

In the above tables Rosetti's determination of the amount of the terrestrial atmospheric absorption has been used. It may be well, however, to give the results obtained by using other estimates of this quantity. Taking Langley's transmission coefficient when the sun is in the zenith as 59 per cent., compared to Rosetti's 71 per cent., the temperature would be multiplied by  $\sqrt[4]{(71/59)}$  and thus become  $5773 \times 1.054$ , which is  $6085^\circ$  absolute. And, as in the previous memoir, to make the case general, if any later investigation shows the zenith transmission coefficient to be  $x$  per cent., the effective absolute temperature becomes

$$5773^\circ \times \sqrt[4]{(71/x)}.$$

It may also be of interest to see what effect is produced if absorption in the atmosphere of the sun itself is taken into account. First, considering the falling off in radiation from the central to the peripheral parts of the sun's disc, we may deduce that, if the absorption were everywhere equal to that at the centre, the radiation would be multiplied by  $4/3$  and the temperature would become

$$5773^\circ \times \sqrt[4]{(4/3)} = 5773 \times 1.074 = 6201^\circ.$$

Secondly, assuming Wilson and Rambaut's\* result for the total loss due to absorption in the solar atmosphere as equal to one-third, our estimate of the temperature would have to be multiplied by  $\sqrt[4]{(3/2)}$ , and we get finally

$$6201^\circ \times \sqrt[4]{(3/2)} = 6201^\circ \times 1.107 = 6863^\circ \text{ absolute} = 6590^\circ \text{ C.}$$

I wish to express my thanks to Dr. Rambaut for some valuable suggestions during the progress of the work.

“On the Constitution of Copper-Tin Alloys.” By C. T. HEYCOCK, F.R.S., and F. H. NEVILLE, F.R.S. Received December 9,—  
Read December 12, 1901.

In February, 1901,† we read a short paper on the results of chilling copper-tin alloys, and at the Glasgow meeting of the British Association, 1901, we gave an account of some of the conclusions that we had arrived at concerning the nature of the alloys rich in copper.‡ The present paper extends our conclusions to all alloys of copper and tin, and the accompanying diagram presents the result in a concise but very complete form.

\* “The Absorption of, Heat in the Solar Atmosphere,” ‘Proceedings Royal Irish Academy,’ 1892, vol. 2, No. 2.

† ‘Roy. Soc. Proc.,’ vol. 68, p. 171.

‡ ‘Report on Alloys,’ Sec. B.

No one dealing with a subject which has been so much studied can give a comprehensive view of the phenomena without largely utilising the results of previous workers. For example, in the pyrometric work needed to determine the freezing-point curve ACDGH of our diagram we have been helped in some important particulars, such as the singularities at G and H, by the results already obtained by Sir W. Roberts-Austen and Dr. Stansfield.\* This is still more the case with regard to the evolutions of heat which take place in the solid alloys as they cool, and which are important indications of internal change. The eutectic line  $b' C'$ , and the very valuable curve XD' E' F', are also due to them. We have, however, re-examined and verified by experiment almost the whole of these pyrometric data.

The microscopic examination of the *unchilled* alloys is also not new, interesting results having been obtained by Charpy and by Stead; for example, the existence of the compounds  $Cu_3Sn$  and  $CuSn$  has been strongly suspected, if not quite proved. But it is our opinion that conclusive results will never be obtained except by the examination of alloys systematically chilled at selected temperatures, and it is in this method, and in the interpretation of results derived from it, that the new part of the work is to be found. Moreover, even with the help of the chilled alloys, the interpretation would have been very imperfect without the aid of Professor Bakhuis Roozeboom's Theory of Solid Solutions. We are also indebted to that gentleman for many valuable suggestions directly concerning these alloys, and for kind encouragement.

The method and purpose of chilling the alloys can be described in a few words. A number of small ingots of the same alloy, each weighing about 5 grammes, were melted and slowly cooled, and at selected temperatures ingots were withdrawn from the furnace and chilled by immersion in cold water. We thus, to a very large extent, stereotype the structure existing in the alloy at the selected temperature, and we can examine it in the usual way by polishing and etching. If the alloy was partly liquid when withdrawn from the furnace, it generally became more or less granulated by the process of chilling, and the microscope then showed it to consist of large copper-rich crystals formed before the chill and surrounded by a network of much smaller, but very similar, crystals formed during the chill, the whole being embedded in tin-rich mother substance. We can thus determine by the microscope how near to complete solidification the alloy was at the moment of chilling. It was in this way that we traced the branches *Ab* and *l<sub>1</sub>def* of the solidus. In the above case it is hardly correct to say that the structure existing before the chill is stereotyped by it, but it is sufficiently recorded. On the other hand, when an alloy has solidified before the moment of chilling, further changes are either

\* 'Fourth Report on Alloys,' February, 1897.



wholly arrested, or forced to occur on so minute a scale as to be invisible. This is well seen in the photographs 4, 5, 6, of the paper published in February, 1901.\*

Inasmuch as the evidence for our statements consists largely of a photographic record of the structure of the various chilled alloys it cannot be given in detail in the present paper, but some of this evidence has already been published in our two papers referred to above. We shall content ourselves at this moment with offering such an explanation of the annexed diagram as will make our conclusions intelligible.

In the diagram the *atomic* percentage of tin in the alloy, and also the percentage by *weight* of tin, are stated at the top. The atomic percentage, being the horizontal ordinate in the diagram, appears as a scale of equal distances, and therefore the percentage by weight is indicated on a gradually increasing scale; but by intraposition, any intermediate percentage can easily be found. The margin of the figure on the left corresponds to pure copper, that on the right to pure tin. The temperature scale is plotted vertically in degrees Centigrade.

In such a diagram, if we travel down a vertical line from the top to the bottom, we are considering the same alloy (so far as total percentage is concerned) at different temperatures, and, therefore, in different states of aggregation. Each closed compartment of the diagram corresponds to a different state of aggregation, and the phases making up the aggregates are indicated for each compartment. We can, therefore, from the position of the point, determine at once the state of the alloy.

The following phases occur:—

(1) Liquid.

(2) (3) (4) Mixed crystals of three types,  $\alpha$ ,  $\beta$ ,  $\gamma$ .

Each of these is a uniform solid solution containing copper and tin, but of variable percentage as in the case of a liquid solution.

(5) The body E', which composes the whole alloy at the point E'. This phase is certainly in many cases the pure compound  $\text{Cu}_3\text{Sn}$ , but there may be compartments in which the phase which we shall still call E' is a solid solution of  $\text{Cu}_3\text{Sn}$  and some other body.

(6) The body H, which first appears in certain alloys when they have cooled to a temperature of  $400^\circ \text{C}$ . There are various reasons, some of which we shall give at a later period, for believing that pure H is the compound  $\text{CuSn}$ , but we have not yet obtained conclusive proof that it habitually crystallises in the pure state.

(7) The solid crystallising on the branch IK, which must be pure tin.

Each of the above six solids can exist in contact with the liquid at appropriate temperatures and concentrations.

\* 'Roy. Soc. Proc.,' vol. 68.

(8) There is also the substance  $D'$ , which is never found in contact with the liquid. The substance  $D'$  is pure at the point  $D'$ , where we believe it to be the compound  $\text{Cu}_4\text{Sn}$ . This phase will be considered somewhat later.

The relations of the first seven phases can best be stated by considering the solidus (or, as we are inclined to call it, the melting-point curve). The solidus is a broken line consisting of the branches  $Ab$ ,  $ldef$ ,  $E_2E_3$ , and  $H'H''$ .

The solidus and the liquidus (or freezing-point curve) are so related that if we draw a horizontal, that is, an isothermal line, cutting the solidus and liquidus, the points of intersection give the percentage compositions of the solid and liquid that can exist in equilibrium at the given temperature. To take an example, the isothermal at  $900^\circ\text{C}$ . cuts the lines  $Ab$  and  $ABLC$  in points which correspond respectively to a uniform solid containing 3 atomic per cents. of tin, and a liquid containing 11 atomic per cents. These two would be in equilibrium, for when the liquid was cooled it would begin to deposit the solid, and when the solid was heated it would begin to melt and form the liquid.

Whenever a branch of the solidus is sloping, as  $Ab$ , or curved, as  $ldef$ , the solid phase is one of a series of mixed crystals. On the other hand, when a branch of the solidus is vertical, as we have drawn  $E_2E_3$  and  $H'H''$ , one can infer that mixed crystals are not formed. It is possible that we are wrong in drawing  $E_2E_3$  and  $H'H''$  quite vertical; the phase  $E'$  may here consist of  $\text{Cu}_3\text{Sn}$  having some  $H$  in solid solution, and the phase  $H$  may also contain some  $\text{Cu}_3\text{Sn}$  or tin in solid solution, in which cases the solidus would not be a vertical straight line. But we have several reasons, some of which will be stated later, for thinking that the mutual solubility of these bodies is not great.

The angle  $C$  of the liquidus indicates that the composition of the solid phase changes abruptly at this temperature, for while the branch  $ABC$  corresponds to the solidus  $Ab$ , the branch  $CD$  corresponds to the solidus  $lc$ . The angle  $C$  was a great stumbling-block to us so long as we only examined alloys that had not been chilled, but Roozeboom's theory explains in the most perfect manner all the phenomena at this angle. It tells us that just above the temperature  $C$  the cooling saturated liquid deposits, and is in equilibrium with, the  $\alpha$  mixed crystal whose composition is given by the point  $b$ , while just below the temperature  $C$  the liquid forms  $\beta$  mixed crystals, much richer in tin and given in composition by the point  $l$ . Thus, as the saturated liquid cools through the temperature  $C$  an isothermal transformation  $\alpha + \text{liquid} = \beta$  takes place. The heat evolved by this reaction is well marked in the cooling curves. No uniform mixed crystals of percentages between  $b$  and  $l$  can exist. The angle  $D$  probably indicates

another break in the series of mixed crystals, but we have not been able to detect a corresponding break in the solidus. However, we propose to call the mixed crystals of the branch *cdef*  $\gamma$  mixed crystals to distinguish them from the  $\beta$  crystals of the branch *lc*, and at Professor Roozeboom's suggestion we have drawn a sloping line from *c* to record the possible gap in the series between the last of the  $\beta$  crystals and the first of the  $\gamma$ .

Thus the branch ABLC of the liquidus deposits  $\alpha$  mixed crystals, the branch CD deposits  $\beta$  mixed crystals, and the branch DEFG deposits  $\gamma$  mixed crystals.

The branch GH of the liquidus deposits crystalline plates of the substance E', which is nearly or quite pure  $\text{Cu}_3\text{Sn}$ .

The branch HI deposits crystals of the substance H, which we think is probably  $\text{CuSn}$ , although it may have an impurity in solid solution.

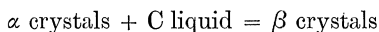
The liquid of the branch IK deposits crystals of pure tin.

Below the lines *Ablcdef*,  $\text{E}_3\text{H}'$ , and  $\text{H}'\text{K}'$  the alloys should be wholly solid, but on account of imperfect transformations this is not in practice everywhere the case.

The points B, L, C, D, E, F, G, H, I divide the alloys into groups having special qualities. We shall now trace the complete cooling of an alloy from each group.

1. *The AB Alloys, containing less than 5 atomic per cents. of Tin.*—When these alloys begin to solidify they form, while in the area *AbC*, a mixture of  $\alpha$  crystals and liquid. When the temperature of an alloy has fallen below the line *Ab*, it consists of uniform  $\alpha$  crystals embedded in a very little tin-rich mother substance, which owes its existence to imperfect adjustment of the equilibrium between solid and liquid during the last stages of solidification. This small residue of mother substance is absorbed at temperatures below *bC* by the  $\alpha$  crystals, and modifies their margins, but, in spite of some deceptive appearances, these alloys, at all temperatures below *Ab*, consist substantially of one phase, namely, the uniform solid solution  $\alpha$ .

2. *The BL Alloys, containing from 5 to 13 atomic per cents. of Tin.*—These alloys commence to solidify by the formation of  $\alpha$  crystals, but when the temperature C is reached the reaction



commences and continues until the C liquid is all exhausted. Thus, when the temperature begins to fall below C, the alloy is wholly solid and consists of  $\alpha$  crystals of the percentage *b* embedded in  $\beta$  crystals of the *l* percentage. These  $\beta$  crystals are uniform and play the part of a mother substance to the  $\alpha$  crystals, which now grow at the expense of the  $\beta$ , while the solid alloy cools through the range of temperature *bb'*. This growth in the solid is very remarkable in alloys near the

composition  $l$ , and accounts for the fantastic angular shapes seen in the  $\alpha$  combs of slowly cooled alloys. Our photograph 1, in Plate 2, of the 'Proceedings,' vol. 68, shows this angularity well. In this photograph the  $\alpha$  combs are dark. When the temperature falls below  $500^{\circ}$  C. (the eutectic line of Roberts-Austen and Stansfield) the residual  $\beta$  decomposes into a very minute eutectic of  $\alpha$  and the tin-rich body  $D'$ , which we believe is  $\text{Cu}_4\text{Sn}$ . Thus at all temperatures below  $b'C'$  this group of alloys form a complex of  $\alpha + D'$ .

3. *The LC Alloys, containing from about 13 to 15.5 atomic per cents. of Tin.*—These alloys commence their solidification with the formation of  $\alpha$  crystals, but at the C temperature these are completely changed into  $\beta$  of the percentage  $l$ , and then the  $\beta$  reacts along the lines  $lc$  and  $CD$  with the residual liquid. When the temperature has fallen to the solidus  $lc$  the alloy is a uniform solid solution. It is a mass of  $\beta$  crystals, chemically identical, but forming crystalline grains differently oriented and therefore showing, after etching, differences of brightness on tilting or rotating. (The Stead effect.) This uniform solid solution continues to exist until the temperature falls below the line  $IC'$ , which is comparable to a freezing-point curve, inasmuch as on cooling to a point on this line, the uniform  $\beta$  becomes saturated with  $\alpha$ , and below the line the  $\alpha$  crystallises out in large copper-rich crystals. Finally, as before, at  $500^{\circ}$  C. the residual  $\beta$  breaks up into the  $C'$  eutectic. Below the  $b'C'$  line these alloys, like the previous group, consist of the complex  $\alpha + D'$ . We have verified all this repeatedly, chilled samples of the alloy  $\text{Sn}_{14}$  showing everything very clearly. The  $C'$  eutectic has often, of course, been previously observed in unchilled alloys, but, so far as we know, without its real nature being discovered.

4. *The CD Alloys, containing from 15.5 to 20 atomic per cents. of Tin.*—These alloys begin to solidify by forming large, comparatively copper-rich combs of  $\beta$ , and when just solid are a uniform mass of  $\beta$  or  $\gamma$  crystals. This uniform solid solution persists so long as the temperature is above the line  $C'XD'$ . These solid solutions are very homogeneous, and we have not been able to find any difference between  $\beta$  and  $\gamma$  crystals. When the temperature falls below  $C'XD'$ , the phase  $D'$  crystallises out in ribands at the borders of the crystal grains of solid solution, as well as in the form of a fern leaf or rosette scattered through these grains. The effect is well shown by photograph 6, Plate 3, of the 'Proceedings,' vol. 68, and the cause of the pattern is discussed in that paper. The substance between the crystals of  $D'$  is, however, uniform until the temperature  $X$  is reached, when the residual solid solution breaks up into the  $C'$  eutectic complex of  $\alpha$  and  $D'$ . The fact that the eutectic point  $X$  of the  $CD$  alloys is a little lower than  $C'$  is evident in the pyrometric curves of Roberts-Austen and Stansfield, and we have abundantly verified it. But Professor Roozeboom suggests,

and we have little doubt on the point, that the true eutectic angle for all alloys from B to D is at C', and that the apparent depression of X is a retardation due to the difficulty experienced by the  $\alpha$  in crystallising from the solid solution without a nucleus of its own kind. Thus, in the region XD<sub>2</sub>D' the alloys are a complex of  $\beta$  and D', while below XD<sub>2</sub> they form a complex of  $\alpha$  and D'. As we have said before, we feel no doubt that this D' is the compound Cu<sub>4</sub>Sn.

The alloy Sn<sub>20</sub>, although it undergoes a well-marked exothermic transformation at the D' temperature, remains substantially uniform. The fact that it has recrystallised is, however, shown by minute traces of the C' eutectic, visible between the large crystals of Cu<sub>4</sub>Sn. It may be that the chemical compound Cu<sub>4</sub>Sn does not exist *above* the temperature D'.

5. *The DE Alloys, containing from 20 to 25 atomic per cents. of Tin.*—Between the liquidus and solidus these alloys contain primary combs of  $\gamma$ . On the solidus these combs fill the alloy, and just below it they form a uniform solid solution, but it is very difficult in this region to avoid a commencement of the transformation proper to the D'E' curve. However, our chilled alloys afford abundant evidence that the normal state of alloys between *de* and D'E' is that of a uniform solid solution. When the temperature falls to a point on the curve D'E', long, straight, very uniform tin-rich bars separate out of the solid solution. These are very slender and scanty near D', but become massive and abundant as we approach E', and at that point fill the whole alloy. These bars are really plates of E', seen more or less edgewise, and their appearance of greater or less breadth is partly due to their inclination. These plates, the first appearance of the E' phase, must be either pure Cu<sub>3</sub>Sn or mixed crystals of Cu<sub>3</sub>Sn and Cu<sub>4</sub>Sn; we are not at present able to decide this point. Thus, in the area D'E'E<sub>2</sub>F'E', the alloys are a complex of E' +  $\gamma$ . But Roberts-Austen and Stansfield have proved that these DE alloys show, when they fall to the temperature D', an evolution of heat. This must be due to the conversion of the residual  $\gamma$  into D', so that below D'E'' the alloys form the complex D' + E'.

6. *The EF Alloys, containing from 25 to about 27.5 atomic per cents. of Tin.*—These go through the same stages of  $\gamma$  + liq., then pure  $\gamma$ , then  $\gamma$  + E', but at the temperature G the residual  $\gamma$  breaks up into E' and the G liquid.

It may be noted here that the triangular area *lxf* forms an island of typical uniform solid solution, which could only have been discovered by the examination of chilled alloys.

7. *The FG Alloys, containing from 27.5 to 42 atomic per cents. of Tin.*—These alloys, like the preceding, begin by forming the complex  $\gamma$  + liquid; their state, when the temperature G is reached, being  $\gamma$  crystals of the *f* percentage and liquid of the G percentage. The isothermal transformation  $\gamma$  crystals = E' + G liquid, now begins.



Cooling curves show that this change is exothermic and abrupt, much heat being evolved by the alloys near  $f$ , but little by alloys near  $G$ . Herein the transformation at  $G$  is the reverse of the transformation at  $C$ . The change from the rounded  $\gamma$  crystals to the plates of  $E'$  with liberation of liquid is perfectly shown by our photographs of alloys chilled near the  $G$  temperature.

When an  $FG$  alloy has cooled below  $G$  the phase  $E'$  crystallises out of a liquid which is becoming richer and richer in tin. This process goes on between the  $G$  temperature of  $633^\circ$  and the  $H$  temperature of  $400^\circ$ . Below  $400^\circ$  the  $FG$  alloys follow the same course as the next group.

8. *The GH Alloys, containing from 42 to about 87.5 atomic per cents. of Tin.*—When these alloys begin to crystallise they deposit plates of  $E'$ , and this process goes on until the liquid has the composition  $H$  and the temperature is  $400^\circ$ . At this temperature the body  $E'$  becomes less stable than the body  $H$ , and the reaction  $E' + \text{liquid} = H$ , commences. This reaction ought to complete itself isothermally until either all the  $E'$  or all the liquid is transformed; but in our experiments we find that the reaction is soon arrested through the plates of  $E'$  becoming completely coated with  $H$ , and thus protected against further action by the liquid. When this has occurred, the temperature begins to fall again, and  $H$  crystallises out of the liquid until the eutectic point  $I$  is reached.

The result of this imperfect reaction is that we have four compartments in the space  $E_3SUH$ , in each of which one of the three phases that exist would be absent if the equilibrium transformations had been completed. This part of the figure assumes that the formula of the  $H$ -body is  $CuSn$ . If this should prove erroneous the line  $H'T$  would have to be shifted, but otherwise the diagram would be unchanged. In the four compartments of the area  $E_3SUH$ , Professor Roozeboom has suggested the excellent plan of placing a bracket round the symbol of the phase that has no right to be present.

9. *The HI Alloys, containing from 87.5 to 98.3 atomic per cents. of Tin.*—In these alloys the solid first forming is  $H$ , and the diagram sufficiently explains itself.

10. *The IK Alloys, with more than 98.3 atomic per cents. of Tin.*—These alloys contain combs of pure tin in a eutectic of  $H + Sn$ .

#### *Some Observations and Qualifications.*

*The Solidus.*—We have drawn this everywhere as a definite line, but our method of determining it, by the inspection of chilled alloys, is probably not so exact as the method by which the liquidus has been determined, and therefore further work on the solidus is desirable. We think that a determination of the *melting* point as distinguished from the *freezing* point would be a promising plan.

*The Phase D'.*—The great similarity in the character of this phase from the moment when it first appears in the C' eutectic of  $\text{Sn}_6$ , to the moment when it begins to appear as fern leaf in  $\text{Sn}_{16}$ , and gradually grows in amount until it fills the alloy at  $\text{Sn}_{20}$ , strongly inclines us to think that it is everywhere  $\text{Cu}_4\text{Sn}$ , and not a solid solution isomorphous with this compound. Perhaps the best argument for the view that D' is pure  $\text{Cu}_4\text{Sn}$  can be found in the fact that Roberts-Austen and Stansfield's line of eutectics ( $\text{XD}_2$  in our figure) extends to  $\text{Sn}_{20}$ .

*The Phase E'.*—Between the percentages D' and E' there is, as we have said, some uncertainty as to the composition of this phase; indeed, at one time we thought that there was another singularity between these points. But on the right of  $\text{Sn}_{25}$  E' must be pure, or nearly pure,  $\text{Cu}_3\text{Sn}$ . The following experiments bear on this question.

We found that E' and H were but little attacked by hydrochloric acid in the cold, and not at all attacked so long as free tin was present. We therefore chilled the alloys  $\text{Sn}_{35}$ ,  $\text{Sn}_{50}$ , and  $\text{Sn}_{65}$  at  $450^\circ$ , a temperature at which they consist only of plates of E' and liquid. They were then exposed for a week or more to strong hydrochloric acid, the acid being tested and changed every day. At first large quantities of tin, but not a trace of copper, dissolved, but gradually less tin came into solution, and when no more tin would dissolve a little copper was found in solution. At this stage the alloy consisted of separate plates of E' and a good deal of black mud. The mud was thoroughly washed away and the plates of E' analysed. Two analyses of each alloy were made.

The  $\text{Sn}_{35}$  gave 39.1—39.1 per cent. Sn.

The  $\text{Sn}_{50}$  gave 38.5—38.8     "     "

The  $\text{Sn}_{65}$  gave 41.7—42.2     "     "

while

$\text{Cu}_3\text{Sn}$  requires 38.35 per cent. Sn.

Considering the great difficulty of avoiding the presence of H in the plates of E' analysed, we think the above conclusive.

By similarly treating the alloy  $\text{Sn}_{90}$ , in which there should theoretically be no E', we obtained a beautiful and clean sample of H in brilliant spear-like leaflets. This contained 61 per cent. of tin, while  $\text{CuSn}$  requires 65 per cent., so that we have not yet obtained  $\text{CuSn}$  in a state of purity.

One reason of some weight in support of the formula  $\text{CuSn}$  is that H must be the body in solution in the liquid alloys of the branch IK of the freezing-point curve; and as we showed in 1890, the value of the depression of the freezing point of the tin points to a molecule in solution containing only one atom of copper.

We have to thank Miss D. Marshall, Lecturer of Girton College, and Mr. W. Fearnside, B.A., of Sidney College, for much help during the experiments.