110. *Intermetallic Compounds formed in Mercury. Part III. The Zn–Fe System and Part of the Sn–Fe System.*

By Alexander Smith Russell and Henry Anthony Montagu Lyons.

This work continues that reported in the two preceding papers. The *compounds* of zinc and iron found are Zn_2Fe_5, Zn_2Fe_6Hg, $ZnFe_4$, $Zn_2Fe_{12}Hg$, and $ZnFe_8Hg$; and of tin and iron, $SnFe_2$ and $SnFe_6Hg$. There are probably also three further compounds intermediate in composition between the two tin–iron compounds named: they await further investigation and are not described here. The compounds found are all new. In a preliminary account of part of this work (*Nature*, 1930, **125**, 89) the existence of ZnFe and $ZnFe_8$ was reported. The former has not been substantiated, although similarity between the systems Zn–Fe and Zn–Cu, subsequently observed, suggests it as a possibility. The latter was not considered at the time as possibly compounded with mercury, but is now found to be $ZnFe_8Hg$. Previous reports of compounds of zinc and iron are confined to the zinc-rich compounds Zn_3Fe and Zn_7Fe, the former being formed at 777°, the latter from Zn_3Fe and liquid at 662° (von Vegesack, *Z. anorg. Chem.*, 1907, **52**, 30; Raydt and Tammann, *ibid.*, 1913, **83**, 257). Evidence for the existence of at least one compound of tin and iron, depending upon thermal arrests at 893°, 780°, and 496°, was obtained by Isaac and Tammann (*ibid.*, 1907, **53**, 281) but the formulæ were quite undetermined. Compound formation between iron and mercury has not previously been examined.

The seven compounds whose empirical formulæ have been given were quite insoluble in mercury. Their amalgams were close to iron amalgam in reducing power towards oxidising agents in sulphuric acid. They reduced permanganate, dichromate, and quinquevalent vanadium rapidly, reduced mercuric ions to metal and ferric ions to ferrous quantitatively, reduced quadrivalent vanadium and uranyl ions to a small extent only, and had no effect on cupric or stannic ions in sulphuric acid. They are thus similar to tin–copper and zinc–copper compounds previously studied, and were accordingly investigated by similar methods. In the "hard-shaking" method the amalgam was vigorously shaken with acidified permanganate for ½ minute after the permanganate had been decolorised. The final changes then occurring were $Zn \longrightarrow Zn^{\cdot\cdot}$ and $Fe \longrightarrow Fe^{\cdot\cdot}$ for zinc compounds, and $Sn \longrightarrow Sn^{\cdot\cdot\cdot\cdot}$ and $Fe \longrightarrow Fe^{\cdot\cdot}$ for tin compounds, any mercury temporarily oxidised to the mercuric state being reduced back to metal. The liquid was then decanted through a filter, the amalgam washed twice with dilute acid, and liquid and washings titrated with standard permanganate. The ratio of the standard permanganate used in oxidising the compounds in the amalgam to that required to titrate the ferrous ions produced is theoretically for the compound $ZnFe_xHg_y$, $(2 + 2x)/x$, and for the compound $SnFe_xHg_y$, $(4 + 2x)/x$. For a pure iron amalgam the experimental value of this ratio was within 1% of 2·0, the theoretical value, showing that the method was reliable. In the "soft-shaking" method the amalgam was gently shaken with acidified permanganate for ¼ minute, the latter being kept in excess. The changes then occurring were $Zn \longrightarrow Zn^{\cdot\cdot}$, $Fe \longrightarrow Fe^{\cdot\cdot\cdot}$, and $Hg \longrightarrow Hg^{\cdot\cdot}$ for zinc compounds, and $Sn \longrightarrow Sn^{\cdot\cdot\cdot\cdot}$, $Fe \longrightarrow Fe^{\cdot\cdot\cdot}$, and $Hg \longrightarrow Hg^{\cdot\cdot}$ for tin compounds. The solution and its washings were then titrated with standard oxalic acid to determine the excess of permanganate. The hot solution was shaken for a minute with a cadmium amalgam which reduced the mercuric ions to metal and the ferric ions to ferrous, but, as control experiments showed, had no reducing effect on the stannic ions. This liquid was decanted through a filter and with its washings titrated with standard permanganate. The ratio of the permanganate used in oxidising the compound in the amalgam to that required to titrate the ferrous ions finally is, theoretically, for the compound $ZnFe_xHg_y$, $(2 + 3x + 2y)/x$, and, for the compound $SnFe_xHg_y$, $(4 + 3x + 2y)/x$. For a pure iron amalgam the value of the ratio determined by the method just described was within 1% of 3·0, the theoretical value, since no mercury takes part in the reduction in this case (see p. 843). Provided that consistent values of the permanganate titre can be obtained for both "hard-shaking" and "soft-shaking" experiments, the empirical formula of any compound present should be determinable without the necessity of the difficult determination of zinc or tin. The former experiment gives the value for x, and the latter that for y. The theoretical values of the volumes of $N/10$-permanganate required to titrate the iron produced by oxidation with 20 c.c. of $N/10$-permanganate for each of the compounds found are given below. Although they are not very diverse, they are sufficiently so to characterise the compounds found.

Formula.	Zn_2Fe_5.	Zn_2Fe_6Hg.	$ZnFe_4$.	$Zn_2Fe_{12}Hg$.	$ZnFe_8Hg$.	$SnFe_2$.	$SnFe_6Hg$.
C.c. (hard-shaking) ...	7·14	7·50	8·00	8·57	8·89	5·00	7·50
C.c. (soft-shaking) ...	5·26	5·00	5·71	5·71	5·71	4·00	5·00

In all cases where mercury was indicated by the permanganate results, it was first confirmed by qualitative analysis and then determined without difficulty by a volumetric method. All the reducing agents tried except stannous sulphate reduced both ferric and mercuric ions. Stannous sulphate in sulphuric acid was found to react with mercuric ions at the ordinary temperature without appreciably reacting with ferric ions, but it was impracticable to employ it owing to the difficulty of removing the small quantity of metallic mercury formed before titration of the remaining stannous sulphate with iodine. The simplest way was as follows: 50 c.c. of *N*/10-permanganate were shaken with the amalgam by the soft-shaking method. After titration with standard oxalic acid, the solution was divided into two parts. The first was shaken vigorously with cadmium amalgam to remove mercuric ions, the ferrous ions, also resulting, being then oxidised in the cold with permanganate. This was then shaken vigorously for a minute with a copper amalgam. Ferric iron was reduced to ferrous with equivalent production of copper sulphate which was determined by the thiosulphate method. The second half of the solution was directly shaken with the same copper amalgam for the same period and the copper determined with the same thiosulphate solution. In the second case both ferric and mercuric ions are reduced, the former as before, the latter to the metal which dissolves in the amalgam and is thus removed from the solution. It can easily be shown that the difference between the two thiosulphate titres bears the same ratio to twice the smaller thiosulphate titre as the number of atoms of mercury to that of iron. The method was proved to be satisfactory by determining the thiosulphate titres resulting from different known volumes of mercuric and ferric ions in presence of manganous and zinc ions, and by its use on the well-defined compound Zn_2Cu_6Hg.

EXPERIMENTAL.

Preparation of Zn_2Fe_5 *and of* Zn_2Fe_6Hg.—5 G. of zinc were dissolved in 300 g. of mercury, and into this, 3 g. of iron were electrolysed. The viscous mass stood for a day before it was examined for compounds. On repeated hard shaking, zinc alone was found to be oxidised until nearly 3·5 g. of it had been removed. Iron was then oxidised in slowly increasing quantities until the permanganate titre from hard shaking reached 7·1 or 7·2 c.c. for ten successive oxidations with 20 c.c. of $N/10$-permanganate. At this point the titre from soft shaking varied only from 5·2 to 5·3 c.c. calculated on 20 c.c. of $N/10$-permanganate, and no mercury was detected in the liquid. These values strongly suggest the presence of Zn_2Fe_5. After standing over-night, the amalgam contained free tin. When it was removed by oxidation, the titres were 7·5 c.c. for hard shaking and 5·0 c.c. for soft shaking, and mercury was easily detected in the partly reduced permanganate solution. These values indicate Zn_2Fe_6Hg. This compound did not dissociate appreciably during the day on which it was examined, and there was no difficulty in obtaining consistent values for both titres. 3 G. of zinc were now added to the amalgam in an endeavour to obtain evidence of a compound richer in zinc than Zn_2Fe_5. The whole was set aside at ordinary temperature for 7 days to ensure adequate time for combination. Free zinc was again removed by the very laborious process of oxidation with acidified permanganate till a point was reached at which iron was detected in the solution. At this point the titres obtained indicated Zn_2Fe_5, the same result as before. No repetition of the experiment gave any indication of ZnFe, a possible compound, since ZnCu, Zn_2Cu_5, and Zn_2Cu_6Hg have been found previously, and Zn_2Fe_5 and Zn_2Fe_6Hg in this work. ZnFe, if it existed, was much less likely to be missed if the free zinc was slowly removed than if it were rapidly removed by the tungsten-film method (Russell and Rowell, J., 1926, 1883). In eight experiments in which excess of free zinc was removed by the latter method, Zn_2Fe_5 resulted in three cases and Zn_2Fe_6Hg in five, the titres being either 7·1 and 5·3 or 7·5 and 5·0 c.c. It was concluded that Zn_2Fe_6Hg is the more stable of the two, and that they are related by the expression $6Zn_2Fe_5 + 5Hg \rightleftharpoons 5Zn_2Fe_6Hg + 2Zn$.

Formation of $ZnFe_4$, $Zn_2Fe_{12}Hg$, *and* $ZnFe_8Hg$.—The last was found to be a stable compound, and the richest in iron content of all those yet examined. It was formed from an amalgam of Zn_2Fe_6Hg, on which tungsten had earlier been deposited, by 12 hours' warming at 100° with dilute sulphuric acid. During the first hour's heating, hydrogen was appreciably evolved, showing that Zn_2Fe_6Hg was unstable at 100°. The hard-shaking titres obtained were consistently 8·9—9·0 c.c., and the soft-shaking titres 5·6—5·75 c.c. Mercury was detected qualitatively. After a week's standing at ordinary temperature, no changes from these values were found. They correspond with $ZnFe_8Hg$.

At ordinary temperature and in absence of the catalytic tungsten, the change from Zn_2Fe_6Hg to $ZnFe_8Hg$ was sufficiently slow to indicate compounds intermediate in composition. The amount of decomposition is evidently a function of time, temperature, amount of catalyst present, and probably concentration of the mass of zinc and iron in the mercury. A detailed examination of this has still to be done. Numerous experiments have shown, however, that when amalgams of Zn_2Fe_6Hg had stood for different times, and the free zinc was removed either by acid when tungsten was present or by oxidation with permanganate when it was absent, or by filtration of the amalgam through a ground-glass filter of Gooch type with pores sufficiently large to allow mercury to pass through under the low pressure of a water pump, invariably one of three sets of titres was obtained: 8·0 and 5·7, 8·6 and 5·7, or 8·9 and 5·7 c.c. Thus, after one hour's heating at 100° with dilute acid in absence of tungsten, and removal of the free zinc formed, 8·0 and 5·7 c.c. were obtained, indicating $ZnFe_4$. This was kept for a week at ordinary temperature; free zinc was again found, and on its removal 8·6 and 5·7 c.c. were obtained, indicating $Zn_2Fe_{12}Hg$. This was examined daily for the next 3 days; it did not dissociate appreciably. At the end of a week some free zinc was found, and on its removal after two weeks the titres indicated the compound $ZnFe_8Hg$. This did not change in the next 4 weeks to any compound richer in iron. In the filtration experiments, the free zinc was not wholly removed by the first filtration despite the fact that the amount present was many times smaller than the solubility of zinc in mercury: it was sorbed on the insoluble paste of compound. The paste was therefore treated with 200 g. of pure mercury, kept for 15 minutes, and filtered again, the process being repeated till the mercury filtrate was found to contain no zinc. Of the two intermediate compounds found, $Zn_2Fe_{12}Hg$ was obtained in repetitions of the experiment always, and $ZnFe_4$ sometimes.

It can be objected that $ZnFe_4$ and $Zn_2Fe_{12}Hg$ may be simply mixtures in different proportions of the stable compounds Zn_2Fe_6Hg and $ZnFe_8Hg$. The latter certainly looks as if it might be made up of $ZnFe_4$ and $ZnFe_8Hg$ in equimolecular proportion. This objection can only be adequately met by a more detailed examination of the problem than has yet been given, but meanwhile it may be said that (*a*) it is unlikely that, if mixtures are possible, there should be two of them only and of such a composition as to appear to be $ZnFe_4$ and $ZnFe_{12}Hg$; (*b*) that it is unlikely that $ZnFe_4$ with no mercury in its composition could be made up of compounds containing mercury. In favour of the objection, however, is the unlikelihood that the points at which one compound had broken up completely into zinc and a second without any of the second being broken up, should often be found experimentally. Experience, however, of both the Sn–Cu and the Zn–Cu system (in mercury) suggests that the break up of a compound is very rapid once it begins: the decomposition is not a continuous or gradual change. A compound may remain stable for a long time and then quite rapidly break up into free tin or zinc and a new compound. If this were true also of zinc–iron compounds the point in favour of the objection may not be valid.

When the mass of iron in 250 g. of mercury is less than 1 g., and the zinc is added to the iron amalgam instead of the iron being electrolysed into the zinc amalgam, $ZnFe_8Hg$ is the only compound definitely formed. The chance of forming compounds between zinc and iron is obviously much smaller in this case, since the soluble zinc has to combine with an insoluble paste of iron instead of with atoms of iron obtained from electrolysis. In this case, however, the possibility of other compounds is indicated, although their composition cannot be determined. If $ZnFe_8Hg$ were the only compound formed in these circumstances, it is to be expected that, as soon as the excess of zinc had been removed, the permanganate titre from hard shaking would rise rapidly from 0 to about 8·9 c.c. In all experiments made, however, about half of the iron put into the amalgam is removed before the point is reached, after which the titre of 8·9 c.c. becomes constant. A typical set of readings obtained with an amalgam containing about 0·6 g. of iron when free zinc had been removed by oxidation is as follows: 0·0, 0·6, 7·9, 8·3, 8·4, 8·5, 8·6, 8·6, 8·9, 8·9, 8·9, 8·9, 8·9, 8·9, 1·3, . . ., the dots representing the point at which all of the zinc and iron had been removed from the amalgam. An iron amalgam to which no zinc had been added gave under similar conditions a succession of values varying from 10·0 to 10·1 c.c. In one of the experiments, the mercury content was determined by the soft-shaking method after the maximum titre by hard-shaking had been attained and found to be, as before, one atom of mercury for each molecule of $ZnFe_8$.

Preparation of $SnFe_2$ *and* $SnFe_6Hg$.—10 G. of tin were added to 300 g. of mercury. Into this were electrolysed about 5 g. of iron. The viscous mass was examined after a few hours' standing by the hard-shaking method. Until about 5 g. of tin had been removed by oxidation, no iron was found in the solutions obtained by shaking portions of 20 c.c. of $N/10$-permanganate, acidified with sulphuric acid, with the amalgam. As soon as the presence of iron was shown by the fact that the solution after hard-shaking could be titrated with permanganate, measurements were begun. Six successive measurements gave titres of 5·0 c.c. for hard-shaking, and four successive measurements gave 4·0 c.c. for soft-shaking, indicating a compound $SnFe_2$. Mercury was tested for in the partly reduced solution resulting from soft-shaking and found to be absent. This confirms the absence of combined mercury in the compound established by the quantitative measurements. To this amalgam 2 g. of tin were added. After 24 hours it was examined. No compound richer in tin than $SnFe_2$ was found; as soon as the free tin had been removed, the permanganate titres indicated the presence of $SnFe_2$ as before. During the next 3 days this amalgam was kept at 100° and vigorously shaken from time to time with acidified permanganate to remove any tin which may have dissociated from the compound. The composition of the tin–iron complex was then determined. The permanganate titres obtained were consistently 7·5 and 5·0 c.c. for hard- and soft-shaking respectively, and these values remained constant till the amalgam was exhausted. They correspond with a stable compound $SnFe_6Hg$. Repetitions of these experiments gave $SnFe_2$ as the initial and $SnFe_6Hg$ as the final product. No compound richer in iron than the latter appeared to be formed by decomposition of the former. Between these compounds there were indications of $SnFe_3Hg$, $SnFe_4Hg_2$, and $SnFe_5$, but they will not be further discussed until more work has been done upon them.

The Reaction between $SnFe_2$ *or* $SnCu_2$ *and Ferric Sulphate.*—In preliminary work it was found that when ferric sulphate oxidised an amalgam of $SnCu_2$, the tin was oxidised to the stannic state without apparently going through the stannous state. This has now been confirmed by Mr. P. V. F. Cazalet, and a similar effect with $SnFe_2$ has been found by Mr. J. Howitt and us. When a tin amalgam is vigorously shaken with 20 c.c. of *N*/10-ferric sulphate in sulphuric acid, the tin oxidised is shown by quantitative determination to be wholly in the stannous state, for, on this supposition, the solution resulting should require 40 c.c. of *N*/10-permanganate for titration, which is the experimental result (Russell and Evans, J., 1925, **127**, 2226). Tin amalgam, however, does not reduce stannic to stannous ions in sulphuric acid, and it is concluded therefore that ferric ions do not react appreciably with stannous ions at ordinary temperature. It is consequently expected that, when an amalgam of $SnCu_2$ reduces ferric sulphate quantitatively, the changes occurring would be $Sn \longrightarrow Sn^{\cdot\cdot}$ and $Cu \longrightarrow Cu^{\cdot\cdot}$. On this supposition the permanganate titre for 20 c.c. *N*/10-ferric sulphate can be calculated to be 26·67 c.c. of *N*/10-solution. The experimental value, however, was invariably 20·0, showing that there were no stannous ions produced to be titrated by the extra volume (6·67 c.c.) of *N*/10-permanganate. If they had been temporarily produced they could not have been oxidised by ferric or cupric ions, since neither of these react with stannous ions. The tin in the compound must accordingly have been directly oxidised to the stannic state.

When $SnFe_2$ was shaken vigorously with ferric sulphate, the iron oxidised was wholly in the ferrous state. It can be calculated that if stannous ions only are formed, 20 c.c. of $N/10$-ferric sulphate should result in a titre of 33·33 c.c. of $N/10$-permanganate, and, if stannic ions are formed, a titre of 25 c.c. The latter value was invariably found experimentally. In this compound also, therefore, tin is directly oxidised to the stannic condition by ferric sulphate. Similar experiments with other tin–copper and tin–iron compounds containing mercury apparently lead to the same conclusion, but the point at issue can only be tested with mercury-free compounds. If the compound contains mercury, ferric sulphate will oxidise it to the mercurous condition, and mercurous ions may be capable of oxidising stannous to stannic ions under the experimental conditions. Tin would therefore appear as stannic in the solution after vigorous shaking even if it were first oxidised to the stannous state.

Discussion of Results.

The existence of $SnFe_2$, $SnCu_2$, and Zn_2Cu_2, of $SnFe_6Hg$, Zn_2Cu_6Hg, and Zn_2Fe_6Hg, and of Zn_2Cu_5 and Zn_2Fe_5 suggests that iron and copper are equivalent, and that one atom of tin is equivalent to two atoms of zinc in these compounds. It is agreed that copper has only one valency electron in the metallic state. It follows that iron has only one, at least in these compounds. If this is so, all the compounds described in this paper have a total of 6, 9, or 12 valency electrons or some simple multiple of these numbers like all the tin–copper and the zinc–copper compounds described earlier: Zn_2Fe_5 has 9, Zn_2Fe_6Hg 12, $ZnFe_4$ 6, $Zn_2Fe_{12}Hg$ 18, $ZnFe_8Hg$ 12, $SnFe_2$ 6, and $SnFe_6Hg$ 12. These numbers appear to be characteristic. Whether the compounds are formed between metals of even valency like mercury and zinc and those of odd valency (in the above sense) like iron and copper, or whether between metals of the B sub-group and metals of the transition and pre-transition groups it is too early yet to say. Work on the Mn–Cu–Hg system now in progress may throw light on this point, for manganese acts like a bivalent metal in such compounds as have been examined, and is a member of the pre-transition group of metals.

The number of valency electrons in iron when uncombined (as in mercury) is not known and cannot be deduced from the above results. It is remarkable, however, that iron neither combines with mercury nor shows in mercury the reducing power which it has in the free state. Iron in mercury is very similar to copper in reducing power (Russell, Evans, and Rowell, J., 1926, 1872). It has been tacitly assumed hitherto that this passivity was due to combination with mercury since all the other elements of atomic numbers 22—29 combine with mercury (see p. 891).

In Table I the principal compounds of the four series so far investigated are arranged for comparison. Four compounds provisionally found but not yet reported are included with the sign (?). The zinc compounds are formulated with two atoms of zinc, since these are equivalent to one atom of tin. The arrangement is made to emphasise the number of atoms of copper or iron found associated with one of tin or two of zinc. It is clear that on present results zinc and iron show the widest range of compositions, and tin and copper the narrowest.

TABLE I.

"Univalent" atoms per tin atom.	Formulæ.			
	Sn–Cu.	Sn–Fe.	Zn–Cu.	Zn–Fe.
2	$SnCu_2$	$SnFe_2$	Zn_2Cu_2	—
3	$SnCu_3Hg$	$SnFe_3Hg$ (?)	—	—
4	$SnCu_4Hg_2$	$SnFe_4Hg_2$ (?)	—	—
5		$SnFe_5$ (?)	Zn_2Cu_5	Zn_2Fe_5
6		$SnFe_6Hg$	Zn_2Cu_6Hg	Zn_2Fe_6Hg
8			$Zn_2Cu_8Hg_3$(?)	Zn_2Fe_8
12				$Zn_2Fe_{12}Hg$
16				$Zn_2Fe_{16}Hg_2$

Only one of the investigated compounds, Zn_2Cu_2, agrees with Hume-Rothery's rule for "β-phases," *viz.*, that the ratio of valency electrons to atoms is 1·5. This ratio varies from 2 in $SnCu_2$ and $SnFe_2$ to 1·2 in $Zn_2Fe_{12}Hg$ and $Zn_2Fe_{16}Hg_2$.

The fact that tin in $SnCu_2$ and in $SnFe_2$, but not in a tin amalgam, is oxidised by ferric sulphate directly to the stannic state is further evidence of the compound nature of these complexes.

Summary.

1. Five new compounds of iron and zinc are formed in mercury at ordinary temperature. Three of these form ternary compounds with mercury.

2. Two new compounds of iron and tin are similarly formed. One of these forms a ternary compound with mercury. There is some evidence also of the existence of three further compounds.

3. Similarities in the empirical formulæ of compounds of the Sn–Fe, Sn–Cu, Zn–Fe, and Zn–Cu systems suggest that iron and copper are equivalent. Iron has accordingly only one valency electron in these compounds.

4. The generalisation that all compounds of the Sn–Cu and Zn–Cu systems which are formed in mercury at ordinary temperature, so far investigated, have a total of valency electrons equal to 6, 9, or

12, or some simple multiple of these numbers, is applicable also to compounds of the Zn–Fe and Sn–Fe systems so far investigated.

5. Iron does not form a compound with mercury, yet in mercury its action towards reducing agents resembles closely that of copper. This form of passivity is not due to metallic compound formation.

6. In the compounds $SnFe_2$ and $SnCu_2$, tin is oxidised directly to the stannic state by ferric sulphate in conditions such that tin itself is oxidised quantitatively to the stannous condition.

Dr. Lee's Laboratory,
Christ Church, Oxford.

[*Received, January 7th,* 1932.]