THESIS

THE EFFECTS OF RAPID COOLING UPON METALS AND ALLOYS

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General Introduction.

It is of great importance to the engineer to be as fully acquainted as possible with the mechanical properties of the metals and alloys which he employs. Many series of experiments have been carried out by various observers with the object of determining the manner in which the mechanical properties of an alloy vary with its composition and with its previous history, but no general principles have been deduced from these scattered observations. During a preliminary study of the available data, the writer strongly felt the necessity of knowing the constitution and structural arrangement of the various alloys of which the mechanical properties had been determined. Many observations of the structure of metals and alloys subjected to various thermal and mechanical treatments have been made, but the results of these leave several difficulties unsolved. Accordingly the present investigation of the effect of rapid cooling was undertaken.

The physical properties of a metal which has solidified quickly may differ greatly from those of the same metal allowed to crystallise slowly. The difference in properties produced by varying the rate of cooling is accompanied by variation in the structure of the metal, that is, in the size and shape of the crystal aggregates or grains. In alloys, still greater relative change in properties may be caused by varying the rate of cooling, and the change in structure is not necessarily confined to the size and shape of the grains, but the manner of distribution of the grains, and even the proximate constitution of the mixture may be more or less completely altered. The exact connection between change of structure and change of properties cannot be exactly specified at present, but in general an alteration of constitution is more important than one of crystal size.

It had seemed likely to the writer for some time that the constitution of a rapidly cooled alloy should be possible of calculation from the equilibrium diagram ; Part I deals with this problem in a fairly thorough manner. The conditions which govern crystal growth are but imperfectly apprehended at present, so that structure must be investigated experimentally ; Part II deals with the structure of various selected metals and alloys, but though the observations are numerous the results are not of general applicability like those of Part I, since each metal and each series of alloys exhibits its own structural peculiarities, and there is great difficulty when studying one cause of structural variation to eliminate all others.

PART I. The Quantitative Effect of the Rate of Cooling upon the Constitution of Binary Alloys.

1. The Process of Crystallisation of Binary Alloys of a Simple Type.

In a simple type of alloy of two metals each solid component is capable of holding in solution a certain limited proportion of the other, and the two solid solutions when present together form an eutectic. The diagram illustrating the physico-chemical conditions of equilibrium of the series is of the form of Fig. 1, where temperatures are represented by ordinates, and the composition of the alloys, in percentages of the two components **A** and **B**, by abscissae. The broken line **CED** is the liquidus or freezing point curve - that is, the locus of the temperatures at which the various molten alloys of the series begin to solidify when cooled ; a point above CED represents a mixture which is wholly liquid, while one immediately below the line represents a mixture which is partly liquid and partly solid. The broken line CHKD is the solidus or melting point curve - that is, the locus of the temperatures at which the various solid alloys begin to liquefy when heated ; a point below CHKD represents a mixture which is wholly solid, while one immediately above the line represents a mixture which is partly solid and partly liquid. The points H and K represent respectively the limiting composition of the solid solution of B in A, and the limiting composition of the solid solution of A in B ; of the first of these solutions, called α, the metal A constitutes the greater portion, while in the second, called β, B is in excess of A. The lines PH and RK represent the changes in the limiting compositions of the solutions α and β at temperatures below HK. The point E, at which the two branches of the liquidus intersect, represents the eutectic alloy of the series.

The equilibrium diagram, Fig. 1, is divided by the various lines into a number of fields, each having a distinct signification. A point in the triangular space CEH, included between the liquidus and solidus, indicates a mixture which is partly liquid and partly solid ; the solid portion contains more of A and less of B than the liquid portion, and consists of crystals of the α-solution having a composition which varies with the temperature. Similarly a point within the triangular area DEK represents a mixture of β-crystals and liquid. An alloy of which the composition lies to the left of H solidifies completely at a temperature above HK to a mass of homogeneous α-crystals ; one with a composition represented by a point to the right of K also becomes completely solid above HK, and consists of homogeneous β-crystals. An alloy having a composition between H and E, when the temperature just reaches HK, is formed of saturated α-crystals of composition H and liquid of composition E ; the liquid solidifies at the constant temperature of the line HK as the eutectic mixture of the series, a conglomerate of tiny crystals of the saturated α- and β-solutions. When the composition of the alloy lies between E and K, the β-crystals first formed reach the saturation composition K, and the rest of the mass solidifies as the eutectic E. Thus all alloys between H and K contain both α- and β-crystals.

The earlier products of solidification are frequently termed primary crystals, in order to distinguish them from the secondary eutectic or other crystallisation. The manner in which the composition of a primary crystal changes during the period of its formation is important. Consider the case of an alloy X, Fig. 2, containing a less proportion of the metal B than is necessary to saturate the α-solution at the eutectic temperature. Draw a vertical line - that is, one of constant composition - through X, cutting the liquidus at x' and the solidus at x". When the liquid alloy is cooled, x' is the temperature at which it commences to solidify, and x''' is the temperature of complete solidification ; or, if the solid alloy be heated, x''' is the temperature at which melting commences, and x' is that of complete liquefaction. If attention is confined, for convenience, to the process of solidification of the melted alloy, the composition of the first tiny crystals is given by x'', the intersection with the solidus of the horizontal line through x'. At any subsequent stage of solidification the compositions of the solid and liquid portions of the mass are represented by the intersections with the solidus and liquidus, respectively, of a horizontal line drawn at the temperature of the mixture in accordance with the vertical scale of the diagram. Thus, at the temperature of the line pq, the alloy is a mixture of crystals of composition p with liquid of composition q. The total composition of the alloy is represented on the line pq by the point o, vertically below X, so that, by elementary geometry, the proportion of p-crystals is the fraction oq/pq, and the proportion of q-liquid is po/pq of the whole alloy. From x' to x''' the proportion of liquid steadily decreases and that of the crystals increases. At x''' the liquid vanishes, the composition of the last droplets being given by x'''', the intersection with the liquidus of the horizontal through x'''.

In an alloy represented by a point like Y, lying between H and E, the earlier part of the process of solidification is like that of X, but the completion is otherwise. When the temperature has just fallen to that of the line HE the composition of the crystals is given by H and that of the liquid by E. The liquid E solidifies at constant temperature to form the eutectic, while the composition of the primary crystals remains unaltered, so that when the temperature commences to fall below HE the just solid alloy consists of primary crystals and eutectic in the proportion of $y'''E$ to Hy''' ; or $y'''E/HE$ of the whole consists of primary crystals, and Hy'''/HE is formed of eutectic.

Returning to the alloy X, the process by which the solid portion changes from a few crystals of composition x'' to a homogeneous mass of composition x''' is of a duplex character. If just above the temperature pq all the crystals were removed from the liquid, a slight fall of temperature would bring about the generation of tiny crystals of composition p. But when the previously formed crystals are not removed, and the conditions are those of equilibrium, the whole of the solid portion of the mixture attains the composition p at this temperature. There is a mutual action of diffusion between the solid and liquid portions, whereby the crystals formed at a higher temperature are enabled to assume, at the temperature pq, the only composition which is consistent with chemical equilibrium between solid and liquid at this temperature. If the process of solidification be supposed to take place is a series of small steps, at each step the crystals already formed change their composition, by diffusion, to that consistent with the new conditions of equilibrium, and there is also a small growth of entirely new material of the correct equilibrium composition.

In the above it has been supposed that the conditions of cooling are such that the alloy is enabled to be in a state of perfect physico-chemical equilibrium at the end of each small interval of temperature, but this is not so in practice. With ordinary rates of cooling, at any temperature within the interval of solidification, the composition of the liquid and of the most recently formed crystals probably approximate closely to those conditional with equilibrium, but such is not the case with the whole mass of solid. The process of diffusion, by which an alteration is effected in the composition of the primary crystals as the temperature falls, is a very slow one. It is much hindered also by the fact that the new growth is usually deposited around an already existing crystal, and forms an envelope which is for the moment in equilibrium with the liquid, and therefore more or less effectually screens the core. Thus, when solidification is completed, each crystal grain varies in composition from its centre to its external surface, giving a common and easily recognised type of structure. Further, any lack of equilibrium during solidification of an alloy having a composition to the left of H, such as X, causes the temperature of complete solidification to be lowered, but this does not fall below HE if surfusion be prevented ; in an alloy having a composition between H and K, like Y, the proportion of eutectic is greater when there is imperfect than when there is perfect equilibrium. These last two statements will be understood by a reference to Fig.2. Suppose that the alloy X cools to pq under conditions of perfect equilibrium. Then at this temperature the fraction oq/pq of the whole mass is solid. Suppose the crystals to be removed and the liquid to be cooled to $x'''x''''$, again under conditions of perfect equilibrium. Then the new crop of crystals is $q'x''''/x'''x''''$ of the portion not removed, and $x'''q'/x'''x''''$ of liquid remains. Thus the mass is not completely solid at the temperature x''', but a fraction equal to $\left(x'''q'/x'''x'''' . po/pq\right)$ of the original amount is still liquid. The sluggishness of diffusion may be conveniently regarded as equivalent to the removal of the crystals from the liquid at various stages in the process of solidification, so that an effect similar to the above is the result. If the rate of cooling of the alloy be very rapid, diffusion is almost entirely prevented ; this is equivalent to replacing the two large steps of Fig. 2 by a great number of small ones. The temperature of complete solidification of an alloy to the left of H is then lowered to the eutectic temperature, and the proportion of eutectic in an alloy having a composition between H and E is increased. The proportion of eutectic present in an alloy under these conditions may be now determined.

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2. Determination of the Proportions of Solid and Liquid in a Rapidly Cooled Alloy.

In considering the subject from a mathematical standpoint certain assumptions are required for the purpose of removing complexities difficult to treat accurately. The first assumption is that the manner of cooling is such that diffusion within the solid parts of the alloy is entirely prevented except during small intervals of temperature which may be varied at will, while diffusion within the liquid portion is always perfect ; consequently, each tiny crystal has the equilibrium composition corresponding with the temperature at the end of the interval within which it was formed. In an actual alloy there would be some diffusion within the solid portions, and a defective diffusion within the liquid parts of the mass. The second assumption is that all liquid remaining when the eutectic temperature is reached solidifies at this temperature ; in the absence of surfusion this would be actually the case. It is further assumed, for the present, that both liquidus and solidus curves, CE and CH, are straight lines ; for an actual series of alloys they are somewhat curved, but any desired degree of accuracy may be secured by subdividing the lines into sections short enough to be regarded as straight.

Consider an alloy represented by the point X, Fig. 3. Let its period of solidification be divided into a number of stages, as in the previous paragraph, the crystals being removed at the end of each stage. At the end of the first stage the two parts of the mixture are in the proportions,

$$\left.\begin{aligned} \text{Solid} &= \frac{oq}{pq} \\[2ex] \text{Liquid} &= \frac{po}{pq} \end{aligned}\right\} \quad \text{of the whole mass.}$$

At the end of the second stage the proportions are,

$$\left.\begin{array}{l}\text{Solid} = \dfrac{q's}{ts} \\[2ex] \text{Liquid} = \dfrac{tq'}{ts}\end{array}\right\} \text{ of the mass remaining after the removal of the first crop of crystals.}$$

That is, at the end of the second stage,

$$\left.\begin{array}{l}\text{Solid} = \dfrac{oq}{pq} + \dfrac{q's}{ts}\cdot\dfrac{po}{pq} \\[2ex] \text{Liquid} = \dfrac{tq'}{ts}\cdot\dfrac{po}{pq}\end{array}\right\} \text{ of the original mass.}$$

And so on, for subsequent stages. If the various steps extend over equal temperature intervals,

$oq = q's = s'u$ &c., = say m,

$lp = p't = t'v$ &c., = say n.

Put $x''x' = a$. Then,

$$\left.\begin{array}{lll} pq = a + m - n\,, & ts = a + 2m - 2n\,, & vu = a + 3m - 3n\,, \\ po = a - n\,, & to' = a - 2n\,, & vo'' = a - 3n\,, \\ & tq' = a + m - 2n\,, & vs' = a + 2m - 3n\,, \end{array}\right\} \text{ \&c.}$$

And the proportions of solid and liquid may be written,

At end of first stage,

$$\left.\begin{array}{l}\text{Solid} = \dfrac{m}{a+m-n} \\[2ex] \text{Liquid} = \dfrac{a-n}{a+m-n}\end{array}\right\} \text{ of original mass.}$$

At end of second stage,

$$\left.\begin{array}{l}\text{Solid} = \dfrac{m}{a+m-n} + \dfrac{m}{a+2m-2n}\cdot\dfrac{a-n}{a+m-n} \\[2ex] \text{Liquid} = \dfrac{a+m-2n}{a+2m-2n}\cdot\dfrac{a-n}{a+m-n}\end{array}\right\} \text{ of original mass.}$$

At end of third stage,

$$\text{Solid} = \frac{m}{a+m-n} + \frac{m}{a+2m-2n}\cdot\frac{a-n}{a+m-n} + \frac{m}{a+3m-3n}\cdot\frac{a+m-2n}{a+2m-2n}\cdot\frac{a-n}{a+m-n}$$

$$\text{Liquid} = \frac{a+2m-3n}{a+3m-3n} \cdot \frac{a+m-2n}{a+2m-2n} \cdot \frac{a-n}{a+m-n}$$

of original mass ; and so on.

At end of r-th stage,

$$\left.\begin{aligned}\text{Solid} &= \frac{m}{a+m-n} + \frac{m}{a+2m-2n} \cdot \frac{a-n}{a+m-n} + \cdots \\ &\quad \cdots + \frac{m}{a+rm-rn} \cdot \frac{a+(r-2)m-(r-1)n}{a+(r-1)m-(r-1)n} \cdot \ldots \cdot \frac{a-n}{a+m-n}\end{aligned}\right\} \cdots (1)$$

$$\left.\text{Liquid} = \frac{a+(r-1)m-rn}{a+rm-rn} \cdot \frac{a+(r-2)m-(r-1)n}{a+(r-1)m-(r-1)n} \cdot \ldots \cdot \frac{a-n}{a+m-n}\right\} \cdots (2)$$

of original mass.

It is simpler to determine the proportion of the liquid than of the solid portion of a mixture. The expression (2) gives the proportional amount of liquid remaining in an alloy at the end of a period of rapid cooling ; if solidification has been completed, (2) gives the amount of liquid present at the eutectic temperature, that is, the amount of eutectic present in the solid alloy. The degree of approximation to an accurate mathematical result for the case of an indefinitely great rapidity of cooling depends upon the number of steps taken, that is, upon the value of r, and for a reasonably accurate result this value must be considerable. A variation in the value of r is an artificial manner of representing a variation in the rate of cooling ; it is not possible to specify the actual rate of cooling which corresponds with a particular value of r, ~~and~~ for the relation between r and the rate of cooling is different for different alloys.

When r is increased indefinitely the expression (2) becomes an interesting example of a continued product of numbers, each less than unity, the value of which is finite. That the value is not zero follows from the fact that an increase in the value of r is only obtained by subdividing the steps, and each subdivision increases the value of the product. Thus, referring to Fig. 3, if the interval between x"x' and ts be considered a single step - that is, if equilibrium conditions prevail throughout this period - the amount of liquid at the end of this step is,

$$\frac{to'}{ts} = \frac{a-2n}{a+2m-2n}$$ of that present at x'.

If the period be divided into two equal steps by the line pq, the first crop of crystals being effectually removed at this temperature, the amount of liquid at the end of the second step is,

$$\frac{tq'}{ts} \cdot \frac{po}{pq} = \frac{a+m-2n}{a+2m-2n} \cdot \frac{a-n}{a+m-n}$$ of that present at x'.

Now,

$$\frac{a-2n}{a+2m-2n} = \frac{a-2n}{a+2m-2n} \cdot \frac{a+m-n}{a+m-n} = \frac{a^2+am-3an-2mn+2n^2}{(a+2m-2n)(a+m-n)}$$

And,

$$\frac{a+m-2n}{a+2m-2n} \cdot \frac{a-n}{a+m-n} = \frac{a^2+am-3an-mn+2n^2}{(a+2m-2n)(a+m-n)}$$

So that the subdivision of the one step into two has increased the proportional quantity of liquid by,

$$\frac{mn}{(a+2m-2n)(a+m-n)}$$ of that present at x'. ------ (3)

Similarly any other increase in the number of steps of the process causes a further increase in the amount of liquid left at the end. The quantity (3) is the amount of liquid necessary to convert the crystals of composition p, removed at the end of the first step, to the equilibrium composition t at the end of the second step. For, in order that the product shall have the composition t, the proportion of s-liquid which must diffuse into the p-crystals is,

$$\frac{\text{s-liquid}}{\text{p-crystals}} = \frac{p't}{ts} = \frac{n}{a+2m-2n}$$

And since the actual amount of p-crystals is,

$$\frac{oq}{po} = \frac{m}{a+m-n} \quad \text{of the whole alloy,}$$

The liquid necessary for the reaction is,

$$\frac{m}{a+m-n} \cdot \frac{n}{a+2m-2n} \quad \text{of the whole alloy.}$$

At the end of any subsequent stage the increased proportion of liquid over that conditional with equilibrium is less than the amount necessary to bring the whole of the crystals to the equilibrium composition corresponding with this temperature, since some of the increased liquid has crystallised at intermediate stages.

If the process of solidification were accomplished in one step - in other words, if conditions of perfect equilibrium prevailed during the whole period of crystallisation of the solid solution - the proportional amount of liquid left in the mixture X, Fig. 3, at the eutectic temperature would be,

$$\frac{Hx'''}{HE} = \frac{a-rn}{a+rm-rn} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

Any subdivision of the process results in a greater proportion of liquid, equal to,

$$\frac{a-rn+Q}{a+rm-rn}$$

where Q is a quantity which depends upon the actual alloy, and upon the number of steps into which the period of solidification is supposed to be divided - that is, upon the extent to which diffusion is operative in the solid parts of the alloy. The expression (2) may be written in the above form ; the details of the transformation are straightforward and uninteresting, and the result is that at the end of the r-th step, Liquid =

$$\frac{1}{a+r(m-n)}\left[a-rn+\frac{{}^{r}C_2\,mn}{\{a+(r-1)(m-n)\}}+\frac{{}^{r}C_3\,mn(m-2n)}{\{a+(r-1)(m-n)\}\{a+(r-2)(m-n)\}}\right.$$

$$+\cdots\frac{{}^{r}C_{s-1}\,mn(m-2n)(2m-3n)\cdots\cdots\{(s-3)m-(s-2)n\}}{\{a+(r-1)(m-n)\}\text{-----}\{a+(r-s+2)(m-n)\}}\cdots\cdots$$

$$\left.\cdots+\frac{mn(m-2n)(2m-3n)\cdots\cdots\{(r-2)m-(r-1)n\}}{\{a+(r-1)(m-n)\}\text{------}(a+m-n)}\right]\text{ ----- }(5)$$

where $${}^{r}C_2=\frac{r(r-1)}{1.2},\quad {}^{r}C_3=\frac{r(r-1)(r-2)}{1.2.3},\quad \&c.$$

The form of the expression (5) is unwieldy, but the continued product (2) can be evaluated conveniently if the notation is changed as follows. In Fig. 4 let the angle ACE be θ , and let ACH be ϕ . Let the difference of temperature between the freezing point C of the pure metal A and the freezing point x' of an alloy X be y_0 ; and let the difference of temperature between the freezing point C and some other temperature q of the partially solidified mixture be y. Let the temperature interval for a small step in the process of solidification be δy. Then the former notation is related to the new notation as follows,

$$x'x'' = a = y_0(\tan\theta - \tan\phi)$$

$$q's = m = \delta y.\tan\theta$$

$$p't = n = \delta y.\tan\phi$$

The proportion of liquid left in a slowly cooled alloy X at any temperature q during the period of freezing is easily obtained as,

$$\text{Liquid at temperature q (slow cooling)} = \frac{po}{pq}$$

$$= \frac{y_0\tan\theta - y\tan\phi}{y(\tan\theta-\tan\phi)}\text{ ---- }(6)$$

If solidification is completed above the eutectic temperature the melting point of the alloy is obtained by equating the expression (6) to zero, which gives,

$$y = y_0 \cdot \frac{\tan\theta}{\tan\phi}$$

as the difference between the freezing point of the pure metal and the melting point of the alloy. If the proportion of eutectic is required in an eutectiferous alloy it is obtained by inserting in (6) the value of y appropriate to the eutectic temperature.

For excessively rapid cooling the proportion of liquid left in the alloy X may be obtained by substitution in the expression (2),

Proportion of liquid (rapid cooling)

$$= \frac{y_0(\tan\theta-\tan\phi)-\delta y.\tan\phi}{(y_0+\delta y)(\tan\theta-\tan\phi)} \cdot \frac{y_0(\tan\theta-\tan\phi)+\delta y(\tan\theta-2\tan\phi)}{(y_0+2\delta y)(\tan\theta-\tan\phi)} \cdot \\ \cdots\cdots\cdots \cdot \frac{y_0(\tan\theta-\tan\phi)+\delta y\{(r-1)\tan\theta-r\tan\phi\}}{(y_0+r.\delta y)(\tan\theta-\tan\phi)}$$

Writing $y_1 = y_0+\delta y$, $y_2 = y_0+2\delta y$, &c., the expression becomes,

$$\frac{y_0(\tan\theta-\tan\phi)-\delta y\tan\phi}{y_1(\tan\theta-\tan\phi)} \cdot \frac{y_1(\tan\theta-\tan\phi)-\delta y\tan\phi}{y_2(\tan\theta-\tan\phi)} \cdot\cdots\cdots \cdot \frac{y_{r-1}(\tan\theta-\tan\phi)-\delta y\tan\phi}{y_r(\tan\theta-\tan\phi)}$$

And after re-arranging,

$$\frac{y_0(\tan\theta-\tan\phi)-\delta y\tan\phi}{y_r(\tan\theta-\tan\phi)} \cdot \left[\left\{1-\frac{\delta y\tan\phi}{y_1(\tan\theta-\tan\phi)}\right\}\left\{1-\frac{\delta y\tan\phi}{y_2(\tan\theta-\tan\phi)}\right\}\cdots\cdots\left\{1-\frac{\delta y\tan\phi}{y_{r-1}(\tan\theta-\tan\phi)}\right\}\right]$$

Proceeding to the limit, multiplying and collecting the terms within the square bracket, and writing c for $\frac{\tan\phi}{\tan\theta-\tan\phi}$, gives,

$$\frac{y_0}{y_r}\Big[1 - c.\delta y\sum\frac{1}{y} + (c.\delta y)^2\sum(\text{products of } \tfrac{1}{y} \text{ in pairs}) \\ -(c.\delta y)^3\sum(\text{products of } \tfrac{1}{y} \text{ in threes}) + \cdots \text{\&c.}\Big]$$

Now the series within the square bracket is convergent, and so long as no great number of terms are necessary the expression may be rewritten, with only a slight deviation from perfect accuracy, as,

Proportion of liquid (rapid cooling)

$$= \frac{y_o}{y_r}\left[1 - c\int_{y_o}^{y_r}\frac{dy}{y} + c^2\int_{y_o}^{y_r}\frac{dy}{y}\left(\int_{y_o}^{y_r}\frac{dy}{y}\right) - \&c.\right]$$

$$= \frac{y_o}{y_r}\left[1 - c.\log_\epsilon\frac{y_r}{y_o} + \frac{1}{\underline{|2}}\left(c.\log_\epsilon\frac{y_r}{y_o}\right)^2 - \frac{1}{\underline{|3}}\left(c.\log_\epsilon\frac{y_r}{y_o}\right)^3 + \&c.\right]$$

$$= \frac{y_o}{y_r}\cdot\epsilon^{-c\log_\epsilon\frac{y_r}{y_o}}$$

$$= \epsilon^{-(c+1)\log_\epsilon\frac{y_r}{y_o}}$$

$$= \left(\frac{y_r}{y_o}\right)^{-(c+1)}$$

$$= \left(\frac{y_o}{y_r}\right)^{c+1}$$

$$= \left(\frac{y_o}{y_r}\right)^{\frac{\tan\theta}{\tan\theta - \tan\phi}} \qquad \text{-------------} (7)$$

It is to be noted that if the separating crystals are of constant composition, as when they consist of a pure metal or metallic compound, the corresponding solidus is a vertical straight line, and $\tan\phi = 0$. The proportion of liquid for rapid cooling is then $\frac{y_o}{y_r}$, exactly the same as for slow cooling. This result, which is almost self evident, follows at once from the original assumptions.

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3. The Constitution of Rapidly Cooled Lead-Tin Alloys.

To illustrate the kind of results obtained by the above method the lead-rich alloys of the lead-tin series have been chosen. Most of the equilibrium conditions for this series have been determined recently with great accuracy by Rosenhain and Tucker. The liquidus for the lead-rich alloys is slightly curved, and is shown as a fine line in Fig. 5 ; the eutectic point is at 62.93 per cent. of tin and 183° C. The corresponding solidus has not been determined exactly ; the limiting concentration of the lead-rich solution is close to 16 per cent. of tin.

For the present purpose both solidus and liquidus have been assumed straight, and the intersection of these lines with the eutectic line have been taken at 16 and 63 per cent. of tin, respectively ; the assumed liquidus and solidus are shown as thick lines in Fig. 5. The curvature of the liquidus is taken into account in a subsequent calculation. The temperature interval between the freezing point of lead (328° C.) and that of the eutectic (183° C.) has been divided into ten equal parts ; the corresponding points of division on the liquidus represent nine lead-rich alloys, numbered I, II, III, &c., for which the calculations have been made. In order to show the effect of different rates of cooling the interval between the freezing point of lead and that of the eutectic has been divided into 10, 20, 50, 100, and 200 steps, respectively, and the corresponding proportions of liquid left at 183° have been calculated from the expression (2), page 14. These are given in Table I, together with the proportions of liquid left in the various alloys when the rate of cooling is indefinitely rapid,as calculated from the expression (7), and also the proportions of liquid obtained under equilibrium conditions.

TABLE I. Liquid remaining in various lead-tin alloys at the eutectic temperature after different rates of cooling. Liquidus and solidus assumed straight.

No. of alloy	Freezing Point degrees C.	Tin per cent.	Proportion of liquid left at 183°						
			∞ Steps	200 Steps	100 Steps	50 Steps	20 Steps	10 Steps	Equilibrium
I	313·5	6·3	·04566	·04519	·04470	·04370	·04047	·03420	·00000
II	299·0	12·6	·11563	·11510	·11456	·11344	·11002	·10370	·00000
III	284·5	18·9	·19912	·19859	·19804	·19691	·19356	·18746	·06170
IV	270·0	25·2	·29281	·29230	·29179	·29068	·28759	·28194	·19574
V	255·5	31·5	·39490	·39443	·39398	·39299	·39023	·38521	·32979
VI	241·0	37·8	·50443	·50385	·50346	·50256	·50026	·49602	·46383
VII	226·5	44·1	·61996	·61966	·61935	·61859	·61683	·61350	·59787
VIII	212·0	50·4	·74148	·74127	·74105	·74045	·73930	·73698	·73191
IX	197·5	56·7	·86829	·86818	·86807	·86785	·86716	·86596	·86596

The values given in the fourth and in the last columns of Table I are plotted in the form of a diagram in the upper part of Fig. 5, where the proportion of liquid remaining in each alloy at 183° is set vertically downwards along the line representing the composition of the alloy. The straight line from 16 to 63 per cent. of tin shows the variation in the proportion of liquid with change in the composition of the alloy when the conditions are those of equilibrium ; the curved line from pure lead to 63 per cent. of tin indicates the larger proportion of liquid found when cooling is indefinitely rapid. For clearness the space between them is shown black. Since the liquid remaining in any alloy at 183° solidifies at this temperature in the form of the lead-tin eutectic, the diagram also represents the proportion of eutectic present in the various solid alloys under the stated conditions.

This diagram is of peculiar interest in connection with Tammann's method of determining the ends of an eutectic line. The method consists in noting, for a number of alloys having compositions between that of the eutectic and that of the saturated solid solution, the time during which the temperature remains stationary at the eutectic freezing point ; if the conditions of cooling are identical for all the alloys these times are proportional to the amounts of eutectic solidifying, and when time is plotted against composition the point at which the proportion of eutectic is zero - that is, the limit of saturation of the solid solution - is found by extrapolation. The difficulties in accurately applying this method are considerable, but the chief objection to the results obtained by most of the investigators who have employed it is in the small quantities of material they have used, and the common accompaniment of rather rapid cooling. As a consequence, nearly all the published data give curved lines like the curved one of Fig. 5. The latter gives the upper limit to the proportion of eutectic when the cooling is very rapid, while the straight line gives the lower limit corresponding with equilibrium. The experimental curves mentioned fall between these two limits ; they give too low a saturation point for the solid solution, that is, too long an eutectic line. The mere fact that they are curved is conclusive evidence either that the rate of cooling of the alloys has been too rapid to give results consistent with equilibrium, or that there have been other sources of error, since for equilibrium the proportion of eutectic varies simply with the composition of the alloy, so that all curves of this nature should be straight lines.

The equation to the curve which represents the proportion of eutectic in a series of rapidly cooled alloys is obtained from (7) by inserting the value of y_r - say y_E - corresponding with the eutectic temperature. The expression may be also written somewhat more conveniently. Let E be the proportion of eutectic in a rapidly cooled alloy ; let X be the percentage of the metal B in the alloy ; let X_S be the percentage of the metal B in the saturated A-rich solid solution ; and let X_E be the percentage of the metal B in the eutectic. Then, referring to Fig. 4,

$$X = y_o \tan\theta \ ; \quad X_S = y_E \tan\phi \ ; \quad X_E = y_E \tan\theta \ ;$$

And,

$$E = \left(\frac{X}{X_E}\right)^{\frac{X_E}{X_E - X_S}} \quad \text{------------} (7a)$$

is the equation to the curve ; E is the ordinate corresponding with the abscissa X, and the other terms are constants proper to the series of alloys. For the lead-rich alloys of the lead-tin series,

$$E = \left(\frac{X}{63}\right)^{\frac{63}{47}}$$

gives the proportion of eutectic in a very rapidly cooled alloy X.

It is clear from Fig. 5 that a much closer approximation to the true saturation point is found by extrapolation through points obtained from alloys rich in eutectic than from those containing only a small proportion of eutectic, whenever the rate of cooling falls short of the extreme slowness necessary to ensure equilibrium. The same fact is brought out still more clearly in Fig. 8, which shows the various apparent positions of the saturation point as determined from the proportion of eutectic in the rapidly cooled alloys, in the manner detailed on page 30. The real saturation point is at H, 16 per cent. of tin ; the points h_1, h_2, h_3, &c., are obtained for alloys I, II, III, &c., respectively, when rapidly cooled, and correspond with the percentages of tin given in the bottom line of Table IV. They actually represent the average composition of the non-uniform primary crystals of each alloy. The horizontal scale of Fig. 8 is more open than that of Fig. 5 in order that the various points shall be clearly separated.

It is interesting to determine what proportion of an alloy has crystallised at any instant during its period of solidification. This is easily calculated, by the methods given already, both for a very rapidly cooled and for a very slowly cooled alloy. Table II gives the proportion of solid matter in each of the nine chosen alloys at nine equidistant temperatures between the freezing point of lead and that of the lead-tin eutectic, and also at the eutectic temperature, when the alloys are very rapidly cooled ; Table III gives corresponding figures for the same alloys when in perfect equilibrium, the liquidus and solidus being assumed straight.

TABLE II. Proportion of primary crystals in very quickly cooled lead-tin alloys at various temperatures. Liquidus and solidus assumed straight.

No. of alloy		I	II	III	IV	V	VI	VII	VIII	IX
Tin per cent.		6·3	12·6	18·9	25·2	31·5	37·8	44·1	50·4	56·7
Temperature, degrees C.	313·5	·000								
	299·0	·605	·000							
	284·5	·771	·419	·000						
	270·0	·844	·605	·320	·000					
	255·5	·884	·707	·496	·258	·000				
	241·0	·909	·771	·605	·419	·217	·000			
	226·5	·926	·814	·679	·528	·363	·187	·000		
	212·0	·938	·844	·732	·605	·467	·320	·164	·000	
	197·5	·947	·867	·771	·663	·545	·419	·286	·146	·000
	183·0	·954	·884	·801	·707	·605	·496	·380	·258	·132

TABLE III. Proportion of primary crystals in lead-tin alloys under conditions of equilibrium at various temperatures. Liquidus and solidus assumed straight.

No. of alloy	I	II	III	IV	V	VI	VII	VIII	IX
Tin per cent.	6·3	12·6	18·9	25·2	31·5	37·8	44·1	50·4	56·7
Temperature, degrees C.									
313·5	·000								
299·0	·670	·000							
284·5	·894	·447	·000						
270·0	1·000	·670	·335	·000					
255·5	1·000	·804	·536	·268	·000				
241·0	1·000	·894	·670	·447	·223	·000			
226·5	1·000	·957	·766	·574	·383	·191	·000		
212·0	1·000	1·000	·838	·670	·503	·335	·168	·000	
197·5	1·000	1·000	·894	·745	·596	·447	·298	·149	·000
183·0	1·000	1·000	·938	·804	·670	·536	·402	·268	·134

The above values are represented diagrammatically in Fig. 6. From the freezing point of each alloy is drawn to the right a short horizontal line, the length of which represents unit quantity of the mixture ; verticals are drawn from the ends of this line to the eutectic line. From the left-hand vertical line, at each of the temperatures given in the first column of Table II, the corresponding proportion of primary crystals in the quickly cooled alloy is set out horizontally, and the points so obtained are joined by a curve. The proportion of liquid present in the mixture at any temperature is obviously given by the horizontal distance between this curve and the right-hand vertical boundary of the rectangle. The portion of each rectangle which represents solid matter is labelled S, and that representing liquid is marked L. In the same way as for the rapidly cooled alloys, a curve for each slowly cooled alloy is plotted from the data of Table III ; each of the latter curves lies to the right of the corresponding one of the former series, in accordance with the fact that there is more solid and less liquid matter in the slowly cooled alloys. The space between each pair of curves, shown black for clearness, exhibits the effect of rapid cooling in reducing the proportion of primary crystals. For rapid cooling the spaces marked L include the narrow dark areas ; for slow cooling the dark areas are to be reckoned as parts of the spaces marked S. The alloys I and II, when slowly cooled, become completely solid at temperatures above 183°, and at these temperatures the difference between quickly cooled and slowly cooled alloy is greatest. In alloys near the eutectic composition, like VIII and IX, the effect of rapid cooling is very small.

If the curves of Fig. 6 are differentiated, either by a graphical or by a mathematical method, other curves are obtained which represent the varying rate of solidification during the period of freezing of each alloy. Such curves are drawn in Fig. 7 for alloys I, III, and VII, the original curves, which differ only in scale from those of Fig. 6, being shown in full lines, and the derived rate curves in dotted lines. The initial rate of crystallisation is the same for both slow and rapid cooling. From the expression (6), page 17, it follows that,

Proportion of solid at any temperature (slow cooling)

= 1 - Proportion of liquid

$$= 1 - \frac{y_0 \tan\theta - y \tan\phi}{y(\tan\theta - \tan\phi)} = \frac{\tan\theta}{\tan\theta - \tan\phi} \cdot \frac{y - y_0}{y}$$

Differentiating this with respect to y,

$$\text{Rate of solidification (slow cooling)} = \frac{\tan\theta}{\tan\theta - \tan\phi} \cdot \frac{y_0}{y^2} \quad ---- (8)$$

At the freezing point, $y = y_0$, so that for both slow and rapid cooling,

$$\text{Rate of solidification at freezing point} = \frac{\tan\theta}{\tan\theta - \tan\phi} \cdot \frac{1}{y_0}$$

$$= \frac{63}{47} \cdot \frac{1}{y_0} \text{, for lead-tin alloys.}$$

The above rate of solidification is in respect of fall of temperature, but it is convenient also to express the rate with regard to the composition of the crystals ; this does not alter the shape of the curves if the solidus is straight, since the composition of the crystals formed at any temperature varies directly as the distance of that temperature from the freezing point of the pure metal, that is, ~~with~~ directly as y. Hence,

Rate of solidification with respect to composition (slow cooling)

$$= \frac{\tan\theta}{\tan\theta - \tan\phi} \cdot \frac{y_0}{y} \cdot \frac{1}{\text{Composition of crystals}}$$

And the rate at the freezing point

$$= \frac{63}{47} \cdot \frac{1}{\text{initial composition of crystals}}$$, for lead-tin alloys.

Thus the rate of solidification at the freezing point of alloy I, with respect to composition is

$$\frac{63}{47} \cdot \frac{1}{1{\cdot}6} = 0{\cdot}8378$$

Or, more simply, using the notation of page 13 ,

Rate of solidification with respect to composition

$$= \frac{\text{Proportion of Solid deposited}}{\text{Change of composition of Solid}}$$

$$= \frac{\frac{m}{a+r(m-n)}\cdot(\text{pre-existing liquid}) + \frac{n}{a+r(m-n)}\cdot(\text{pre-Existing Solid})}{n}$$

$$= \frac{\frac{m}{a+r(m-n)}\cdot\frac{a-rn}{a+r(m-n)} + \frac{n}{a+r(m-n)}\cdot\frac{rm}{a+r(m-n)}}{n}$$

$$= \frac{m}{n}\cdot\frac{a}{\{a+r(m-n)\}^2} \quad \text{-----------------} (9)$$

At the freezing point, r = 0 , and the rate is

$$\frac{m}{n}\cdot\frac{1}{a} = \frac{\tan\theta}{\tan\phi}\cdot\frac{1}{a}$$

That is, for alloy I the rate is $\frac{63}{16}\cdot\frac{1}{4{\cdot}7}$, the same as above.

For alloys containing no eutectic, the rate of solidification at the melting point, when the last drop of liquid solidifies, is,

$$\frac{m}{n}\cdot\frac{rn}{\{rn+r(m-n)\}^2} = \frac{1}{rm}$$

$$= \frac{1}{\text{horizontal distance between solidus and liquidus at melting point}}$$

since, at this point, $a = rn$. Thus the slowly cooled alloy becomes completely solid when

$$y\tan\phi = y_0\tan\theta = 6{\cdot}3$$

The corresponding value of rm is, $\tan\theta(y-y_0) = y_0\tan\theta\left(\frac{\tan\theta}{\tan\phi}-1\right)$

$$= 6{\cdot}3 \times \frac{47}{16}$$

$$= 18{\cdot}51$$

a value which may be measured, of course, upon the equilibrium diagram.

The final rate of solidification $= \frac{1}{18{\cdot}51} = 0{\cdot}0540$

The rate of solidification at the melting point of an alloy which contains eutectic, and any intermediate rates, may be obtained by substituting suitable values in (9), but in Fig. 7 the differentiation has been performed graphically except for the initial and final points of each curve.

For rapidly cooled alloys, the rate of solidification with respect to fall of temperature is obtained from the expression (7), page 19, thus,

Proportion of solid at any temperature (rapid cooling)

$= 1$ - Proportion of liquid

$$= 1 - \left(\frac{y_0}{y}\right)^{c+1}$$

Differentiating this with respect to y gives,

Rate of solidification (rapid cooling) $= (c+1)\left(\frac{y_0}{y}\right)^{c+1}\cdot\frac{1}{y}$ --- (10)

Or. with regard to composition, as explained above,

$$\text{Rate of solidification} = (c+1)\left(\frac{y_0}{y}\right)^{c+1} \cdot \frac{1}{\text{Composition of crystals just being formed}}$$

But the proportion of liquid remaining at this temperature is,

$$\left(\frac{y_0}{y}\right)^{c+1}$$

Therefore the rate of solidification is,

$$\frac{\tan\theta}{\tan\theta - \tan\phi} \cdot \frac{\text{Proportion of liquid}}{\text{Composition of separating crystals}} \quad \text{------} (11)$$

At the freezing point, $y = y_0$, so that (10) reduces to

$$\frac{\tan\theta}{\tan\theta - \tan\phi} \cdot \frac{1}{y_0}$$

which is identical with the result for slow cooling. The expression (11) may be obtained very simply thus,

Rate of solidification with respect to composition

$$= \frac{\text{Proportion of solid deposited}}{\text{Change of composition of solid}}$$

$$= \frac{\dfrac{m}{a + r(m-n)} \cdot (\text{liquid})}{n}$$

Now, $\dfrac{m}{n} = \dfrac{\tan\theta}{\tan\phi}$

And, $\dfrac{\text{Composition of separating crystals}}{a + r(m-n)} = \dfrac{\tan\phi}{\tan\theta - \tan\phi}$, by simple geometry.

Therefore the rate of solidification is,

$$\frac{\tan\theta}{\tan\theta - \tan\phi} \cdot \frac{\text{Proportion of liquid}}{\text{Composition of separating crystals}}$$

as before. The final rate of solidification of the primary crystals of the rapidly cooled alloy I is,

$$\frac{63}{47} \times \frac{\cdot 04566}{16} = 0\cdot 0038$$

where the proportion of liquid remaining at 183° has been taken from Table I. Intermediate values may be obtained by suitable substitution, or by graphical means as in Fig. 7. From the rate curves of Fig 7 it is possible to deduce the theoretical forms of cooling curve which correspond with a very slow and with a very rapid rate of cooling.

From the data given in Table II the average composition of the primary crystals of each rapidly cooled alloy at the stated temperatures may be calculated, if, as already assumed, the composition of the liquid is always that indicated by the liquidus. The point which represents the average composition of the crystals is a point on the apparent solidus for that particular alloy when rapidly cooled. The average composition of the primary crystals, by simple arithmetic, is,

$$\frac{(\text{Composition of alloy}) - (\text{proportion of liquid} \cdot \text{Composition of liquid})}{\text{proportion of Solid}}$$

Thus, for alloy I, at a temperature of 270°, the proportion of solid (see Table II) is 0.844, and the proportion of liquid is 0.156. The composition of the alloy is 6.3 per cent. of tin, and that of the liquid part of it is 25.2 per cent. of tin. Hence,

Average composition of primary crystals of alloy I at 270°

$$= \frac{6{\cdot}3 - ({\cdot}156 \times 25{\cdot}2)}{{\cdot}844} = 2.81 \text{ per cent. of tin.}$$

For very slow cooling the composition (from Fig. 5) is 6.4 per cent. of tin, so that the effect of rapid cooling is to cause a very considerable shift of the apparent solidus to the left. Values calculated in this manner for the alloys I to IX at various temperatures are given in Table IV, and the corresponding solidus curves are drawn as fine lines in Fig. 8. Certain published solidus curves for slowly cooled alloys show the same kind of hollow curvature as these, but it must not be concluded on that account that the experimental work was faulty.

TABLE IV. Average composition of primary crystals of rapidly cooled lead-tin alloys at various temperatures.

	No. of alloy	I	II	III	IV	V	VI	VII	VIII	IX	Equilibrium Composition
	Tin per cent.	6.3	12.6	18.9	25.2	31.5	37.8	44.1	50.4	56.7	
Temperature, degrees C.	313.5	1.60									1.6
	299.0	2.19	3.20								3.2
	284.5	2.56	3.87	4.80							4.8
	270.0	2.81	4.37	5.50	6.40						6.4
	255.5	2.99	4.77	6.09	7.09	8.00					8.0
	241.0	3.15	5.12	6.56	7.73	8.80	9.60				9.6
	226.5	3.28	5.40	6.98	8.29	9.39	10.43	11.20			11.2
	212.0	3.38	5.61	7.36	8.74	9.93	11.03	12.01	12.80		12.8
	197.5	3.48	5.84	7.68	9.19	10.46	11.60	12.62	13.56	14.40	14.4
	183.0	3.57	5.99	7.94	9.53	10.93	12.22	13.27	14.15	15.30	16.0

In order to show the effect of varying the rate of cooling, the values given in Table V have been obtained in the same manner as those above, but with a greater degree of accuracy ; they represent the average composition of the primary crystals of alloy I at the eutectic temperature, corresponding with the various proportions of liquid left in this alloy as listed in Table I. Under conditions of equilibrium the alloy I, of course, becomes completely solid at a temperature far above that of the eutectic point. The figures of Table V are not valuable in themselves, since the real rate of cooling cannot be specified, but they show the approach towards equilibrium conditions, on account of the greater opportunity for diffusion, as the rate of cooling is decreased.

TABLE V. Apparent saturation point for alloy I at different rates of cooling.

Rate of cooling, represented by number of steps in freezing process.	Average composition of primary crystals at 183°C. Tin, per cent.
∞	3.587
200	3.616
100	3.647
50	3.709
20	3.908
10	4.292

- o - o -

4. Calculation of the Constitution of Quickly Cooled Alloys when the Curvature of Solidus and Liquidus is Considerable.

When the liquidus and solidus are only slightly curved, the calculation of the proportion of liquid or of eutectic in quickly cooled alloys, based upon the assumption of a straight liquidus and solidus, gives results which are not seriously erroneous ; this is particularly the case when, as with the lead-tin alloys, the curve oscillates about the straight line. Sometimes the degree of curvature is considerable, and the liquidus or solidus lies wholly on one side of the straight line drawn from the freezing point of the pure metal to the eutectic point, or to the saturation point, as the case may be. Now the proportion of solid formed during a small fall of temperature depends upon the angles of slope of the solidus and liquidus, and upon the horizontal distance between these lines in the region considered. Hence if the liquidus is convex and the solidus is concave upwards the proportion of liquid in quickly cooled alloys is greater than for a liquidus and solidus assumed straight ; if the liquidus is concave and the solidus is convex upwards the proportion of liquid is less ; if both are curved in the same direction the effect depends upon the mean inclination of the lines and their degree of curvature in a given region.

When the curvature is such that it must be allowed for, the expression (2), page 14, is quite suitable for purposes of calculation when correct values of m and n, which now vary from point to point, are inserted. A better and less tedious method is to divide the portion of the equilibrium diagram under consideration into a number of parts by horizontal straight lines, between each adjacent pair of which the solidus and liquidus differ but slightly from straight lines, and then to make use of expression (7), page 19, or more conveniently (7a), page 23, for each part ; there is no necessity that the parts should be equal, in fact their size is better regulated by the degree of curvature of solidus and liquidus. In Fig. 9 the compositions of the alloys U, V, W, and X are supposed to be chosen so that the sections u'v', v'w', w'x' of the liquidus, and the sections u"v", v"w", w"x" of the solidus do not deviate from straight lines by more than some arbitrarily chosen small quantity. The lines v'u' and v"u" are produced to intersect in C_U , w'v' and w"v" to meet in C_V , and so on ; through C_U , C_V , &c., vertical lines are drawn to meet u'u" in u, v'v" in v, &c., respectively.

The proportion of liquid in the rapidly cooled alloy U at the temperature vv' is then,

$$\left(\frac{u\,u'}{u_{,}\,v'}\right)^{\frac{u_{,}v'}{v''v'}}$$

Similarly the proportion of liquid in the rapidly cooled alloy V at the temperature ww' is,

$$\left(\frac{v\,v'}{v_{,}\,w'}\right)^{\frac{v_{,}w'}{w''w'}}$$

Hence the proportion of liquid in U at the temperature ww' is,

$$\left(\frac{u\,u'}{u_{,}\,v'}\right)^{\frac{u_{,}v'}{v''v'}} \cdot \left(\frac{v\,v'}{v_{,}\,w'}\right)^{\frac{v_{,}w'}{w''w'}}$$

The proportion of liquid in U at the temperature xx' is,

$$\left(\frac{u\,u'}{u_{,}\,v'}\right)^{\frac{u_{,}v'}{v''v'}} \cdot \left(\frac{v\,v'}{v_{,}\,w'}\right)^{\frac{v_{,}w'}{w''w'}} \cdot \left(\frac{w\,w'}{w_{,}\,x'}\right)^{\frac{w_{,}x'}{x''x'}}$$

and so on. The simplest method of procedure is to determine numerically the proportion of liquid in each quickly cooled alloy at the freezing temperature of the chosen alloy next below it, and to perform the necessary multiplication afterwards. It is therefore most convenient to begin with the chosen alloy which has the lowest freezing point.

This method has been applied to the lead-tin alloys, and the results, given in Table VI, show that in this case the effect of curvature of the liquidus is negligible. The calculations were made for nine alloys, of which the freezing temperatures are the same as for those chosen when the liquidus was assumed straight ; the compositions, and the equilibrium proportions of liquid for the two sets of alloys are therefore different, and do not admit of direct comparison in the tables. In Fig. **20** the open circles indicate points plotted for an assumed straight liquidus, corresponding with the figures given in the fourth column of Table I, and the black dots show the results obtained by making use of the true curved liquidus. It is easily seen that the distances of the former points from the curve drawn through the latter ones are very small. In a slowly cooled alloy any curvature of the liquidus and solidus is without effect upon the proportion of eutectic present under conditions of equilibrium at the eutectic temperature ; this proportion depends only upon the composition of the alloy, the composition of the eutectic, and the composition of the saturated primary crystals.

TABLE VI. Liquid remaining in various lead-tin alloys at the eutectic temperature. True curved liquidus employed.

No. of alloy	Freezing point degrees C.	Tin per cent.	Liquid at 183°	
			Rapid cooling	Equilibrium
I a	313·5	5·4	·03355	·00000
II a	299·0	11·0	·09183	·00000
III a	284·5	16·8	·16647	·01702
IV a	270·0	23·4	·26364	·15745
V a	255·5	30·8	·38341	·31489
VI a	241·0	38·1	·51024	·47021
VII a	226·5	44·8	·63343	·61277
VIII a	212·0	50·7	·74724	·73830
IX a	197·5	56·3	·85994	·85745

The same method is applied below to the more useful alloys of the copper-tin and copper-zinc series, for which the results are of some practical importance. The fact that in these alloys the various branches of the liquidus end at transition points, instead of at eutectic points, alters nothing in the method of calculation.

Apart from errors in the experimental determination of the equilibrium diagram, there are others introduced into the calculations by insufficiently close approximation of the short straight sections to the true curves, and by defective draughtsmanship ; these, while preventing the attainment of mathematical accuracy, may be reduced by ordinary care and trouble to quantities altogether negligible in practice. The intersections of the chosen portions of the solidus and liquidus are not infrequently bad ones - that is, the lines are inclined at only a small angle to each other - or the intersection may even lie off the drawing paper ; the horizontal positions of such points are then best checked by calculation. Thus, if C_V is the intersection of w'v' with w"v", and $C_V v$ is drawn vertically, then by simple geometry,

$$\frac{v_1'w'}{v_1''w''} = \frac{vv'}{vv''} = \frac{vv'' + v''v'}{vv''}$$

Or,

$$vv'' = \frac{v_1''w'' \, . \, v''v'}{v'w' - v_1''w''}$$

And $vv_o = vv' - v_o v''$, is the distance of the vertical line $C_V v$ from CA. The distances $v_1''w''$, $v''w'$, $v_1'w'$, and $v_o v''$ are all obtained from the diagram.

When the liquidus and solidus are curved it does not always happen that corresponding sections of these lines are convergent upwards ; they sometimes converge downwards, and occasionally become sensibly parallel for a short distance. It is necessary , therefore, to enquire what corresponding change there is in the expression which gives the quantity of liquid present in a rapidly cooled alloy.

When the liquidus and solidus converge downwards the conditions are as represented in Fig. 10, which should be compared with Fig. 4. Here m and n, θ and ϕ, are measured as before, but y and y_0 are measured upwards instead of downwards, and X, X_S, and X_E are measured from the right instead of from the left. Obviously,

$$n > m, \quad y_0 > y, \quad \tan\phi > \tan\theta, \quad X_S > X_E, \quad X > X_E .$$

The quantity of liquid present in a rapidly cooled alloy, therefore, is more conveniently written in this case as,

$$\left(\frac{y_r}{y_0}\right)^{\frac{\tan\theta}{\tan\phi - \tan\theta}} \quad \text{or} \quad \left(\frac{X_E}{X}\right)^{\frac{X_E}{X_S - X_E}}$$

When the liquidus and solidus are parallel, as in Fig. 11, m = n, and a is the same for all alloys. Hence the expression (2) becomes,

$$\text{Liquid} = \frac{a-m}{a} \cdot \frac{a-m}{a} \cdot \text{-----} \text{ to } r \text{ factors,}$$

$$= \left(1 - \frac{m}{a}\right)^r$$

The limiting value of this expression, when r is large and m is small, is,

$$\epsilon^{-\frac{rm}{a}} = \epsilon^{-\frac{M}{a}}$$

Where M is written for rm and is equal to the difference between the composition of the original alloy and that of the liquid portion of it at the given temperature ; in Fig. 11, for the alloy X, at the temperature pq, M = oq, and a = x''x'. The same result may be obtained from (7a). For, when liquidus and solidus are parallel, $X_E = X + M$, and $X_E - X_S = a$; X is indefinitely large, and M is finite. Therefore,

$$\left(\frac{X_E}{X}\right)^{-\frac{X_E}{X_E - X_S}} = \left(\frac{X+M}{X}\right)^{-\frac{X+M}{a}} = \left(1 + \frac{M}{X}\right)^{-\frac{X}{a}}$$

$$= \epsilon^{-\frac{M}{X}\cdot\frac{X}{a}}, \text{ in the limit, } = \epsilon^{-\frac{M}{a}}$$

5. The Copper-Tin Alloys.

Fig. 12 shows the portion of the equilibrium diagram to be dealt with, drawn from the experimental results of Roberts-Austen and Stansfield, of Heycock and Neville, and of Shepherd and Blough. The percentages of tin which correspond with the various critical points of the diagram are ,

$a = 9$, $b = 22.5$, $B = 25.5$,
$b_1 = 27.2$, $c = 28$, $C = 31.9$,
$d_1 = 38.4$, $c_1 = 41$, $D = 58$.

These are believed to be as nearly correct as they can be fixed at present ; future experiments may show small errors in some or all of these points. The liquidus curves AB, BC, and CD have been determined with very considerable accuracy, but the solidus curves Aa, bb_1, and cc_1 require further investigation in order to determine their exact forms. Any correction of the equilibrium diagram will necessitate, of course, a corresponding correction of the results of this paragraph.

In alloys containing less than 25.5 per cent. of tin the copper-rich crystals, designated α , crystallise from the liquid. The branch AB of the liquidus is of fairly uniform curvature, and for the purpose of calculating the constitution of rapidly cooled alloys the curve has been divided into eight equal parts, giving seven alloys of which the compositions are set forth in Table VII. The proportion of liquid remaining in each of these alloys at the temperature aB has been calculated by the method outlined in the preceding paragraph, and the results are plotted in the upper left-hand corner of Fig. 12. The ordinates of the straight line drawn from 9 to 25.5 per cent. of tin represent the constitution of alloys when in equilibrium ; the ordinates of the black area represent the excess of liquid occasioned by very rapid cooling, exactly as in Fig. 5.

By taking a larger number of alloys than the seven chosen, a slight correction would be made in the calculated proportion of liquid for rapid cooling, but excessive subdivision of the liquidus merely entails laborious calculations for the sake of an unnecessary and often spurious accuracy.

For alloys containing 25.5 to 31.9 per cent. of tin, in which the primary crystallisation consists of the β-solution, the liquidus BC is so nearly straight that it has been assumed accurately so, and the proportion of liquid has been calculated in the same manner as for the lead-tin alloys in paragraph 3, the proportionate error being probably of the same order as in that case. The alloys chosen for calculation are given in Table VIII. The straight lines CB and b_1b meet at 14.2 per cent. of tin, and the curve which represents the proportion of liquid in the rapidly cooled alloys is shown carried back to this percentage in the upper middle part of Fig. 12. The proportion of C-liquid in the rapidly cooled alloy B is 0.178 of the whole.

Between 31.9 and 58 per cent. of tin, where the primary crystals are designated γ, the curvature of the liquidus is fairly uniform, but that of the solidus is not so. It is necessary to choose mixtures at such intervals as correspond with quite short sections of the strongly curved part of the solidus ; nine have been taken, their compositions being as given in Table VII. The calculated results are exhibited by a curve as before, shown in the upper right-hand part of Fig. 12, and, similarly to the case of the β-crystallisation, this curve is dotted back to 25.7 per cent. of tin, the position of the intersection of the first portions of the solidus and liquidus. The proportion of D-liquid in the rapidly cooled alloy C is 0.048.

For the branch of the liquidus immediately to the right of D the crystallising substance is the compound Cu_3Sn, which separates in a sensibly pure state from the liquid. Under the limitations imposed by the initial assumptions, no change of constitution is caused here by varying the rate of cooling. This series of alloys is therefore left at the point D.

TABLE VII. Liquid remaining in various copper-tin alloys at the first transition temperature below their respective freezing points. True liquidus and solidus curves employed.

No. of alloy	Freezing point degrees C.	Tin per cent.	Primary crystals	Proportion of liquid at transition temperature	
				Rapid cooling	Equilibrium
I	1062	3·50	α	·07240	·00000
II	1036	6·95	α	·17048	·00000
III	1005	10·40	α	·28547	·08485
IV	971	13·65	α	·40903	·28182
V	933	16·80	α	·54391	·47273
VI	890	19·85	α	·68875	·65758
VII	844	22·75	α	·84093	·83333
alloys intermediate between VII and C are given in Table VIII					
C	745	31·90	γ	·04782	·00000
VIII	728	38·55	γ	·15034	·00000
IX	717	41·80	γ	·21997	·04706
X	704	45·10	γ	·31972	·24118
XI	694	47·20	γ	·40644	·36471
XII	683	49·40	γ	·51395	·49412
XIII	671	51·55	γ	·62882	·62059
XIV	659	53·70	γ	·74983	·74706
XV	647	55·85	γ	·87412	·87353

It is a matter of some interest ts emphasise the necessity of allowing for curvature in the calculations, by showing the differences in the results obtained when liquidus and solidus are assumed straight. In Fig. 13 the proportions ~~for~~ of liquid and solid for the α and γ periods of crystallisation, as drawn already in Fig. 12, are compared, on an enlarged scale, with those calculated when the lines AB in the one case, and CD, cc_1 in the other are assumed straight ; the former results are shown by full dots and lines, and the latter by open circles and broken lines. The numerical data for the assumed straight liquidus and solidus are given in Table VIII. For the α-crystallisation the curvature of the liquidus AB has the effect of diminishing the amount of solid formed during a small fall of temperature, as compared with what would be formed if AB were straight ; in the upper diagram of Fig. 13, therefore, the continuous curve lies below the dotted one. For the γ-crystallisation the curvature of the liquidus CD would have an effect similar to that of AB, but this is more than nullified by the strong reverse curvature of the solidus cc_1, and in the lower diagram of Fig. 13 the continuous curve lies above the dotted one. In both cases the proportional error caused by assuming the curved lines of the equilibrium diagram to be straight is seen to be very large, more especially for γ ; it follows, of course, that a small correction in the shape of the lines may make an important change in the calculated constitution of the rapidly cooled alloys.

TABLE VIII. Liquid remaining in various copper-tin alloys at the first transition temperature below their respective freezing points. Each branch of liquidus and solidus assumed straight.

No. of alloy	Tin per cent.	Primary crystals	Proportion of liquid at transition temperature	
			Rapid Cooling	Equilibrium
1	5·0	α	·08063	·00000
2	10·0	α	·23535	·06061
3	15·0	α	·44040	·36364
4	20·0	α	·68697	·66667
5	25·0	α	·96986	·96970
B	25·5	β	·17760	·00000
6	27·7	β	·35234	·10638
7	29·2	β	·52866	·42553
8	31·3	β	·87563	·87231
9	32·0	γ	·05536	·00000
10	39·0	γ	·19464	·00000
11	44·0	γ	·34602	·17647
12	49·0	γ	·54066	·47059
13	54·0	γ	·77855	·76471

So far the transformations which take place in the partly liquid alloys have been neglected. Under conditions of equilibrium there is a transition of α + B to β at the temperature aB, of β + C to γ at the temperature b_1C, and of γ to Cu_3Sn + D at the temperature d_1D. It is in accordance with the original assumptions to consider the first two of these changes to be suppressed when the rate of cooling is indefinitely rapid. Now an alloy containing less than 25.5 per cent. of tin, at the temperature aB, consists of α-crystals and B-liquid. If the rate of cooling is very rapid the B-liquid has no time to react with the α-crystals to form β-crystals, but it behaves as if it were an independent liquid alloy of composition B, and deposits β-crystals as if the α-crystals did not form part of the mixture. At the temperature b_1C a quantity of C-liquid, which as stated already is 0.178 of the B-liquid, is left. Similarly, any liquid left at C deposits γ-crystals independently of the previous formation of α and β, and leaves a residue of 0.048 of its own weight of D-liquid at the temperature d_1D.

The very slowly cooled alloys experience changes after they have become completely solid, but for the present purpose these are not considered. The upper diagram of Fig. 14 shows the constitution of just solid alloys when in a condition of equilibrium ; the temperature of each alloy containing less than 41 per cent. of tin is supposed to be just below that of its proper point on the broken solidus line $Aabb_1cc_1$, Fig. 12 ; for those containing 41 to 58 per cent. of tin the temperature is supposed to be just above dc_1D, so that no account is taken of the formation of Cu_3Sn. This arrangement is made merely for convenience in comparing results. The lower diagram of Fig. 14 represents the constitution of the very rapidly cooled alloys ; the temperature is supposed to be just above d_1D, and the extreme rapidity of cooling is supposed to preclude any change in the solid phases. The two diagrams, taken together, show what profound differences of constitution may be caused by varying the rate of cooling. Take, for instance, an alloy containing 7 per cent. of tin ; when solid and in a condition of equilibrium this consists entirely of homogeneous α-crystals, but when very rapidly cooled to just above the temperature of d_1D it would consist of roughly 83 per cent of α , 14 per cent. of β , 2.9 per cent. of γ , and 0.1 per cent. would still remain liquid. Or choose an alloy containing 20 per cent. of tin ; under equilibrium conditions, at a temperature just below that of aB, this consists of 18.5 per cent. of α and 81.5 per cent. of β ; but when rapidly cooled to the same temperature it would contain about 31 per cent. of α , 57 per cent. of β , and 12 per cent. of liquid ; if quickly cooled to just above d_1D this liquid would deposit 11.5 per cent. of γ , the remaining 0.5 per cent. of the alloy being still liquid. Further instances may be taken from the diagrams, or from Table IX, which contains the numerical data from which the diagrams have been drawn.

TABLE IX. Constitution of rapidly cooled copper-tin alloys at a temperature of 635° C.

No. of alloy	Tin per cent.	α	Liquid at B	β	Liquid at C	γ	Liquid at D
I	3·50	·9276	·0724	·0595	·0129	·0123	·0006
II	6·95	·8295	·1705	·1402	·0303	·0289	·0014
III	10·40	·7145	·2855	·2348	·0507	·0483	·0024
IV	13·65	·5910	·4090	·3364	·0726	·0691	·0035
V	16·80	·4561	·5439	·4474	·0965	·0919	·0046
VI	19·85	·3113	·6887	·5664	·1223	·1165	·0058
VII	22·75	·1591	·8409	·6916	·1493	·1422	·0071
B	25·50	·0000	1·0000	·8224	·1776	·1691	·0085
6	27·70			·6477	·3523	·3355	·0168
7	29·20			·4713	·5287	·5035	·0252
8	31·30			·1244	·8756	·8338	·0418
C	31·90			·0000	1·0000	·9522	·0478
VIII	38·55					·8497	·1503
IX	41·80					·7800	·2200
X	45·10					·6803	·3197
XI	47·20					·5936	·4064
XII	49·40					·4861	·5139
XIII	51·55					·3712	·6288
XIV	53·70					·2502	·7498
XV	55·85					·1259	·8741

The forms of the apparent solidus curves for the various alloys of Table VII have been determined, both for their own individual interest, and also for comparison with those obtained in the simpler case of the lead-tin series, illustrated in Fig. 8. Fig. 15 shows the solidus curves for α-crystals, and Fig. 16 for γ-crystals. The former differ but little in shape from the lead-tin curves, except that the initial rate of crystallisation is somewhat reduced by the curvature of the copper-tin liquidus. The curves for γ-crystals clearly show the influence of the peculiar form of the true solidus. The data for these diagrams are given in Tables X and XI for α, and in Tables XII and XIII for γ.

TABLE X. Proportion of primary α-crystals in rapidly cooled copper-tin alloys at various temperatures.

No. of alloy		I	II	III	IV	V	VI	VII
Tin per cent.		3·50	6·95	10·40	13·65	16·80	19·85	22·75
Temperature, degrees C.	1062	·000						
	1036	·575	·000					
	1005	·746	·403	·000				
	971	·823	·583	·302	·000			
	933	·867	·687	·475	·248	·000		
	890	·895	·752	·586	·406	·210	·000	
	844	·914	·797	·661	·514	·353	·181	·000
	795	·928	·830	·715	·591	·456	·311	·159

TABLE XI. Average composition of primary α-crystals in rapidly cooled copper-tin alloys at various temperatures.

No. of alloy		I	II	III	IV	V	VI	VII
Tin per cent.		3·50	6·95	10·40	13·65	16·80	19·85	22·75
Temperature, degrees C.	1062	0·70						
	1036	0·95	1·45					
	1005	1·15	1·84	2·40				
	971	1·32	2·16	2·89	3·50			
	933	1·46	2·46	3·33	4·11	4·75		
	890	1·58	2·70	3·72	4·58	5·33	6·05	
	844	1·69	2·92	4·06	5·04	5·89	6·74	7·50
	795	1·79	3·15	4·38	5·45	6·42	7·33	8·18

TABLE XII. Proportion of primary γ-crystals in rapidly cooled copper-tin alloys at various temperatures.

No. of alloy		C	VIII	IX	X	XI	XII	XIII	XIV	XV
Tin per cent.		31·90	38·55	41·80	45·10	47·20	49·40	51·55	53·70	55·85
Temperature, degrees C.	745	·000								
	728	·682	·000							
	717	·783	·317	·000						
	704	·850	·530	·312	·000					
	694	·882	·630	·459	·213	·000				
	683	·907	·707	·572	·378	·209	·000			
	671	·924	·761	·650	·492	·354	·183	·000		
	659	·936	·800	·707	·574	·458	·315	·161	·000	
	647	·945	·828	·748	·634	·535	·412	·281	·142	·000
	635	·952	·850	·780	·680	·594	·486	·371	·250	·126

TABLE XIII. Average composition of primary γ-crystals in rapidly cooled copper-tin alloys at various temperatures.

No. of alloy		C	VIII	IX	X	XI	XII	XIII	XIV	XV
Tin per cent.		31·90	38·55	41·80	45·10	47·20	49·40	51·55	53·70	55·85
Temperature, degrees C.	745	28·00								
	728	28·80	30·45							
	717	29·16	31·54	32·80						
	704	29·58	32·74	34·52	36·40					
	694	29·85	33·47	35·42	37·37	38·40				
	683	30·11	34·06	36·12	38·02	38·90	39·45			
	671	30·28	34·47	36·55	38·43	39·26	39·78	40·15		
	659	30·41	34·76	36·87	38·71	39·49	40·03	40·37	40·60	
	647	30·51	34·95	37·07	38·90	39·68	40·19	40·53	40·70	40·85
	635	30·59	35·12	37·23	39·03	39·81	40·31	40·62	40·80	40·95

6. The Copper-Zinc Alloys.

The portion of the equilibrium diagram to be considered is drawn in Fig. 17 from the experimental results of Roberts-Austen, of Shepherd, and of Tafel. The compositions corresponding with the various critical points are,

$a = 29$, $b = 36$, $B = 37$,

$b_1 = 55$, $c = 60.7$, $C = 61$,

per cent. of zinc. As in the case of the copper-tin alloys, there may be small errors in the positions of these points. The solidus curves for α- and β-crystals probably differ little from straight lines ; the forms of the liquidus curves are probably not quite so accurately determined as those of copper-tin. Few of the alloys containing more than 60 per cent. of zinc are of practical importance, and the corresponding part of the equilibrium diagram is somewhat defective, so that the crystallisation of only α and β is considered here.

The α-crystals separate from liquid alloys containing less than 37 per cent. of zinc. The curvature of the branch AB of the liquidus is approximately uniform, and the line does not depart greatly from straightness ; it was divided into four equal parts, giving three alloys containing 9.30, 18.65, and 27.85 per cent. of zinc, respectively. These are probably sufficient for the present purpose. The numerical data are given in Table XIV, and are plotted, in the same manner as before, in the upper part of Fig. 17. A similar procedure was followed for the branch BC. The proportion of C-liquid left in the rapidly cooled alloy B is very small, only 0.0043. Comparison of the curves shown in Fig. 17 with those obtained when AB and BC are assumed straight gives results like that of Fig. 13 for the copper-tin α-crystals ; the correct figures correspond with a greater proportion of liquid than when the liquidus is assumed straight, the difference in the case of the α-crystals being small, but for β considerable. The figures for the assumed straight liquidus are not of particular interest, and accordingly have not been tabulated here.

TABLE XIV. Liquid remaining in various copper-zinc alloys at the first transition temperature below their respective freezing points. True liquidus and solidus curves employed.

No. of alloy	Freezing point degrees C.	Zinc per cent.	Primary Crystals	Proportion of liquid at transition temperature	
				Rapid Cooling	Equilibrium
I	1048	9·30	α	·00924	·00000
II	1007	18·65	α	·07514	·00000
III	959	27·85	α	·30455	·00000
B	905	37·00	β	·00429	·00000
IV	896	43·10	β	·06311	·00000
V	881	49·15	β	·18526	·00000
VI	860	55·15	β	·42312	·00250

In Fig. 18 the constitutions of slowly and of rapidly cooled alloys are compared, just as in Fig. 14. Each slowly cooled alloy containing less than 55 per cent. of zinc is supposed to be at a temperature just below the corresponding point on $Aabb_1$, and those containing from 55 to 61 per cent. of zinc to be at a temperature just above b_1C ; the quickly cooled alloys are also supposed to be at the latter temperature. The results are not so striking as in the case of the copper-tin alloys, chiefly on account of the closeness of the points b and B, Fig. 17, to each other. The calculated figures are given in Table XV.

TABLE XV. Constitution of rapidly cooled copper-zinc alloys at a temperature of 830° C.

No. of alloy	Zinc, per cent.	α	Liquid at B	β	Liquid at C
I	9·30	·9908	·0092	·0092	·0000
II	18·65	·9249	·0751	·0748	·0003
III	27·85	·6954	·3046	·3033	·0013
B	37·00	·0000	1·0000	·9957	·0043
IV	43·10			·9369	·0631
V	49·15			·8147	·1853
VI	55·15			·5769	·4231

7. The Copper-Nickel Alloys.

The method of the preceding paragraphs may be extended to alloys of two metals which show complete mutual solubility when solid. A suitable example is afforded by the copper-nickel alloys.

The equilibrium diagram, Fig. 19, is due to Guertler and Tammann, and to Kurnakow and Zemczuzny. The curvature of liquidus and solidus is greatest in the middle region of the diagram. The nine alloys for which the calculations have been made have their freezing points situated at equal intervals between the freezing point of nickel and that of copper ; a somewhat better choice, more in accordance with the variations of curvature, might have been made.

There is now, of course, no eutectic or transition temperature for the partly liquid alloys, and mixtures cooled with extreme rapidity would only become completely solid at the freezing point of copper, according to the original assumptions. The process of solidification, however, may be supposed interrupted at any desired temperature, and the differences of constitution between slowly and rapidly cooled alloys at this temperature may be represented by a diagram of the same form as in previous examples. In the upper part of Fig. 19 such diagrams have been drawn for the four temperatures 1118°, 1187°, 1256°, and 1324°, corresponding with the freezing points of the alloys numbered I, III, V, and VII, respectively. The data are given in Table XVI.

TABLE XVI. Liquid remaining in quickly cooled copper-nickel alloys at various temperatures during partial solidification.

No. of alloy	Freezing point degrees C.	Nickel per cent	Proportion of liquid at temperature, degrees C.								
			1393	1358	1324	1290	1256	1221	1187	1153	1118
I	1118	6·6									1·00000
II	1153	13·6								1·00000	·52856
III	1187	20·7							1·00000	·64042	·33850
IV	1221	28·2						1·00000	·66073	·42315	·22366
V	1256	37·1					1·00000	·60728	·40125	·25697	·13582
VI	1290	46·9				1·00000	·53643	·32576	·21524	·13785	·07286
VII	1324	57·8			1·00000	·42236	·22656	·13762	·09091	·05822	·03077
VIII	1358	69·0		1·00000	·32874	·13885	·07448	·04524	·02989	·01914	·01012
IX	1393	82·5	1·00000	·17848	·05867	·02478	·01329	·00807	·00533	·00342	·00181

Below the real solidus has been plotted for each alloy the apparent solidus. All alloys of the series, when just solid and in a condition of equilibrium, are formed of homogeneous crystals. In each quickly cooled alloy the average composition of the crystals gradually approaches that of the whole mixture as more and more of the mass becomes solid. The shape of the apparent solidus for alloy IX is similar to those drawn for the lead-tin alloys, but mixtures containing more copper than IX show a reversed curvature of the lower part of the apparent solidus, corresponding with the reversed inclination of the real solidus to the liquidus at the copper end of the diagram. The average compositions of the primary crystals for the nine chosen alloys, at various temperatures, are given in Table XVII.

TABLE XVII. Average composition of primary crystals of rapidly cooled copper-nickel alloys at various temperatures during partial solidification.

No. of alloy		I	II	III	IV	V	VI	VII	VIII	IX
Nickel per cent.		6.6	13.6	20.7	28.2	37.1	46.9	57.8	69.0	82.5
Temperature, degrees C.	1118	15.60	21.44	27.92	34.42	41.89	50.07	59.43	69.63	82.64
	1153		27.80	33.34	38.92	45.22	52.23	60.53	70.08	82.73
	1187			38.50	42.79	48.10	54.08	61.52	70.49	82.83
	1221				46.60	50.86	55.93	62.52	70.94	82.94
	1256					54.40	58.24	63.86	71.57	83.12
	1290						61.20	65.77	72.56	83.41
	1324							68.90	74.48	84.04
	1358								78.10	85.43
	1393									89.20

8. Calculation of the Constitution of Alloys cooled at Ordinary Rates.

For an actual alloy the rate of cooling lies between the extreme slowness necessary for equilibrium, and the extreme rapidity for which the preceding calculations have been made. The proportion of liquid in the mixture at any temperature during the period of partial solidification also lies between those calculated for the two extreme conditions. The difficulty of specifying the rate of cooling at a point in a mass of metal has been mentioned already, but it may be possible to determine the proportion of liquid or of eutectic in each of a series of alloys, all cooled under approximately similar conditions at a rate within the range of those realised in manufacturing or experimental work, without determining what this rate is.

The examination of many of the experimental results emanating from Prof. Tammann's laboratory shows that the shape of the curve, which represents the proportion of eutectic in the just solid alloys of a series cooled at a moderately slow rate, is ~~of a form~~ similar to that obtained by calculation for very rapid cooling. Moreover, the curves plotted from the figures in the various columns of Table I are all of similar shape. It is probable, therefore, that the curves which represent the proportion of liquid or of eutectic for different rates of cooling can be referred to one general equation. Now for equilibrium conditions the curve is a straight line. If, as before, E is the proportion of eutectic in the just solid alloy, X is the composition of the alloy, X_E is the composition of the eutectic, and X_S is that of the saturated solid solution, the expression (4), page 16, may be rewritten as,

$$E\,(\text{slow cooling}) = \frac{X - X_S}{X_E - X_S} \qquad \text{-------} (4a)$$

And for extremely rapid cooling the expression (7a),

$$E\,(\text{rapid cooling}) = \left(\frac{X}{X_E}\right)^{\frac{X_E}{X_E - X_S}}$$

has been given already. These are two particular cases of the general equation,

$$E = \left(\frac{X - x}{X_E - x}\right)^{\frac{X_E - x}{X_E - X_S}} \qquad \text{-----------}(12)$$

where x is a quantity which varies with the rate of cooling, and has a value between zero and X_S. For very slow cooling, $x = X_S$, and (12) reduces to (4a). For very rapid cooling, $x = 0$, and (12) reduces to (7a). At any intermediate rate the curve cuts the axis of composition at a point between zero and X_S, and the composition for this point is x, since by putting $x = X$ in (12) the value of E becomes zero.

The quantity x is a convenient means of defining the rate of cooling, though it does not specify the rate of loss of heat. To know the rate of fall of temperature or the rate of loss of heat of a mass of alloy conveys no information as to the structure of the mixture, unless one is already familiar with this particular alloy ; for some changes of phase are very sluggish, while others are extremely energetic, and a rate of loss of heat which might be regarded, from its effects, as rapid in the one case, would be characterised as slow cooling in the other. On the contrary, a statement of the ratio of x to X_S, after a perusal of this paragraph, should convey a fairly definite idea of the structural condition of an alloy, quite irrespective of the component metals or of the energy involved in the change of phase.

For cases in which the curvature of liquidus and solidus is negligible, the expression (12) is regarded as representing very closely the proportion of liquid in an alloy during the process of solidification,for all rates of cooling, but this expression requires experimental verification, since it has been deduced only indirectly from physical facts. There is certainly a close agreement between the quantities calculated from (12) and those given in the various columns of Table I, but even with the rate specified there as " 10 steps " the conditions approximate far more closely to great rapidity than to great slowness. In Fig. 20 three curves have been drawn for the lead-tin alloys, from equation (12), between the curve representing the proportion of liquid in very rapidly cooled alloys and the straight line representing the conditions for very slowly cooled ones ; the values of x chosen for the new curves, which are drawn with fine lines, are 4, 8, and 12 per cent. of tin. The data for these curves are given in Table XVIII. For cases of transition similar curves can be drawn. Curves of this kind are compared in the following paragraph with some of the experimental curves published from Prof. Tammann's laboratory, but the various defects of the latter are too great to allow them to be employed to decide whether equation (12) accurately represents the conditions prevailing at intermediate rates of cooling. It has to be remembered, also, that the rate of cooling of an actual mass of metal, except when special precautions are taken, is very far from uniform, and that the value of x is therefore different for different parts of the mass.

TABLE XVIII. Liquid remaining in various lead-tin alloys at the eutectic temperature after different rates of cooling. Liquidus and solidus assumed straight.

No. of alloy	Tin per cent.	Proportion of liquid left at 183°C.		
		$x = 4$	$x = 8$	$x = 12$
I	6·3	·01703	·00000	·00000
II	12·6	·08915	·05482	·00806
III	18·9	·17772	·15046	·11412
IV	25·2	·27669	·25659	·23070
V	31·5	·38356	·36970	·35231
VI	37·8	·49693	·48815	·47738
VII	44·1	·61585	·61097	·60509
VIII	50·4	·73965	·73751	·73498
IX	56·7	·86784	·86731	·86669

The proportion of liquid present in an alloy, cooled at a moderate rate, at a temperature between its freezing point and its eutectic or transition point, cannot be found by the present method, unless some assumption be made as to the manner in which the quantity x varies with the temperature of the partially liquid alloy. Thus, the sectional method of calculation, employed in the case of rapid cooling when the curvature of liquidus and solidus is to be allowed for, cannot be used in conjunction with (12) to get corresponding results for moderate rates of cooling, without some such arbitrary assumption.

When solidus and liquidus are both sensibly straight lines, the variation of x with the temperature cannot differ much from a linear relation also, since the extreme values of x vary according to two straight lines, the solidus and the vertical boundary $X = 0$. In other words, if a lead-tin alloy, containing x_0 per cent. of tin, is cooled at such a rate that it just solidifies at the eutectic temperature without any formation of eutectic, an alloy containing $x_0/2$ per cent. of tin may be expected to become just completely solid at a temperature midway between the freezing point of lead and that of the lead-tin eutectic. Though the assumption of this linear variation of x with the temperature requires verification, there is such a strong probability of its substantial accuracy that it has been made use of to work out the corresponding conditions in lead-tin alloys cooled at moderate rates. Taking the same three values of x as before, namely 4, 8, and 12 per cent. of tin, measured at the eutectic temperature, as defining the rate of cooling of the alloys, the proportions of solid and liquid in the mixtures I to IX, at nine equidistant temperatures, have been calculated. The proportions of primary crystals present in the mixtures are set forth in Table XIX. From these proportions the average composition of the non-uniform crystals has been determined, in the same way as in paragraph 3 ; the data are given in Table XX. The corresponding solidus curves are drawn in Figs. 21, 22, and 23, which differ from each other and from Fig. 8 only as regards the rate of cooling. The four sets of solidus curves for each of the alloys I, III, and VII are compared in Fig. 24; if those for the other six alloys were inserted here there would be too much overlapping and confusion to allow of easy comparison. The assumption of the linear variation of x with temperature is readily seen to give apparent solidus curves of correct form, and of correct manner of change of form with change in the rate of cooling. In these calculations the liquidus has been assumed straight for convenience, since the error caused by this assumption, as shown in paragraph 4, is extremely small.

TABLE XIX. Proportion of primary crystals at various temperatures in lead-tin alloys cooled at moderate rates. Liquidus and solidus assumed straight.

No. of alloy		I	II	III	IV	V	VI	VII	VIII	IX
Tin per cent		6·3	12·6	18·9	25·2	31·5	37·8	44·1	50·4	56·7
						$x = 4$				
Temperature, degrees C.	313·5	·000								
	299·0	·616	·000							
	284·5	·790	·424	·000						
	270·0	·868	·616	·323	·000					
	255·5	·911	·723	·503	·260	·000				
	241·0	·937	·790	·616	·424	·218	·000			
	226·5	·955	·836	·694	·536	·367	·188	·000		
	212·0	·967	·868	·749	·616	·474	·323	·165	·000	
	197·5	·976	·892	·790	·677	·554	·424	·288	·147	·000
	183·0	·983	·911	·822	·723	·616	·503	·384	·260	·132
						$x = 8$				
Temperature, degrees C.	313·5	·000								
	299·0	·630	·000							
	284·5	·815	·430	·000						
	270·0	·899	·630	·326	·000					
	255·5	·945	·743	·512	·262	·000				
	241·0	·973	·815	·630	·430	·220	·000			
	226·5	·991	·864	·712	·546	·371	·189	·000		
	212·0	1·000	·899	·771	·630	·482	·326	·165	·000	
	197·5	1·000	·925	·815	·694	·565	·430	·291	·148	·000
	183·0	1·000	·945	·850	·743	·630	·512	·389	·262	·133
						$x = 12$				
Temperature, degrees C.	313·5	·000								
	299·0	·648	·000							
	284·5	·848	·438	·000						
	270·0	·941	·648	·330	·000					
	255·5	·992	·769	·523	·265	·000				
	241·0	1·000	·848	·648	·438	·221	·000			
	226·5	1·000	·902	·735	·559	·377	·190	·000		
	212·0	1·000	·941	·799	·648	·491	·330	·166	·000	
	197·5	1·000	·970	·848	·716	·578	·438	·294	·148	·000
	183·0	1·000	·992	·886	·769	·648	·523	·395	·265	·133

TABLE XX. Average composition of primary crystals at various temperatures in lead-tin alloys cooled at moderate rates. Liquidus and solidus assumed straight.

No. of alloy		I	II	III	IV	V	VI	VII	VIII	IX
Tin per cent.		6.3	12.6	18.9	25.2	31.5	37.8	44.1	50.4	56.7
$x = 4$										
Temperature, degrees C.	313.5	1.60								
	299.0	2.37	3.20							
	284.5	2.95	4.03	4.80						
	270.0	3.43	4.75	5.70	6.40					
	255.5	3.84	5.36	6.44	7.27	8.00				
	241.0	4.18	5.90	7.11	8.09	8.90	9.60			
	226.5	4.52	6.42	7.78	8.84	9.76	10.58	11.20		
	212.0	4.80	6.85	8.34	9.50	10.53	11.39	12.18	12.80	
	197.5	5.06	7.26	8.85	10.16	11.21	12.12	12.95	13.81	14.40
	183.0	5.32	7.68	9.36	10.72	11.87	12.90	13.78	14.54	15.45
$x = 8$										
Temperature, degrees C.	313.5	1.60								
	299.0	2.60	3.20							
	284.5	3.44	4.26	4.80						
	270.0	4.18	5.20	5.89	6.40					
	255.5	4.83	6.06	6.90	7.44	8.00				
	241.0	5.42	6.88	7.79	8.49	9.18	9.60			
	226.5	5.96	7.64	8.71	9.49	10.13	10.74	11.20		
	212.0	6.30	8.35	9.55	10.40	11.18	11.75	12.24	12.80	
	197.5	6.30	9.02	10.32	11.31	12.09	12.74	13.37	14.12	14.40
	183.0	6.30	9.67	11.12	12.13	13.00	13.77	14.40	14.88	15.60
$x = 12$										
Temperature, degrees C.	313.5	1.60								
	299.0	2.88	3.20							
	284.5	4.04	4.52	4.80						
	270.0	5.12	5.76	6.12	6.40					
	255.5	6.10	6.92	7.40	7.74	8.00				
	241.0	6.30	8.08	8.63	9.04	9.28	9.60			
	226.5	6.30	9.18	9.81	10.29	10.66	10.95	11.20		
	212.0	6.30	10.23	10.98	11.51	11.91	12.21	12.47	12.80	
	197.5	6.30	11.24	12.13	12.71	13.10	13.54	13.84	14.12	14.40
	183.0	6.30	12.19	13.23	13.85	14.38	14.82	15.14	15.43	15.80

If the solidus and liquidus are much curved the expression (12) is not directly applicable. The curve which shows the proportion of liquid in the very rapidly cooled alloys is not represented by (7b), since, as shown in Fig. 13, this curve may lie either above or below that given by (7b), according to the shape of the solidus and of the liquidus. It is necessary, therefore, in such a case, to express the numerical results, obtained by substituting variable values of X_E and X_S in (7b), in terms of the actual fixed values of these quantities. The index of the fraction X/X_E is then found to vary with X, instead of being constant as it is when liquidus and solidus are straight. The equation may be of the form,

$$E = \left(\frac{X}{X_E}\right)^{c\cdot\frac{X_E}{X_E - X_S} + z} \qquad (13)$$

where c is a constant, and z consists of one or more terms, positive or negative, to be found for each case. In order to determine c and z for any series it is necessary to calculate the index of the fraction X/X_E for a number of alloys of this series, and to discover the manner in which the index varies.

A simple example is that of the α-crystallisation of the copper-tin series, for which some data have been given already in paragraph 5. When the proportions of liquid in the chosen alloys were calculated, the values of X_E and X_S were taken to vary in accordance with the slope of the liquidus, as explained fully in paragraph 4 ; but for the present purpose X_E and X_S are constant, since the proportion of liquid is required to be expressed in terms of the actual compositions of the saturated solid solution and the liquid phase. Referring to the beginning of paragraph 5, X_E is equal to the proportion of tin at the point B, Fig. 12, that is, 25.5 per cent. ; and X_S is equal to that at a, 9 per cent. Hence,

$$\frac{X_E}{X_E - X_S} = \frac{25\cdot5}{25\cdot5 - 9} = 1\cdot545$$

In Table XXI are given the compositions of the various alloys for which the calculations were previously performed, the proportion of liquid remaining in each at the transition temperature after very rapid cooling, and the value of the index $n = \frac{\log E}{\log \frac{X}{X_E}}$. The values of n, when plotted against the compositions of the corresponding alloys, are found to lie very closely upon a straight line, the uppermost of Fig. 25, represented by the equation,

$$n = 0{\cdot}83\left(\frac{X_E}{X_E - X_S}\right) + 0{\cdot}29\left(\frac{X}{X_E}\right) \qquad \text{-----} (14)$$

The proportion of liquid remaining at the transition temperature, in an alloy of composition X, after very rapid cooling, is thus,

$$E = \left(\frac{X}{X_E}\right)^{0{\cdot}83\left(\frac{X_E}{X_E - X_S}\right) + 0{\cdot}29\left(\frac{X}{X_E}\right)} \qquad \text{--------} (15)$$

The values of n calculated from (14) are listed in Table XXI ; they differ but slightly from the true ones on the line above them.

TABLE XXI. Variation in the index of X/X_E with variation of composition in copper-tin alloys which reject α-crystals primarily ; and proportion of liquid left at the transition temperature in alloys cooled at moderate rates.

No. of alloy	I	II	III	IV	V	VI.	VII
Tin per cent. = X	3·50	6·95	10·40	13·65	16·80	19·85	22·75
X/X_E	·1373	·2733	·4088	·5366	·6604	·7803	·8943
Proportion of liquid, for $x=0$, = E	·0724	·1705	·2855	·4090	·5439	·6887	·8409
$n = \frac{\log E}{\log X/X_E}$	1·323	1·364	1·401	1·436	1·468	1·503	1·550
n, for $x=0$, calculated from (14)	1·322	1·361	1·401	1·438	1·474	1·508	1·541
n, for $x=0$, calculated from (18)	1·323	1·361	1·400	1·436	1·471	1·505	1·537
n, for $x=3$, calculated from (18)	1·193	1·222	1·251	1·279	1·305	1·331	1·355
n, for $x=6$, calculated from (18)	—	1·099	1·116	1·132	1·147	1·162	1·176
E, for $x=0$, calculated from (18)	·0723	·1711	·2859	·4091	·5431	·6885	·8420
E, for $x=3$, Calculated from (18)	·0106	·1192	·2487	·3843	·5283	·6806	·8379
E, for $x=6$, calculated from (18)	·0000	·0361	·1900	·3468	·5078	·6720	·8364

The form of the equation for intermediate rates of cooling must satisfy the condition that $n = 1$ when $x = X_S$; in other words, the curve which represents the proportion of liquid must become the straight line passing through the saturation point of the solid solution when the rate of cooling is indefinitely slow. It follows that one or both of the numerical multipliers in (14) must vary with the value of x.

In order to determine the manner of variation of n with the rate of cooling it is preferable to write the expression (15) in a somewhat different form, and then to apply the result (12). It is to be noted that (7a) may be written,

$$E \text{ (rapid cooling)} = \left(\frac{X}{X_E}\right)^{1 + \frac{X_S}{X_E - X_S}} \qquad \text{-------(7b)}$$

A comparison of this with (15), bearing in mind that the numerical factors in (15) have to vary with the value of x, and that the limiting value of n is unity, shows that the latter expression may be written,

$$E \text{ (rapid cooling)} = \left(\frac{X}{X_E}\right)^{1 + a\cdot\frac{X_S}{X_E - X_S}\left(b + \frac{X}{X_E}\right)} \qquad \text{---(16)}$$

where a and b are numerical constants. Or, more generally, for any rate of cooling characterised by the quantity x,

$$E = \left(\frac{X - x}{X_E - x}\right)^{1 + a\cdot\frac{X_S - x}{X_E - X_S}\left(b + \frac{X - x}{X_E - x}\right)} \qquad \text{-----(17)}$$

For the case of the copper-tin α-crystals, the constants $a = 0.52$, $b = 1.00$, give a close approximation to the actual value of the index n, and

$$E = \left(\frac{X - x}{X_E - x}\right)^{1 + \cdot 52\frac{X_S - x}{X_E - X_S}\left(1 + \frac{X - x}{X_E - x}\right)} \qquad \text{------(18)}$$

is accordingly taken to represent the proportion of liquid in such an alloy, of composition X, at the transition temperature, when cooled at a rate characterised by the quantity x. This form of expression is adopted because it is the simplest equation which fulfils the numerical conditions for n, and reduces to the limiting forms (4a) and (7a). The values of n obtained from (18) when $x = 0$, that is, for very rapid cooling, are inserted in Table XXI ; they differ slightly from those obtained from (15) because the numerical constants in both expressions are only taken to two significant figures, a degree of accuracy which seems sufficient in the present state of the subject.

The first test of (18) consists in inserting a value of x, and in examining the shape and position of the curve which represents the proportion of liquid in the various alloys of the series when cooled at a rate characterised by this particular value of x. The two values, $x = 3$, and $x = 6$, have been chosen, and the calculated values of n and of E are set forth in Table XXI. From Fig. 26, where the proportions of liquid are plotted to a base of composition, it can be seen that the curves for the two intermediate rates of cooling are just such as would be expected from the previous results of this paragraph, as regards both shape and general position. The values of n are plotted in Fig. 25.

A more searching test of (18) is to employ it in the determination of the apparent solidus curves of the various alloys, for moderate rates of cooling. This involves the calculation of the proportion of liquid present in each of a number of alloys at a series of different temperatures. Now the constants in (18) are those for the transition temperature, 795° C., and one or both of them may be different for a different temperature. The proportions of α-crystals present in the very rapidly cooled alloys at a number of different temperatures have been given already in Table X, and these figures allow of the determination of the value of n for a number of alloys at each chosen temperature. The values of n thus obtained are given in Table XXII, and are plotted in Fig. 27, from which it is readily seen that for each temperature n varies with the composition of the alloy in an approximately linear manner, and may be represented therefore by an expression of the form of (16). The values of the constants, a and b, are easily calculated, and are set forth in Table XXIII. In Table XXII the values of n calculated by using the tabulated constants, a and b, are compared with the actual values of n.

TABLE XXII. Variation in the index of χ/χ_E with variation of temperature for a number of very rapidly cooled copper-tin alloys which reject α-crystals primarily.

Temperature	No. of alloy	I	II	III	IV	V	VI	VII
	Tin per cent.	3.50	6.95	10.40	13.65	16.80	19.85	22.75
1036	n - actual	1.248						
	n - formula	1.248						
1005	n - actual	1.259	1.280					
	n - formula	1.260	1.280					
971	n - actual	1.272	1.296	1.323				
	n - formula	1.272	1.296	1.321				
933	n - actual	1.285	1.314	1.345	1.374			
	n - formula	1.284	1.314	1.344	1.373			
890	n - actual	1.298	1.330	1.362	1.392	1.416		
	n - formula	1.298	1.329	1.361	1.390	1.419		
844	n - actual	1.310	1.346	1.380	1.411	1.438	1.465	
	n - formula	1.310	1.344	1.377	1.409	1.439	1.469	
795	n - actual	1.323	1.364	1.401	1.436	1.468	1.503	1.550
	n - formula	1.323	1.361	1.400	1.436	1.471	1.505	1.537

TABLE XXIII. Variation in the values of a and b with variation of temperature.

Temperature	X_E	X_S	X_S/X_E-X_S	a	b
1036	6·95	1·45	·2637	0·13	6·73
1005	10·40	2·40	·3000	0·20	4·00
971	13·65	3·50	·3448	0·28	2·56
933	16·80	4·75	·3942	0·37	1·74
890	19·85	6·05	·4384	0·41	1·48
844	22·75	7·50	·4918	0·45	1·25
795	25·50	9·00	·5455	0·52	1·00

There is one further difficulty to be overcome before the numerical work can be carried out, namely, the determination of the manner in which x varies with the temperature. Now the copper-tin solidus line Aa, Fig. 12, so far as is known, is straight, and the argument applied in the case of the lead-tin alloys - namely, that the extreme values of x vary according to two straight lines, the solidus and the vertical boundary $X = 0$, and that therefore the intermediate values probably vary in a linear manner also - is as legitimate here as before. The variation of x with the temperature is thus assumed to be linear, and corresponding values at different temperatures, intermediate between the freezing point of copper and the transition point of the α-solution, are given in Table XXIV for values of 3 and 6 at the transition temperature.

TABLE XXIV. Values of x at various temperatures for copper-tin alloys cooled at moderate rates.

Temperature	x_1	x_2
Freezing point of copper, 1084°	0·00	0·00
" " " alloy I, 1062°	0·23	0·46
" " " " II, 1036°	0·50	1·00
" " " " III, 1005°	0·82	1·64
" " " " IV, 971°	1·17	2·35
" " " " V, 933°	1·57	3·13
" " " " VI, 890°	2·01	4·03
" " " " VII, 844°	2·49	4·98
Transition temperature, 795°	3·00	6·00

The proportion of liquid in each of the chosen alloys, numbered I to VII, can be now determined at each chosen temperature by inserting the appropriate values of the various quantities in (17). Thus, for alloy III, at the temperature 971°, cooled at a rate characterised by $x = 3$ at the transition temperature, the values of the constants are $a = 0.28$, $b = 2.56$, and the equation to be used is,

$$E = \left(\frac{X - x}{X_E - x}\right)^{1 + 0\cdot28 \frac{X_S - x}{X_E - X_S}\left(2\cdot56 + \frac{X - x}{X_E - x}\right)}$$

At this temperature $X_E = 13.65$, $X_S = 3.50$, $x = 1.17$; the composition of the alloy is $X = 10.40$. The value of the index, therefore, is,

$$n = 1 + 0\cdot28\ \frac{3\cdot50 - 1\cdot17}{13\cdot65 - 3\cdot50}\left(2\cdot56 + \frac{10\cdot40 - 1\cdot17}{13\cdot65 - 1\cdot17}\right) = 1\cdot212$$

And the proportion of liquid in the mixture is,

$$E = \left(\frac{10\cdot40 - 1\cdot17}{13\cdot65 - 1\cdot17}\right)^{1\cdot212} = 0\cdot6936$$

The calculated proportions of α-crystals in the various alloys at the chosen temperatures are given in Table XXV, and from these the average composition of the crystals in each case has been determined, just as in previous examples, and set out in Table XXVI. The apparent solidus curves for the two different rates of cooling are plotted from the data of Table XXVI in Figs. 28 and 29. In Fig. 30 the various solidus curves for alloys I and V, for different rates of cooling, are compared together ; those for the other alloys offer a similar comparison, but their insertion here would make the diagram needlessly intricate.

TABLE XXV. Proportion of primary α-crystals at various temperatures in copper-tin alloys cooled at moderate rates.

No. of alloy		I	II	III	IV	V	VI	VII
Tin per cent.		3·50	6·95	10·40	13·65	16·80	19·85	22·75
					$x = 3$			
Temperature, degrees C.	1062	·000						
	1036	·589	·000					
	1005	·774	·410	·000				
	971	·861	·601	·306	·000			
	933	·911	·714	·488	·251	·000		
	890	·948	·789	·606	·416	·213	·000	
	844	·972	·842	·689	·530	·361	·183	·000
	795	·989	·881	·751	·616	·472	·319	·162
					$x = 6$			
Temperature, degrees C.	1062	·000						
	1036	·607	·000					
	1005	·812	·420	·000				
	971	·916	·626	·312	·000			
	933	·980	·754	·505	·255	·000		
	890	1·000	·844	·637	·428	·216	·000	
	844	1·000	·911	·734	·556	·372	·186	·000
	795	1·000	·964	·810	·653	·492	·328	·164

TABLE XXVI. Average composition of primary α-crystals at various temperatures in copper-tin alloys cooled at moderate rates.

No. of alloy		I	II	III	IV	V	VI	VII
Tin per cent.		3·50	6·95	10·40	13·65	16·80	19·85	22·75
$x = 3$								
Temperature, degrees C.	1062	0·70						
	1036	1·09	1·45					
	1005	1·49	1·99	2·40				
	971	1·86	2·50	3·03	3·50			
	933	2·20	3·00	3·68	4·26	4·75		
	890	2·60	3·50	4·26	4·95	5·54	6·05	
	844	2·95	3·99	4·83	5·58	6·26	6·89	7·50
	795	3·26	4·44	5·39	6·26	7·08	7·77	8·52
$x = 6$								
Temperature, degrees C.	1062	0·70						
	1036	1·27	1·45					
	1005	1·90	2·19	2·40				
	971	2·57	2·95	3·23	3·50			
	933	3·23	3·74	4·13	4·43	4·75		
	890	3·50	4·56	5·01	5·37	5·74	6·05	
	844	3·50	5·41	5·92	6·38	6·75	7·15	7·50
	795	3·50	6·26	6·86	7·35	7·83	8·26	8·72

A more complex example than the above is that of the γ-crystallisation of the copper-tin alloys, for which some data were given in paragraph 5. Here the values of X, and the fixed values of X_E and X_S, must be measured from the point of intersection of the solidus and liquidus, which is at about 25.7 per cent. of tin. Thus,

$X_E = 58 - 25.7 = 32.3$, and $X_S = 41 - 25.7 = 15.3$.

The variation in the index n for this case is set forth in Table XXVII, and is plotted in Fig. 31. A curve through the points appears roughly hyperbolic, but a solution gives two straight lines as the nearest simple approximation ; these lines are represented by the equations,

$$\left.\begin{aligned} n_1 &= 1 + 1{\cdot}11\,\frac{X_S}{X_E - X_S}\left(0{\cdot}65 + \frac{X}{X_E}\right), \quad \text{when } \frac{X}{X_E} \text{ is less than } 0{\cdot}615 \\ n_2 &= 1 + 1{\cdot}11\,\frac{X_S}{X_E - X_S}\left(1{\cdot}88 - \frac{X}{X_E}\right), \quad \text{when } \frac{X}{X_E} \text{ is greater than } 0{\cdot}615 \end{aligned}\right\} (19)$$

That is, the values of the constants a and b are 1.11 and 0.65, or - 1.11 and - 1.88, according as X/X_E is less or greater than 0.615. The proportion of liquid left at the transition temperature in an alloy of composition X, cooled at a rate characterised by the quantity x, if the method just used above is employed here, is given by one or other of the expressions,

$$\left.\begin{aligned} E &= \left(\frac{X - x}{X_E - x}\right)^{1 + 1{\cdot}11\frac{X_S - x}{X_E - X_S}\left(0{\cdot}65 + \frac{X - x}{X_E - x}\right)} \\ E &= \left(\frac{X - x}{X_E - x}\right)^{1 + 1{\cdot}11\frac{X_S - x}{X_E - X_S}\left(1{\cdot}88 - \frac{X - x}{X_E - x}\right)} \end{aligned}\right\} --- (20)$$

according as $\frac{X - x}{X_E - x}$ is less or greater than 0.615. Numerical values of the proportion of liquid have been calculated, and are given in Table XXVII, for the alloys C to XV of paragraph 5, when x = 5.1 , and when x = 10.2 . The corresponding curves are drawn in Fig. 32, from which they appear to be of fairly satisfactory form and position, though not entirely so, the portions of each curve in the neighbourhood of the point at which the change in the form of n occurs being defective, and indicating that the approximation taken is not of sufficient accuracy.

TABLE XXVII. Variation in the index of X/X_E with variation of composition in copper-tin alloys which reject γ-crystals primarily; and proportion of liquid left at the transition temperature in various alloys cooled at moderate rates.

No. of alloy	C	VIII	IX	X	XI	XII	XIII	XIV	XV
Tin per cent.	31·90	38·55	41·80	45·10	47·20	49·40	51·55	53·70	55·85
Tin per cent. − 25·7 = X	6·20	12·85	16·10	19·40	21·50	23·70	25·85	28·00	30·15
X/X_E	·1920	·3978	·4984	·6005	·6656	·7336	·8003	·8668	·9334
E (actual)	·0478	·1503	·2200	·3197	·4064	·5140	·6288	·7498	·8741
n (actual) = $\frac{\log E}{\log X/X_E}$	1·842	2·056	2·175	2·236	2·212	2·149	2·084	2·013	1·953
n, for $x=0$, calculated from (20)	1·841	2·047	2·147	2·249	2·213	2·145	2·079	2·012	1·946
n, for $x=5{\cdot}1$, calculated from (20)	1·460	1·623	1·702	1·783	1·835	1·797	1·744	1·691	1·639
n, for $x=10{\cdot}2$, calculated from (20)	—	1·256	1·305	1·355	1·387	1·419	1·390	1·358	1·325
E, for $x=0$, calculated from (20)	·0478	·1515	·2242	·3178	·4061	·5145	·6294	·7499	·8746
E, for $x=5{\cdot}1$, calculated from (20)	·0092	·1303	·2142	·3180	·3951	·5048	·6238	·7473	·8736
E, for $x=10{\cdot}2$, calculated from (20)	·0000	·0697	·1784	·3050	·3945	·4968	·6189	·7452	·8730

TABLE XXVIII. Variation in the index of X/X_E with variation of temperature for a number of copper-tin alloys which reject γ-crystals primarily.

No. of alloy	C	VIII	IX	X	XI	XII	XIII	XIV	XV
Tin per cent.	31·90	38·55	41·80	45·10	47·20	49·40	51·55	53·70	55·85
X	6·20	12·85	16·10	19·40	21·50	23·70	25·85	28·00	30·15
Temperature, degrees C. 728	1·571								
717	1·599	1·689							
704	1·666	1·833	2·008						
694	1·721	1·932	2·123	2·331					
683	1·771	2·009	2·195	2·373	2·409				
671	1·805	2·048	2·219	2·358	2·369	2·324			
659	1·826	2·064	2·216	2·324	2·319	2·269	2·202		
647	1·837	2·064	2·199	2·281	2·266	2·208	2·141	2·068	
635	1·842	2·056	2·175	2·236	2·212	2·149	2·084	2·013	1·953

When the apparent solidus curves are required for these intermediate rates of cooling, difficulties are encountered. The numerical values of n at various temperatures, for the chosen alloys, are easily calculated, just as before ; they are set out in Table XXVIII. When these are plotted, as in Fig. 33, a complex system of curves is revealed, and only the extreme members of the system can be even approximately represented by an equation of simple form. It has been considered advisable, therefore, to terminate the present discussion at this point. The complexity of the curves of Fig. 33 may be traced chiefly to the peculiar form of the solidus for the γ-crystals. Recently published diagrams for other series of alloys go to show that solidus curves in general may be expected to depart much more from straightness than was formerly considered likely ; but, on the other hand, a reversed curvature is unusual, and suggests a change of phase. It is probable, therefore, that in the larger number of cases the methods of this paragraph will be at least fairly satisfactory. For complex cases careful experimental determinations are desirable ; a valuable check upon the experimental results can be always obtained by making a few calculations for the extreme condition of indefinitely rapid cooling.

In the case of the γ-crystals of the copper-tin alloys, the difficulty of determining the variation of x with the temperature is greater than for α, on account of the curvature of the solidus. The most probable solution would appear to consist in making the fraction x/X_S constant for all temperatures, but its accuracy has not been tested ; it is in agreement, of course, with the assumption made in the case of the straight solidus.

9. Some Experimental Determinations of the Proportion of Eutectic present in Binary Alloys cooled at Moderate Rates.

No special experiments have been yet carried out by the writer to determine the form assumed by the curve representing the proportion of liquid present in each of a series of alloys when cooled at definite rates, and to discover the modifying effects of surfusion, mass of transforming material, and quality of transformation. In order that the results of such experiments shall have their full value, it is necessary that the solidus curve for the series of alloys under examination be known with a fair approach to accuracy. The number of solidus curves which have been determined with any considerable accuracy is very limited. This in itself is evidence of the difficulty of mapping such curves. The thermal method, so successful for obtaining points on the liquidus, is of little use for points on the solidus. Fig. 7 furnishes the explanation in a graphical manner ; the rate of solidification is high when crystals begin to form, but diminishes rapidly afterwards. The rate of evolution of heat, and the consequent change in the slope of the cooling curve, therefore, while quite strongly marked at the freezing point of an alloy, are almost indistinguishable at the melting point, and the difference between the two conditions is somewhat accentuated by the slower rate of cooling at the lower temperature. A heating curve, as a means of detecting the melting point, is better than a cooling curve, but is not satisfactory. The microscopical method, though one of trial and error, is capable of giving the best results. A sample of the solid alloy, carefully annealed and brought to a state of equilibrium, is heated for a short time at some definite temperature, and is then examined for signs of incipient melting. If these are not found, the alloy is reheated to a temperature a few degrees higher than before, re-examined, and so on, until it is quite clear that melting has commenced. In this way the melting point of the actual specimen can be fixed within a very few degrees. Whether or not the temperature so determined is a point on the true solidus curve depends upon the condition of the alloy at the time of the experiment. If the alloy is one which should contain no eutectic, and if it has been insufficiently annealed, the observed melting point will be lower than the true one. Such an alloy, but slightly within the saturation limit, may actually contain some eutectic, and its melting point will be the eutectic point ; in an alloy somewhat less rich than this the external envelope of each primary crystal may have a composition only just less than that of saturation, and so on. For a series of alloys, which have all received a similar and insufficient annealing treatment, the apparent saturation limit of the primary crystals will be reduced, the solidus will be depressed and will merge gradually into the eutectic line instead of meeting the latter abruptly ; its form will be somewhat like that of the dotted curve in Fig. 34. The conditions are probably too complex and uncertain for any useful calculation, but the possibility of error of the kind described requires considerable care for its complete avoidance. A curve of the form sketched in Fig. 34 should be certainly received with caution, though the solidus at the aluminium end of the aluminium-zinc series, determined by Rosenhain and Archbutt with great care, has this form, and the most recently determined iron-carbon solidus is of a similar shape.

When the proportion of liquid left at the eutectic temperature or transition temperature of an alloy is required, the thermal method possesses some advantages of convenience over a microscopical examination. The thermal method was first suggested by Tammann, though chiefly as an aid to determine the saturation limit of the solid solution. There is considerable difficulty in cooling successive mixtures of a series under strictly comparable conditions, and the experimental results secured at Gottingen under Tammann's direction leave much to be desired. In a general way, however, they are in agreement with the results of the preceding paragraphs, as a few examples will show.

The first example to be taken is that of the lead-tin alloys, for which the theoretical conditions have been fully worked out already. Table XXIX gives the time of solidification of the eutectic present in alloys cooled at a moderately slow rate, as determined by Degens. If each time is plotted against the composition of the corresponding alloy, a mean curve through the points gives a maximum time of about 735 seconds for an alloy consisting of pure eutectic - 63 per cent. of tin - and a zero time at about 8 per cent. of tin. The real saturation limit of the solid solution at the eutectic temperature is 16 per cent. of tin, and the curve for a cooling rate characterised by $x = 8$ is to be found in Fig. 20. This is reproduced in Fig. 35, and the experimentally determined proportion of eutectic for each alloy, given by the solidification time in seconds divided by the maximum time of 735 seconds, as listed in Table XXIX, is marked upon the diagram. The experimental points lie somewhat irregularly, but group themselves fairly well about the curve.

TABLE XXIX. Time of solidification of eutectic in various lead-tin alloys - Degens.

Tin per cent.	Time of Solidification Seconds	Proportion of Eutectic = time/735
7·79	5	·0068
9·22	12	·0163
12·92	30	·0408
19·94	100	·1361
23·54	160	·2177
28·81	230	·3130
31·30	285	·3878
36·61	350	·4762
43·50	440	·5987
51·87	540	·7348
56·49	630	·8572
60·61	705	·9592

Another simple series is that of aluminium and tin, for which the equilibrium diagram is drawn in Fig. 36 from the experimental results of Shepherd, and of Gwyer. The former judged, from observations of the density of annealed alloys, that the saturation limit of the aluminium-rich solid solution was at about 20 per cent. of tin, but he did not determine the form of the solidus curve ; the latter observed the time of solidification of the eutectic present in each of a number of the alloys to be as represented by the small circles in the upper part of Fig. 36. Shepherd's value for the saturation limit, though the method of determination is unsatisfactory, was at first regarded as fairly accurate ; the solidus was assumed straight, the liquidus being of such a form that this assumption cannot cause much error. A number of alloys were chosen, of which the compositions are given in Table XXX, and the calculation of the proportion of liquid left in each at the eutectic temperature, after very rapid cooling, was made in the manner already fully described ; the numerical results are given below and are plotted in Fig. 37. The values of the index of X/X_E were then calculated as explained in the case of the copper-tin alloys ; these values are given in Table XXX, and are plotted to a very open scale in Fig. 38. It is not possible to represent accurately the variation of the index by a simple expression, but the constant value n = 1.076 gives the nearest simple approximation. This is equivalent to,

$$n = 1 + \cdot 30 \frac{X_S}{X_E - X_S}$$

where $X_E = 99.52$ and $X_S = 20$ per cent. of tin. For slower rates of cooling the proportion of liquid is then given approximately by the general equation,

$$E = \left(\frac{X - x}{X_E - x}\right)^{1 + \cdot 30 \frac{X_S - x}{X_E - X_S}}$$

For Gwyer's results the value of x is about 5 per cent. of tin ; the corresponding calculated proportions of eutectic are given in Table XXXI and are plotted in Fig. 37, where the dots represent Gwyer's results. There is not nearly such good agreement here as in the previous example, due partly to the somewhat rough approximation taken for obtaining the calculated results, and partly to irregularity in the experimental points. These points lie in such a manner as to suggest that Shepherd's estimate of the saturation limit is not correct. Accordingly some alloys, containing 5, 10, 15, and 20 per cent. of tin respectively, were prepared, and annealed for an extended period at the melting point of tin. On account of the long time necessary to obtain equilibrium conditions in the aluminium-tin solution, these experiments are not complete at the time of writing. It is quite clear, nevertheless, that aluminium cannot dissolve as much as 20 per cent. of tin. Fig. 39 is a section of the 20 per cent.

alloy after 14 days' annealing at 232° C., the same treatment as that accorded in Shepherd's experiments ; the white spots show that a very considerable proportion of the tin has not been absorbed.

TABLE XXX. Calculated proportions of eutectic in aluminium-tin alloys

Tin per cent.	Proportion of eutectic very rapid Cooling	Value of n	Proportion of Eutectic $x = 5$
10	·08546	1·070	·0448
25	·22929	1·066	·1936
40	·37884	1·065	·3498
60	·58196	1·070	·5643
70	·68463	1·077	·6733
75	·73625		
80	·78811	1·090	·7832
85	·84038		
90	·89335	1·121	·8939
93	·92567		
96	·95874		
98	·98159		

TABLE XXXI. Times of solidification of eutectic in aluminium-tin alloys - Gwyer.

Tin per cent.	Time of Solidification Seconds	Proportion of eutectic = time/350
5·1	5	·0143
10·1	30	·0857
15·1	40	·1143
25·1	70	·2000
40·0	115	·3286
50·1	150	·4286
60·0	190	·5429
70·0	230	·6572
80·0	280	·8000
81·4	290	·8286
85·0	295	·8429
90·0	330	·9429
97·8	340	·9715
100·0	350	

A third example, of more practical importance than the previous two, is furnished by the aluminium-rich alloys of the aluminium-copper series. Fig. 40 shows the equilibrium diagram for the series, drawn from the experimental results of Carpenter and Edwards, of Curry, and of Gwyer. The saturation limit of the aluminium-rich solution, designated η , is at about 10 per cent. of ~~tin~~ copper ; as in the previous case the form of the solidus has not been determined, and is here assumed straight. Table XXXII gives the results of calculations, performed in the same manner as before, for a number of alloys ; the proportions of liquid are plotted in Fig. 41. The variation in the index of X/X_E for very rapid cooling is closely represented by a straight line, as shown in Fig. 42, and the corresponding general equation for the proportion of eutectic in an alloy of the series is,

$$E = \left(\frac{X - x}{X_E - x}\right)^{1 + \cdot 33 \frac{X_S - x}{X_E - X_S}\left(2\cdot 00 + \frac{X - x}{X_E - x}\right)}$$

Experimental determinations of the time of solidification of the eutectic in a number of alloys of this series have been made by Gwyer, and are set forth in Table XXXIII ; a mean curve through the points gives a maximum time of solidification of about 290 seconds, and a value of $x = 3$ as representing the rate of solidification. The experimental points, though few in number, are shown in Fig. 41 to lie closely about the curve calculated for this value of x.

A fair idea of the relative magnitude of the experimental errors to be expected in these determinations is given by the left-hand portion of the time diagram for eutectic, which refers to those alloys in which the primary crystals are of $CuAl_2$ (Fig. 40). This compound forms no solid solution, or one of extreme tenuity, and the proportion of eutectic for alloys between F and G should be represented by the same straight line, whatever the rate of cooling. A mean line through the experimental points, however, shows distinct curvature, and the individual points have irregular positions.

TABLE XXXII. Calculated proportions of eutectic in aluminium-copper alloys.

Copper per cent.	Proportion of eutectic very rapid Cooling	Value of n	Proportion of eutectic $x = 3$
5	'08671	1·317	'0386
10	'20829	1·349	'1728
15	'35320	1·373	·3310
20	'51887	1·396	'5069
25	·70459	1·419	·7001
30	'91110	1·438	'9105

TABLE XXXIII. Times of solidification of eutectic in aluminium-copper alloys - Gwyer.

Copper per cent.	Time of Solidification Seconds	Proportion of eutectic $= \text{time}/290$
10	50	'1724
20	150	'5172
25	200	'6896
30	260	'8965

The proportion of eutectic in an alloy may be determined microscopically when the conditions are favourable. The area of the regions occupied by eutectic, as measured upon a micrograph, divided by the whole area of the micrograph, gives a more or less close approximation to the proportion of eutectic by volume. A better value is obtained by averaging the results obtained from a number of sections of the same alloy. The ratio of the density of the eutectic to the mean density of the alloy can be obtained approximately by simple calculation from the proportions of the two metals contained in each, and the proportion of eutectic by weight can be thus found. When a compound is present its density must be determined by direct experiment. In using the micrographic method it is necessary for good results that the primary crystals and eutectic be distributed with fair uniformity, that the boundary of each is easily distinguishable, that the magnification of the micrograph is such that the unavoidable errors in determining the areas are of relatively small magnitude, and that each constituent is present in appreciable quantity. It follows that the measurement can be made satisfactorily only when the rate of cooling is not very rapid, and when the composition of the alloy is somewhat remote from both that of the eutectic and of the saturated solid solution. Rapid cooling usually means small crystals and ill-defined boundaries ; a very small proportion of one constituent means a relatively large error in determining its area. Satisfactory measurements have been made by Desch, Sauveur, and others for slowly cooled alloys, and the method is in use as a rapid and fairly reliable means of estimating the composition of certain classes of industrial alloys, such as steels and brasses.

10. Experimental Determination of the Proportions of the Constituents when a Transition is involved.

In the case of an alloy in which an eutectic is formed it has been seen that the heat evolved at the freezing point of the eutectic is proportional to the amount of eutectic present - that is, to the amount of liquid present just above ~~at~~ the eutectic temperature - and this holds good for any rate of cooling, provided that the composition of the eutectic remains unaltered, and that the temperature remains sensibly constant while the eutectic solidifies. In the case of transformation of the constituents of an alloy, at a fixed transition temperature, the heat evolved may be proportional to the amount of transformed liquid, but this is not necessarily the same as the total amount of liquid at the transition temperature; and the effect depends greatly on the rate of cooling. With extremely rapid cooling, that is, when the proportion of liquid left at the transition temperature in any particular alloy is a maximum, the transformation may be entirely suppressed, and there is no heat evolved. At a slower rate of cooling only a part of the liquid reacts with the crystals, and the heat evolved is less than would have been the case if the reaction had been completed. It may be also that the degree of completeness of the reaction, when the rate of cooling of a number of alloys has been the same, varies with the composition of the alloy ; the reaction would be expected to take place more completely when there was a comparatively small proportion of primary crystals than when there was much primary solid and little liquid.

Further, while the maximum proportion of liquid at the transition temperature aB, Fig. 43, is obtained in an alloy having the composition of the point B on the liquidus, the maximum evolution of heat with very slow cooling is obtained in an alloy of the composition b, that of the secondary solid. This is due to the fact that the reacting substances, a and B, are present in quantities which vary in opposite directions ~~with~~ when the composition of the alloy is changed, and that the proportional amount of the product is governed by the quantity of the liquid B involved in the reaction, that is, the quantity which becomes solid at this temperature. This does not mean, of course, that all the heat evolved is due simply to the solidification of B. If the rate of cooling is very slow, and the composition of the alloy lies to the left of b, the whole of the liquid remaining at the transition temperature crystallises at this temperature ; if the composition of the alloy lies between b and B all the α-crystals disappear and only a portion of the liquid, bearing the fixed ratio, $\frac{b - a}{B - b}$, to the quantity of primary α-crystals, solidifies at the transition temperature, the letters a, b, and B being used to represent the compositions corresponding to those points on the diagram.

Now suppose that the rate of cooling is relatively rapid until the transition temperature is reached, and that the temperature is then kept constant until the transformation is completed ; the proportion of the secondary product, β , for any particular mixture is the same as before, but the proportion of reacting liquid is greater, some of the liquid which now solidifies being material which would have crystallised at a higher temperature under conditions of equilibrium. So long as the composition of the alloy lies to the left of b it is clear that again all the liquid solidifies at the transition temperature, and the alloy becomes a completely solid mixture of α and β. When the composition lies between b and B all the primary crystals disappear as a result of the transition, and the proportion of liquid which is necessary for the process, that is, the proportion of liquid which solidifies at the transition temperature is,

$$(\text{proportion of primary crystals}) \cdot \frac{b - (\text{mean composition of primary crystals})}{B - b} \quad ---- (21)$$

Thus the proportion of liquid involved in the reaction no longer bears a constant ratio to the proportion of primary crystals, but depends upon the average composition of these, which varies with the composition of the alloy when the rate of cooling is constant. If h represents the composition corresponding to the apparent saturation point of the α-solution, and X is the composition of the alloy, the ratio of liquid to solid when the transition temperature is just reached is given by the fraction $\frac{X-h}{B-X}$. And it follows that when X lies between b and B, the proportion of liquid solidifying at the transition temperature is,

$$(\text{total proportion of liquid}) \cdot \frac{B-X}{X-h} \cdot \frac{b-h}{B-b} \qquad \text{------}(22)$$

Now the fraction $\frac{B-X}{B-b}$ is constant for any particular alloy, while the total proportion of liquid and the numerical fraction $\frac{b-h}{X-h}$ vary with the rate of cooling, both becoming greater as the rate of cooling is made more rapid ; hence the proportion of liquid which solidifies in a particular mixture at the transition temperature increases as the rate of cooling is made more rapid, provided that the transformation is completed. For any particular rate of cooling the maximum proportion of crystallising liquid is always obtained for the alloy which has the composition b.

There is no series very suitable for illustrating the foregoing remarks. The usual defect, from the illustrative point of view, is that the composition of the secondary solid is too near that of the liquid to allow of any great departure from the straight line in that part of the curve of proportion of crystallising liquid which refers to alloys between points like b and B, Fig. 43. The copper-tin alloys containing less than 25.5 per cent. of tin make quite a good example, however, if the composition of the secondary solid β is assumed to be, not at b = 22.5 per cent. of tin, as in Fig. 12, but much nearer to a = 9 per cent. of tin ; it has been taken for the present purpose at 12 per cent. of tin. This arbitrary change, of course, has no effect upon the relative proportions of solid and liquid existing just above the transition temperature, and the data of Tables X, XI, XXV, and XXVI can be used to calculate the relative amounts of transforming liquid. The proportion of liquid which crystallises at the transition temperature in alloys containing 0 to 12 per cent. of tin is the total amount of liquid present just before transition commences, as given in those tables ; for alloys containing 12 to 25.5 per cent. of tin the total liquid given in the tables is to be multiplied by the appropriate fraction, obtained by substituting in (22). The fractions found in this manner are set forth in Table XXXIV for various alloys cooled at four different rates. The results are plotted in Fig. 44 ; the portion of this diagram to the left of the vertical dotted line at 12 per cent. of tin is identical with the corresponding part of Fig. 26, except as to scale ; the part to the right of the dotted line is that newly determined.

When the rate of cooling through the transition temperature is not slow enough to allow the reaction to be completed, the proportion of the secondary solid is a certain fraction of that obtained under the previous conditions ; this fraction probably varies somewhat with the composition of the alloy, as well as with the rate of cooling, and may be different in different parts of the same mass.

TABLE XXXIV. Proportion of liquid solidifying in copper-tin alloys during the transition of α to β when the transformation is completed. The composition of β is assumed to be 12 per cent. of tin, and the results are intended only for an illustrative purpose.

No. of alloy Tin per cent.	I 3·50	II 6·95	III 10·40	IV 13·65	V 16·80	VI 19·85	VII 22·75
$x = 0$							
Mean Composition of α	1·79	3·15	4·38	5·45	6·42	7·33	8·18
Total liquid	·0724	·1705	·2855	·4090	·5439	·6888	·8409
Liquid Solidifying	·0724	·1705	·2855	·2868	·1884	·1075	·0449
$x = 3$							
Mean Composition of α	3·26	4·44	5·39	6·26	7·08	7·77	8·52
Total liquid	·0106	·1192	·2487	·3843	·5283	·6806	·8379
Liquid Solidifying	·0106	·1192	·2487	·2619	·1720	·0999	·0418
$x = 6$							
Mean Composition of α	3·50	6·26	6·86	7·35	7·83	8·26	8·72
Total liquid	·0000	·0361	·1900	·3468	·5078	·6720	·8364
Liquid solidifying	·0000	·0361	·1900	·2249	·1520	·0909	·0399
$x = X_s = 9$							
Mean Composition of α	3·50	6·95	9·00	9·00	9·00	9·00	9·00
Total liquid	·0000	·0000	·0848	·2818	·4727	·6576	·8334
Liquid Solidifying	·0000	·0000	·0848	·1596	·1172	·0761	·0370

The actual connection between the quantity of heat evolved and the proportion of liquid which solidifies at the transition temperature is less simple than might be thought at first ; it is of importance if the constitution of the alloy is to be determined by thermal means. Let ϵ_1 be the intrinsic energy of α per unit weight, let ϵ_2 be that of β , and ϵ_3 that of the liquid, all measured at the transition temperature. The change of energy at the transition temperature may not be all manifested thermally, so that the symbols must be taken as applying to energy which is so manifested, though the argument is equally valid as regards energy manifested in other ways.

Suppose first that cooling is so slow that equilibrium conditions prevail throughout the process. Then the energy of unit weight of an alloy just before transition is

$$(1-E)\epsilon_1 + E\epsilon_3$$

where E is used for the proportion of liquid just before transition. If L be the proportion of liquid remaining just after transition, P the proportion of α , and Q the proportion of β , the energy per unit weight of the transformed alloy is,

$$P\epsilon_1 + Q\epsilon_2 + L\epsilon_3$$

Hence the heat evolved or absorbed during transition, per unit weight, is,

$$\left\{(1-E)\epsilon_1 + E\epsilon_3\right\} - \left\{P\epsilon_1 + Q\epsilon_2 + L\epsilon_3\right\} \quad ---- (23)$$

After transition there may be some α or some liquid left in the mixture, according as the composition of the alloy lies between a and b or between b and B, Fig. 43. Let k be the ratio of α to liquid to form β , that is, the ratio $\frac{B-b}{b-a}$, Fig. 43.

If α is in excess, L = 0 , and the heat evolved during transition is,

$$\left\{(1-E)\epsilon_1 + E\epsilon_3\right\} - \left\{P\epsilon_1 + Q\epsilon_2\right\}$$

Now the amount of α involved in the reaction is $(1 - E) - P$, and the amount of liquid involved is E. Therefore,

$$k = \frac{1-E-P}{E}$$

Or,

$$P = 1-E(1+k)$$

And,

$$Q = 1-P = E(1+k)$$

Therefore the heat evolved is,

$$\left[(1-E)\epsilon_1 + E\epsilon_3\right] - \left[\left\{1-E(1+k)\right\}\epsilon_1 + E(1+k)\epsilon_2\right]$$

$$= E\left\{\epsilon_1 k - \epsilon_2(1+k) + \epsilon_3\right\} \text{ - - - - - - - } (24)$$

which is proportional to E, the amount of liquid involved in the reaction, since all the terms within the bracket are constant.

If the liquid is in excess, $P = 0$, and the heat evolved during transition is,

$$\left\{(1-E)\epsilon_1 + E\epsilon_3\right\} - \left\{Q\epsilon_2 + L\epsilon_3\right\}$$

In this case the amount of α which participates in the reaction is $1 - E$, and the amount of participating liquid is $E - L$. Therefore,

$$k = \frac{1-E}{E-L}$$

Or,

$$L = \frac{E(1+k)-1}{k}$$

And,

$$Q = 1-L = (1-E)\frac{1+k}{k}$$

Therefore the heat evolved is,

$$\left\{(1-E)\epsilon_1 + E\epsilon_3\right\} - \left\{(1-E)\cdot\frac{1+k}{k}\cdot\epsilon_2 + \frac{E(1+k)-1}{k}\cdot\epsilon_3\right\}$$

$$= (1-E)\left\{\epsilon_1 - \epsilon_2\cdot\frac{1+k}{k} + \epsilon_3\cdot\frac{1}{k}\right\}$$

$$= \left(\frac{1-E}{k}\right)\left\{\epsilon_1 k - \epsilon_2(1+k) + \epsilon_3\right\}$$

$$= (E-L)\left\{\epsilon_1 k - \epsilon_2(1+k) + \epsilon_3\right\} \text{ - - - - - - - } (25)$$

which is the same proportion of $E - L$, the amount of liquid involved in the reaction, as in (24). Thus, in either case, the heat evolved during transition is a constant multiple of the amount of participating liquid.

Suppose next that cooling is comparatively rapid above the transition temperature, but very slow through the transition temperature, so that the transformation is allowed to complete itself. Let E' be the proportion of liquid just before transition commences. The average composition of the primary crystals is different from their equilibrium composition, and the energy per unit weight is correspondingly different ; let it be ϵ_1'. The conditions after transition are exactly the same as in the first case. Hence the heat evolved or absorbed during transition is,

$$\left\{(1-E')\epsilon_1' + E'\epsilon_3\right\} - \left\{P\epsilon_1 + Q\epsilon_2 + L\epsilon_3\right\} \quad ---- (26)$$

But since the mean composition of the primary crystals varies both with the composition of the alloy and the rate of cooling, the ratio of α to liquid to form β is correspondingly variable. For a particular alloy, X, cooled at a particular rate, let this ratio be k' ; this is the ratio $\frac{B-b}{b-h}$ of page 83.

If α is in excess, $L = 0$. The amount of primary crystals participating in the reaction is $(1 - E') - P$, and the amount of participating liquid is E'. Therefore,

$$k' = \frac{1-E'-P}{E'}$$

Or,

$$P = 1-E'(1+k')$$

And,

$$Q = 1-P = E'(1+k')$$

Therefore the heat evolved is,

$$\left[(1-E')\epsilon_1' + E'\epsilon_3\right] - \left[\left\{1-E'(1+k')\right\}\epsilon_1 + E'(1+k')\epsilon_2\right]$$

$$= E'\left\{\epsilon_1(1+k') - \epsilon_1' - \epsilon_2(1+k') + \epsilon_3\right\} + (\epsilon_1'-\epsilon_1)$$

$$= E'(\epsilon_3-\epsilon_2) + k'E'(\epsilon_1-\epsilon_2) + (1-E')(\epsilon_1'-\epsilon_1) \quad ---- (27)$$

For a constant rate of cooling above the transition temperature, as the composition of the alloy is changed so that X increases, the fraction E' increases, and k' also increases, while $\epsilon_1'-\epsilon_1$ decreases, since h approaches a. Therefore the heat evolved according to (27) consists of a portion, $E'(\epsilon_3-\epsilon_2)$, which is a constant multiple of the proportion of participating liquid, a second portion, $k'E'(\epsilon_1-\epsilon_2)$, which forms an increasing multiple of the participating liquid as X moves towards b, and a third portion, $(1-E')(\epsilon_1'-\epsilon_1)$, which is the heat evolved in the conversion of the non-saturated inhomogeneous α-crystals to saturated homogeneous α-crystals, and diminishes as X moves towards b.

For an alloy of constant composition X, as the rate of cooling is made more rapid the fraction E' increases, but k' decreases, and $\epsilon_1'-\epsilon_1$ increases, since h recedes from a. The quantity $k'E'(\epsilon_1-\epsilon_2)$ is therefore a diminishing multiple of the proportion of participating liquid as the rate of cooling is quicker, while the quantity $(1-E')(\epsilon_1'-\epsilon_1)$ may either increase or diminish according to the particular metals in the mixture.

If the liquid is in excess, $P = 0$. The amount of primary crystals participating in the reaction is $1 - E'$, and the amount of the participating liquid is $E' - L$. Therefore,

$$k' = \frac{1-E'}{E'-L}$$

Or,

$$L = \frac{E'(1+k')-1}{k'}$$

And,

$$Q = 1 - L = (1-E')\cdot\frac{1+k'}{k'}$$

Therefore the heat evolved is,

$$\left[(1-E')\epsilon_1' + E'\epsilon_3\right] - \left[\left\{(1-E')\cdot\frac{1+k'}{k'}\cdot\epsilon_2 + \frac{E'(1+k')-1}{k'}\cdot\epsilon_3\right]\right.$$

$$= (1-E')\left\{\epsilon_1' - \epsilon_2\cdot\frac{1+k'}{k'} + \epsilon_3\cdot\frac{1}{k'}\right\}$$

$$= \frac{(1-E')}{k'}\left\{\epsilon_1'k' - \epsilon_2(1+k') + \epsilon_3\right\}$$

$$= (E'-L)\left\{\epsilon_1'k' - \epsilon_2(1+k') + \epsilon_3\right\}$$

$$= (E'-L)(\epsilon_3-\epsilon_2) + k'(E'-L)(\epsilon_1'-\epsilon_2) \qquad \text{------} \quad (28)$$

If the composition of the alloy is changed while the rate of cooling above the transition temperature is kept constant, or if the rate of cooling of a particular alloy is varied, the effects are similar to the corresponding ones described with regard to (27), but there is now no term relating to α-crystals alone since these disappear entirely during transition.

Suppose lastly that the rate of cooling is not made very slow through the transition temperature ; then the transformation is only partially accomplished. In alloys having a composition to the left of b there will be usually some liquid remaining after the process of transformation has ceased ; in alloys with a composition between b and B there will be usually some α-crystals remaining, so that in the general case the three phases α , β, and liquid will be present together below the transition temperature. The heat evolved during transition is,

$$\left\{(1-E')\epsilon_1' + E'\epsilon_3\right\} - \left\{P'\epsilon_1'' + Q'\epsilon_2 + L'\epsilon_3\right\} \quad ----(29)$$

where P', Q', and L' are the proportions of α, β, and liquid left in the mixture after the incomplete transformation, at a temperature just below that of aB, Fig. 43. Let k" be the ratio of α to liquid to form β , in a particular alloy cooled at a particular rate. Then since the richer parts of the α-crystals are the outer parts of the crystals, and are consequently those first attacked by the liquid during the reaction, the value of k" lies between that of k, and that of k' for the same alloy cooled at the same rate under the preceding conditions. Further, on account of their inhomogeneity, the energy per unit weight of the α-crystals existing before transition is not the same as the energy per unit weight of the α-crystals which do not react ; the first is accordingly lettered ϵ_1' , and the second ϵ_1'' in (29). It is supposed that ϵ_3 and ϵ_2 have their equilibrium values ; as regards ϵ_3 this is in accordance with the original hypothesis, but it is by no means certain that the β-solution formed during incomplete transition must necessarily have the composition B.

The determination of the quantities P', Q', and L' for alloys of various compositions, cooled at different rates, offers difficulties which have not yet been overcome, so that the determination, by thermal means, of the constitution of an alloy which has suffered an incomplete transition is a problem which still remains to be solved. It is clear from (27) and (28) that the heat evolved when the rate of cooling is other than very slow is not in general proportional to the amount of transforming liquid, and the curves obtained experimentally from measurements of the time during which the temperature remains constant at that of transition may be expected to differ in form from the curves which represent the proportion of transforming liquid, like those of Fig. 44. This conclusion is apparently borne out by some of the Gottingen results, in which the experimental curves are convex where those of Fig. 44 are concave ; other experimental curves even show a reversal of curvature, but this may be due to experimental errors ; others, like that indicated by the small circles at the top of Fig. 45, have a curvature similar to that of Fig. 44.

It must not be forgotten that a transition which is incomplete when the temperature commences to fall again may proceed over a considerable interval of temperature, possibly at an increasing rate and with recalescence, so that a solution of (29) is not by any means a complete solution of the whole problem. Much depends upon the energy involved in a transformation. For instance, in the case of the formation of $CuAl_2$ at the transition temperature F, Fig. 40, the change is so energetic that the time results plot very closely to a straight line, though the rate of cooling is not excessively slow. On the other hand, in the copper-lead series, though two of the three phases present at the transition temperature are liquid, the reaction is sluggish, and the time results, even with a fairly slow rate of cooling, may plot to a curve instead of a straight line, Fig. 46.

As regards the micrographic determination of the proportions of the constituents in cases where transition occurs, the same considerations apply as in the simpler case when an eutectic is formed. But there is now the added objection that a partially accomplished transition often gives rise to such a minute subdivision of the original crystals that it is quite impossible to form an accurate estimate of the relative proportions of the constituents by visual examination. Thus in this case the micrographical method is of more limited application than before. The value of the different experimental means varies largely in different cases, and can be truly found only after careful trial.

Summary of Part I.

The constitution of an alloy of simple type, when very rapidly cooled, can be written down at once if the liquidus and solidus are sensibly straight, and if certain hypothetical conditions are approximately fulfilled.

In whatever way the liquidus and solidus are curved, and however complex is the series of alloys, the constitution after very rapid cooling can be still determined by an extension of the same method, provided the hypothetical conditions remain approximately fulfilled.

The constitution of alloys cooled at rates intermediate between very fast and very slow can be determined, with a probably close approach to accuracy, by a further extension of the method, unless the conditions are unusually complex.

The constitution of alloys of the series lead-tin, copper-tin, copper-zinc, and copper-nickel have been calculated for different rates of cooling, and the calculated results for certain lead-tin, aluminium-tin, and aluminium-copper alloys have been compared with experimental results.

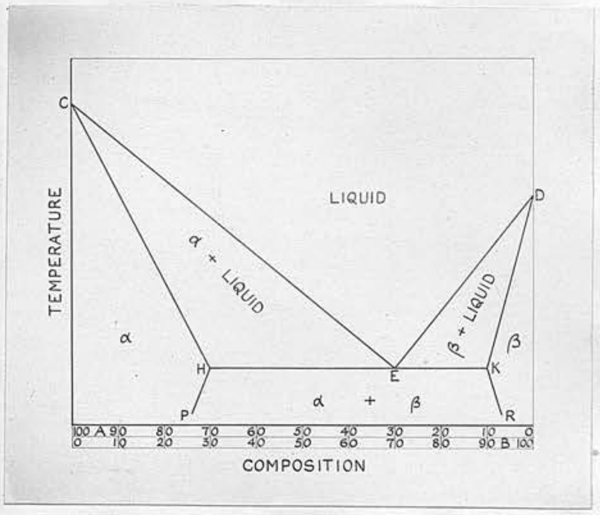

FIG. 1. Typical Equilibrium diagram for a Series of alloys in which the Structural Constituents are two Solid Solutions, α and β, and an Eutectic E.

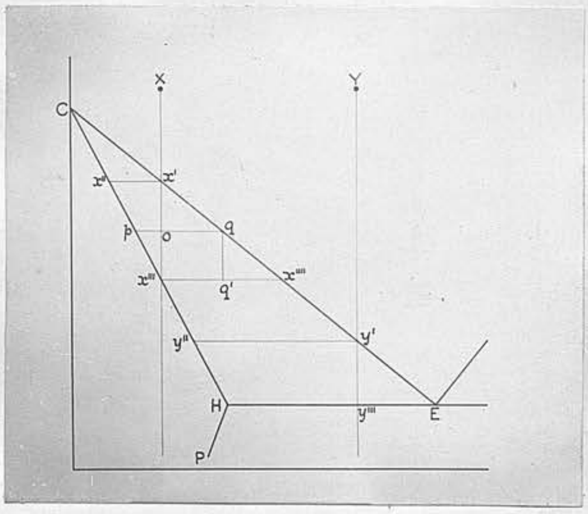

FIG. 2. Part of Equilibrium diagram, illustrating manner of Solidification of two alloys X and Y

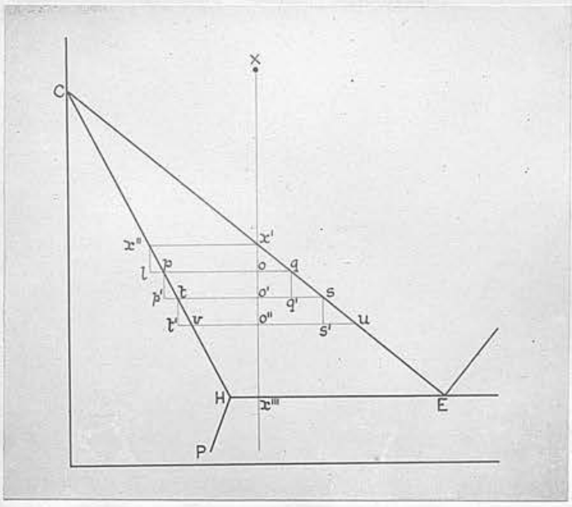

FIG. 3. Part of Equilibrium diagram, in which the period of Solidification of the alloy X is divided into a number of stages

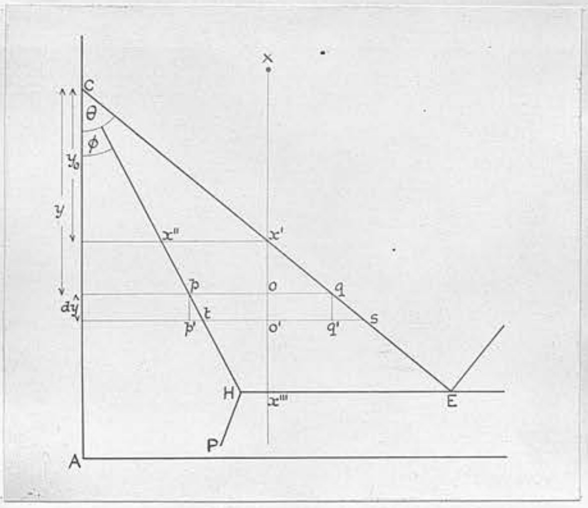

FIG. 4. Similar to Fig 3, but with notation suitable for infinitesimal steps.

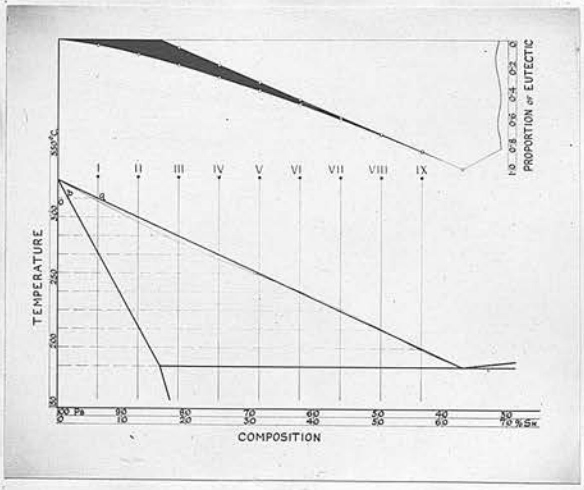

FIG. 5. Part of Equilibrium diagram for lead-tin alloys. The black area at the top represents the difference in the proportions of Eutectic Contained in alloys Cooled with extreme Slowness and with extreme rapidity.

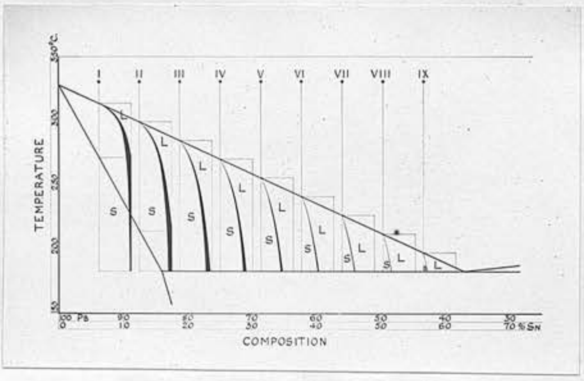

FIG. 6. Part of Equilibrium diagram for lead-tin alloys, Showing the relative proportions of liquid and Solid for very Slow and for very rapid Cooling.

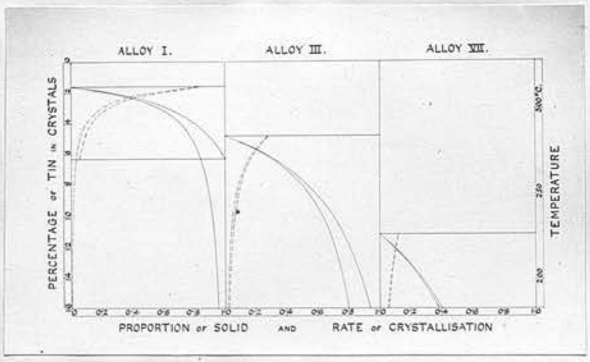

FIG. 7. Diagrams Similar to those of Fig. 6. The dotted curves are obtained by differentiating the full-line curves, and represent the varying rate of crystallisation.

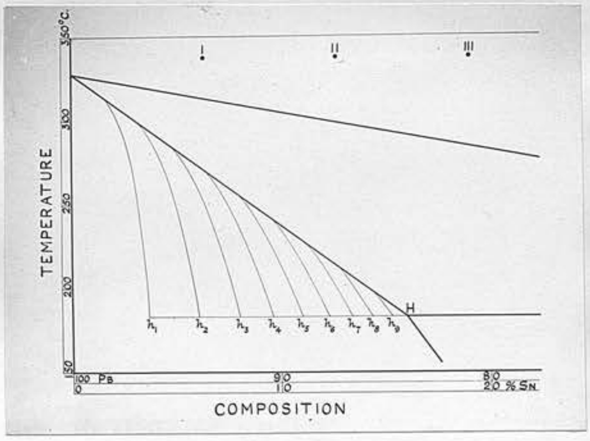

FIG. 8. Part of Equilibrium diagram for lead-tin alloys, Showing the apparent forms of Solidus and the apparent positions of the Saturation points obtained from rapidly Cooled alloys.

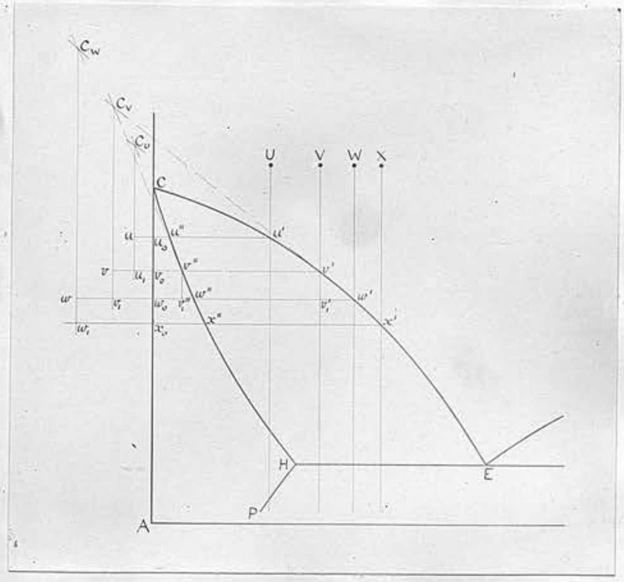

FIG. 9. Part of Equilibrium diagram, illustrating the method employed for calculating the proportion of liquid in rapidly cooled alloys when the curvature of liquidus and solidus is considerable.

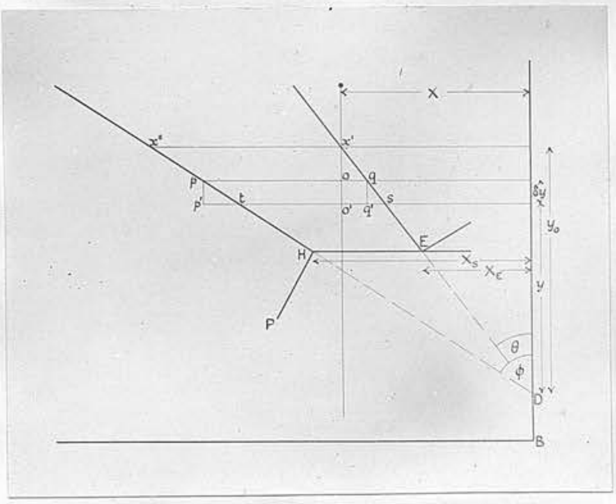

FIG. 10. Part of Equilibrium diagram with solidus and liquidus convergent downwards, and notation suitable for infinitesimal steps.

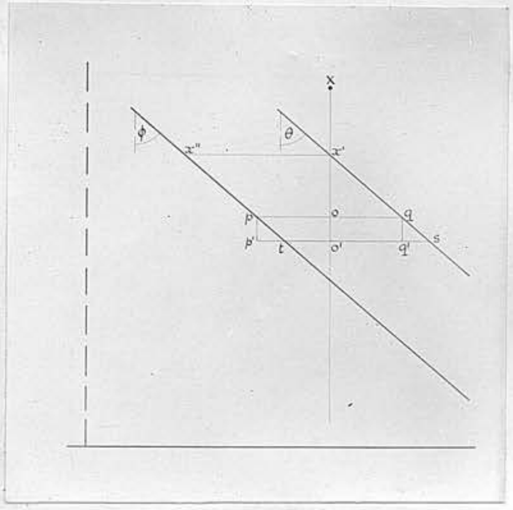

FIG. 11. Part of equilibrium diagram, with solidus and liquidus parallel.

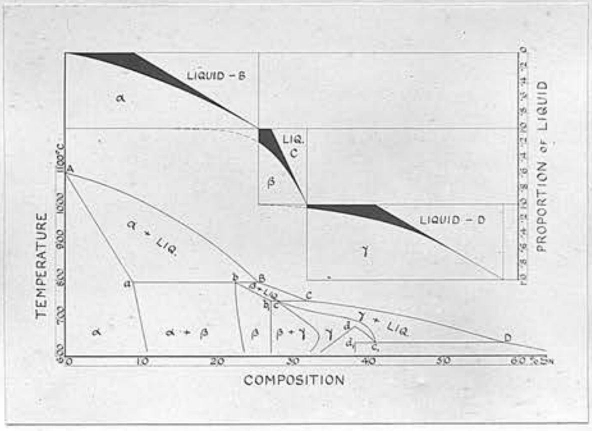

FIG. 12. Part of Equilibrium diagram for copper-tin alloys, and diagrams indicating the increase in the proportion of liquid caused by rapidly cooling alloys which reject α-, β-, and γ-crystals, respectively.

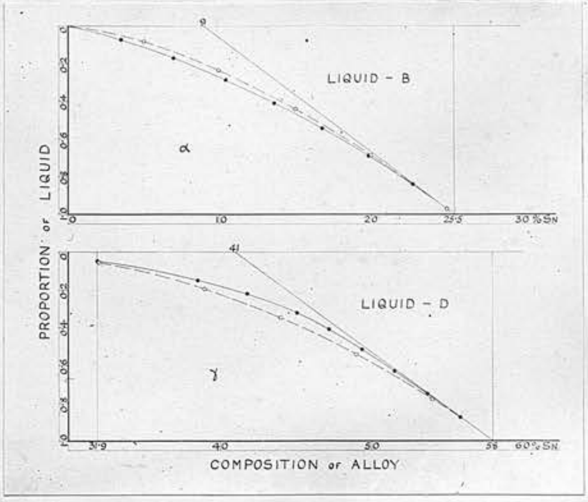

FIG. 13. Diagrams showing the calculated proportion of liquid in rapidly cooled copper-tin alloys from which α-crystals and γ-crystals separate; ○, when liquidus and solidus are assumed straight; ●, when their actual curved forms are employed.

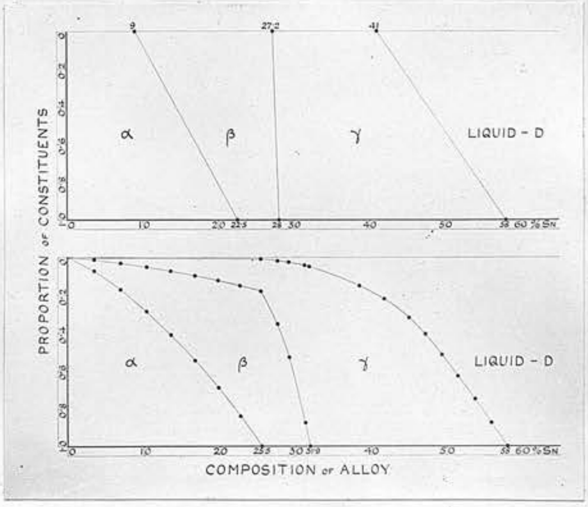

FIG. 14. Diagrams showing, above, the constitution of copper-tin alloys in a condition of equilibrium, and, below, their constitution when very rapidly cooled.

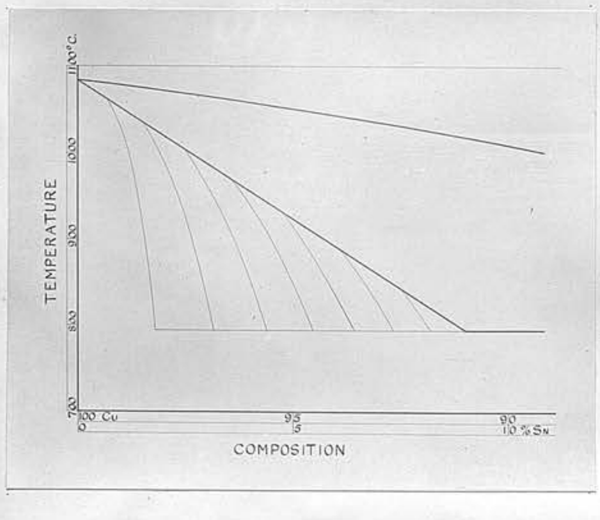

FIG. 15. Part of equilibrium diagram for copper-tin alloys, showing the apparent forms of solidus obtained from rapidly cooled alloys which reject α-crystals.

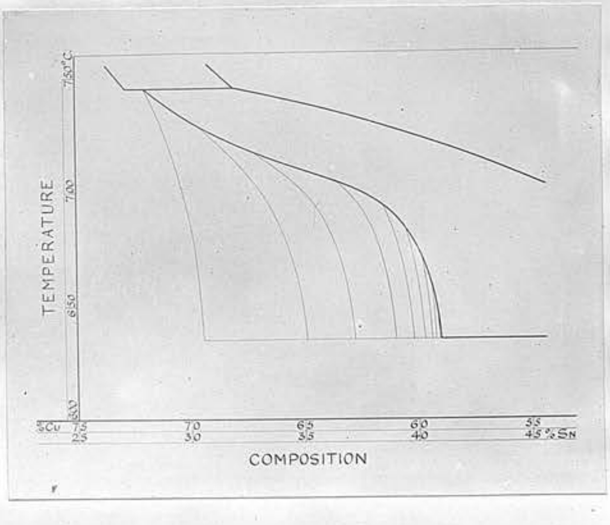

FIG. 16. Part of equilibrium diagram for copper-tin alloys, showing the apparent forms of solidus obtained from rapidly cooled alloys which reject γ-crystals.

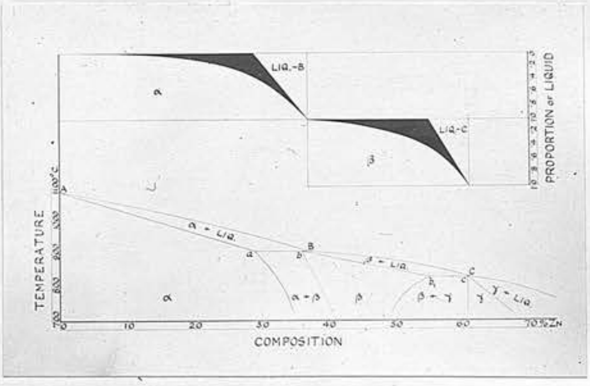

FIG. 17. Part of equilibrium diagram for copper-zinc alloys, and diagrams indicating the increase in the proportion of liquid caused by rapidly cooling alloys which reject α- and β-crystals, respectively.

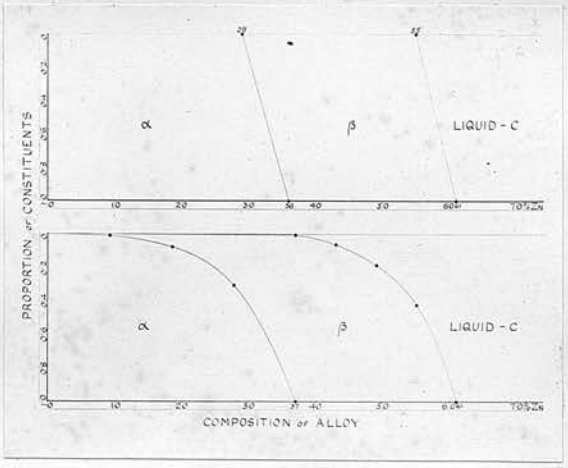

FIG. 18. Diagrams showing, above, the constitution of copper-zinc alloys in a condition of equilibrium, and, below, their constitution when very rapidly cooled.

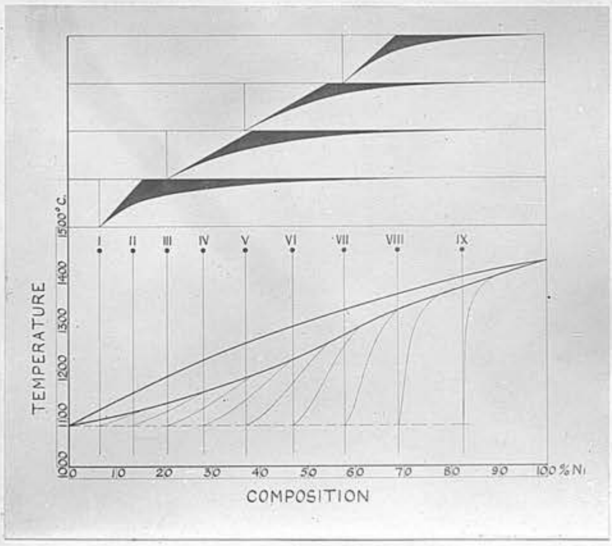

FIG. 19. Equilibrium diagram for copper-nickel alloys; diagrams showing the increase in the proportion of liquid in rapidly cooled alloys at four selected temperatures; and apparent solidus curves of nine chosen alloys.

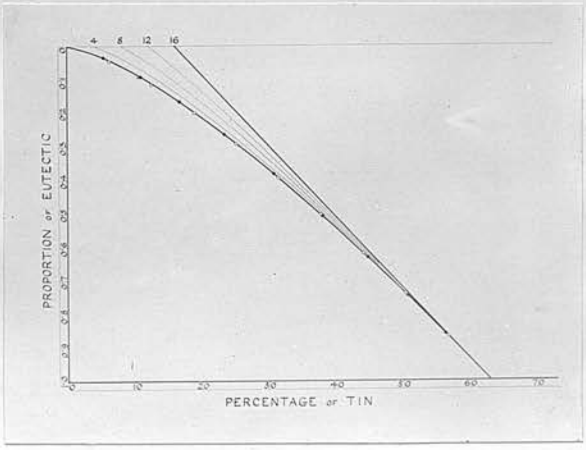

FIG. 20. Diagram showing the calculated proportion of Eutectic in lead-tin alloys cooled with extreme rapidity;
O, when liquidus is assumed straight;
●, when true curved liquidus is employed.
The fine lines through 4, 8, and 12 per cent. of tin indicate the calculated proportion of Eutectic for three intermediate rates of cooling.

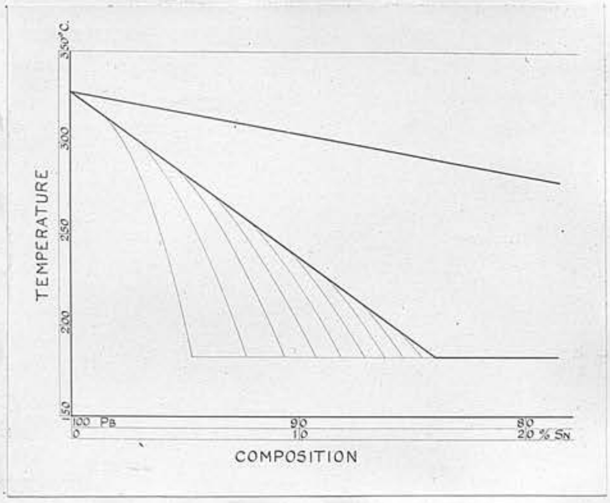

FIG. 21. Part of equilibrium diagram for lead-tin alloys, showing apparent Solidus curves for a rate of cooling characterised by $x = 4$ per cent. of tin.

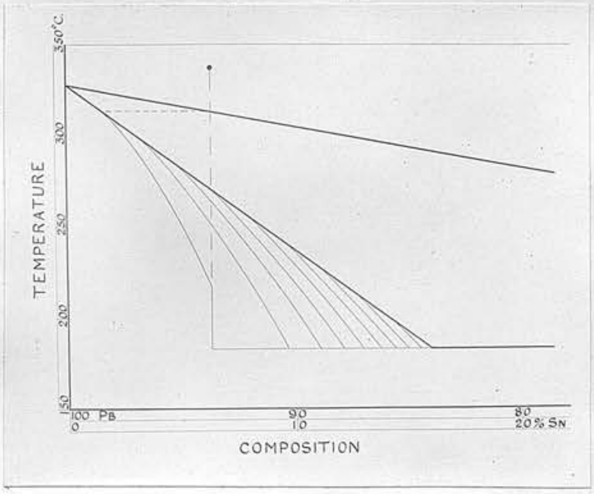

FIG. 22. Part of equilibrium diagram for lead-tin alloys, showing apparent Solidus curves for a rate of cooling characterised by $x = 8$. per cent. of tin.

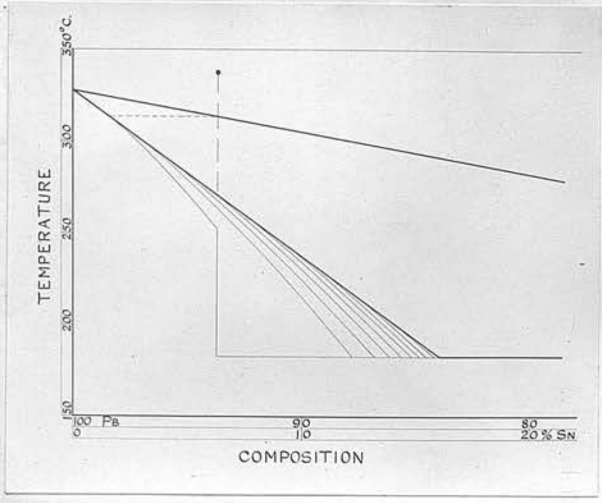

FIG. 23. Part of equilibrium diagram for lead-tin alloys, showing apparent Solidus curves for a rate of cooling characterised by $x = 12$. per cent. of tin.

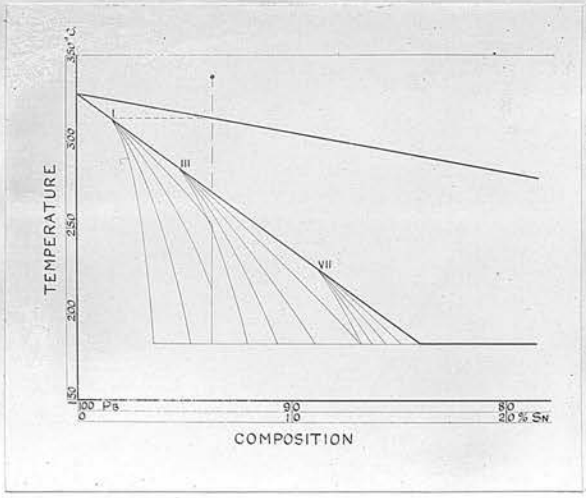

FIG. 24. Part of equilibrium diagram for lead-tin alloys, Comparing Solidus curves of alloys I, III, and VII, at rates of cooling characterised by values of x of 0, 4, 8, 12, and 16. per cent. of tin.

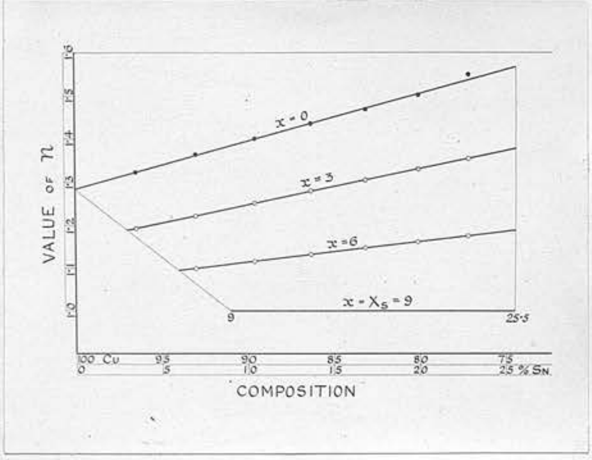

FIG. 25. Diagram showing the variation in the index n, at four different rates of cooling, for copper-tin alloys which reject α-crystals

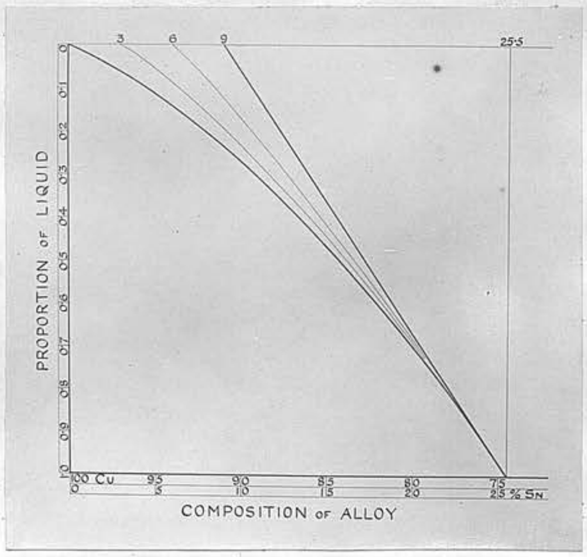

FIG. 26. Diagram showing the calculated proportion of liquid, at the transition temperature, in copper-tin alloys which reject α-crystals, cooled at four different rates.

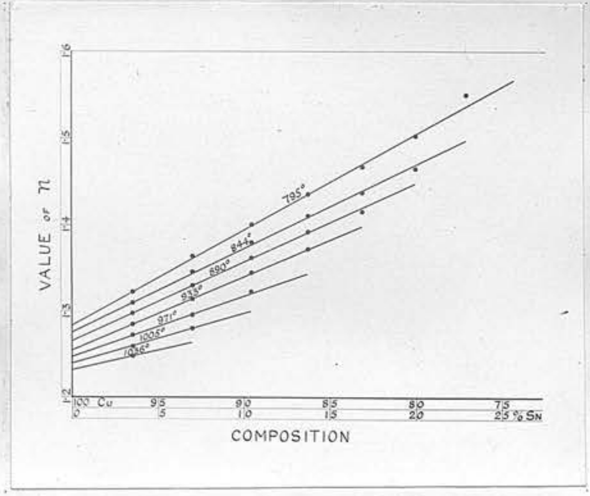

FIG. 27. Diagram showing the variation in the index n, at different temperatures, for very rapidly cooled copper-tin alloys which reject α-crystals.

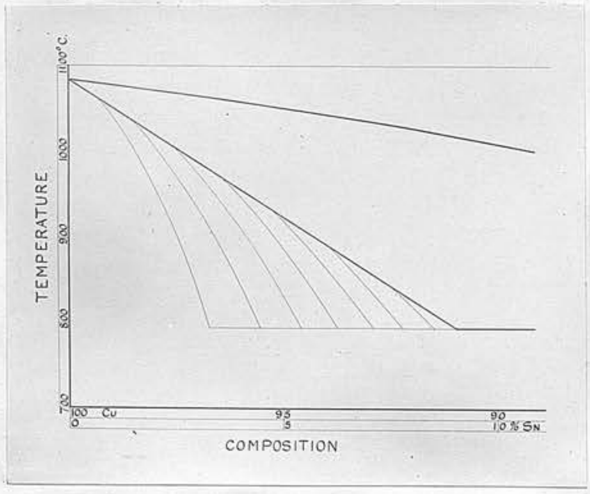

FIG. 28. Part of equilibrium diagram for copper-tin alloys, showing apparent solidus curves of α-crystals, for a rate of cooling characterised by $x = 3$ per cent. of tin.

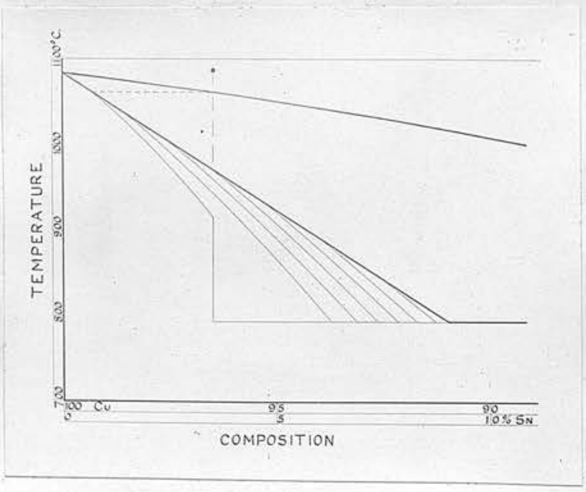

FIG. 29. Part of equilibrium diagram for copper-tin alloys, showing apparent solidus curves of α-crystals, for a rate of cooling characterised by $x = 6$ per cent. of tin

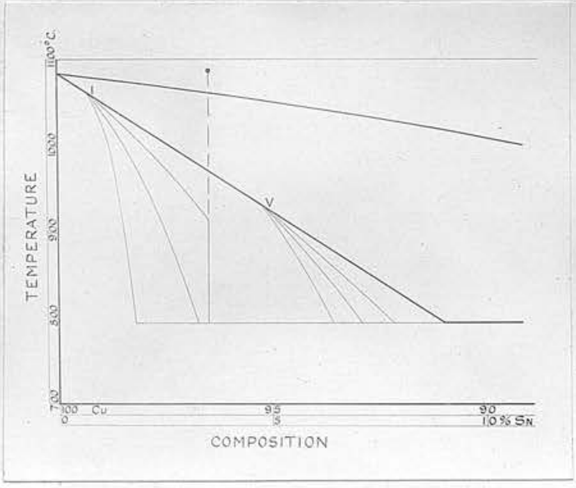

FIG. 30. Part of equilibrium diagram for copper-tin alloys, comparing solidus curves of alloys I and V, at rates of cooling characterised by values of x of 0, 3, 6, and 9. per cent. of tin.

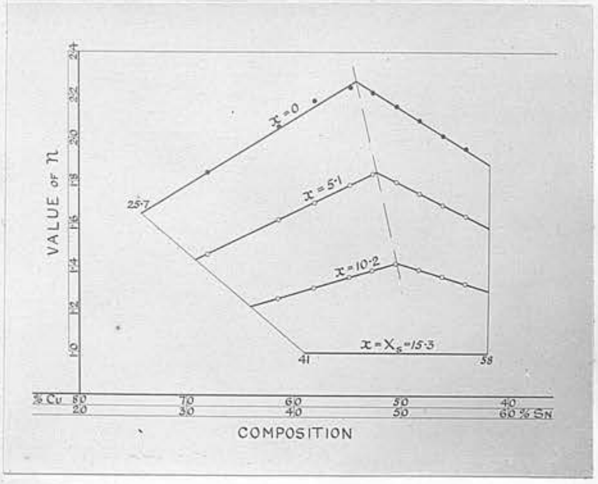

FIG. 31. Diagram showing the variation in the index n, at four different rates of cooling, for copper-tin alloys which reject γ-crystals.

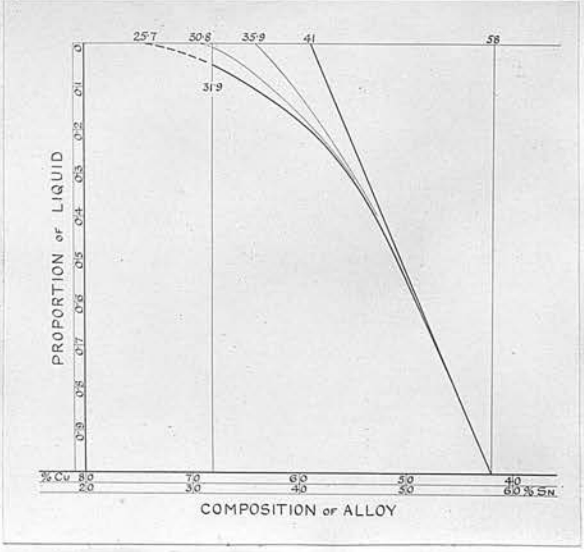

FIG. 32. Diagram showing the calculated proportion of liquid, at the transition temperature, in copper-tin alloys which reject γ-crystals, cooled at four different rates.

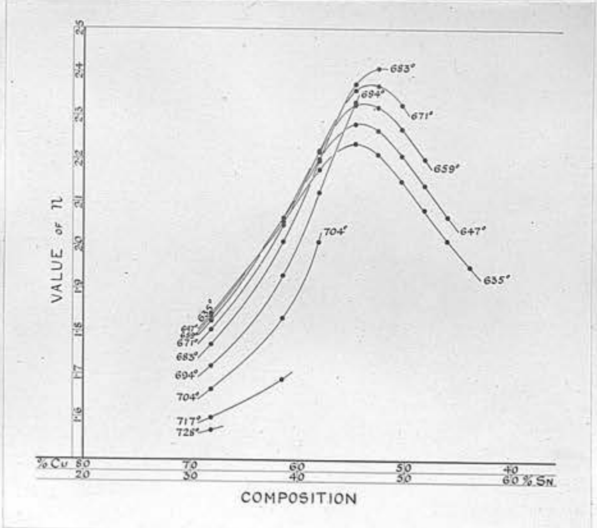

FIG. 33. Diagram showing the variation in the index n, at different temperatures, for very rapidly cooled copper-tin alloys which reject γ-crystals.

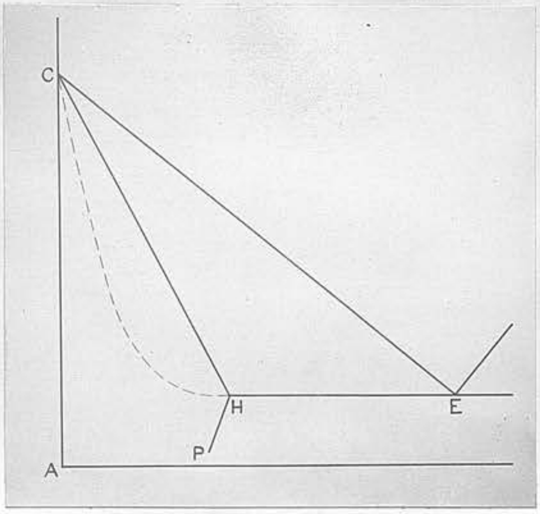

FIG. 34. Sketch showing dotted the shape of solidus to be expected when determined by reheating alloys which are in a condition of imperfect Equilibrium.

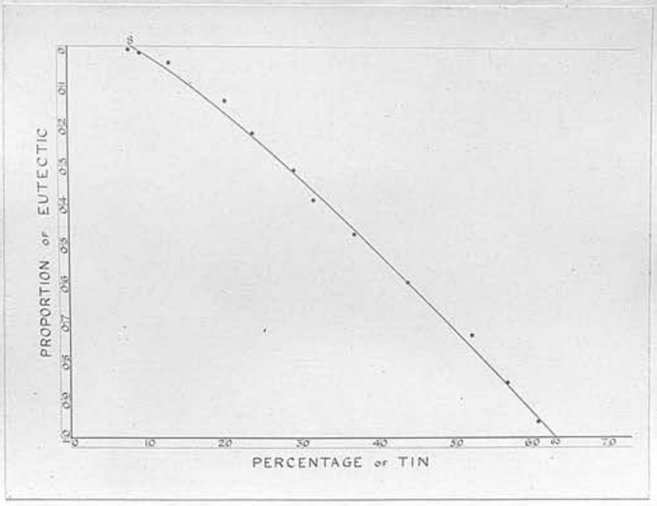

FIG. 35. Diagram showing the proportion of Eutectic in lead-tin alloys cooled at a moderate rate. The points represent the experimental observations of Degens, and the curve is calculated for $x = 8$ per cent. of tin.

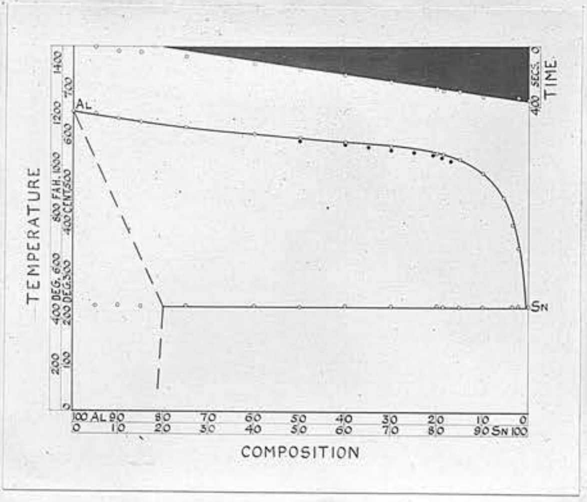

FIG. 36. Equilibrium diagram for aluminium-tin alloys; ●, Shepherd; O, Gwyer.

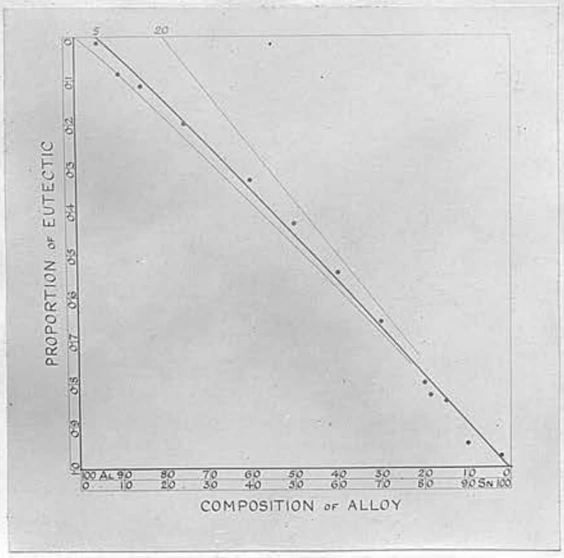

FIG. 37. Diagram showing the proportion of eutectic in aluminium-tin alloys cooled at a moderate rate. The points represent the experimental observations of Gwyer, and the curve is calculated for $x = 5$ per cent. of tin.

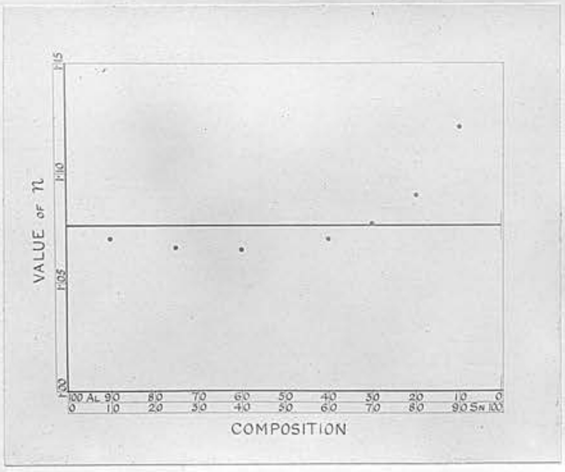

FIG. 38. Diagram showing the variation in the index n for very rapidly cooled aluminium-tin alloys.

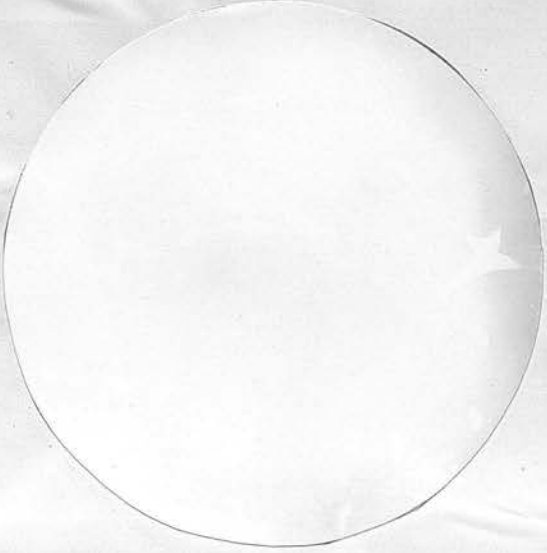

FIG. 39. Aluminium-tin alloy, containing 20 per cent. of tin, annealed at 230° C. for 14 days; etched with caustic potash; magnified 100 diameters

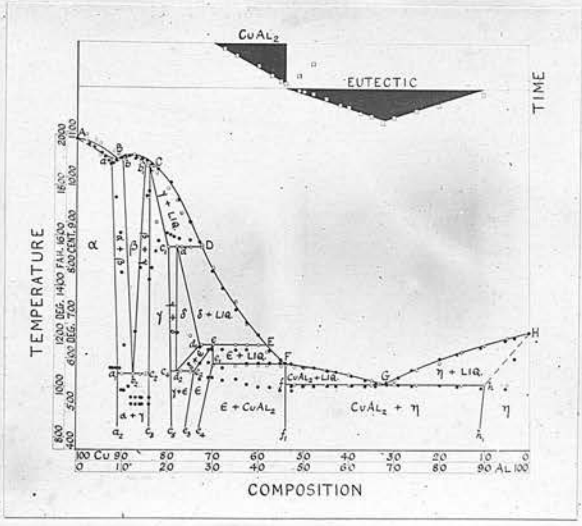

FIG. 40. Equilibrium diagram for Copper–aluminium alloys; ●, Carpenter and Edwards; ○, Curry; □, Gwyer.

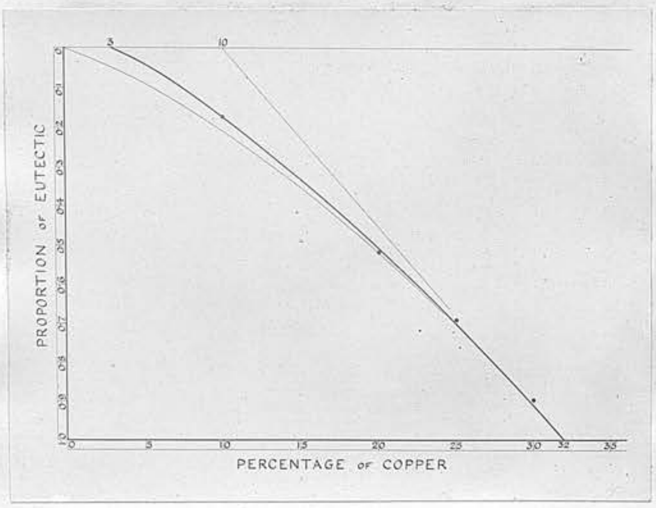

FIG. 41. Diagram showing the proportion of eutectic in aluminium–copper alloys cooled at a moderate rate. The points represent the Experimental observations of Gwyer, and the curve is calculated for $x = 3$ per cent. of copper.

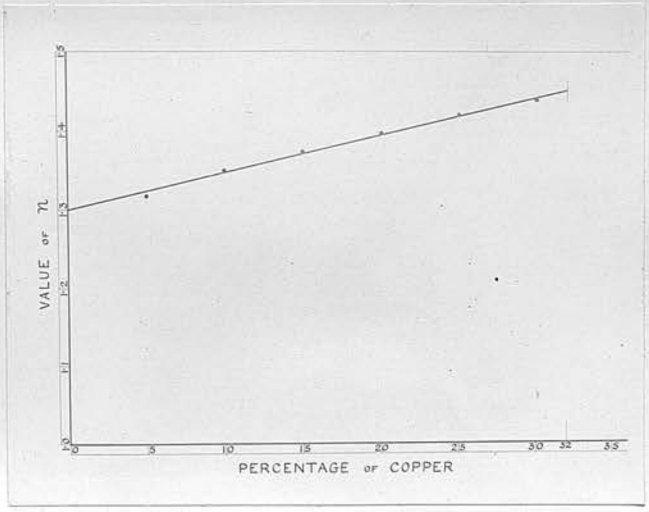

FIG. 42. Diagram showing the variation in the index n for very rapidly cooled aluminium–copper alloys.

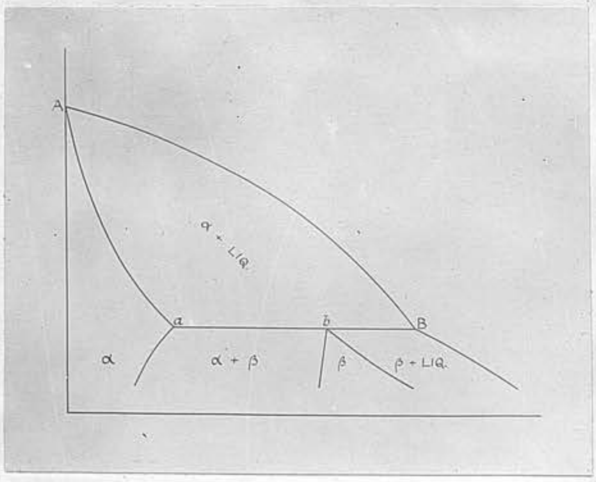

FIG. 43. Part of typical Equilibrium diagram for a series of alloys in which the partly solid mixtures experience a transition

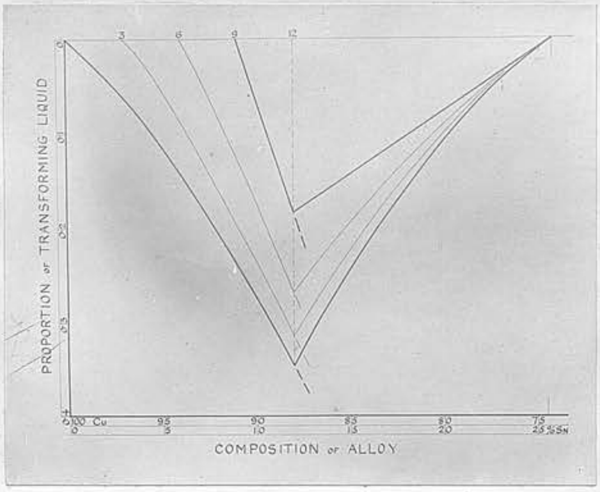

FIG. 44. Diagram showing the proportion of liquid involved in the transition of α to β in copper-tin alloys cooled at different rates. The composition of β is assumed as 12 per cent of tin, and the temperature is supposed to remain stationary at 795° until the transformation is completed. The diagram is illustrative only.

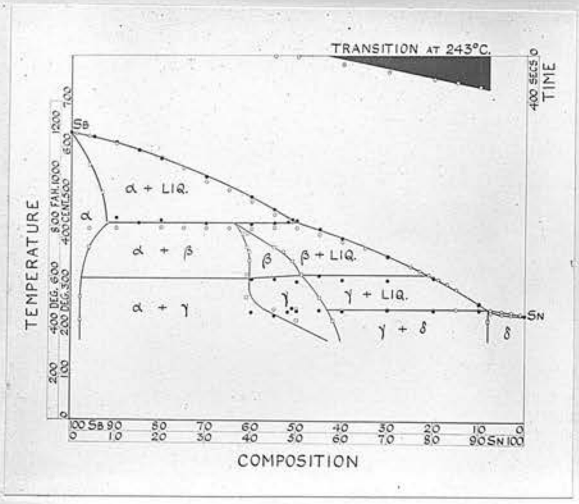

FIG. 45. Equilibrium diagram for antimony-tin alloys; ●, Reinders; ○, Williams; □, Gallagher.

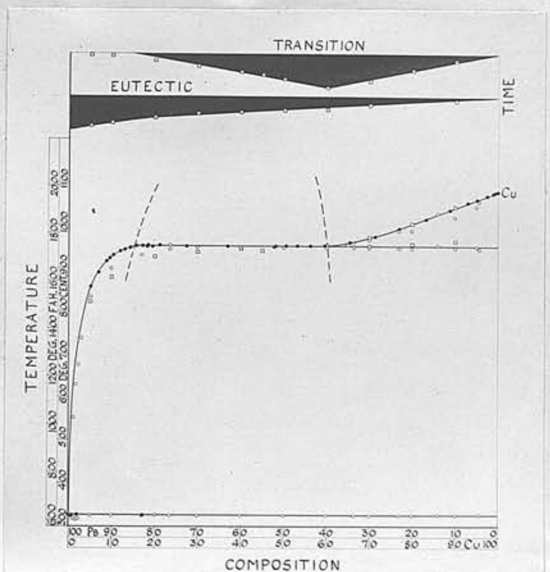

FIG. 46. Equilibrium diagrams for Copper-lead alloys; ●, Heycock & Neville; ○, Roberts-Austen; □, Friedrich and Leroux.