formulæ of the zinc compounds found in mercury and of those found by *X*-ray or thermal methods.

TABLE I.

General formula.	X-Ray.	Hg.	X-Ray.	Hg.	X-Ray.	Hg.
Zn ₇ X	Zn ₇ Mn	Zn ₇ Mn				
Zn ₂₁ X ₅		Zn ₄ Mn	Zn ₂₁ Co ₅	Zn _{4.2} Co	Zn ₂₁ Ni ₅	Zn _{4.2} Ni
Zn ₃ X	Zn ₃ Mn	Zn ₃ Mn		Zn ₃ Co	Zn ₃ Ni	Zn ₃ Ni
ZnX					ZnNi	ZnNi

The formulæ of compounds obtained by the mercury method are, as has been stated, approximate only; the suffix 4.2 does not differentiate between a ratio of 21 : 5 and say 25 : 6 or 17 : 4. The *X*-ray work on the Zn-Mn system was done by Parravano and Montoro (*Mem. R. Accad. Italia Sci. Fis. Mat. Nat.*, 1930, 1, Chim., No. 4), on the Zn-Co system by Ekman (*Z. physikal. Chem.*, 1931, B, 12, 57), and on the Zn-Ni system by Ekman (*loc. cit.*), Tamaru (*Bull. Inst. Phys. Chem. Res. Tokyo*, 1932, 11, 90), Tafel (*Metal-lurgie*, 1907, 4, 781; 1908, 5, 413), and Vigouroux and Bourbon (*Bull. Soc. chim.*, 1911, 9, 873).

In Table II the formulæ of the three compounds found by the mercury method in the Al-Fe system are compared with all those known from *X*-ray and thermal work (Bradley and Jay, *J. Iron Steel Inst.*, 1932, 125, 339; *Proc. Roy. Soc.*, 1932, A, 136, 210; Osawa, *Sci. Rep. Tohoku*, 1933, 22, 803) and with those of three compounds of the Al-Cu system (see *Trans. Faraday Soc.*, 1929, 25, 367).

TABLE II.

X-Ray.	Hg.	X-Ray.
Al ₃ Fe, Al ₅ Fe ₂ , Al ₂ Fe		
AlFe	AlFe, Al ₄ Fe ₃	AlCu, Al ₄ Cu ₉
AlFe ₃	AlFe ₃	AlCu ₃

Table III similarly gives the approximate empirical formulæ of compounds of the Sn-Mn and the Sn-Co system, found by the various methods, and also those of the Sn-Fe system to which reference has been made above.

TABLE III.

General formula.	Thermal.	Hg.	Thermal.	Hg.	X-Ray.	Hg.
Sn ₃ X		Sn ₃ Mn				
Sn ₂ X		Sn ₂ Mn		Sn ₂ Co	Sn ₂ Fe	
SnX	SnMn	SnMn	SnCo		SnFe	
SnX ₂	SnMn ₂	SnMn ₂	SnCo ₂	SnCo ₂	SnFe ₂	SnFe ₂
SnX ₃						SnFe ₃
Sn ₃ X ₃₁	SnMn ₄					
SnX ₅						SnFe ₅

No *X*-ray work has yet been done on the first two systems. The thermal work on the Sn-Mn system was done by Williams (*Z. anorg. Chem.*, 1907, 55, 24), that on the Sn-Co system by Schemtschuschny and Belynsky (*ibid.*, 1908, 59, 364) and by Lewkonja (*ibid.*, p. 293).

EXPERIMENTAL.

Compounds of Tin and Manganese.—0.5 G. of manganese was obtained electrolytically in 250 g. of mercury, in which 8 g. of tin had earlier been completely dissolved, by the method of Russell, Evans, and Rowell (J., 1926, 1872). After 24 hours, oxidation with permanganate in acid solution of the amalgam revealed tin only, showing that there was no free manganese (which is more reactive than free tin) and that any compounds formed between tin and manganese were less reactive than tin itself. The oxidation of the amalgam was continued with ferric sulphate in acid solution until manganese ions were detected in the ferrous sulphate. At this stage the atomic proportion of tin to manganese was calculated to be approximately 3. The amalgam was then treated with successive quantities of 30 c.c. of *N*/10-permanganate in sulphuric acid and the total manganese determined volumetrically by the sodium bismuthate method, until this content was found constant (Found : 40.7—41.0 c.c. *N*/10-KMnO₄. Sn₃Mn

oxidised to Sn^{IV} and Mn^{II} requires 40.7 c.c.). The tin was now determined by oxidising the amalgam with 50 c.c. of $N/10$ -permanganate and weighing the purified stannic oxide thereby obtained (Found : 0.163 g. Sn_3Mn requires SnO_2 , 0.1615 g.). The absence of mercury from the compound was proved both by qualitative tests and by the agreement of the manganese and tin determinations in fixing the empirical formula of the compound as Sn_3Mn . After these determinations had been confirmed the amalgam was heated at 100° for an hour and re-examined. It was found to have decomposed into free tin and a compound richer in manganese. The free tin was removed and the compound was examined as before (Found : 44.8, 45.1 c.c. $N/10$ - KMnO_4 . Sn_2Mn requires 45.0 c.c. Found : 0.153 g. SnO_2 . Sn_2Mn requires 0.1507 g.).

The amalgam containing Sn_2Mn , after having been heated for 2 hours and then kept for 24 hours, was found to have decomposed into free tin and a compound of empirical formula SnMn . By the addition of tin to different concentrations of manganese in mercury, and by electrolysing different amounts of manganese into tin amalgams of fixed concentration it was possible to get a fourth compound SnMn_2 and to confirm the formulæ of the other three compounds. In amalgams containing approximately 3% or more of tin and manganese, free tin was obtained when a compound was decomposed by heat. In much weaker amalgams, containing approximately 0.5% or less of tin and manganese, free manganese was obtained when decomposition occurred. The series of decompositions which have led to the finding of these tin-manganese compounds is similar to those occurring in the Zn-Cu and Sn-Cu systems. The four Sn-Mn compounds found are insoluble in mercury. They are definitely less reactive towards oxidising agents than tin, and, *a fortiori*, than manganese. Each reduces U^{VI} to U^{IV} , V^{V} to V^{III} , and, slowly, Cu^{II} to metal in sulphuric acid solution.

Compounds of Zinc and Manganese.—This system behaves very similarly to that just described and was investigated by similar methods. In analytical work manganese only was determined by the volumetric method; zinc was not determined. Mercury was not a constituent of the three compounds (see Table I).

Compounds of Zinc and Cobalt.—2 G. of cobalt were obtained electrolytically in 250 g. of a 2.5% zinc amalgam from cobalt sulphate in sulphuric acid solution. After it had stood for several days, zinc free from cobalt was found to be oxidised by acidified permanganate. This excess of uncombined zinc was then removed by reacting with acid in presence of tungsten as catalyst (Russell and Rowell, J., 1926, 1881). Oxidation was then continued with permanganate until cobalt ions were detectable in the liquid. At this stage the amalgam was oxidised by successive quantities of 30 c.c. of $N/10$ -permanganate in sulphuric acid solution. No mercury was oxidised. The cobalt in the liquid was determined without separation of zinc or manganese ions as Co_3O_4 after precipitation by α -nitroso- β -naphthol; the zinc was separated from cobalt and manganese and determined in neutral solution as phosphate. The results gave an atomic ratio $\text{Zn}/\text{Co} = 4.1\text{--}4.3$, so this compound is probably the $\text{Zn}_{21}\text{Co}_5$ found by Ekman (*loc. cit.*). It was insoluble in mercury and reduced V^{V} to V^{II} , U^{VI} to U^{IV} quickly, and Cu^{II} to copper without difficulty. On being heated for $\frac{1}{2}$ hour on the water-bath with 8N-sulphuric acid, zinc was liberated, as shown by the marked evolution of hydrogen. When the evolution had ceased, the amalgam was again quantitatively oxidised by successive quantities of 30 c.c. of $N/10$ -permanganate. Again mercury was absent. Cobalt and zinc were determined as before. The results agreed in fixing the empirical formula of the compound as Zn_3Co . This compound was remarkably stable and did not further decompose when heated at 100° . It was quite insoluble in mercury; it reduced U^{VI} to U^{IV} , but V^{V} only to V^{III} , and Cu^{II} to copper very slowly, in sulphuric acid solution.

Repetition of the process which had given $\text{Zn}_{4.2}\text{Co}$ with different quantities of zinc and cobalt gave Zn_3Co oftener than $\text{Zn}_{4.2}\text{Co}$. With the former compound, decomposition at 100° afforded the latter. When the order of adding zinc and cobalt to mercury was reversed, the only compound obtained with certainty had the empirical formula ZnCo_4 . To 400 g. of a 0.5% amalgam of cobalt were added 10 g. of zinc, and the whole left for 7 hours. Tungsten was then deposited on the amalgam, and the whole heated at 100° for an hour with 4N-sulphuric acid to remove the excess of zinc. Oxidation of the amalgam by 25 c.c. of $N/10$ -permanganate then gave 0.0795 g. of Co_3O_4 (Calc. for ZnCo_4 : 0.0803 g.).

Compounds of Zinc and Nickel.—The procedure here was very similar to that with cobalt. Nickel was determined with dimethylglyoxime. The compound obtained after the removal of excess of zinc gave an atomic ratio $\text{Zn}/\text{Ni} = 4.1\text{--}4.3$. It had very similar reducing properties to the corresponding compound of zinc and cobalt, and decomposed to a compound of approximate empirical formula Zn_3Ni . This, however, further decomposed on prolonged

treatment with 4*N*-sulphuric acid at 100° to uncombined zinc and ZnNi which was stable. No further compounds were obtained by altering the proportions of zinc and nickel, or the order in which they were brought together in mercury. In none of them was mercury present as a constituent.

Compounds of Aluminium and Iron.—Attempts to form Al-Fe compounds in mercury by the addition of aluminium to iron amalgams at ordinary temperature were unsuccessful. The surface of the amalgam always became oxidised and hot; sometimes there was a pyrophoric effect. When the action subsided, the whole of the iron had been removed from the mercury. As iron amalgams of the concentrations employed (0.5—3%) do not show these oxidation effects characteristic of aluminium amalgams, it would seem that when aluminium was added to the iron amalgam combination with iron ensued and the resulting complex was sufficiently reactive to be oxidised immediately in the air. If this is the explanation of the effect it is unlikely that the aluminium-rich (and, therefore, probably highly reactive) compounds which have been reported (Table II) will be obtained by the mercury method. A simple method of obtaining iron-rich compounds consisted in adding aluminium foil to amalgams containing either Zn-Fe or Sn-Fe compounds. In the first case aluminium was found completely to displace the zinc, and in the second case the tin. To a 3% amalgam of iron in 250 g. of mercury were added 8 g. of zinc. After 24 hours, the excess of zinc was removed by the tungsten method. To the Zn-Fe compound was then added aluminium foil and a little 2*N*-sulphuric acid, and the whole was heated at 50°. Qualitative tests showed that zinc was being rapidly removed from the amalgam. After an hour the excess of aluminium was removed by acid, and the compound in the amalgam examined by the usual method. It contained aluminium and iron but no zinc or mercury. Excess of aluminium was added to this, and the amalgam set aside for a day. Then the free aluminium was removed with acid, and the compound examined. Aluminium was determined gravimetrically as oxide, and iron volumetrically by reduction to ferrous iron with zinc amalgam and titration with *N*/10-permanganate. The results agreed in settling the empirical formula of the compound as AlFe. This lost aluminium when heated with sulphuric acid at 100° for a short time. The new compound was analysed for aluminium and iron as before, and found to have the approximate formula Al₄Fe₉. On standing for several days this compound became AlFe₃, which did not further decompose. On the addition of aluminium to this last compound Al₄Fe₉ was more often obtained than AlFe. With AlFe₃, though not with the other compounds, there was a tendency in dilute amalgams to combine with mercury: in one experiment a compound of approximate empirical formula Al₂Fe₆Hg₃ was obtained. Aluminium and iron were determined as described above, and mercury by the volumetric thiocyanate method with ferric iron as indicator.

DISCUSSION OF RESULTS.

It is seen that the transition elements iron, cobalt, and nickel and the pre-transition element manganese differ sharply from copper in that they form compounds with zinc, aluminium, and tin in mercury without the last being present as constituent. Binary compounds of iron, cobalt, nickel, or manganese with zinc, aluminium, or tin are therefore suitable for the purpose of comparing the empirical formulæ obtained by the usual processes of metallurgy and by the mercury method.

It is clear from Tables I, II, and III that in these different systems there is good agreement over the range of formulæ and in some cases exact agreement of empirical formulæ. Where, as in the Al-Fe system, compounds obtained by *X*-ray or thermal methods have not been found by the mercury method, there are good reasons for their non-occurrence, indicated partly in the present work and partly, by analogy, in work on previous systems. Where compounds obtained by the mercury system are new, they have formulæ which seem reasonable on other grounds. For instance, iron was shown by Russell and Lyons (J., 1932, 857) to be equivalent to copper in zinc and tin compounds when atoms of iron or copper are in excess in the molecule. It is reasonable, therefore, to expect that Al₄Fe₉ corresponds with Al₄Cu₉, with 21 valency electrons to 13 atoms, identified by Bradley and Thewlis (*Phil. Mag.*, 1928, 6, 878; *Proc. Roy. Soc.*, 1926, A, 112, 678). The tables show also that manganese, iron, and cobalt are equivalent when united in excess with tin, and that manganese, cobalt, and nickel are equivalent when united in excess with zinc. Now Ekman (*loc. cit.*) has shown that the nine transition

metals are equivalent when united with excess of zinc atoms in compounds of the type $Zn_{21}Fe_5$. It would appear from Table I that manganese also belongs to this class. It seems then that in binary compounds between tin, aluminium, or zinc and manganese, iron, cobalt, or nickel, the last four are equivalent whether or not they are in excess in the molecule of the intermetallic compound. The reason for distinguishing between excess of atoms of a transition metal in a molecule and excess of atoms of zinc, aluminium, or tin, is that when the former are not in excess they do not appear to contribute any valency electrons to the system of electrons in the molecule. In the other case, however, as the results now show, not only are the transition metals and manganese equivalent, but each contributes one electron per atom to the system. This is a new generalisation. It is part of an extension of the criterion of an intermetallic compound first laid down by Hume-Rothery (*J. Inst. Metals*, 1926, **35**, 295), involving fixed ratios between valency electrons and number of atoms in the molecule and the assignment of different valency electrons in different circumstances to transition and pre-transition metals. This subject has been discussed by Russell (*Nature*, 1934, **133**, 217).

Despite the fact that compounds formed in mercury cannot at present be investigated by the X-ray method, there is satisfactory evidence of a chemical nature that they are the same kind of compound as those investigated and substantiated by workers with the X-ray and other physical methods. As there is no reason to believe that the ternary and quaternary compounds (Russell, *loc. cit.*) formed in mercury differ in kind from the binary compounds, the mercury method promises to be useful in investigations in fields where physical methods are at present inapplicable.

SUMMARY.

Intermetallic compounds Zn_7Mn , Zn_4Mn , Zn_3Mn , $Zn_{4.2}Co$, Zn_3Co , $ZnCo_4$, $Zn_{4.2}Ni$, Zn_3Ni , $ZnNi$, $AlFe$, Al_4Fe_9 , $AlFe_3$, Sn_3Mn , Sn_2Mn , $SnMn$, $SnMn_2$, Sn_2Co , and $SnCo_2$ have been found by the mercury method and analysed without their removal from the mercury. The formulæ in italics represent new compounds. The agreement of these empirical formulæ with those obtained by thermal and X-ray methods in the six systems is satisfactory. It is concluded that the compounds investigated by the mercury method are the same as those investigated and characterised by workers with physical methods.

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