THE CONSTITUTION OF THE COPPER-TIN ALLOYS

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The alloys of copper and tin stand next in importance to those of iron and carbon. Naturally they have been the subject of a great many investigations, some of which have done much toward clearing up the mystery which surrounds the constitution of the series. But, for the most part, the investigations have resulted in increasing the number of data, without in any way permitting of generalizations.

They have been examined as to their density, their heat and electrical conductivities, their electromotive force, and in many other respects, but in nearly every case, the determinations have been made upon bronzes of unknown physical treatment, and as we shall see later, the data obtained apply only to the particular specimens examined. A comparative examination of the data collected shows one thing and no more; namely, that the relation between properties of the different percentage compositions is an additive one. But if one tries to draw any more definite conclusions than that, he is soon lost in a mass of contradictions.

For example, in Fig. 1,[1] if one decides that the measure-

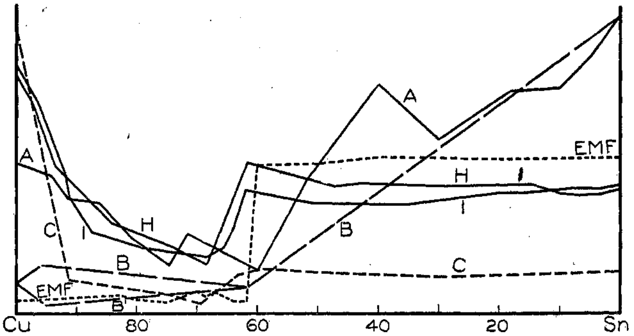

Fig. 1

E. M. F.	Electromotive Force	I	Induction Balance
C	Electrical Conductivity	H	Heat Conductivity
B	Specific Volume, annealed	A	Specific Volume, cast

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[1] Quoted with additions from Stansfield. 3d Report of the Alloys Research Com. 1895. For the sake of brevity, we will speak of a bronze as being of a certain percent, meaning thereby the percentage of copper. Thus, a 60 percent bronze contains 60 percent of copper and the rest, 40 percent, tin.

ment of electrical conductivity (C) is to be the criterion of where irregularities occur in the properties of the series, then the singular points will be found at about 61 percent or Cu_3Sn, 68 percent or Cu_4Sn and at 90 percent. However, the heat conductivity (H) shows not only these three points but also an irregularity at 50 percent, as does also the induction balance (I); but the only marked irregularity in the electromotive force (E. M. F.) is at 61 percent, while the maximum tensile strength is at 81 percent.

Density determinations on this series of alloys give quite hopeless results, for while it is not difficult to show that the densities are abnormal, Fig. 1, it is almost impossible to show what they really are. Curve A represents the density of the cast bronzes and curve B that of the annealed bronze. From zero to 61 percent copper, the densities are fairly readily determined, but the large size of the crystals of Cu_3Sn do not readily break down upon annealing, and consequently equilibrium is reached with great slowness.

With bronzes containing more copper than 61 percent, there are two serious obstacles in the way of an accurate determination of the densities. First, the best determinations that we could get showed that the density was practically constant between 61 and 100 percent of copper. Secondly, these alloys dissolve gas while molten, and are never free from blow-holes. It was shown by Riche that the cast and annealed alloys gave different densities, and we were able to show that the density of the quenched alloys was about 0.05 of a unit greater than that of the annealed specimen. In our complete paper we hope to return to this subject, but for the present we can only say that because of the difficulties already mentioned, the densities or specific volumes can in no way help us in determining the constitution.

The first real step in the solution of this problem, was made when Roberts-Austen and Stansfield published their determinations of the cooling curves for the complete series of alloys. It is true that the freezing-point curve had been determined previously by Heycock and Neville and by Le

Chatelier, but neither of them was able to use the results obtained to explain the constitution.

Stansfield's curves, showing the liquidus, and the transformations in the solid, formed the basis upon which Heycock and Neville constructed an approximate equilibrium diagram.

From Stansfield's determination of the liquidus, Fig. 2,[1] we see that it has six branches, from which it follows that there must be six possible solid phases which can crystallize from the molten alloys. An examination of the physical properties as heretofore determined shows that all of the physical properties of this series are abnormal, and the results are fairly conclusive that the abnormality occurs at about 61 percent of copper. But Stansfield's determination of the liquidus shows six branches, and there must be six solid phases possible, so that whereas there are at least six different solid phases, the physical properties show only one of them and it is merely an accident that they show that one. From a comparison of these data we see how useless it is to attack this problem in an unsystematic manner.

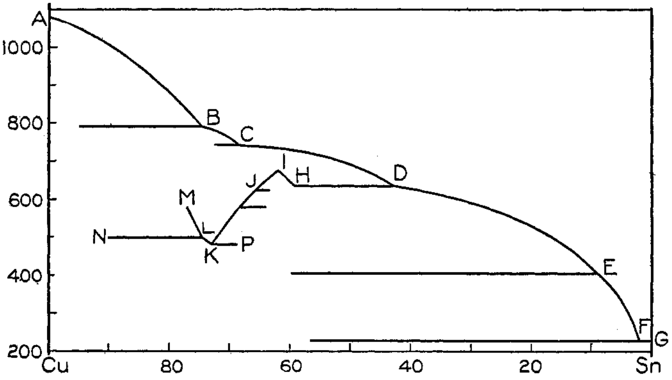

Fig. 2

Just what may be the composition of these six solid phases cannot be told from the diagram. The method of Tammann will indicate approximately what the compositions may be, but it is open to the objection that it assumes that equilibrium

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[1] Fourth Report of the Alloys Research Committee, 1897.

is reached during the time of cooling down of the alloy. As a matter of fact, it frequently takes a considerable length of time for these reactions to take place, and in this case, at least, the method is not a success.

The next method which promises assistance is the analytical method of Bancroft.

We chose lead as the third component, because it was known to form neither compounds nor solid solutions with either copper or tin. In this way it was hoped that the complications might not be increased by adding the third component. Another reason for using lead is that it is easily separated from copper and tin, and allows of very accurate determination. A third component having been decided upon, it was necessary to determine approximately the freezing-point surface for the ternary system. From any mixture from which samples were to be taken for analysis, it was necessary to assure ourselves that the temperature at which the sample was taken was within the field in which the solid phase in question was stable. These points having been determined, analyses were made from the results of which the composition of the solid phases have been calculated.

Certain precautions are necessary in analyzing these alloys, otherwise the results obtained may be quite seriously affected. For lead, tin, and copper the method of solution in nitric acid is used commercially. In fact, however, it is not accurate. Neither lead nor copper can be separated quantitatively from tin by nitric acid. As shown in a previous paper, the stannic oxide always contains lead, and although some writers state that copper can be separated from tin by nitric acid of a certain concentration, reference to the original paper shows that the author worked with bronzes holding never more than 5 percent of tin. On 0.5 gram samples it is not surprising that he was able to detect "only a trace of copper" in his stannic oxide. Previous experience having shown that tin and lead could easily be separated by distilling off the tin as chloride in a stream of HCl gas, it was thought well to try this method for copper, tin and lead. The results were perfectly satisfactory. The method is as follows:

About 2 grams of the molten alloy are sucked up into a narrow glass tube 2.5 mm in diameter. This sample was then cut into suitable lengths, weighed and placed in a pig similar to the one described in a previous paper. In passing, it should be observed that the glass tubing is always warmed to about the temperature of the alloy before sucking up the sample, and even for samples melting at 900° this soft glass tube, if first heated to redness, can still be used for taking the sample if one works quickly. The alloy is now dissolved by aqua regia varying the proportions of nitric and hydrochloric acids according to the copper content of the alloy. Thus for alloys up to 30 percent copper, one part concentrated HNO_3 to 7–9 of concentrated HCl works more rapidly. Alloys rich in copper will require a greater concentration of nitric acid. Thus for alloys above 60 percent copper, the usual 1 : 4 aqua regia works best. Alloys very rich in lead, 40–90 percent, will require a greater proportion of nitric acid, while those of about 60 percent Pb, 30 percent Sn and 10 percent Cu may require to be first dissolved in diluted nitric acid, brought *nearly* to dryness, and cooled, then concentrated HCl run in and the usual procedure followed.

The alloy being completely dissolved, the pig is placed horizontally in an arsenic furnace, a slow current of air passed through it, and heated gently until completely dry, that is, until the copper chloride turns brown. Of course, if the tin is to be determined, the liquid distilled over must be caught and saved as it will contain a large part of the tin.

The pig having been brought to dryness is now placed in a paraffin bath and heated to 200°, a current of HCl gas being run through the pig to assist in carrying over the tin. At the temperature of boiling sulphur, $CuCl_2$ distils off. In from thirty minutes to an hour, depending on the composition of the alloy, all of the tin will have been carried over. The tip of the outlet tube of the pig and the thistle tube being rinsed into the beaker containing the tin solution, the solution, which must not be boiled or evaporated, is partially neutralized with ammonia and the tin precipitated with hydrogen sulphide. After washing, it may be ignited to oxide and weighed, or, better, it may be just dissolved in HCl and precipitated as oxide by KNO_3 or $(NH_4)_2SO_4$ as directed in Fresenius. The reason for the second precipitation is to get rid of the excess of chlorides, which are so difficult to wash out of the sulphide and which, if present on ignition, cause a part of the tin to volatilize. The determination of the tin is by no means as accurate as that of the other two metals.

The residue of copper and lead chlorides in the pig is now washed, put into an evaporating dish, and the pig rinsed with conc. HCl to remove the adherent lead chloride. After the excess of HCl has been evaporated, strong HNO_3 is added and the chlorides evaporated to dryness, more conc. HNO_3 added and again evaporated until the lead and copper chlorides are completely changed to nitrates. With small quantities of lead one or at most two evaporations will suffice. For larger amounts of lead a third evaporation will be necessary.

The nitrates of lead and copper are now taken up with water containing about 10 cc of conc. HNO_3, and electrolyzed either in a Classen dish, which is tedious, or with a rotating cathode.

When no more lead or copper is precipitated, the solution is evaporated to dryness, about 1 gram $NaNO_3$ added, taken up with 25 cc of water and again electrolyzed. By this process, all of the lead and copper are precipitated and the only error in the determination of these two components is the error of weighing. With the tin, on the other hand, an error of 0.2–0.4 percent results even with careful work, and it is for that reason that we felt justified, after making some preliminary experiments, in getting tin by difference and basing our calculations on the figures for lead and copper. That this is quite justified will appear in the course of the analyses.

It should be stated that, if instead of adding 10 cc of KNO_3 to the nitrates, as above, 0.5 cc HNO_3 and about 10 grams $NaNO_3$ are added, the first electrolysis will run out practically all of the lead and copper (start slowly), and for ordinary work the concentration and second electrolysis can be omitted. There seldom remains over 0.05 percent of either metal in the electrolyte, under these circumstances.

The alloys were melted in an atmosphere of coal gas, so that except for a deposit of carbon at high temperatures, the surface of the alloy remained bright throughout the course of the experiment.

The furnace used was a specially constructed Fletcher gas furnace made for us by the Buffalo Dental Manufacturing Company, and of such dimensions that a 00 graphite crucible just fitted tightly against the opening in the lid, leaving the whole mouth of the crucible free for manipulation.

Results.—The following results were obtained for the branch AB of the liquidus.

	Concentrations		Percent Sn in solid phase
	Initial	Final	
1	Cu, 89.89 Pb, 5.02 Sn, 5.09	Cu, 83.04 Pb, 8.37 Sn, 8.59	— 0.16
2	Cu, 78.75 Pb, 10.54 Sn, 10.71	Cu, 72.14 Pb, 14.58 Sn, 13.28	+ 4.00
3	Cu, 79.98 Pb, 10.09 Sn, 9.93	Cu, 73.39 Pb, 14.02 Sn, 12.59	+ 2.42
	Cu, 75.93 Pb, 11.46 Sn, 12.61	Cu, 70.28 Pb, 14.20 Sn, 15.52	+ 0.442

The minus sign indicates that 0.16 percent lead crystallized with the copper. This is doubtless due to analytical error. Thus by analytical methods we have proved positively that copper forms a solid solution with tin and we have also shown that the percentage of tin so absorbed varies over at least 5 percent. It will be shown in the metallographic section that, on careful annealing, copper will absorb as much as 13 percent of tin, and the variation found on analysis is probably due to the different rates of crystallization. It was not possible to wait for equilibrium to be reached.

The limiting concentration of tin in copper could be shown analytically also, if necessary, by allowing a certain amount of crystals to form and then holding the temperature constant until equilibrium had been reached. Of course, where a compound crystallizes, this difficulty is not encountered. Nor is it so serious when working at lower temperatures. The α-crystals of Heycock and Neville are therefore as they had suspected, a solid solution of tin and copper, the limiting concentration on rapid cooling being about 5 percent of tin.

The following results were obtained for branch BC, of the liquidus:

	Concentrations		Percent Cu in solid phase
	Initial	Final	
1	Cu, 69.14 Pb, 1.64 Sn, 29.22	Cu, 67.34 Pb, 2.00 Sn, 30.66	77.31
2	Cu, 70.33 Pb, 2.09 Sn, 27.58	Cu, 68.49 Pb, 2.89 Sn, 28.62	75.10
3	Cu, 68.86 Pb, 7.46 Sn, 23.68	Cu, 55.99 Pb, 23.63 Sn, 20.38	74.80
4	Cu, 67.31 Pb, 4.87 Sn, 7.82	Cu, 64.37 Pb, 7.40 Sn, 28.23	73.09
5	Cu, 66.55 Pb, 3.09 Sn, 30.36	Cu, 65.68 Pb, 3.69 Sn, 30.63	70.73

From the above results we see that the crystals which separate from bronzes containing between 68 and 74 percent of copper, are a solid solution in which the copper content varies between 70 and 78 percent. As is to be expected the alloys richer in copper yielded β-crystals richer in copper.

For the branch CD of the liquidus, the following results were obtained:

	Concentrations		Percent Cu in solid phase
	Initial	Final	
1	Cu, 59.50 Pb, 3.37 Sn, 37.13	Cu, 58.11 Pb, 3.98 Sn, 37.91	67.76
2	Cu, 62.11 Pb, 2.86 Sn, 35.03	Cu, 61.10 Pb, 3.46 Sn, 35.44	66.93
3	Cu, 59.45 Pb, 3.63 Sn, 36.92	Cu, 57.15 Pb, 4.87 Sn, 37.98	66.41
4	Cu, 54.99 Pb, 4.98 Sn, 40.03	Cu, 52.28 Pb, 6.34 Sn, 41.38	64.90
5	Cu, 62.02 Pb, 1.06 Sn, 36.92	Cu, 61.12 Pb, 1.47 Sn, 37.41	64.39
6	Cu, 62.73 Pb, 1.08 Sn, 36.19	Cu, 61.39 Pb, 1.97 Sn, 36.64	64.35
7	Cu, 59.98 Pb, 4.11 Sn, 35.91	Cu, 56.92 Pb, 7.35 Sn, 35.73	63.85
8	Cu, 54.59 Pb, 4.67 Sn, 40.74	Cu, 49.75 Pb, 8.31 Sn, 41.94	60.80

The results here show that the γ-crystals are a solid solution of tin in copper, the percent of copper varying between 60 and 68 percent. Many analyses were made necessary by the fact that the crystals being small the mother-liquor which one can pipette off, becomes very scanty before any great change of concentration has occurred. And it was also desirable to settle beyond question that the γ-crystals were mixed crystals and not a compound.

Branch DE of the liquidus:

	Concentrations		Percent Cu in solid phase
	Initial[1]	Final	
1	Cu, 30.0 Pb, 12.0 Sn, 58.0	Cu, 14.23 Pb, 17.82 Sn, 67.95	62.50
2	Cu, 34.0 Pb, 10.0 Sn, 56.0	Cu, 14.64 Pb, 17.24 Sn, 68.12	60.91
3	Cu, 30.0 Pb, 15.0 Sn, 55.0	Cu, 15.64 Pb, 22.08 Sn, 62.28	60.43

Mean, 61.3
Theory for Cu_3Sn, 61.6

When it is remembered that these were the first analyses made and that the extrapolation is across a range of 25 to 30 percent, we feel justified in concluding that the solid phase which separates from bronzes containing between 8 and 43 percent copper is the compound Cu_3Sn.

In the ternary system the change from the field of the phase CD to that of the field for DE is readily noticeable with the naked eye. With a little practice the location of the boundary curve between the two can be easily detected to within 3 percent on ingots which have not cooled too rapidly. The presence of the lead makes the large plates of Cu_3Sn stand out very sharply on the surface of the ingots.

An examination of the ternary diagram shows that the phase crystallizing along branch EF of the liquidus, Fig. 2, exists in a comparatively small field. It would be very

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[1] This series of initial concentrations were weighed out to milligrams on hundred gram lots, so that no analysis was deemed necessary. This assumption was confirmed by analysis.

difficult to determine this phase by starting with the initial concentration lying within the field for the crystallization of the phase in question. The range of concentration possible is not over 3 percent and the location of the field is such that a slight error in analysis would result in an enormous error in the calculation so that it is necessary to use some other method. From the most advantageous point which could be chosen an error of 0.2 percent in the analysis would extrapolate to an error of between 5 and 20 percent in the calculation of the position of the solid phase. The method which must be used is a combination of the analytical method with a method of transformation. It is found possible to start with the initial concentration lying outside of the field for the solid phase and if properly selected it is possible to cause the first phase which separates to disappear and the position of the melt to enter the field of the phase whose position is sought. This method is so helpful where one has to deal with small fields, that a word about it may not be out of place.

Let us suppose that we wish to determine analytically the composition of the phase which is stable in field IV of Fig 3. We know that the phase is of a composition approaching

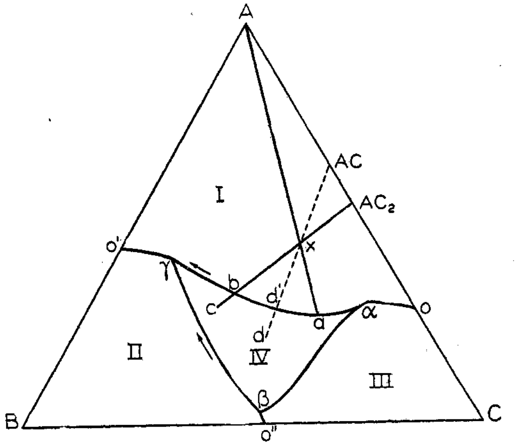

Fig. 3

that of the point AC_2, the problem being to distinguish whether it is the phase AC_2 or the neighboring compositions AC and

AC_3. If we know the freezing-point surface of the field, α, β, γ, we can select a temperature and composition such that by holding the temperature constant at some point within field IV all of the first crystals which separated from the melt, will be transformed into crystals which are stable within field IV. Thus on cooling an alloy of the composition x, crystals of A will first separate along xa. When the mother-liquor reaches the composition a, AC_2 begins to separate. As the temperature falls, the composition of the melt moves along the boundary curve towards the lower quintuple point γ. This change can occur only by A redissolving as AC_2 separates. This reaction progresses until at the composition indicated by b, all A has disappeared and we have left only the solid phase AC_2 and the melt. Further cooling will tend to move the composition of the melt along the line xbc.[1] The path followed by the changing composition of the mother-liquor is indicated by the heavy lines $xabc$.

If therefore we hold the alloy x for a sufficiently long time at the temperature c, and if the alloy has been properly stirred to break up the larger masses and insure equilibrium, an analysis of the mother-liquor and the solid (which may be mixed with mother-liquor) will show the composition of the solid phase. If our surmise as to the composition of the solid phase has been correct, then the extrapolation will indicate AC_2. If the phase is AC, the composition of the melt will have reached the point d instead of progressing to c. Thus by choosing several compositions and analyzing, we can arrive at the composition of the solid phase. If the compound were ternary, the problem would be attacked in a similar way.

It may be objected that the method necessitates some foreknowledge of the composition of the phase in question, but this objection is not as reasonable as it might seem. We are dealing with a case in which it is impossible to separate and analyze the crystals. The microscopic methods will help, but would be very delicate for such a case. Since there is not

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[1] Geer: Jour. Phys. Chem. 8, 257 (1904).

sufficient change of concentration inside the field to allow of accurate extrapolation, the transformation method suggested is the only one now available.

It was mentioned above, that the analysis of the solid, with whatever mother-liquid it might hold, would be desirable. This gives us three points for determining the composition of the phase. First, the initial concentration; second, the mother-liquid, plus a small amount of admixed solid; and third, the solid, with a greater or less amount of mother-liquid. This last composition can be made to approach much nearer to the composition of the solid phase than does the initial concentration, thus increasing the accuracy without an increase in the experimental difficulties.

The limitations to the application of this method of transformation are those of manipulation. If an alloy is too rich in copper, as Cu 30 percent, Pb 1 percent, Sn 69 percent, there will not be enough mother-liquor left at 227° to pipette off, nor will the change from Cu_3Sn to the next tin-rich phase be rapid enough for practical purposes. Even a 20 percent copper alloy had not completely changed over, on holding for five days at 227°, although the mass of Cu_3Sn crystals was removed, broken up in a mortar and stirred into the melt. By very careful work we were able to obtain the following results:

It will be seen that some of the results show percentages of copper which are out of the region for the phase studied. This means that crystals of the solid phase were sucked up with the mother-liquor. This is not an uncommon occurrence where the crystals are small. Thus, in certain analyses, the sample pipetted off showed an increase in copper and a decrease in lead, *i. e.*, a reversal, while a third sample taken at a somewhat lower temperature fell back into line and all three points lay on the same straight line. It is evident that if more crystals than mother-liquid are sucked up in the sample, the concentration may vary anywhere between that of the pure solid phase and the initial concentration.

Of all of these analyses, the last three were by far the

	Concentrations		Percent Cu in solid phase
	Initial	Final	
1	Cu, 13.907 Pb, 4.046 Sn, 82.047	Cu, 12.513 Pb, 4.287 Sn, 83.200	37.25
2	Cu, 14.248 Pb, 4.645 Sn, 81.107	Cu, 2.734 Pb, 7.237 Sn, 89.929	34.82
3	Cu, 18.46 Pb, 2.23 Sn, 79.31	Cu, 5.81 Pb, 3.43 Sn, 90.66	41.7
4	Cu, 18.10 Pb, 3.69 Sn, 78.21	Cu, 11.19 Pb, 4.75 Sn, 84.06	42.2
5	Cu, 12.88 Pb, 3.07 Sn, 84.05	Cu, 6.06 Pb, 3.81 Sn, 90.19	41.1
6	Cu, 21.231 Pb, 4.154 Sn, 74.615	Cu, 2.875 Pb, 8.777 Sn, 88.348	37.72
7	Cu, 21.301 Pb, 3.091 Sn, 75.608	Cu, 4.048 Pb, 6.149 Sn, 89.803	38.74
8	Cu, 24.219 Pb, 2.513 Sn, 73.268	Cu, 2.177 Pb, 5.846 Sn, 91.977	38.53

best. The conditions were better than in the first five, and the changes of concentration were greater. All of them agree in showing that the solid phase is certainly not CuSn, and that its composition does not fall at any simple molecular proportion.

Since the temperature limits of the field for this phase are quite small, it was thought necessary to use some kind of a thermostat, which would be more constant than the electric furnace. Consequently a large boiling tube was lowered into the furnace. This tube had suspended in it a crucible containing the alloy. A simple condenser at the top served to return the condensed liquid. Boiling quinoline gives a very constant temperature of about 230°, which temperature was the most advantageous for the investigation of this phase. The boiling liquid serves to balance the variations in voltage on the line, and the electrical heating minimizes the danger from fire, should the boiling tube break. Metal tubes were not found to be satisfactory. With this arrangement, it was found possible to keep the alloys at the temperature of boiling quinoline for weeks at a time. As a result of all of the analyses, we are able to say definitely that of all the phases which can separate from their respective branches of the liquidus, only one is a definite compound. The remainder are solid solutions whose compositions vary with the temperature.

III. Microscopic study

In what has gone before, we have considered only such phases as might exist in contact with the melt. It will now be worth while to investigate the significance of the evolutions of heat detected in the solid alloys.

If we examine the heat changes shown in Stansfield's diagram, Fig. 2, the curve HIJKLM suggests at once changes in the solid which resemble those which occur in the freezing of a liquid alloy. It must be remembered that this diagram was obtained under certain fixed conditions, and that certain assumptions were made, which may or may not have been warranted.

In the first place, all of these data were obtained by means of cooling curves. This means that the reactions were liable to supercooling. Very careful measurements made with the aid of heating curves have shown that supercooling does occur in the determination of these temperatures. Thus on the heating curves the inversion temperatures did not vary more than two-tenths of a degree (measuring directly to microvolts) while the cooling curves showed often as much as 20° supercooling. It follows therefore, that the points actually determined by Stansfield and by Heycock and Neville, will have to be revised.

During our study of these temperatures, we were able to establish that branches NL and KP of the curve given in Fig. 3 were continuous and that the branch LM is not properly located.

A second assumption made in the determination of the constitution of these alloys is that the heat changes observed are necessarily the *only* changes which here exist. There is *no warrant* for such an assumption.

Before examining the results of our investigations, we must give attention to the equilibrium diagram worked out by Heycock and Neville. This diagram is reproduced in Fig. 4.

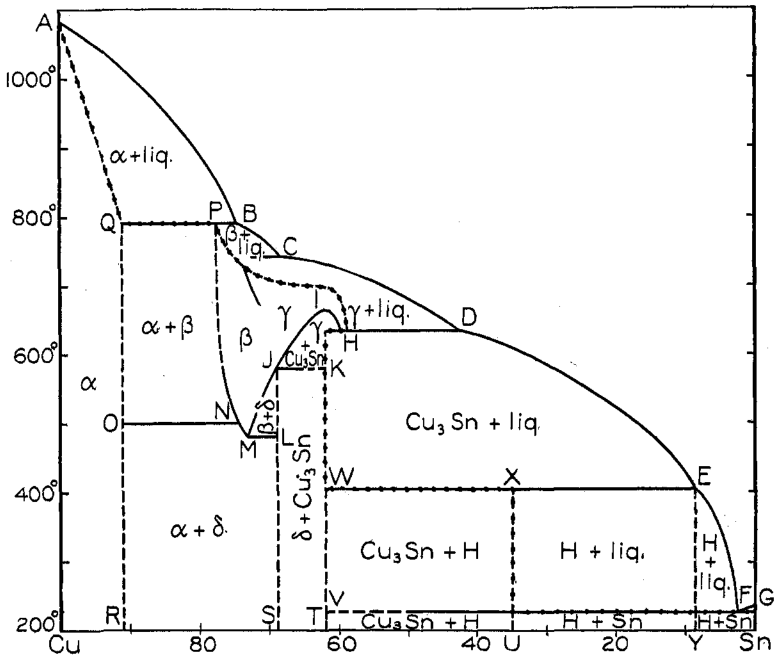

Fig. 4

Assuming the temperatures indicated by Stansfield to be correct, and that the inversions there indicated were the *only* ones, these two pioneers worked out what seemed to them to be the correct interpretation of the data.

They readily saw that copper crystallized from the copper-rich bronzes as a solid solution, and they placed the limiting concentration at 9 percent of tin. They did not determine whether or not this limit was changed by change of temperature after the alloy had become solid. Consequently, they drew the line QR vertical.

The shape of the triangular field PHIJMN was so suggestive that they were a little misled as to the nature of the alloys in this region. The V shape of this field suggested that the alloys were a homogeneous solid solution which was in contact with the γ-crystals on one side, and with the α-crystals on the other. That being true, the point M becomes the eutectoid concentration and temperature. Of course it is absolutely necessary that the temperatures of line LM and NO be identical, otherwise we would have α, β, δ, and vapor existing over the range of temperatures of MN, a condition which is impossible from a theoretical point of view.

These investigators were unable to locate within the field PHIJMN the region for pure β, pure γ, and the mixtures of β and γ. It will be found, by trying to draw in the imaginary limits of these fields, that there is no arrangement which will satisfy the demands of the theory. It becomes evident therefore, that either their microscopic data, or the pyrometric data, or both must be in error.

When we look for the reason for these very skilful investigators having been unable to solve this problem, we find it in the second of the assumptions mentioned above. In investigating this region, they assumed that the only changes were those indicated by the pyrometer. Consequently, by preparing specimens by quenching from temperatures in this region, they chose only those temperatures which were indicated by the heat changes. This error is not entirely the fault of these particular men but is one which they learned from their predecessors in this kind of work. In fact, there has not been any investigation of the much studied iron-carbon alloys in which this same blunder has not occurred. It was only natural for Heycock and Neville to make a similar mistake.

In undertaking the study of these alloys it seemed to us that the only way to be sure that nothing was overlooked was to make the study thorough. It was decided that it would be better to examine every percentage, at intervals of 10°, throughout this region. In order to do this, it was necessary to arrange a thermostat in which a high temperature could be maintained constant for long periods of time. This result was finally obtained by means of an electrically heated lead bath, which was equipped with a stirrer. The pyrometer placed in the lead gave the temperature, and the ingots treated were protected by means of shields of Jena glass. A current of coal gas prevented oxidation. The ingots after having been held at the desired temperature for a sufficiently long time were removed and quenched instantly by immersing in a large vessel of cold water. The ingots being relatively small, and the time which elapsed between their removal from the bath and the time they reached the water being much less than a second, we were able to fix the structure present in the alloy at the temperature in question. Duplicates assured us that the method was reliable. As a result of our investigations the diagram submitted in Fig. 5 is thought to express the constitution of the copper-tin alloys. In Fig. 6 the crosses indicate the compositions and temperatures at which annealings and quenchings were made.

In Fig. 2 it is seen that the pyrometer shows the presence of the quadruple point as far over as 95 percent of copper. However, this is a case of quite rapid cooling. In Fig. 5 we have shown this quadruple point only as far as 90 percent. The reason for doing so is that investigations of the curve at lower temperatures would seem to require that for conditions of equilibrium the quadruple point can scarcely extend beyond 90 percent of copper. This likewise, when annealed for a considerable time at temperatures between 200° and 700°, becomes perfectly homogeneous as far over as 87 percent of copper.

Field I is the region for the pure α-crystals of which the

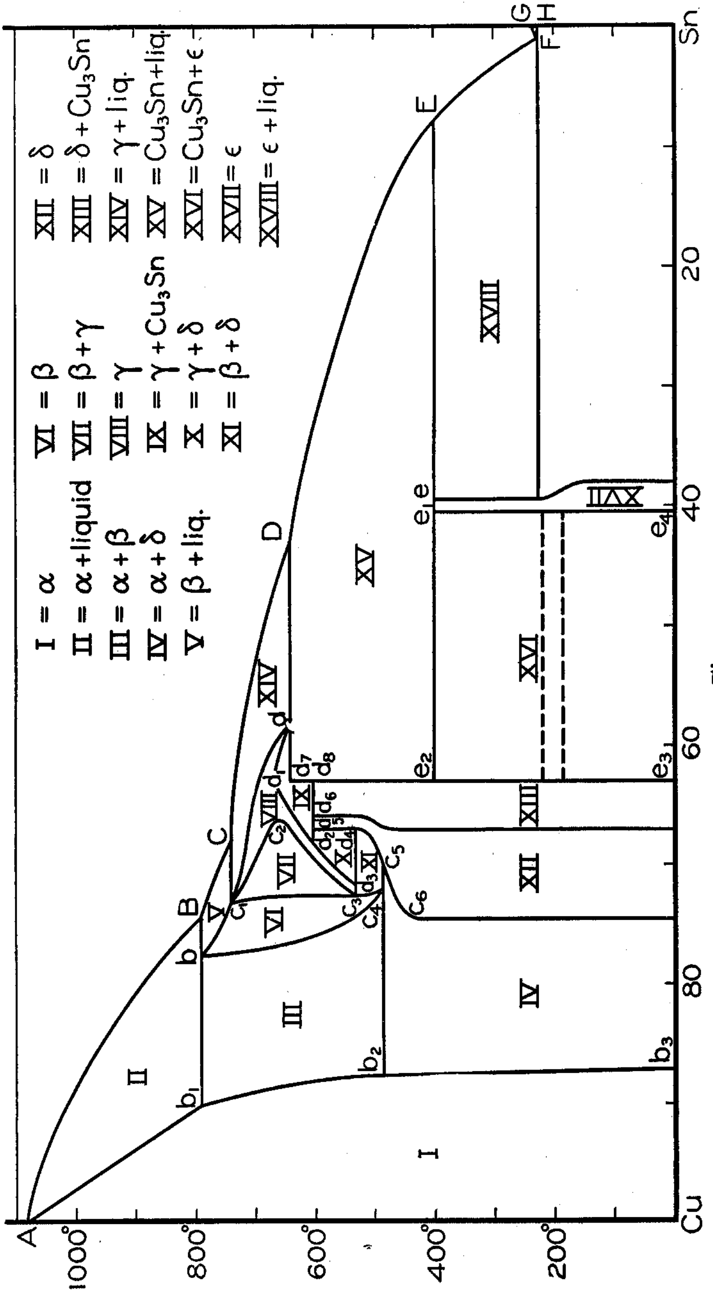
I = α
II = α + liquid
III = α + β
IV = α + δ
V = β + liq.
VI = β
VII = β + γ
VIII = γ
IX = γ + Cu_3Sn
X = γ + δ
XI = β + δ
XII = δ
XIII = δ + Cu_3Sn
XIV = γ + liq.
XV = Cu_3Sn + liq.
XVI = Cu_3Sn + ε
XVII = ε
XVIII = ε + liq.
A
B
C
D
E
F
G
H
b
b_1
b_2
b_3
c_1
c_2
c_3
c_4
c_5
c_6
d
d_1
d_2
d_3
d_4
d_5
d_6
d_7
d_8
e
e_1
e_2
e_3
e_4
1000°
800°
600°
400°
200°
Cu
80
60
40
20
Sn

Fig. 5

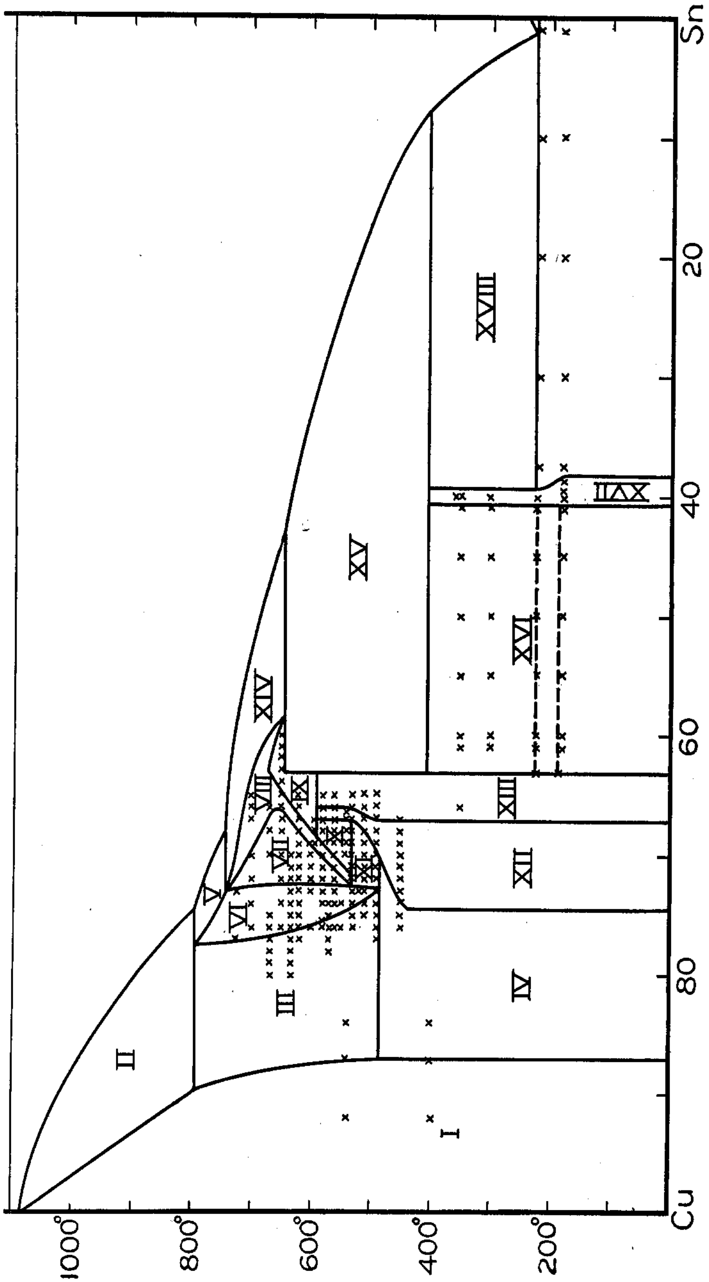
1000°
800°
600°
400°
200°
Cu
80
60
40
20
Sn
I
II
III
IV
V
VI
VII
VIII
IX
X
XI
XII
XIII
XIV
XV
XVI
XVII
XVIII

Fig. 6

tin concentration is seen to vary with temperature and to reach the maximum of about 13 percent.

Field II is the field in which α-crystals are stable in contact with the melt. As indicated by the line Bb_1, alloys with these concentrations consist of two phases, α and β.

As indicated by the line c_5b_2 the β-crystals break down at a temperature of 486° with the formation of the succeeding phase which we have called δ.

Field V is the region for β-crystals in contact with the melt.

Field VI gives the region for homogeneous β.

Field VII is the region for a mixture of the crystals β and γ.

Field VIII is the region for pure γ. This field is very peculiar in shape, but the existence of the slender arm $c_2c_3d_1$ has been verified very carefully. The chief trouble in determining the relation in this region lies in the fact that it is so very narrow. On this account it is likely to be missed unless specimens are taken at least for every percent of change in concentration. Once the field is located it cannot be mistaken for the region on either side of it. The branch $c_2c_3d_3d_1$ is of course homogeneous. But Field VII consists very clearly of a mixture of yellow and white crystals, β and γ. However, region X differs from region VII, and consists wholly of white crystals whose behavior shows the alloys to be a mixture of two kinds of crystals. The differences are distinctly marked and warrant interpreting this region as consisting of two solid phases.

Below the line d_3d_4 the change of the structure in the alloy is very striking. Instead of consisting of the mixture of the white crystals in Field X, we have now a mixture of brilliant yellow crystals in the white matrix. This change is so striking and so impossible of explanation, according to the diagram of Heycock and Neville, that we were led to believe in the existence of the line d_3d_4 long before we were able to verify it experimentally.

The phase δ, which is formed entirely through transformation in the solid, was for a long time considered to be the compound Cu_4Sn. That such is not the case is shown by the fact that the composition Cu_4Sn is not homogeneous over the temperatures at which it is necessary for the compound to exist. It is found that alloys having 1 percent less copper than the composition Cu_4Sn are homogeneous, and we have, therefore, designated the phase merely as δ. It is a solid solution whose composition varies remarkably with changing temperatures as indicated by the lines bounding Field XII. Thus while alloys containing between 70 to 74 percent of copper are inhomogeneous at temperatures above $d_4c_5c_6$, they are perfectly homogeneous below the lines of c_5c_6. We were able to say that the lines c_6c_7, d_6, and d_7 fall almost vertically, the variation being not greater than 1 percent in composition.

Field XIII consists of a mixture of δ and Cu_3Sn resulting from the breaking down of the γ-crystals along the line d_2d_8.

Our results agree with those of Heycock and Neville as to the breaking down of γ with the formation of Cu_3Sn at the composition of that compound.

Field XV is the region for Cu_3Sn already in contact with the melt.

Field XVI is the region for Cu_3Sn and the next phase ε.

As we found from analytical data, this phase ε could not be the compound CuSn, and a careful study of the annealed and quenched alloy has shown it to occupy the region of Field XVII.

Field XVIII is the region for ε in contact with the melt.

Whether or not pure tin or a solid solution separates along the liquidus FG is a matter of little importance.

In addition to the changes in the solid which have been recorded for the copper-rich alloys, we found two other heat changes in the alloys containing from 41 to 61.5 percent of copper. The first of these changes is at 218° and occurs at the same temperature in all of the above-mentioned concentrations. The second change is likewise one at constant temperature and is found at 182°.

The heat effect is small in the lower change but quite large in that at 218°. At present we are unable to give a satisfactory explanation as to the cause of these changes. At first sight one might attribute the upper change to lag in the eutectic change, but the 218° point is very distinct from that of the eutectic. On the other hand, the suggestion that the 182° change is related to the supposed allotropic modification of tin, at 170°, is not borne out by the fact that these two changes do not occur in the alloys in which tin is *one* of the solid phases. Even when the 25 percent alloy is poured into water, and the resulting shot (which are of a very fine-grained structure) are annealed for three weeks at 150°, there is no evidence of these two heat changes on the heating or cooling curves. Nor are these two changes to be detected in the alloys richer in copper than Cu_3Sn, *i. e.*, 61.5 percent.

Our attention was first directed to these phenomena by the change in microstructure which the alloys undergo when annealed for a long time at about 180°. For the present, however, it seems better to publish the data available, and leave the discussion of these relatively unimportant changes for the completed paper.

In our complete paper we will publish the photographs showing the structures which are characteristic of each region, and show more in detail the method of investigation. For the present, the diagram submitted will suffice to indicate the nature of these important alloys as well as the value of more *systematic* investigation of alloys. The great importance of the time factor in establishing equilibrium relations is emphasized by the difference between this diagram and those previously published. The assumption made by the earlier investigators, *i. e.*, that the reactions involved were instantaneous, has been disproved. It has also been shown that the pyrometric evidence alone is not sufficient to establish such diagrams. These assumptions are so obviously in error that there would seem to be no need of calling attention to them, but the literature shows them to have been made by nearly every student of alloys.

The general results of this paper are as follows:

1. The phases which can coexist with the melt are the α, β, and γ solid solutions, the compound Cu_3Sn, the ε solid solution, and pure tin.
2. Below 600° the δ solid solution can exist. This phase was previously supposed to be the compound Cu_4Sn.
3. The complete concentration-temperature diagram has been worked out for temperatures above 219°.
4. Mixtures of Cu_3Sn and the ε crystals show heat effects at 218° and at 182°. The nature of these changes is still in doubt.

In conclusion, we wish to thank Professor Bancroft, who has directed and encouraged this investigation since it was begun some three years ago. His kindly criticism has always been available, and without it, it is very doubtful whether or not the results obtained would have been possible.

The expenses of the investigation have been met by grants from the Carnegie Institution of Washington, to which full credit must be given. A part of the pyrometric work was done in the Geophysical Laboratory of the Carnegie Institution, and we wish to thank Dr A. L. Day for the facilities afforded.

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