334. *Intermetallic Compounds formed in Mercury. Part IV. Summary of Work on the* Sn–Cu, Sn–Fe, Zn–Cu, Zn–Fe, Cd–Cu, Hg–Cu, Mn–Cu, *and* Zn–Mn *Systems.*

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THIS paper summarises extensions of previous work on the Sn–Cu, Zn–Cu, Zn–Fe, and Sn–Fe systems (this vol., pp. 842, 852, 857) and new work on the Hg–Cu, Cd–Cu, Zn–Mn, and Mn–Cu systems. The methods of investigation are the chemical ones described earlier; 44 new compounds are mentioned.

Copper Mercurides.—The new compounds formed in mercury have empirical formulæ Cu_4Hg, Cu_5Hg_2, Cu_8Hg_5, Cu_5Hg_8, Cu_2Hg_5, $CuHg_4$, Cu_7Hg, and $CuHg_3$. The first three of these, the compound CuHg earlier reported, and the next three, may be respectively formulated as S, S_2T, ST_2, T, T_2U, TU_2, and U respectively, where S, T, and U represent Cu_4Hg, Cu_2Hg_2, and $CuHg_4$ respectively. Four of the compounds thus appear to be analogous to U_3O_8 or Fe_3O_4, *i.e.*, compounds of simpler ones. The eight compounds found may, therefore, be reduced to Cu_7Hg, Cu_4Hg, CuHg, $CuHg_2$, and $CuHg_4$. In previous work, CuHg and possibly Cu_8Hg_5 have been found by *X*-ray methods (Katoh, *Z. physikal. Chem.*, 1929, *B*, **6**, 27; *Bull. Chem. Soc. Japan*, 1930, **5**, 13; Terrey and Wright, *Phil. Mag.*, 1928, **6**, 1055); two compounds of undetermined formulæ were found by thermal and micrographic work by Tammann, Mansuri, and Stassfurth (*Z. anorg. Chem.*, 1923, **132**, 65; 1925, **143**, 357).

Relation of the Systems.—In Table I the principal compounds of six systems investigated are arranged for comparison. The arrangement is that described earlier (this vol., p. 865). Compounds previously announced are given in parentheses.

The table brings out the equivalence of copper and iron, and the close, although not exact, similarity of the formulæ of the compounds of cadmium and copper and of those of zinc and iron. It may also be seen that most of the compounds containing combined

TABLE I.

"Univalent" atoms per tin atom.	System. Sn–Cu.	Sn–Fe.	Zn–Cu.	Cd–Cu.	Zn–Fe.	Hg–Cu.
1/2						Hg_4Cu
2/3						Hg_6Cu
6/5	Sn_3Cu_4					
2	($SnCu_2$)	($SnFe_2$)	(Zn_2Cu_5)			(Hg_3Cu_2)
3	($SnCu_3$, $SnCu_3Hg$)	($SnFe_3$, $SnFe_3Hg$)				
4	($SnCu_4Hg_2$)	$SnFe_4Hg_{\frac{1}{2}}$		$CdCu_4$		
5		$SnFe_5$	(Zn_3Cu_5)	Cd_2Cu_5	(Zn_2Fe_5)	Hg_2Cu_5
6		($SnFe_4Hg$)	(Zn_2Cu_4Hg)	Cd_2Cu_6Hg	(Zn_2Fe_6Hg)	
8			$Zn_2Cu_6Hg_2$	Cd_2Cu_8	(Zn_2Fe_8)	Hg_2Cu_8
10				$Cd_2Cu_{10}Hg_2$	$Zn_2Fe_{10}Hg_2$	
12				$Cd_2Cu_{12}Hg$	$Zn_2Fe_{12}Hg$	
14				$Cd_2Cu_{14}Hg_2$	Zn_2Fe_{14}	Hg_2Cu_{14}
16				$Cd_2Cu_{16}Hg_2$	($Zn_2Fe_{16}Hg_2$)	
18				$Cd_2Cu_{18}Hg$	$Zn_2Fe_{18}Hg$	
20					$Zn_2Fe_{20}Hg_2$	
28				$Cd_2Cu_{28}Hg_2$		

mercury may be formulated as M_2T_x,T_4Hg, or M_2T_x,T_2Hg_2, where T represents Cu or Fe, M is Zn, Cd, or $\frac{1}{2}$Sn, and x has values for such compounds, M_2T_x, as have no mercury of combination. It is seen also that for these values of x, *viz.*, 2, 5, 8, and 14, there is a corresponding mercuride of copper. There is a possibility, therefore, that many of the compounds found may be regarded (*a*) as derivatives of copper mercurides (in which one atom of iron may be substituted for one of copper, and one atom of tin or two atoms of zinc or cadmium for two of mercury), and (*b*) as compounds analogous to U_3O_8 or Fe_3O_4.

Mercurides of Zn_2Cu_5.—This well-defined compound is stable and uncombined with mercury in amalgams more concentrated than 2%. At smaller concentrations, mercurides of definite composition are formed, which, like those of $SnCu_3Hg$ previously investigated (this vol., p. 842), may be in equilibrium with one another. There is, indeed, a striking resemblance between the two series which is brought out in Table II. The new compounds of both series are given without parentheses.

TABLE II.

Zn–Cu.	Sn–Cu.	Valency electrons.
(Zn_2Cu_5)	($SnCu_3Hg$)	9
$Zn_2Cu_5Hg_{1\frac{1}{2}}$	$SnCu_3Hg_{2\frac{1}{2}}$	12
$Zn_2Cu_5Hg_{4\frac{1}{2}}$	($SnCu_3Hg_{5\frac{1}{2}}$)	18
$Zn_2Cu_5Hg_6$	$SnCu_3Hg_7$	21
$Zn_2Cu_5Hg_9$	($SnCu_3Hg_{10}$)	27

Instances of this mercurisation of compounds so that the valency electrons in the empirical formulæ total 9, 12, 21, or simple multiples of these numbers have previously been reported in both the Sn–Cu and the Zn–Cu system. New instances are $SnCu_2$ and $SnCu_2Hg_3$; $Zn_2Cu_8Hg_8$ and $Zn_2Cu_8Hg_{7\frac{1}{2}}$.

Compounds of Manganese and Zinc and of Manganese, Copper, and Mercury.—In the first system three compounds containing no

mercury were found: Zn_7Mn, Zn_4Mn, and Zn_3Mn. The first and third of these have been found by *X*-ray examination by Parravano and Montoro (*Mem. R. Accad. Ital. Sci. Fis. Mat. Nat.*, 1930, **1**, No. 4); Zn_4Mn may be approximately one of the compounds $Zn_{21}X_5$ (X a transition element) found by Eykman (*Z. physikal. Chem.*, 1931, *B*, **12**, 217). Manganese–copper–mercury compounds were very unstable. Independent examination by three of us has enabled the formulæ of four of them to be approximately fixed: $MnCu_9Hg$, $MnCu_{11}Hg_3$, $MnCu_{15}Hg_{10}$, and $MnCu_{17}Hg_{18}$. These may be regarded as derivatives of $Cu_{10}Hg$, $Cu_{12}Hg_3$, $Cu_{16}Hg_{10}$, and $Cu_{18}Hg_{18}$ (the simplest formulæ of three of which have been found experimentally), by the replacement of one of the copper atoms by a manganese atom.

The facts (*a*) that the simpler of the compounds formed in mercury conform to the rules relating valency electrons to atoms in the molecule, discovered by *X*-ray examination (*Ann. Reports*, 1931, **27**, 294), (*b*) that the more complex compounds may in many cases be regarded as made up of these simpler ones (and in a few cases have been found experimentally to dissociate into simpler ones), and (*c*) that compounds whose approximate formulæ conform to no rules, such as the above zinc–manganese compounds or Sn_5Cu_6, have previously been found by *X*-ray or thermal examination, leave little doubt that the compounds formed in mercury are as real and as definite as those formed in the solid state by ordinary methods.

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