108. *Intermetallic Compounds formed in Mercury. Part I. The Tin–Copper System.*

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The possibility that binary intermetallic compounds may be formed by obtaining two metals in mercury at ordinary temperature was first pointed out by Russell (*Nature*, 1930, **125**, 89). It might be assumed *a priori* that if such compounds were formed they would be very unstable or that the presence of mercury as medium or third metal would be a complication. With some metals, however, this is not so. A number of binary and ternary compounds are formed easily, and some of their properties can be investigated without their removal from the mercury. The first system to be investigated, tin and copper, is so far the simplest and most fruitful. The *compounds* found have the empirical formulæ: $SnCu_2$, $SnCu_3Hg$, $Sn_2Cu_6Hg_{11}$, $SnCu_3Hg_{10}$, $SnCu_3Zn$, $Sn_2Cu_6Zn_5$, $Sn_2Cu_6Zn_2Hg_{15}$, $SnCu_4Hg_2$, $SnCu_4Hg_8$, and $SnCu_4Zn_2$. With the exception of the first, these compounds are new. Tin–copper compounds formed by melting the two metals together seem confined to $SnCu_3$ (Mylius and Gromm, *Ber.*, 1894, **27**, 637; Le Chatelier, *Compt. rend.*, 1896, **120**, 835; Bornemann and Sauerwald, *Z. Metallk.*, 1922, **145**, 2451), Sn_8Cu_{31} (Bradley, *Phil. Mag.*, 1928, **6**, 878; Bradley and Thewlis, *Proc. Roy. Soc.*, 1926, *A*, **112**, 678; Bradley and Gregory, *Mem. Manchester Phil. Soc.*, 1927, **72**, 91) and, with much doubt, to $SnCu_2$ (Le Chatelier, *Compt. rend.*, 1896, **120**, 835; Sackur and Pick, *Z. anorg. Chem.*, 1908, **58**, 46; Desch, "Intermetallic Compounds," London, 1914, p. 61).

The phrase *intermetallic compound* is used here merely to mean a combination of two or three metals which on chemical analysis approximately obeys the law of constant proportions, possesses a simple empirical formula, and differs in its solubility in mercury and in its reducing power towards oxidising agents from at least one of the constituent metals. Thus $SnCu_2$ invariably gave on analysis tin and copper in the atomic ratio of 1 : 2; it is quite insoluble in mercury, whereas tin and copper have solubilities at the ordinary temperature of *ca.* 2% and 0·002% respectively; it fails to reduce the cupric ion to the metal and reduces the uranyl to the uranous ion to a small extent, whereas these reductions are easily accomplished by tin in mercury.

The majority of the compounds would not have been found had the obvious procedure of removing them from the mercury before analysis been followed. Removal from the great mass of mercury is simple because the compounds are all insoluble in it, but subsequent treatment, such as distillation under reduced pressure, to remove the last traces of mercury, led to dissociation into the component metals or to a residue of tin and copper in atomic ratio approximately 1 : 4 with a variable mercury content. The instability of the compounds and the power of some of them for combining with different quantities of mercury made an investigation of their formulæ *in situ* in mercury essential, and this is the only one so far carried out in detail. A general method of chemical analysis of the compounds was worked out on the validity of which most of the information obtained about them depends. It was based on simple volumetric methods and on facts suggested by earlier work in this laboratory on amalgams. On account of its importance with regard to the validity of the work to be described, and of its radical departure from the usual way of substantiating the entity of intermetallic compounds (*e.g.*, the thermal method of analysis), it is described in some detail.

EXPERIMENTAL.

Preliminary Experiments.—These were carried out by shaking acidified permanganate in stoppered bottles with amalgams consisting of about 1 g. of a single metal in about 200 g. of mercury. The amalgam was prepared either by direct addition (for bismuth, cadmium, lead, thallium, tin, and zinc) or by electrolysis (for all the other metals mentioned). On simple theory, it is to be expected that so long as the surface of the mercury in contact with the oxidising agent is completely covered by a more reactive metal, that metal should do the whole of the reduction. Experimentally it was found that theory was approximately fulfilled for amalgams of bismuth, cadmium, iron, lead, thallium, tin, and zinc. When one of these was gently shaken with acidified permanganate so that part of the latter only was reduced, no mercuric ions were detected in the partly reduced solution unless the mass of the metal was no more than a few mg. in 200 g. of mercury. (If any had been temporarily formed they are unlikely to have been reduced back to metal in presence of permanganate.) It was deduced that when any one of these metals is oxidised by acidified permanganate it is unaccompanied by mercury either as medium or as part of a complex. The behaviour of iron may be taken as an illustration of this, because there the quantitative proof of the statement is especially simple. An amalgam containing 0·1 g. of iron was shaken gently with 50 c.c. of *N*/10-permanganate until about half the latter had been reduced. The excess was determined by oxalic acid. Iron was determined by reduction, followed by titration with permanganate. If x atoms of iron and y atoms of mercury together reduce the permanganate, the ratio of the permanganate reduced to that required to titrate the iron finally must be $(3x + 2y)/x$. This has a minimum value of 3 when y is zero, *i.e.*, when mercury takes no part in the reduction. This was invariably the experimental value obtained except with iron amalgams containing a few mg. only in about 200 g. of mercury, *e.g.*, 28 c.c. gave 9·3 c.c., 40 c.c. gave 13·5 c.c., 1035 c.c. gave 348 c.c.

When amalgams of cobalt, copper, chromium, manganese, molybdenum, nickel, titanium, tungsten, uranium, and vanadium were similarly shaken with excess of acidified permanganate, mercuric ions were invariably found in the partly reduced solution, implying either that these metals formed a complex with mercury or that they were so similar in reactivity to mercury that the latter accompanied them in the reduction. For amalgams of copper, chromium, manganese, and titanium, however, the latter possibility is excluded. When any of these were vigorously shaken after the permanganate had been decolorised, the solution obtained showed no trace of mercurous or mercuric ions. It was deduced that, for these metals, complexes with mercury had been formed and that these must be more reactive than mercury since they are able to reduce mercuric ions to the metal.

The next set of preliminary experiments were carried out by obtaining two metals, each more reactive than mercury, in an amalgam and observing how they were removed when shaken vigorously with acidified permanganate. It was expected from the results of the first experiments that the more reactive metal, provided it did not form a complex with the second, would be removed without trace of the other until its concentration became very small, that the rest of it would be removed simultaneously with the second metal, and then that this second metal would behave with regard to mercury as the first had done with regard to it. This was found to occur with the following systems: Bi–Cu, Pb–Cu, Bi–Fe, Pb–Fe, Cd–Fe. The following result is illustrative. 0·280 G. of iron was obtained in 250 g. of mercury electrolytically, and 0·653 g. of cadmium added directly. After an hour's standing, the amalgam was shaken vigorously with acidified *N*/10-permanganate, 1 c.c. at a time. Not till 116 c.c. had been reduced was iron detectable in the reduced solution qualitatively. After 118 c.c., cadmium ceased to be detectable in the same solution. For a further 95 c.c., ferrous but no mercurous or mercuric ions were detected. After 5 c.c. more, the amalgam on being shaken broke into a mass of small bubbles, a sign that mercury alone was present. During the last few c.c., both iron and mercury were detectable in the reduced solution. From these data it can be calculated that until 0·646 g. of cadmium had been removed iron took no part in the reduction although present to the extent of 0·280 g. The 3 c.c. of permanganate which oxidised both metals were found on analysis to have oxidised 5 mg. of cadmium and 6 mg. of iron. The remaining 100 c.c. could not have oxidised more than 0·280 g. of iron since some of it had oxidised mercury. The quantities of cadmium and iron accounted for, 0·651 g. and less than 0·286 g. respectively, are in satisfactory agreement with the quantities originally contained in the amalgam.

If, however, the second metal forms a complex with the first, simple theory suggests that the complex would lie between the two metals in reactivity, and, therefore, that the more reactive metal (presumed to be present in excess) would alone be removed by oxidation till it was reduced to the mass required to form the complex with the second metal. The complex would at this point be revealed, provided it was unable to reduce, or was prevented from reducing to metal, the ions of the less reactive metal forming the complex. This is more likely to occur when the oxidation is carried out in presence of excess of permanganate, but it was found to occur even when the shaking with permanganate was vigorous after it had been decolorised. Complex formation was found in the following systems: Sn–Cu, Zn–Cu, Sn–Fe, Zn–Fe, Cd–Cu, Mn–Cu. The details of the first four of these form the subject matter of this and the following papers. In all these systems the reducing powers of the complexes were found to be so close to those of the less reactive metals (copper or iron) that the ions of the latter were not appreciably reduced to metal by the complex by vigorous shaking for short periods. These complexes therefore could be examined both by the methods of hard shaking, and of gentle shaking with permanganate kept in excess, as described below. Tin and copper exemplify this case: 1 g. of tin was added to 0·334 g. of copper in 250 g. of mercury and shaken with 5 c.c. portions of acidified $N/10$-permanganate till the pink colour was just destroyed. (In these circumstances no stannous or cuprous ions can be formed, and it was found that no mercurous or mercuric ions were formed.) For 46 portions no copper was detected in the solution by the addition of ammonia or of potassium iodide. In the next portion, however, and in all subsequent portions until the amalgam was converted into pure mercury, both copper and tin were detected. By the quantitative methods to be described it was found that tin and copper in the amalgam were being oxidised in the atomic ratio of 1 : 2. The 46 portions of 5 c.c. of permanganate had reduced the tin content to 0·317 g. The copper content was then 0·334 g. These masses are very close to the atomic ratio of 1 : 2.

The foregoing results may be summarised as follows. Preliminary work with various metals of the B sub-groups and of the transition or pre-transition groups of the periodic classification suggested strongly that when one metal was being oxidised by permanganate it was either totally uninfluenced by the presence of a second or that it formed a definite complex with it. About 50 such complexes have already been found in the various systems examined. In every case the sum of the valency electrons of the atoms forming the empirical compound is 9 or 12 or some simple multiple of these numbers. In view of this regularity and of the other properties mentioned above, the word " compound " instead of " complex " will be used hereafter.

Quantitative Method of Analysis.—The compounds of tin and copper to be described were very similar in reducing power towards oxidising agents in dilute sulphuric acid, and lie between bismuth and copper, close to the latter. They had no appreciable action on acidified copper, stannous, or stannic sulphates, but could reduce agents whose oxidation–reduction potentials, ε_H, exceeded $+ 0{\cdot}5$ volt; permanganate, dichromate, quinquevalent vanadium, ferric sulphate, and mercuric sulphate were reduced to manganese and chromium sulphates, quadrivalent vanadium, ferrous sulphate, and mercury respectively. Their reactivity exceeded that of mercury sufficiently to prevent the latter from partaking in the reduction until the intermetallic compound was diminished to a few milligrams. From work (Russell and Evans, J., 1927, **125**, 2223) on the more reactive tin and the less reactive copper, it was assumed that the compounds were all 100% efficient as reducing agents, *i.e.*, the mass of material oxidised was exactly equivalent to that of the oxidising agent reduced. When a compound of general formula $SnCu_xHg_y$ was shaken vigorously for a minute in a stoppered bottle with 20 c.c. of *N*/10-permanganate and 50 c.c. of 2*N*-sulphuric acid, all three metals took part in the reduction, but since mercuric ions were reducible to the metal by the compound, stannic and cupric ions in the atomic ratio 1 : x and equivalent to the volume of permanganate reduced remained. In this solution of stannic, cupric, and manganous, but no mercuric ions, copper could be determined without difficulty by the potassium iodide–thiosulphate method. If θ be the volume of *N*/10-thiosulphate required, then $20/\theta = (4 + 2x)/x$, since with permanganate tin is oxidised to stannic and copper to cupric ion, whereas with potassium iodide cupric is reduced to cuprous ion. When the compound was shaken gently with excess of permanganate in sulphuric acid, the mercuric ions produced were not reduced to metal. In this case if θ be calculated on 20 c.c. of $N/10$-permanganate, $20/\theta = (4 + 2x + 2y)/x$, since now, in addition to the same changes as before, mercury is oxidised to mercuric ion. As x is known, y also is known.

In practice, after the amalgam had been vigorously shaken with acidified permanganate, the liquid was decanted through a filter, the amalgam washed with dilute acid, and liquid and washings treated with a few drops of permanganate till the pink colour persisted. Potassium iodide was then added, and copper determined. As a check on the method and the solutions used, a 2% amalgam of copper was treated in the same way. With this, 20 c.c. of $N/10$-permanganate should correspond with 10 c.c. of $N/10$-thiosulphate. It gave as a mean value 10·25 c.c., and this value was used to correct the experimental values obtained with the intermetallic compounds. No experiments were relied upon which had not been checked in this way.

In the experiments in which the permanganate remained in excess, it was found unnecessary to remove mercuric ions before copper was determined. They do not liberate iodine from potassium iodide. The excess of permanganate was most conveniently determined by titration with uranous or titanous sulphate or with oxalic acid, the first two being quicker than the last because they react at the ordinary temperature. Their oxidised forms do not react with potassium iodide. In some experiments mercuric ions were removed, and it was found best to do this by shaking the solution with a 2% cobalt amalgam which does not react with cupric ion, or give ions which liberate iodine from potassium iodide.

Formation and Analysis of $SnCu_2$.—1 G. of tin was dissolved in 200 g. of mercury at the ordinary temperature, and shaken very vigorously for a few minutes in a stoppered bottle with a concentrated solution of copper sulphate in $4N$-sulphuric acid. The tin in the amalgam was at first oxidised to the stannous condition and copper ion reduced to metal, but this was found to combine with the remaining tin to give a compound which proved unable to reduce the cupric ion. After a time, therefore, no diminution of the concentration of cupric ion occurred, and this marked the completion of the formation of the compound.

The compound was not formed by the addition of the requisite quantity of tin to an amalgam of copper at ordinary temperature, or by electrolysing the requisite amount of copper into a tin amalgam. In such circumstances some of the tin remained uncombined when the amalgam was examined within a few hours of being prepared. When this was removed from it by oxidising agents, there remained compounds in which the atomic ratio of tin to copper was either 1 : 3 or 1 : 4. At ordinary temperature, however, the addition of tin to a copper amalgam in an atomic ratio greater than 0·7 gave free tin and the compound $SnCu_2$, the former being completely removed by oxidising agents before the latter.

The compound, examined immediately after preparation, was such that successive portions of 20 c.c. of $N/10$-permanganate gave *consistently* 5·0 c.c. of $N/10$-thiosulphate, both with vigorous shaking and when permanganate was kept in excess, *until the compound was removed wholly from the mercury.* In consequence $x = 2$, $y = 0$, and the empirical formula of the compound is $SnCu_2$. The compound was quite insoluble in mercury when filtered more than once through a ground-glass filter of Gooch type with pores sufficiently large to allow mercury to pass freely under the pressure produced by a water-pump; no traces of copper or of zinc were found in the mercury. Observations on the reducing power of this compound towards uranyl sulphate, quadrivalent vanadium ion, and copper sulphate showed that it was close to, but definitely above, that of copper.

Decomposition of $SnCu_2$.—All preparations of this compound in mercury, when left to stand at ordinary temperature for different times, were found to give uncombined tin and either $SnCu_3Hg_y$ or $SnCu_4Hg_y$, where y is a small integer. The conditions for ensuring stability are still under investigation, but preliminary results point to the following. Concentrations of about 0·5% in mercury are more stable than those of 2—5%. The former tend to decompose into uncombined tin and $SnCu_4Hg_y$, the latter to tin and $SnCu_3Hg_y$. The transitions were simply followed by shaking the amalgams at intervals very vigorously with portions of 20 c.c. of $N/10$-permanganate in acid, and determining the copper ion produced. Before decomposition, θ was constant at 5·0 c.c.; after, it remained zero for many portions and then became 6·0 or 6·7 c.c., remaining constant till the compound was removed from the mercury. The former value corresponds with an atomic ratio of tin to copper of 1 : 3, the latter with one of 1 : 4. If the mercury which is known to be combined with $SnCu_3$ and $SnCu_4$ is omitted, the following equations express what has occurred : $3SnCu_2 = 2SnCu_3 + Sn$; $6SnCu_2 = 3SnCu_4 + 3Sn$. In both cases the tin liberated corresponded in amount with that required by the above equations. Thus, in one experiment 3·25 g. of $SnCu_2$ were left to decompose for 6 hours. At the end of this time 8 portions of 20 c.c. of $N/10$-permanganate failed to oxidise any copper. The ninth portion required 4·5 c.c. of $N/10$-thiosulphate. Thereafter 44 portions gave a mean value of about 6·0 c.c. Further oxidation showed that mercury alone remained. Of the 1060 c.c. of *N*/10-permanganate used, 178 c.c. oxidised tin, the remainder the $SnCu_3$. The calculated figures for the tin and the $SnCu_3$ produced by 3·25 g. of $SnCu_2$ are 176 and 881 respectively. (Mercury did not come into these calculations since with vigorous shaking no mercuric ions were finally produced.)

Formation, Analysis of, and Decomposition of $SnCu_3Hg_y$.—5 G. of tin dissolved in 200 g. of mercury were shaken gently with excess of acidified copper sulphate solution for 5 minutes or until there was no alteration in the concentration of cupric ion. The amalgam, freed from copper sulphate solution, was shaken vigorously with successive portions of acidified *N*/10-permanganate to remove any uncombined tin present, *i.e.*, until the blue colour of cupric ions appeared. The amalgam then contained the compound required. The compound could also be prepared by heating the above quantities of tin and mercury on a water-bath with excess of copper sulphate solution for ½ hour and removing uncombined tin as before. Provided that quantities of the order of 5 g. of compound were made, it could be obtained by adding about 10% in excess of the theoretical amount of tin to a copper amalgam, allowing it to stand for ½ hour, and removing the excess of tin. Attempts to do this with quantities of the order of 1 g. usually resulted in the production of $SnCu_4Hg_2$. It could also be prepared by the decomposition of $SnCu_2$ as mentioned above. Analysis by the general method gave mean values of θ (for 20 c.c. of *N*/10-permanganate) of 6·0 c.c. of *N*/10-thiosulphate, when the shaking was vigorous, and three different values, 5·0, 2·85, and 2·0 c.c., when the shaking was gentle in presence of excess of permanganate. The value 5·0 was obtained when the compound had been freshly prepared, and the other two when it had stood for many hours. Many experiments supported each of these three values when vigorous shaking at the same time gave the uniform value 6·0, but the conditions necessary to obtain the values 2·85 and 2·0 are not yet clearly known. These results give a value of x of 3·0, and values of y, 1·0, 5·5, and 10·0. The empirical formulæ are $SnCu_3Hg$, $Sn_2Cu_6Hg_{11}$, and $SnCu_3Hg_{10}$. Assuming the valency electrons for tin, copper, and mercury to be 4, 1, and 2 respectively, these compounds have 9, 36, and 27 electrons respectively, a result which may be of significance.

Formation of $SnCu_3Zn$ *and* $Sn_2Cu_6Zn_5$.—To 2 g. of $Sn_2Cu_6Hg_{11}$, 5 g. of zinc in 200 g. of mercury were added, allowed to react at ordinary temperature, and the excess of zinc removed. This was quickly done by depositing a film of tungsten on the surface of the amalgam and covering it with dilute sulphuric acid (Russell and Rowell, J., 1926, 1881). When the evolution of hydrogen ceased, the amalgam was shaken with permanganate till the blue colour of copper sulphate appeared, so that any uncombined zinc remaining might be oxidised before the less reactive compound. Then, for 20 c.c. of $N/10$-permanganate in sulphuric acid, whether with vigorous shaking or with the permanganate in excess, the copper obtained was equivalent to 5 c.c. of $N/10$-thiosulphate. On the assumption that the ratio of tin to copper had not been altered by the addition of zinc, this result established that the compound has the formula $SnCu_3Zn$, without any combined mercury, a result confirmed by the determination of zinc volumetrically by the ferrocyanide method. The assumption was justified because when the amalgam of the compound stood for 24 hours, zinc dissociated from it, combined with acid in presence of the tungsten, and so was completely removed. The compound which remained was shown by analysis to be $Sn_2Cu_6Hg_{11}$, one of the forms of $SnCu_3Hg_y$.

The replacement of only one of the mercury atoms of the compound $SnCu_3Hg_y$ by zinc suggested that the first mercury atom might be differently combined with the $SnCu_3$ from the others. Further work still in hand, however, has disposed of this suggestion. A stable compound with approximately 2·5 atoms of zinc appears to be formed, uncombined with mercury. Further, there are conditions in which $SnCu_3Zn$ combines with about 7 or 8 atoms of mercury and the provisional formula for this form, $Sn_2Cu_6Zn_2Hg_{15}$, has been adopted. All of these compounds in presence of acid change ultimately to $SnCu_3Hg_y$ in 24—72 hours at the ordinary temperature.

Preparation and Properties of $SnCu_4Hg_2$.—This compound resulted from the decompositions of $SnCu_2$ and $SnCu_3Hg$ in the circumstances mentioned above. It could also be prepared by adding equal masses, not exceeding 0·5 g., of tin and copper to 200 g. of mercury, allowing the mixture to stand, and removing uncombined tin. On analysis, x was found to be 4·0 and y either 2·0 or approx. 8. The empirical formulæ are consequently $SnCu_4Hg_2$ and $SnCu_4Hg_8$ with valency electrons 12 and 24 respectively. The former compound was usually obtained when the alloy was freshly prepared, the latter when it had stood for some hours, but further conditions have not yet been defined. When zinc in excess was added to either, a compound free from mercury and of empirical formula $SnCu_4Zn_2$ was obtained, analogous to that given by zinc and $SnCu_3Hg$. It was also similarly decomposed by treatment with acid at 100°, regenerating $SnCu_4Hg_2$.

The compound $SnCu_4Hg_2$ as ordinarily prepared was stable in mercury. A preparation of $SnCu_3Hg$ which was stable at the ordinary temperature was converted into $SnCu_4Hg_2$ by an hour's heating on a water-bath in presence of acidified copper sulphate. On cooling and standing, this compound apparently reverted to $SnCu_3Hg$ as shown by the general method of analysis. Thus the number of c.c. of $N/10$-thiosulphate obtained when 20 c.c. of $N/10$-permanganate had been vigorously shaken with the compound changed from 6·7 to 6·0 after decomposition. The latter value was found, however, not to be constant. Successive oxidations with permanganate caused it to rise towards 10·0 c.c., which suggested that copper uncombined with tin was present and being removed increasingly with the $SnCu_3$, as would be expected since it is the less reactive. 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 (*viz.*, 0·002%), but no zinc, was detected in it. The decomposition of $SnCu_4Hg_2$ can therefore be formulated as $SnCu_4Hg_2 = SnCu_3Hg + CuHg$, and its formation from $SnCu_3Hg$ as $5SnCu_3Hg + Cu^{\cdot\cdot} + 3Hg = 4SnCu_4Hg_2 + Sn^{\cdot\cdot}$.

Discussion of Results.

The stability of the compounds formed seems to depend primarily upon their concentration in the mercury in which they are suspended: $SnCu_3Hg_y$ is stable when its concentration is 3% or more of the mercury. At a concentration of one-tenth of this, $SnCu_4Hg_2$ is stable. At one-tenth of its stable concentration, $SnCu_3Hg_y$ decomposes into $SnCu_4Hg_2$ and tin; at ten times its stable concentration $SnCu_4Hg_2$ decomposes into $SnCu_3Hg_y$ and copper. $SnCu_2$ is never very stable. It is more stable, however, at a concentration of 0·3% than at 3%. At the former concentration it appears to decompose directly into $SnCu_4Hg_2$, which is understandable, since at that concentration the intermediate $SnCu_3Hg$ is itself unstable. At the latter concentration it does not decompose beyond $SnCu_3Hg$.

The variability in the mercury content of $SnCu_3Hg$ and $SnCu_4Hg_2$ is a puzzling phenomenon. Freshly prepared $SnCu_3Hg$ seems able to add on either 4½ or 9 additional atoms of mercury, and $SnCu_4Hg_2$ 6 additional atoms. There have been indications also that $SnCu_2$, which usually has no combined mercury, sometimes appears as $SnCu_2Hg_3$. There is thus a possibility that additional mercury atoms in number equal to half that of the valency electrons of the compound may be added.

The compounds are not obviously members of any class known to metallurgists. Hume-Rothery (*J. Inst. Metals*, 1926, **35**, 295) has pointed out that in some cases the compositions of the "β-phases" were such that the ratio of valency electrons to atoms was approximately 3/2. The β-phases round the compositions ZnCu, $AlCu_3$, and $SnCu_5$ in the systems Zn–Cu, Al–Cu, and Sn–Cu, for example, have 3, 6, and 9 electrons to 2, 4, and 6 atoms respectively, copper being regarded as having one electron. Bradley and his collaborators (*loc. cit.*) extended this generalisation to the " γ-phases." These, for example Sn_8Cu_{31}, Zn_8Cu_5, and Al_4Cu_9, have 21 electrons to 13 atoms. The compounds formed in mercury conform rather to the former type, in that most of them have valency electrons in numbers 3, 6, or 9 or simple multiples of these, and not 21; not, however, in having the number of atoms two-thirds of that of the electrons. Only by counting quadrivalent tin as two bivalent atoms can $SnCu_2$ be regarded as one of these compounds. Then $SnCu_3Hg$, $SnCu_3Zn$, and $SnCu_4Hg_2$ could be regarded as compositions of $SnCu_2$ with CuHg or CuZn, both of which conform to the 3-electron–2-atom rule.

It is clear, however, that the number of electrons, 9 or 12, which some of the compounds have, appears to be more significant than the number of atoms which give rise to them, and this is borne out by the study of zinc and copper compounds in the following papers, and by unpublished work on other systems. The compounds which contain different quantities of combined mercury do not stand outside this generalisation; nor do the two compounds of tin, copper, and zinc, $Sn_2Cu_6Zn_2Hg_{15}$ and $Sn_2Cu_6Zn_5$, which have been provisionally examined. The systems Zn–Cu, Zn–Fe, Sn–Fe, Mn–Cu, and others in mercury are at present under investigation, and full discussion is reserved till these results are available.

Summary.

Stable compounds of tin and copper with or without mercury are formed in mercury at the ordinary temperature. A method for determining their empirical formulæ without removing them from the mercury in which they are suspended is described. Three of the compounds are of the form $SnCu_2,(CuHg)_n$, where $n = 0$, 1, and 2. The second ($n = 1$) can have its mercury atom replaced by 1 and probably by 2·5 zinc atoms; it can also exist with either $4\frac{1}{2}$ or 9 additional atoms of mercury. The third ($n = 2$) can have its two atoms of mercury replaced by two atoms of zinc; it can also exist with 6 additional atoms of mercury. All of the compounds have valency electrons equal to 6, 9, or 12, or some simple multiple of these numbers, and to this extent they are akin to the compounds in the Sn–Cu, Zn–Cu, and Al–Cu systems round which the β-phases range.

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