109. *Intermetallic Compounds formed in Mercury. Part II. The Zinc–Copper System.*

By Alexander Smith Russell, Peter Victor Ferdinand Cazalet, and Nevill Maxsted Irvin.

This work is a continuation of that reported in the preceding paper. The compounds formed have the empirical formulæ ZnCu, $ZnCu_3Hg_2$, Zn_2Cu_5, and Zn_2Cu_6Hg. Copper forms CuHg which is partly dissociated in mercury at the ordinary temperature into free copper. The zinc *compounds* except ZnCu are new. Other workers have reported the existence of various zinc–copper compounds, chiefly from a study of the physical properties of alloys, of which $ZnCu_2$, ZnCu, Zn_3Cu_2, Zn_2Cu, Zn_3Cu, and Zn_6Cu have found most support (Mellor, "Treatise on Inorganic and Theoretical Chemistry," London, 1923, IV, 672). The doubt as to whether Zn_2Cu or Zn_3Cu_2 more correctly represents the γ-phase of zinc–copper alloys, on which the physical evidence was conflicting (Desch, "Intermetallic Compounds," London, 1914, p. 97), has apparently been settled by the work of Bradley and his collaborators (*Phil Mag.*, 1928, **6**, 878; *Proc. Roy. Soc.*, 1926, *A*, **112**, 678; *Mem. Manchester Phil. Soc.*, 1927, **72**, 91). Their view is that the compound is Zn_8Cu_5. This and the compound ZnCu, round which the β-phase ranges, are now considered to be the best substantiated compounds. It is almost certain that the former is not formed in mercury, for otherwise it would have been found. On the other hand, there is no evidence from work on zinc–copper alloys that the well-defined compound Zn_2Cu_5 formed in mercury exists.

EXPERIMENTAL.

Formation of ZnCu *and* Zn_2Cu_5.—5 G. of zinc were added to 200 g. of mercury and shaken in a stoppered bottle with a concentrated solution of copper sulphate in 2*N*-sulphuric acid. The zinc at first reduced cupric ion to metal, but this combined with zinc to form a compound unable to reduce cupric ion. Before this quantity of zinc was wholly converted into the zinc–copper compound the amalgam became viscous so that further shaking became difficult. The viscosity was destroyed by separating the mercury from the semi-solid paste by squeezing the amalgam through a handkerchief and adding the mercury to the paste. The resultant mixture was scarcely more viscous than pure mercury. This was shaken with more acidified copper sulphate until it again became viscous, the above process being repeated several times. The final amalgam was then shaken with permanganate acidified with

2*N*-sulphuric acid, to remove uncombined zinc, until the blue colour of cupric ion appeared. After this point, shaking with acidified permanganate whether vigorously, to reduce any mercuric ions formed, or gently, keeping the permanganate in excess, gave consistently for 20 c.c. of *N*/10-permanganate quantities of cupric ion equivalent to 5·0 c.c. of *N*/10-thiosulphate. Hence x and y in the general formula $ZnCu_xHg_y$ are 1 and 0 respectively, since $(2 + 2x + 2y)/x = 20/5$ and $(2 + 2x)/x = 20/5$.

When freshly prepared this compound gave no detectable solubility in mercury and could be kept for weeks at the ordinary temperature without appreciable decomposition. All attempts to prepare from it a compound richer in zinc failed; free zinc and the unchanged compound invariably resulted. The compound Zn_2Cu_5 was most simply prepared from ZnCu by heating the amalgam containing a trace of tungsten upon it for 2 hours on a water-bath with 2*N*-sulphuric acid. Slowly the latter compound decomposed into free zinc and the former compound, the zinc being removed from the system by reacting with the acid in presence of the tungsten catalyst. After a time, the evolution of hydrogen ceased and this marked the completion of the change. The new compound, shaken with successive portions of *N*/10-permanganate, acidified with sulphuric acid, gave consistently cupric ion equivalent to 7·1—7·2 c.c. of *N*/10-thiosulphate per 20 c.c., both with vigorous shaking, and with gentle shaking keeping the permanganate in excess. Hence x and y in the general formula are 2·5 and 0 respectively; the formula is Zn_2Cu_5. This compound was completely insoluble in mercury and stable both at the ordinary temperature and at 100°. The addition of zinc in excess to its amalgam for 30 minutes yielded ZnCu, which remained after the more reactive zinc had been oxidised by permanganate. The two compounds are therefore related by the equation $5ZnCu \rightleftharpoons Zn_2Cu_5 + 3Zn$.

The electrode potentials of these compounds have still to be determined, but observations on their reducing powers towards uranyl sulphate and copper sulphate in acid solution show that they resemble copper closely, the descending order of reactivity being ZnCu, Zn_2Cu_5, Cu. Because of this, neither compound in presence of copper can be removed by oxidation without being accompanied by it, so the obvious method of preparing compounds, *viz.*, the addition of the requisite quantities of zinc to copper amalgams, is inapplicable. Mixtures of zinc and copper, with the latter in excess of that required to form ZnCu, when oxidised, gave zinc ion and cupric ion in approximately constant proportion, suggesting that what was oxidised was a compound. Further examination, however, showed that, as oxidation proceeded, zinc less and less, copper more and more were oxidised, suggesting that as the more reactive compound was diminished in concentration the less reactive copper was taking an increasing part in the reduction.

Preparation of $ZnCu_3Hg_2$ *and* Zn_2Cu_6Hg.—When a dilute amalgam of ZnCu was heated for 4 hours or more at 100° with excess of acidified copper sulphate, with stirring or periodical shaking, a compound was obtained which required 7·5 and 5·0 c.c. of $N/10$-thiosulphate per 20 c.c. of $N/10$-permanganate, according as the shaking was vigorous or the permanganate kept in excess. Hence $x = 3$, $y = 2$, and the empirical formula is $ZnCu_3Hg_2$. This compound was stable in acid at ordinary temperature, completely insoluble in mercury and converted into ZnCu by the addition of excess of zinc to its amalgam for 30 minutes, followed by removal of the excess. The equations $2ZnCu + Cu^{\cdot\cdot} + 2Hg = ZnCu_3Hg_2 + Zn^{\cdot\cdot}$, and $ZnCu_3Hg_2 + 2Zn = 3ZnCu + 2Hg$ represent what has occurred.

When an amalgam of Zn_2Cu_5 was vigorously shaken for 15 minutes with excess of acidified copper sulphate at 100° a new compound was found. Its analysis corresponded to $ZnCu_3Hg_{\frac{1}{2}}$. It was thought that this compound was related to the other, as apparently are $SnCu_3Hg$, $SnCu_3Hg_{5\frac{1}{2}}$, and $SnCu_3Hg_{10}$ or $SnCu_4Hg_2$ and $SnCu_4Hg_8$, but the zinc compounds have not yet been found to change into each other as do the other related compounds; the compound $ZnCu_3Hg_{\frac{1}{2}}$ may be constitutionally different from $ZnCu_3Hg_2$. On standing for a few hours at the ordinary temperature, it decomposed into Zn_2Cu_5 and free copper; the values of the thiosulphate titrations, constant at 7·5 and 6·7 c.c. (for vigorous or gentle shaking respectively) before decomposition, became 7·1 and 7·1 c.c. after. On continued oxidation, the former value slowly rose, not only to 7·5, but towards 10·0, suggesting that free copper was becoming more and more oxidised relatively to the Zn_2Cu_5. That free copper was present was shown by solubility measurements. Before decomposition nothing but the mercury of the amalgam passed through the filter; after, copper in concentration equal to its solubility in mercury, 0·002%, but no zinc, was detected in it. The decomposition of Zn_2Cu_6Hg can therefore be formulated as $Zn_2Cu_6Hg = Zn_2Cu_5 + CuHg$; the equation for its formation, however, cannot be given till it is known how Zn_2Cu_5 decomposes in presence of cupric ion. The decomposition is similar to that of $SnCu_4Hg_2$ into $SnCu_3Hg$ and CuHg. Further, the first is obtained from the second by a method similar to that for the formation of Zn_2Cu_6Hg from Zn_2Cu_5.

The compounds described are those most simply prepared, but there are indications of at least an equal number of others. Thoy are not considered here because the conditions under which they are formed have still to be fully investigated. As with tin compounds, the concentration of zinc–copper material in the mercury appears to be an important factor in determining what a particular procedure will produce. For instance, whereas Zn_2Cu_5 is the usual product obtained by heating an amalgam of ZnCu at 100° for some hours, Zn_2Cu_6Hg has several times been obtained by starting with a different concentration. Again the usual procedure for obtaining the latter, given above, has sometimes resulted in $Zn_2Cu_8Hg_3$ under what appear to be identical conditions.

Formation and Decomposition of CuHg.—Evidence that copper and mercury form a compound which could most simply be represented by the formula CuHg was first given by Joule (J., 1863, **16**, 378; *Mem. Manchester Phil. Soc.*, 1865, **2**, 115). Guntz and de Grieft (*Compt. rend.*, 1912, **154**, 357) gave evidence for the existence of CuHg and Cu_2Hg_3. In each of these cases the compound was obtained as the residue of an amalgam from which the excess mercury had been removed by great pressure. By analogy with the compounds ZnCu and Zn_2Cu_5, it was expected that CuHg and Cu_5Hg_2 might be formed in mercury. The former, but not the latter, has been found.

2 G. of copper were obtained in 200 g. of mercury by electrolysis and examined by the method given above for compounds containing mercury. 20 C.c. of *N*/10-permanganate led to a mean value of 5·75 c.c. of *N*/10-thiosulphate. This figure corresponded closely with a formula Cu_4Hg_3 (Calc.: 5·71 c.c. of *N*/10-thiosulphate). 40 C.c. of *N*/10-permanganate, however, were found to lead to 10·75 and not 11·5 c.c. of *N*/10-thiosulphate. These results suggested that, in addition to a compound of formula approximately CuHg, a constant small quantity of uncombined copper was being oxidised by the permanganate because the difference between the two volumes of permanganate taken, 20 c.c., led to a value of thiosulphate 5·0 c.c. which was proportionately lower than the value obtained with 40 c.c., itself lower than that obtained with 20 c.c. To test this suggestion, portions of *N*/10-permanganate, 1, 2, 3, 4, and 5 c.c., were shaken with the amalgam till the pink colour was just rendered invisible, and the solutions obtained analysed (*a*) for copper quantitatively by the potassium iodide method, (*b*) for mercury qualitatively. In (*a*) 1 c.c. of *N*/10-permanganate should finally require 0·5 or 0·25 c.c. of *N*/10-thiosulphate according as copper only or CuHg was doing the reduction. The values obtained for the portions taken were 0·5, 1·0, 1·5, 1·85, 2·1 c.c. of *N*/10-thio-

sulphate. These showed that, up to 3·5 c.c. of $N/10$-permanganate, the reducing agent was copper only, *i.e.*, with this amalgam at ordinary temperature there was approx. 0·01 g. of copper uncombined or more loosely combined than the rest, and that this is oxidised before the combined copper and therefore is presumably more reactive. Qualitative tests showed that, up to 3 c.c. of permanganate, mercury could not be detected in the oxidised solution. It was detected with 4 c.c. and greater volumes. Qualitative tests for mercury showed also that when all the free copper had been removed from the amalgam by permanganate, a new supply was not instantaneously generated by the amalgam: a time of the order of 15 secs. was required. It is difficult, however, to be sure that all the free copper has been removed before attempting an experiment to determine the formula of the copper–mercury compound. It was found best to shake varying quantities of permanganate, greater than 10 c.c., with the amalgam containing free copper, determine the corresponding values of thiosulphate, and calculate the differences in the thiosulphate titre for 20 c.c. differences in the permanganate titres. The mean value obtained in 10 experiments ranged from 5·0 to 5·20 c.c. For CuHg the value should be 5·0, for $Cu_{13}Hg_{12}$ it should be 5·2. It is deduced that the compound of copper in mercury is not richer in copper than the latter and in view of the difficulty of eliminating free copper entirely, the presence of which would give high results, its formula is probably the former. Since this work was done five additional compounds, ranging from Cu_7Hg to $CuHg_4$, have been found.

Discussion of Results.

There are some points of resemblance between zinc compounds and the tin compounds described in the previous paper. If written as Zn_2Cu_2, ZnCu may be regarded as $SnCu_2$ in which two bivalent atoms replace one quadrivalent. The other zinc compounds have either 9 or 12 valency electrons in the molecules of their empirical formulæ, as have some of the tin compounds. $ZnCu_3Hg_2$ may be written $ZnCu(CuHg)_2$; $SnCu_3Hg$ and $SnCu_4Hg_2$ may be written $SnCu_2(CuHg)$ and $SnCu_2(CuHg)_2$. Zn_2Cu_6Hg and a compound found but not discussed here, *viz.*, $Zn_2Cu_8Hg_3$, may be written $Zn_2Cu_5(CuHg)$ and $Zn_2Cu_5(CuHg)_3$. There is thus both with zinc and tin the possibility of series of compounds of the form $R(CuHg)_n$, where n is a small integer.

Summary.

The methods of formation and decomposition of ZnCu, $ZnCu_3Hg_2$, Zn_2Cu_5, Zn_2Cu_6Hg, and CuHg, compounds formed in mercury at

ordinary temperatures or at 100°, have been studied. The relations of these to each other and to similar compounds of tin, copper, and mercury have been briefly discussed.

DR. LEE'S LABORATORY, CHRIST CHURCH,
OXFORD.

[*Received, October 26th,* 1931.]