Quaternary Intermetallic Compounds

INVESTIGATORS of metallic systems by thermal and X-ray methods have found many binary intermetallic compounds; they have found, however, only a few ternary and no quaternary compounds. If a metal or metals of one class (zinc, tin, cadmium, mercury) reacts in mercury at ordinary temperature with one of another (copper, iron, cobalt, nickel, manganese), many binary and ternary compounds result[1].

Recently we have succeeded in getting three of the first class to unite with copper to form reasonably stable quaternary compounds, the analysis of which by the volumetric processes of the laboratory presented no difficulty. Seven of them were obtained by the reaction between zinc and the simplest ternary compound which forms in mercury, namely, $SnCu_3Hg_7$. Their approximate empirical formulæ are: $Sn_4Cu_{12}Zn_4Hg_3$, $Sn_5Cu_{15}Zn_5Hg_9$, $SnCu_3ZnHg_6$, $SnCu_3ZnHg_9$, $Sn_4Cu_{12}Zn_4Hg_{45}$, $Sn_4Cu_{12}Zn_7Hg_{21}$ and $Sn_4Cu_{12}Zn_7Hg_{33}$. Four others have been prepared by the reaction between tin and the simplest binary compound which forms in mercury, namely, ZnCu. Their approximate empirical formulæ are: $Zn_8Cu_8SnHg_7$, $Zn_6Cu_8SnHg_9$, $Zn_{40}Cu_{40}Sn_5Hg_{14}$ and $Zn_{40}Cu_{40}Sn_{12}Hg_{21}$. Cadmium forms ternaries with copper and mercury without difficulty but not with copper and zinc or with copper and tin. Quaternaries or quinaries including cadmium cannot, in consequence, be so prepared.

Ternary and quaternary compounds formed in mercury, so far as the work has gone, may be regarded as derived from known compounds of mercury and copper in which other metals of the *B* sub-group of the Periodic Classification partly replace the mercury, an atom of the quadrivalent tin counting as two divalent atoms of mercury; zinc, cadmium and mercury being equivalent. Thus $SnCu_3Hg_7$, $SnCu_3ZnHg_6$ and $Sn_4Cu_{12}Zn_7Hg_{21}$ may be regarded as derived from $CuHg_3$, a compound which has been prepared in mercury but otherwise is unknown in metallurgy. (The corresponding $CuZn_3$, however, is well known.) Similarly, $Sn_5Cu_{15}Zn_5Hg_9$, $Zn_{40}Cu_{40}Sn_5Hg_{14}$, and the ternaries (not mentioned above) $Zn_2Cu_5Hg_6$ and $Zn_4Cu_5Hg_4$, may be regarded as derivatives of Hg_8Cu_5, which has been prepared in mercury. (The corresponding Zn_8Cu_5 and Cd_8Cu_5 are well known in metallurgy.)

If this process of derivation is legitimate, our work is brought into line with that done by thermal and X-ray methods. In addition to the binary compounds which form easily in mercury or by other methods, there is the possibility of a large number which do not. Their existence, possible and actual, has enabled us to confirm and extend considerably the rules connecting the numbers of valency electrons and atoms which were put forward first by W. Hume-Rothery[2]; namely, for compounds between such metals as tin, zinc or cadmium and metals like copper, silver or iron, there are characteristic ratios of valency electrons to atoms of 3 : 2, or 21 : 13 or 7 : 4, that is to say, for 21 electrons there may be 14, 13 or 12 atoms in the compound. We find for a given number of electrons there are ranges of atoms. For copper united with a divalent metal of the *B* sub-group there may be for 42 electrons 21, 22, 23, 24, 25, 26, 27 or 28 atoms; for 18 electrons 12, 13, 14, 15 or 16 atoms. In tin-copper compounds, for 42 electrons there may be 14, 15, 16, 17 or 18 atoms, for 28 electrons, 12, 13, 14, 15 or 16 atoms and for 21 electrons, 12, 13 or 14 atoms. It would thus appear that the total number of valency electrons—18, 21, 28 or their multiples—is even more characteristic of an intermetallic compound than the ratio of electrons to atoms.

In reckoning valency electrons, metallurgists count copper and silver as having each one electron, zinc, cadmium and mercury as having each two electrons, and lead and tin as having each four. To fit transition metals like iron, cobalt and nickel into the schemes, they regard their atoms as contributing no valency electrons to the compound. Our results show, however, that in certain compounds (mainly when these metals are in excess) iron, cobalt, nickel, manganese, and possibly other transition and pre-transition metals of the Periodic Classification, may be regarded as having each one electron; in other compounds (mainly when the *B* metal is in excess) the transition metal acts as if it had no electron. Thus, in $SnFe_5$, iron acts as if it had one valency electron; in $Zn_{21}Ni_5$, nickel acts as if it had no valency electron.

My former pupil, Mr. R. P. Lawrence, has helped me in this work.

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[1] Russell, Cazalet, Irvin, Lyons, Kennedy and Howitt, *J. Chem. Soc.*, 841, 852, 857, 2340; 1932. NATURE, **125**, 89, Jan. 18, 1930.

[2] *J. Inst. Metals*, **35**, 295; 1926. *Annual Reports of Chemical Society*, **27**, 294; 1931.

Passage of Hydrogen through Steel

INVESTIGATIONS have recently been carried out by Dr. J. M. Bryan and myself at the Low Temperature Research Station, Cambridge, on the relative rates of corrosion by dilute solutions of citric acid of different samples of mild steel sheets such as are used in the manufacture of tin-plate. In these tests an attempt was made to eliminate edge-corrosion by making the steel sheet the bottom of the corrosion chamber. This was done by cutting off the bottoms of glass bottles, grinding the edges and coating them with pure vaseline to prevent leakages, and applying the sheet. The whole was clamped up tightly in a suitable frame, the sheet itself being in contact on its outer side with a pad of filter paper resting on a wooden block. The chamber thus formed was connected to a gas burette so that the hydrogen formed through the action of the dilute acid could be measured, and the whole apparatus was held at 25° C.

It was found after a given period that the loss in weight of the sheet indicated that the hydrogen-equivalent of the steel dissolved was far in excess of the hydrogen actually collected. This excess was greater than could be accounted for through solution of the hydrogen in the corroding medium, and it appeared therefore that the hydrogen was either absorbed by the metal in considerable qualities or else passed through it and was evolved freely on the outer side. That the latter was more probable was supported by the fact that blisters appeared on the outer side of some of the specimens, showing that the gas passed, at any rate, nearly through the metal and could exert considerable pressures inside it.

A further experiment was therefore carried out in which the metal sheet was clamped so as to form a diaphragm between two flanged hemispherical glass