

A STUDY OF THE ALLOYS OF ALUMINIUM AND LEAD

by

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Dedication

To Dr. A. N. Campbell in  
grateful acknowledgement and appreciation  
of his help in the direction of this research.

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## INTRODUCTION

## Historical Introduction

Due to the fact that the applicability of pure metals in industry is relatively small, the study of metallic alloys takes on increased importance since the alloying of pure metals with one another immensely widens the range of their applicability. Obviously, the process of alloying will produce, from the relatively small number of elementary metals, an infinite number of new metals possessing certain qualities of malleability, fusibility and inalterability which are to be desired for particular purposes. Then too, it may happen that the use in the pure state of a certain metal which possesses a desirable secondary property may be impracticable due to some other property or to the prohibitive costs involved; in such a case, the alloying of the desired metal with some other metal which may advantageously modify the former will make available the desired property. An example of this may be seen in the alloying of gold and silver, desired for their inalterability, with copper in order to increase their hardness and reduce the cost.

The great practical importance of metals and alloys in technical processes was, in part, the reason that they came to be considered as a separate class from other solutions and mixtures governed by the same physico-chemical laws. It was this importance in metallurgical industries, also, that was the motivating cause of many of the earliest and most important researches. In the control of the metallurgical operations of many industries, the study of structure has come to be a very valuable aid to chemical

analysis and the applications are constantly becoming more and more widespread.

Aside from its application in metallurgy, and considered from the standpoint of pure science, the identity of relations in metallic and non-metallic systems is of considerable importance. Methods identical with those used in metallography are employed in the study of the formation and metamorphosis of igneous rocks and have also been used in the investigation of cements and slags. In addition, the applicability of these methods seems capable of still further extension.

As late as 1871, the term "metallography" was employed to denote the description of metals and their properties but this use is now obsolete. The word was reintroduced in 1892 to designate the microscopic structure of metals and alloys; its meaning has since been gradually extended and modified to include investigation of alloys by methods other than microscopical. The definition of metallography is now given as the study of the internal structure of metals and alloys and of its relation to their composition and to their physical, chemical and mechanical properties.

The study of the internal structure of metals and alloys may be considered as a branch of physical chemistry since the structure of the solid depends on the physical and chemical conditions under which it is formed. In particular, the study of structure may thus be considered as belonging to the study of equilibrium of heterogeneous condensed systems. Metallography, while taking into account those factors of the nature and relative quantities of the phases in a system and the transformation of energy accompanying chemical changes which are considered in physical chemistry, also deals with the arrangement of the component

particles in space.

Early work in the study of metallic alloys established the important fact that the chemical, physical and mechanical properties of alloys are directly dependent on their chemical composition, i.e., on the nature and proportions of both the constituent metals and the compounds which they form together, as well as of the isomorphous mixtures and of their various allotropic modifications.

The first record of the examination of metals and alloys by microscopical means appeared as early as 1665, when Robert Hooke described the appearance of lead crystallizing from its alloy with silver. The technique used by the early workers was the examination of the fractured surfaces of alloys by the microscope. However, a better method was developed by Widmannstätten who found that, when certain meteorites were cut and polished and oxidized by heating in air, a characteristic structure was developed. It was later discovered that structures were developed even more distinctly when the specimens were etched with nitric acid. In 1864, H.C. Sorby produced, by a method he devised for the preparation and examination of micro-sections, photomicrographs which compared very favorably with those obtained by later workers.

Metallography continued to progress along with the advancement of the study of the nature of metallic alloys. For some time, there was much controversy as to whether alloys were mechanical mixtures or were to be considered as chemical compounds. In connection with this question, Levol showed that only a few alloys remained homogeneous throughout the process of solidification, most of them being separated into parts which have dif-

ferent fusibilities.

Investigation of the alloys by means of their physical properties was undertaken by Matthiessen who put forward the suggestion that they were solidified solutions which might or might not contain compounds. He carried out his work using alloys containing varying proportions of the same constituents, taking any discontinuous change of properties as possible evidence of the existence of a compound. Matthiessen's work more or less marks the starting point of the consideration of alloys as a branch of physical chemistry.

It had been observed that alloys very frequently melted at temperatures lower than those of their components and after the Raoult law of freezing point depression had been established, it was thought that the study of alloys might be undertaken from this view point. A number of investigations were undertaken along these lines. Ramsay studied the depression produced in the vapor pressure of mercury by the addition of other metals; the depression of the freezing point was studied by Tammann and by Heycock and Neville. In addition, Kapp, as well as Heycock and Neville<sup>1</sup>, determined the complete freezing point curves of certain binary alloys, passing from one end of a series to the other.

Jüptner and Le Chatelier were the first to suggest the application of Gibbs' theory of phases to the study of alloys. The first important application of this was made by Roozeboom who constructed the complete diagram of thermal equilibrium of iron and carbon from the results which Roberts-Austen had previously obtained in the thermal examination of iron and steel.

In 1899, Roozeboom established his well known five types of solid solutions in binary systems from the theoretical stand-

point of the phase rule. The first important application of this idea was made by Heycock and Neville who used it in their study of the alloys of copper and tin. In this same investigation, the method of quenching from determined temperatures was introduced and the microscopical study of the alloys was also dealt with, this latter method of investigation having since developed very rapidly.

Many valuable additions to the study of metallography were contributed by Tammann, among these being a survey of a large number of binary metallic systems which was undertaken in an attempt to establish irregularities between alloys of different metals. The diagrams that he established were not entirely acceptable due to the inferiority of his experimental methods and of the materials with which he was working but the work stimulated interest in the study of metals and alloys and did include some valuable information on the properties of metals.

## Theoretical

### General Phase Rule

It was not until the late nineteenth century that a satisfactory theory dealing with the equilibria of chemical reactions was established. This theory, enunciated by Willard Gibbs, is general in application and is not based on any hypothetical assumptions as to the nature and constitution of matter which might weaken it.

Previous to this, it had been known that chemical reactions did not take place completely in one direction but proceeded to a certain point and then halted. Therefore, various attempts had been made to collect all known cases of chemical and physical equilibria with a view to establishing a general law. Such attempts were made by Wenzel and Berthollet who recognized the influence on the equilibria of systems of the masses of the participating substances. However, the real quantitative study of equilibria was begun by Guldberg and Waage in their general statement and mathematical treatment of the Law of Mass Action which satisfactorily summarized the conditions of equilibria in many cases, both homogeneous and heterogeneous, certain simplifying assumptions having to be made in the latter case. When, however, this law was applied to those systems in which the number of molecular aggregates and the degree of their molecular complexity were not known, it failed since it depended on the kinetic and molecular theories and therefore involved certain assumptions as to the nature and condition of the substances participating in the equilibrium.

It was ten years after this that Willard Gibbs enunciated his general theorem which is now known as the Phase Rule which, considering a system as possessing only three variable factors, namely, temperature, pressure and the concentration of its components, defines the conditions of equilibria as a relationship between the number of so-called phases and the components of a system. Gibbs established this theory on the basis of the laws of thermodynamics (a method of treatment first applied by Horstmann) and achieved his results in a perfectly general way, free of any hypothetical assumption as to the molecular condition of the substances in the equilibrium. By it he showed how all cases of equilibrium could be divided into classes or groups and how similarities in the behavior of apparently different systems and differences in apparently similar systems could be explained.

The phases of a system may be defined as the different homogeneous but physically distinct portions of a system which are marked off in space and separated from the other portions of the system by bounding surfaces. Thus we may consider water as existing in three different phases, ice, water and vapor. A phase, however, need not be chemically simple, although it must be homogeneous; a gaseous mixture or a solution may be considered as a phase. A mixture of solid substances, however, since it is heterogeneous, is not one phase but consist of as many phases as there are substances present.

The components of a system are "the smallest number of independently variable constituents by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation."<sup>12</sup> For example, the system ice - water - vapor has only one component

although there are three phases present. In the case of the equilibrium of the dissociation of calcium carbonate into calcium oxide and carbon dioxide, there are three substances present but the system cannot be considered as one of three components since they are not mutually independent. That is, the composition of any one phase is defined when the other two are taken and the system is therefore considered as one of two components.

The number of degrees of freedom of a system is defined as "the number of variable factors, i.e., temperature, pressure and concentration of the components, which must be fixed arbitrarily in order that the condition of the system may be perfectly defined."<sup>12</sup> Therefore, the system water - vapor has evidently only one degree of freedom; if the temperature is fixed the pressure under which the two phases can co-exist is also fixed. If we consider the system ice - water - vapor we see that, in this case, there are no degrees of freedom and the state of the system with reference to the temperature and pressure of the vapor is defined. If any one of the variables is changed, one of the phases will disappear and the system will no longer consist of three phases. In the case of a system which is a gas or vapor, there are two degrees of freedom, for the temperature and pressure may be arbitrarily changed while the volume remains the same.

The Phase Rule as established by Gibbs and which defines the conditions of equilibrium in terms of the co-existing phases and components, may be stated as follows: "A system consisting of  $n$  components is capable of existing in  $n - 2$  phases only when the temperature, pressure and concentration have fixed and definite values; if there are  $n$  components in  $n - 1$  phases, equilibrium

can exist while one of the factors varies, and if there are only  $n$  phases, two of the varying factors may be arbitrarily fixed."<sup>12</sup>

The following equation is generally given as the expression of the above statement,

$$F = n - r / 2$$

where  $F$  denotes the degrees of freedom of the system,  $n$  the number of components and  $r$  the number of phases. Obviously, therefore, as the number of phases is increased, the number of degrees of freedom becomes less and the condition of the system becomes more and more defined.

When this rule is applied to metallography, however, certain simplifying assumptions may be made. The vapor phase is generally neglected in a consideration of the equilibria of metals since the volatility of metals at their melting points is too small to have any effect. Also, the pressure under which equilibrium conditions are reached is considered to be constant since, in most cases, the freezing point determinations are carried out in vessels which are either open to the atmosphere or connected with other vessels in which the pressure is equal to the atmospheric pressure. Accordingly, the influence of pressure on the freezing point of metals and alloys is neglected in all but very exceptional cases. Thus there is one less variable to consider, leaving only the factors of temperature and concentration to be taken into account. Therefore, in a consideration of metallic alloys, the Phase Rule may be expressed by the formula,

$$F' = n - r / 1$$

### Binary Systems

All solid substances may be classified as being either crystalline or amorphous and we find that alloys belong in the first group. The crystallinity of alloys can very often be recognized by examination of the fracture under a microscope but, in certain cases, the fracture may be conchoidal, i.e., resembling a glass, so that the crystalline character is no longer revealed by the microscope. In such cases, the characteristic cooling curves may be used to prove that the alloys belong to the group of crystalline substances. When an amorphous body is cooled the fall of temperature is regular, due to the continuity between the different intermediate states assumed by the mass as it solidifies. However, when a crystalline body is fused and allowed to cool, the results are quite different. The solidification begins suddenly and, due to the liberation at this stage of the latent heat of crystallization, the temperature is observed to halt. Such an arrest of the temperature is noted when any crystalline substance is allowed to cool and, therefore, alloys as crystalline substances, must all show such a halt on their cooling curves. As a result of the crystalline character of alloys we may expect to observe, in the action of heat on them, phenomena similar to those shown by other crystalline mixtures such as mixtures of fused salts or solutions of salts and water.

In the case of solutions, the freezing point was found to be lowered by the dissolution of the salt in the water and similarly, in the case of fused salts, the freezing points are found to be lowered by the addition of one salt to another. The same phenomenon is observed with metals; Heycock and Neville<sup>1</sup>

demonstrated this with their experiments on the effects of adding small quantities of one metal to another on the temperature of solidification of the latter. In this way it has been determined that the melting point of tin is lowered by the addition of small quantities of silver, copper, nickel and lead; and in like manner that of antimony is lowered by the addition of silver, copper, etc.

However, in a small number of cases, it was observed that, by the addition of one metal to another, the opposite effect of raising the solidification temperature was produced. An example of such a case is found when silver is added to cadmium or zinc, causing their temperatures of solidification to rise. This phenomenon has also been noted in substances other than metals, that is, in the case of certain fused mixtures of salts, e.g., potassium sulphate added to potassium chromate.

The solidification of elementary substances or of definite compounds takes place at one constant temperature but with salt solutions or fused mixtures of salts the solidification takes place in a somewhat different manner. In these cases, solidification begins at a certain definite temperature depending on the composition of the mixture and continues only as the temperature falls. It becomes complete at a second definite temperature which is independent of the composition. In the case of some binary alloys this latter temperature is not the same for all the alloys of a series but such a series may be divided into groups of alloys, each group having a characteristic solidifying temperature. There are rarely more than three groups in such cases.

It is the point at which solidification just commences

that is taken as the point of solidification of a mixture or the crystallization point of an aqueous solution. The curves on which these solidification points are plotted against the corresponding compositions of the mixtures are referred to as fusion curves. Similar curves relating compositions of saturated solutions to corresponding temperature are called solubility curves. These two types of curves are identical in form but this fact was not realized until pointed out by Le Chatelier. The reason that the relationship was not recognized was probably due to the fact that the common practice was to plot these curves with the temperatures as ordinates in one case and as abscissae in the other, which resulted in a difference of orientation for the curves. Nowadays the accepted method of plotting these curves is to plot the arbitrary variable in each case as abscissae and the function of this variable, determined experimentally, as ordinates.

The general procedure in the establishment of the solubility and fusibility curves is somewhat different for each case. When the solubility curve is desired, one finds, at a given temperature, the composition of the liquid in equilibrium in contact with either ice or excess salt. In the case of fusibility, mixtures of known composition are taken and the temperatures of solidification determined for them. The analogy of these two kinds of phenomena becomes quite evident when we consider that the state of saturation of a liquid is unaffected by the presence of a large or small amount of solid substance in contact with it and also that, at the solidification point of a liquid, a state of saturation is considered to exist with respect to the solid substance separating from the liquid, since a very small lowering

of temperature is required to cause the deposit.

When there are several solid substances in different chemical states separating from a liquid mixture, the curve of mutual solubility of two substances will be represented by a number of intersecting branches. There will be a separate branch for each solid substance separating and also one for each of their allotropic forms and for each of their compounds, with these branches intersecting one another and forming a continuous curve which, however, has a certain number of angular points. In the experimental investigation of these curves, with the exception of the case of supersaturation, they can be traced only in the region limited by successive points of intersection.

The existence of these multiple branches in solubility curves was first discovered by Loewel when he was investigating the curves of sodium sulphate, sodium carbonate and magnesium sulphate. Somewhat later than this, Bakhuis Roozeboom drew the same conclusions when studying solutions of calcium chloride and it was finally shown by Le Chatelier that this occurrence must naturally follow as a result of the fundamental laws of energy and that there can be, therefore, no exceptions to this rule.

### Thermal Analysis

The method of investigation of metallic alloys known as thermal analysis is the most widely used and probably the most important method employed today and may, in fact, be regarded as the foundation or basis for all other methods of investigation. The reason for this lies in the fact that, in all but a few

instances, we would be unable to interpret correctly the results obtained by microscopic and other methods of investigation if nothing were known of the diagram of thermal equilibrium of a system which shows what phases we may expect to occur in an alloy of a certain composition cooled under certain conditions.

In metallography, the most important requisite is a knowledge of the phases present in the cold alloy and on this point the establishment of the thermal equilibrium diagram provides much important information. The freezing point curves resulting from the thermal analysis show the temperatures in the neighborhood of the freezing point of the alloy. Any changes in the solidified alloy from one phase to another will also be revealed by means of thermal analysis if the heat effect which accompanies the changes is of sufficient intensity.

The fact that heat is liberated or absorbed when one phase in the alloy changes to another phase is the basis of the method of thermal analysis. The general method is to take either cooling curves or heating curves on which these effects show up. These curves are determined with the specimen in an enclosure which is cooled so that, as far as possible, the loss of heat due to radiation, convection and conduction is uniform.

When the cooling curve of a pure substance is taken in such a way, the curve obtained will be continuous, representing a gradual fall of temperature while the substance is cooling and as long as no solidification takes place. As soon as solid begins to separate out, the heat liberated will cause a halt in the cooling and the temperature will remain constant until the solidification is complete. This, of course, is based on the assumption that there is no supercooling occurring.

In the case of a solution, however, the curve obtained is slightly different. As with a pure substance, the curve is continuous while all is liquid but when a solid phase appears there is heat evolved and the rate of cooling changes. There is, however, no temperature halt on the curve but merely a change of direction at the freezing point of the solution. With continued cooling, the composition of the solution changes as the solid phase separates out and the temperature falls down to the eutectic point. At this point a second solid phase appears, causing the system to become invariant, again supposing there is no supercooling. The temperature now remains constant until the solidification becomes complete, after which the fall of temperature becomes uniform again.

The eutectic halt, that is, the length of time during which the temperature remains constant at the eutectic point, naturally depends on how much of the solution has solidified before this point was reached. Obviously, the halt time will be a maximum for a solution whose composition is represented by that of the eutectic point.

The construction of the equilibrium diagram is accomplished by plotting the temperatures of the halt points on the cooling curves of mixtures of different compositions against these respective compositions. These arrest points are indicated on the cooling curves by the occurrence of breaks or discontinuities. There may also be obtained from the cooling curves certain information regarding the solid phases present. When the times of the constant eutectic halts for different mixtures are plotted against the corresponding compositions of the liquid mixtures, a curve with a maximum is obtained which indicates that only the

pure components are present as solid phases.

The usual procedure is to plot the direct cooling curve as temperature against time but in certain cases the thermal effect of the phase changes is so slight that it does not show up on the direct cooling curve. To overcome this and increase the sensitivity of the cooling curve method, Sykes<sup>2</sup> developed what is known as the differential curve method. In this method, the curve is obtained by plotting the time against the temperature difference between the specimen and its enclosure. This temperature difference is obtained by means of two thermocouples connected differentially, one being put in the specimen and the other in a neutral body in the enclosure.

#### Types of Equilibrium Diagrams

- (1) The components separate out in the pure state:

The typical diagram for such systems is shown in Fig.1. This is the simplest possible equilibrium diagram for two-component systems in which there is no solid solution. Points A and B on the diagram are the melting points of the pure components and C represents a eutectic point. As mentioned before, the dissolution of a substance in a liquid causes a lowering of the freezing point of the liquid and thus when B is added to molten A, the temperature at which solid A is in equilibrium with the liquid will be lower than that of the freezing point of pure A. This lowering of temperature becomes progressively greater as the concentration of B increases and this behavior is represented by the curve AC which gives the compositions of solutions in equilibrium, at different temperatures, with solid A. In the

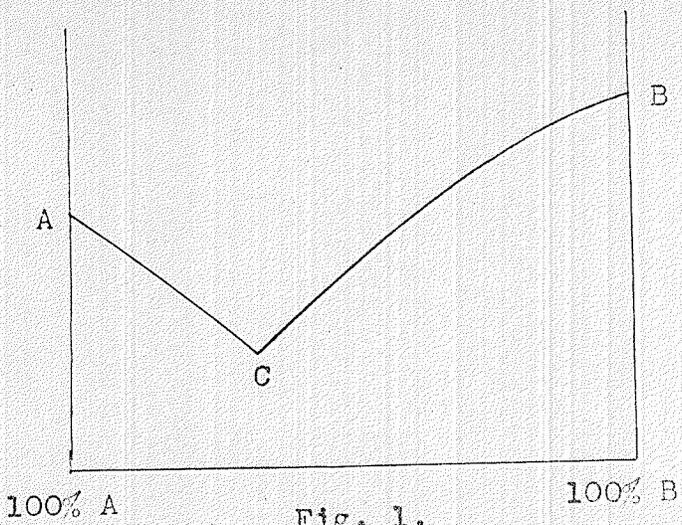


Fig. 1.

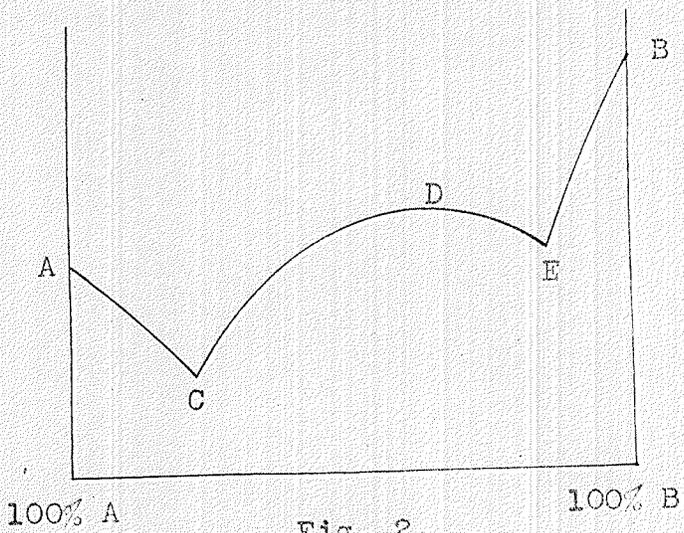


Fig. 2.

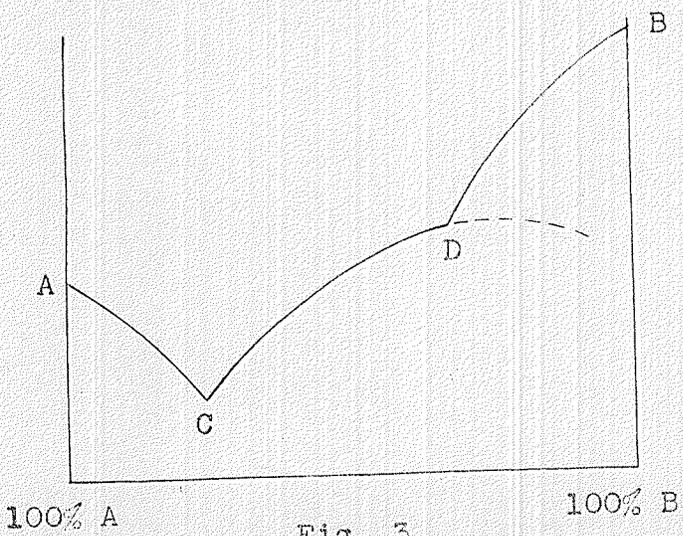


Fig. 3.

same way, we see that BC represents the compositions of solutions at different temperatures in equilibrium with the solid B. At the eutectic point C, both the solid components A and B can exist in equilibrium with a liquid whose composition is represented by C. If, from such a solution, crystals of one of the solid components were to separate, the equilibrium would be upset and the liquid would be supersaturated with respect to the other component. To reestablish equilibrium, crystals of the latter must separate out. At this eutectic point therefore, the separating solid consists of a mixture of both solid components A and B and the temperature will remain constant until all is solid. This constancy of temperature is a characteristic of eutectic mixtures at their freezing points. In this respect, therefore, they resemble pure substances or definite compounds, and it was due in part to this fact and in part to the apparent complete homogeneity of some eutectic mixtures that some early workers mistook them for compounds.

(2) Compounds are formed with a congruent melting point:

A compound with a congruent melting point may be described as one which is capable of stable existence as a solid in equilibrium with a liquid of the same composition. When such a compound is formed by two components, the equilibrium diagram of the system is of the type shown in Fig. 2. There is now a third curve present in addition to the two curves which are the same as those already discussed. This third branch of the equilibrium curve must show a maximum which always occurs at the composition of the compound. That is, the compound has a definite melting point which, by the addition of either of the pure com-

ponents, is lowered in accordance with the curves DC and DE on the diagram. A, B and D are the melting points of the pure components A and B and the compound  $A_xB_y$  respectively. As before, the curve AC gives the compositions of mixtures at different temperatures in equilibrium with A as the separating solid and BE represents the compositions of solutions in equilibrium at different temperatures with B as the solid phase. Along the curve CDE, the compositions of the solutions in which the compound is the solid phase are similarly given. C is the eutectic point where a mixture of pure A and the compound  $A_xB_y$  is in equilibrium in contact with a solution whose composition is represented by the point C. Similarly, E is the eutectic point with B and the compound  $A_xB_y$  as solid phases existing in contact with a solution of the composition of E. The area in which the compound forms, i.e., the area under the curve CDE, does not have any definite limits and may cover a very large part of the diagram in some cases or only a small part in others. The compound may have a melting point which is higher or lower than those of the pure components or it may be intermediate. For each compound with a congruent melting point that two components may form, there will be a curve similar to CDE in Fig. 2 on which a maximum will occur at the composition of the compound.

If the compound were undissociated into its components, the curves CD and DE would be expected to intersect at D instead of forming a continuous curve. In favor of this argument is the fact that D represents the melting point of a pure substance which is lowered by the addition of another substance to the liquid phase. But when the compound is dissociated in the liquid phase, we are dealing with a mixture of molecules in the liquid

phase whose composition varies continuously with the temperature. The curve will therefore be continuous as long as the compound remains unchanged and the maximum on the curve will be rounded and not the point of intersection of two branches. The sharpness of this bend in the curve depends upon the degree of dissociation of the compound in the liquid phase; if the compound is only slightly dissociated the crest of the curve will be fairly sharp and as the degree of dissociation increases the maximum becomes flatter and flatter. Various attempts have been made to calculate directly the degree of dissociation from the extent of flattening of the curve and have given results which are in approximate agreement with the actual facts.

(3) Compounds are formed with incongruent melting points:

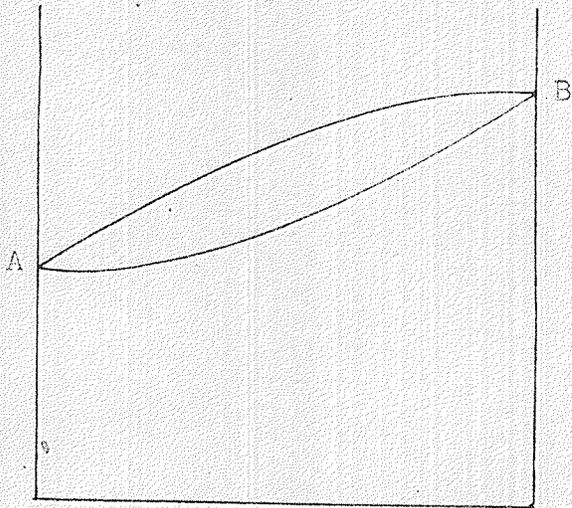
A compound which has an incongruent melting point is one which undergoes decomposition, with the formation of another solid phase, below the temperature of the congruent melting point of the compound. The equilibrium diagram of such a system in which the components form an incongruently melting compound is shown in Fig. 3. In this case the compound can exist stably only in contact with a solution containing an excess of one of the components. In the diagram, the dotted line represents the metastable existence of the compound and the curve formed is like that for a congruently melting compound, i.e., it has a maximum at the composition and congruent melting point of the compound. Actually, however, the compound decomposes into another solid phase and a liquid which has a different composition from that of the compound before the temperature of the congruent melting point is reached. This point where decomposition occurs, point D on the diagram, is known as the incongruent melting point or

peritectic point and represents the limit of stable existence of the compound under the particular pressure assumed. For every compound with an incongruent melting point, formed by two components, there is such a point and the equilibrium diagram of the system would consist of a series of curves with no maxima and would have only one eutectic point.

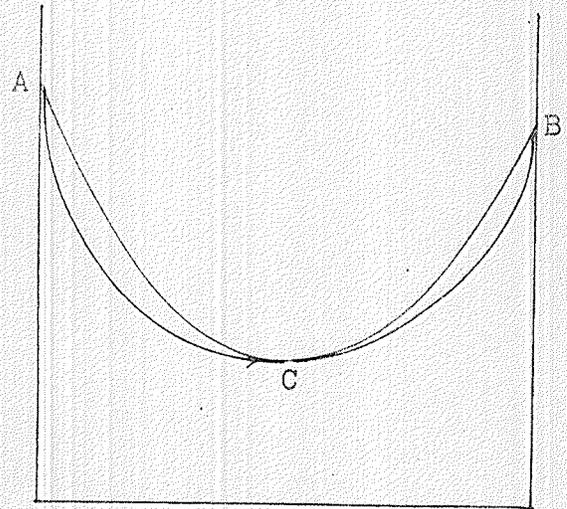
The composition of the compound must be found indirectly since there is no temperature maximum on the equilibrium curve. It can be got by extrapolation of the curve through the metastable or so-called 'hidden' maximum but the results obtained by this method are only approximate. Tammann, however, noticed that the duration of the compound halt time depended on the composition of the mixture taken and that the further away from the composition of the compound it was, the smaller it became. He therefore plotted the duration of the halt time against the original composition of the mixture and obtained two curves which intersected at a point where the compound halt time was a maximum. This point, therefore, gives the composition of the compound and affords a check on the incongruent melting point, since the time of the compound halt is zero at this point.

#### Formation of Solid Solutions

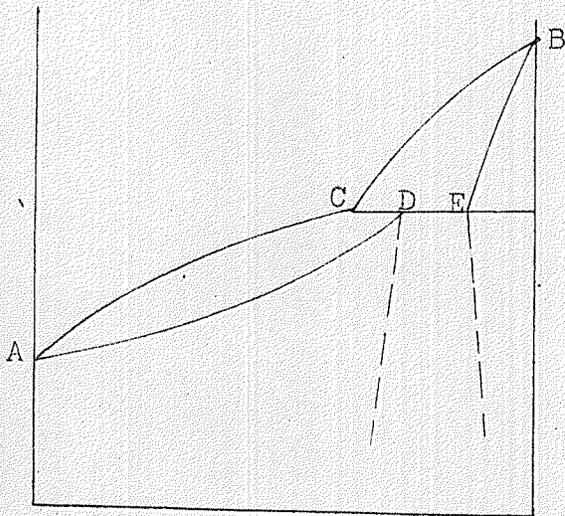
When two components form solid solutions as well as liquid solutions, two curves are required to depict the equilibrium diagram of such a system. This is in part due to the fact that the concentrations of the components are generally different in each phase and one curve therefore relates to the liquid phase while the other relates to the solid phase. The temperature at which solid just begins to separate out from the liquid mixture



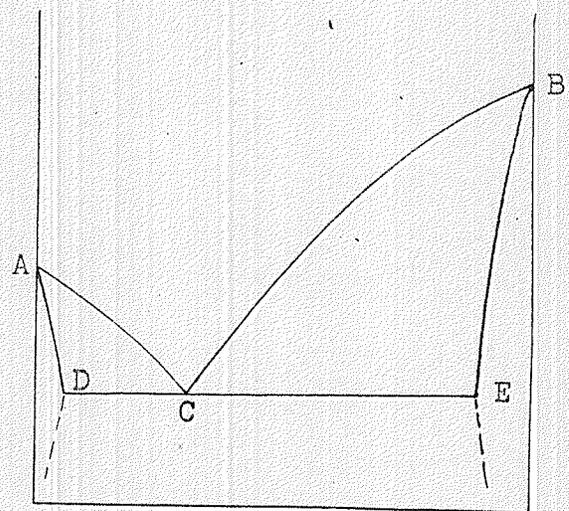
Type I



Type II



Type III



Type IV

Fig. 4.

is known as the freezing point and, therefore, the freezing point curve will be that obtained by plotting temperatures against the compositions of the liquid phase. The point at which the solid solution just begins to liquefy is called the melting point and therefore the melting point curve is obtained by plotting the compositions of the solid solutions against the temperatures. The above curves are also referred to respectively as the liquidus and the solidus.

When a solid solution occurs in a system, the two components may be either completely or only partially miscible in the solid state and therefore it is usual to divide the consideration of the types of solid solution into two sections.

(1) An unbroken series of solid solutions is formed:

When the two components are completely miscible in the solid state there can be only one solid phase present since a solid solution, of course, consists of just one phase. This solid phase will, therefore, be a solid solution of varying composition. It follows that there will be only one liquid phase since the components must also be completely miscible in the liquid state. There can, therefore, never be more than three phases present and the system can never become invariant, while the equilibrium curve must be continuous. There are three types of such systems but one, in which there is a maximum shown by the curve, is very rare, and known only when the components are optical isomers. Therefore, we will only consider the other two types which are as follows:

(a) The freezing points of all mixtures lie between the freezing points of the pure components (Fig. 4, Type I)

The diagram consists of two continuous curves joining

the melting points of the two pure components; these two curves are the freezing point curve and the melting point curve and give the respective compositions of the liquid and solid solutions formed by the components. When a liquid mixture is cooled, the freezing point gives the point where it touches the liquidus curve. By projecting a horizontal from this point to intersect the solidus curve, we get the composition of the corresponding solid phase which separates out.

The relative positions of the solidus and liquidus curves are given by the following rule: "at any given temperature the concentration of that component, by the addition of which the freezing point is depressed, is greater in the liquid than in the solid phase; or, conversely, the concentration of that component, by the addition of which the freezing point is raised, is greater in the solid than in the liquid phase."<sup>12</sup>

(b) The freezing point curve passes through a minimum (Fig. 4, Type II)

There is, in this case as well as in that where the pure components are deposited, a minimum freezing point obtained but here there is a continuous curve through the point and not two curves intersecting. On one side of the minimum the liquidus contains relatively more of one component than does the solidus, while on the other side it contains relatively less. The compositions of the solidus and liquidus are the same at the minimum and, therefore, complete solidification and liquefaction will take place at the same temperature and the solid solution will exhibit a definite melting point.

(2) The components do not form a continuous series of solid solutions:

Partial solid solubility is very much the same as the case

of partial miscibility in the liquid state. The component B is soluble to a certain extent in the solid component A but, if a further quantity is added, the composition of the solid is not changed but another solid phase appears which is a solution of A in solid B. Therefore, at this point we have four phases co-existing namely, solid solution with excess A, solid solution with excess B, liquid solution and vapor, and the system must therefore exhibit an invariant point. At this point the equilibrium curve is no longer continuous but shows a break or discontinuity. There are two types of curves to be considered.

(a) A transition point is exhibited by the freezing point curve (Fig. 4, Type III)

When B is added to the other component A, it causes a rise in the melting point. In accordance with the rule previously given there will be a greater concentration of B in the solid solution than in the liquid. The compositions of both the liquid and solid solutions are given by the curves AC and AD respectively. Similarly the curves BC and BE represent the compositions of the liquid and solid solutions formed when A is added to B, the melting point of the latter being lowered by this addition. At the temperature of the horizontal line CDE there is an equilibrium between the liquid solution, whose composition is represented by C, and the two solid solutions of the compositions D and E. The curve for the solid phases, therefore, exhibits a discontinuity at this temperature and, as a consequence of the change in the solid phase, the freezing point curve or liquidus also shows a break.

(b) The freezing point curve exhibits a eutectic point (Fig. 4, Type IV)

In this case, addition of either one of the components to

the other cause a lowering of the freezing point. This results in two freezing point curves which intersect at a eutectic point where the liquid solution solidifies to a conglomerate of two solid solutions.

At this eutectic point there is equilibrium between the two solid solutions whose compositions are represented by D and E and a liquid solution of the composition of the eutectic point C, and therefore a molten mixture of this composition will solidify entirely at the temperature of the horizontal DCE to a mixture of the two solid solutions. These solid solutions represent the respective end points of the two series of solid solutions of the two metals A and B, D being the saturated solution of B in A and E, a saturated solution of A in B.

The mutual solubility of the two solid components changes with the temperature however, and when solid solutions are formed they do not necessarily remain unchanged in the solid state. It is possible that they may lose their homogeneity at some lower temperature and this fact is of considerable importance in the study of the formation of alloys.

Bakhuys Roozeboom was responsible for the classification of these types of solid solutions. He established them in 1899 from the theory of thermodynamic potential.

#### Incomplete Miscibility in the Liquid State

It is not always the case that alloys melt to a homogeneous liquid; certain pairs of substances form two immiscible liquid layers within certain ranges of temperature and concentration. The degree of immiscibility varies with different pairs of substances.

It is more usual for the mutual solubility of two liquids to increase with rising temperature but in rare instances it is

observed to decrease. Therefore, if we consider two liquid layers formed by two substances A and B as the temperature rises, we see that in the layer in which A is in excess the concentration of B becomes greater and that the layer with excess B becomes increasingly richer in A. That is, the compositions of the two layers are gradually approaching each other as the temperature is raised. Evidently there is a certain temperature at which these two liquid phases do become identical in composition. This temperature is known as the critical solution temperature but its experimental realization is very difficult in the majority of metallic systems, owing to the fact that this temperature is usually higher than that of the boiling points of the metals involved and also because of the difficulty in distinguishing the two layers due to the lack of transparency.

When two metals are almost completely immiscible in one another in the liquid phase at a temperature slightly above the melting point of the higher melting one, the freezing point of either will be unaffected by the presence of the other no matter what the composition. Therefore, for any liquid mixture, the metal with the higher melting point will crystallize out entirely at its normal freezing point and the temperature will then fall to the freezing point of the other metal which will then crystallize out. This is a limiting case and the equilibrium diagram consists merely of two horizontal lines through the respective freezing points of the two metals.

In actual fact, however, such complete immiscibility never takes place and the usual form taken by the equilibrium curve is that shown below in Fig. 5

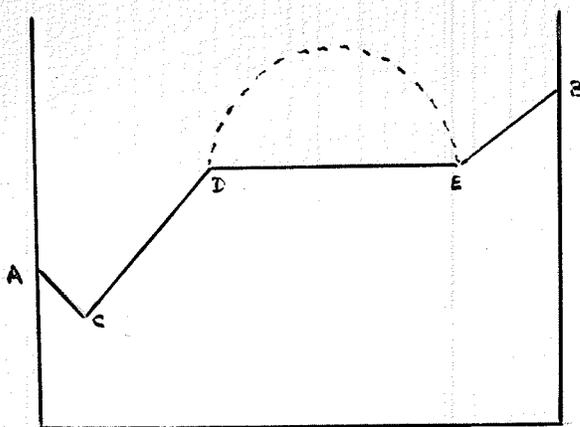


Fig. 5

The freezing point of each pure metal is depressed by the addition of the other. The eutectic point is usually found to be nearer to the freezing point of the more fusible metal and so near to the end of the series as to be practically indistinguishable from the freezing point of the pure metal.

Fig. 5 shows what will happen when liquid mixtures varying composition are cooled, assuming that there are no compounds or solid solutions formed and that both metals crystallize in the pure state. From a mixture rich in B, crystals of B will first be deposited and the temperature will fall in accordance with the curve BE, until the temperature and composition of the point E have been reached. At this point the freezing point curve intersects the miscibility curve which is indicated by the dotted line. If B continued to separate from the molten alloy, the composition of the mixture would reach a point between B and E. This, however, is within the region of immiscibility and therefore the result of crystallization must be the formation of a second liquid phase which has the composition D. We thus have the three phases, solid B and the two liquid phases in contact with one another. The system becomes invariant at this point and further crystallization takes place at constant temperature represented by the horizontal line DE. The mean composition of the liquid alloy changes along

the line ED as the crystallization proceeds until the point D is reached, at which point the liquid alloy of the composition E disappears. This reduces the number of phases present to two and as further cooling takes place the temperature falls, as indicated by the curve DC, with the metal B crystallizing from a homogeneous liquid. This continues until the eutectic point C is reached, after which the process continues in the normal fashion. On the individual cooling curves of molten alloys, the formation of the second liquid phase shows up as a horizontal portion which is exactly like that obtained for the solidification of a eutectic. These cases are usually distinguished microscopically.

The upper part of the curve of liquid solubility lying above the liquidus, cannot be determined by the simple method of thermal analysis, as the development of heat is too small to be detected and thus other methods must be used. The most general method is analysis of samples removed from either layer of an alloy at a temperature at which the alloy is molten. The curve may be traced by changing the temperatures at which samples were taken. The method of quenching the molten alloys and analysing samples may also be used.

The converse condition, of a homogeneous liquid which separates into two phases on heating, is known but is less common.

#### Methods of Cooling

The two general methods used in the determination of cooling curves of fused masses are those known as Plato's method and the much older method of free cooling. These methods are described in general as follows:

(a) Method of free cooling:

In this method the substance under consideration is melted up in a furnace which is fitted with a thermocouple and kept molten for a short time. The heating is then cut off entirely and, as the molten mass cools, readings of the temperature are taken at certain definite intervals of time.

The cooling is fairly rapid in this method and takes place according to Newton's law of cooling. When a body in which no solidification or other thermal effects occur is cooled and temperature readings are plotted against time, the curve obtained is like that shown in Fig. 6.

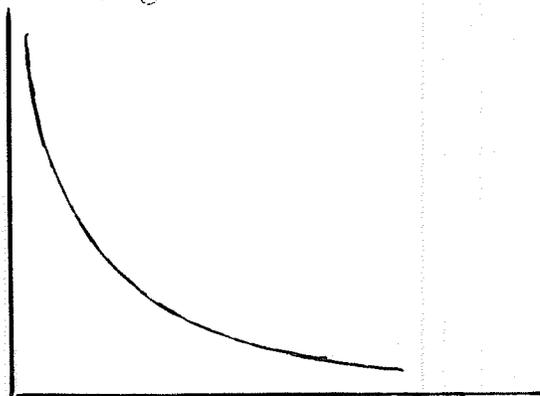


Fig. 6

(b) Method of Plato:

In Plato's method the cooling is restricted. This is usually accomplished by attaching a rheostat to the circuit of the furnace and gradually cutting off the heating current by increasing the resistance. The resistance is usually calibrated and is increased a certain definite amount at definite intervals of time so as to keep the cooling regular. Readings of the temperature are taken at the same intervals of time by means of a thermocouple in the furnace and when plotted against time give a curve like that shown in Fig. 7, provided, of course, that there is no solidification or other thermal phenomenon taking place.

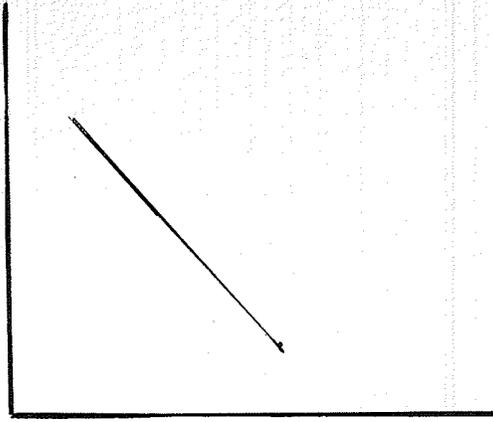


Fig. 7

When any thermal effect takes place in a melt it shows up on the cooling curve as a change of direction of the curve, and thus it would be much easier to detect on a curve like that of gradual cooling than on the other type. This is especially true if the heat effects are very small, since the very slight change of direction that would result would be much more difficult to distinguish on a curved line than on a straight one.

The following are the types of curves to be expected when the method of gradual cooling is used:

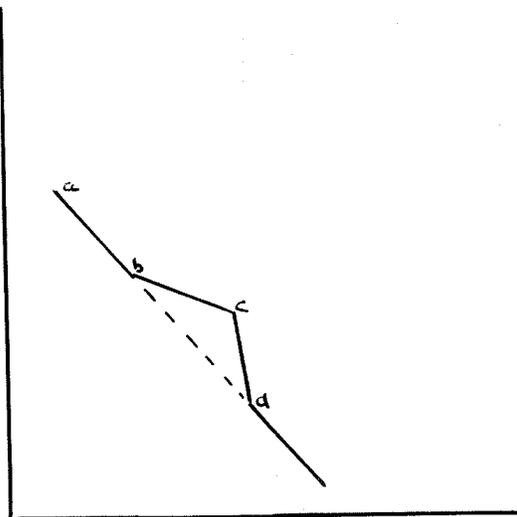


Fig. 8

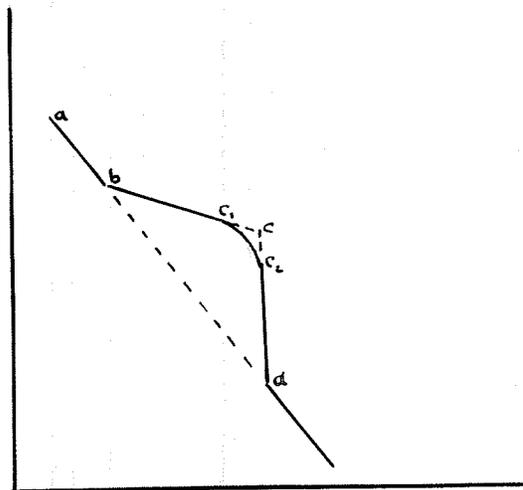


Fig. 9

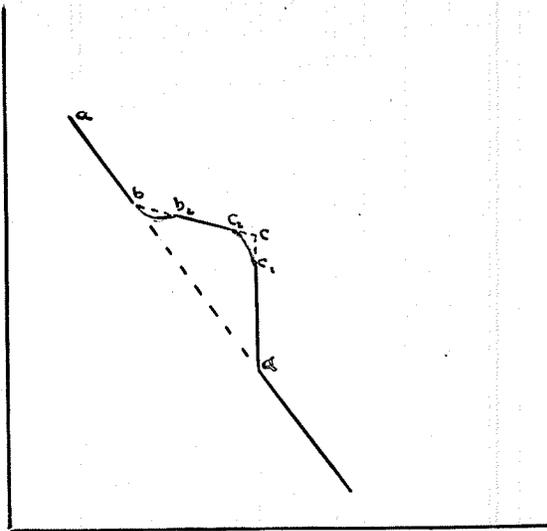


Fig. 10

Fig. 8 represents the ideal case. Along the curve from a to b the cooling is uniform but at b the first trace of solid appears. The rate of cooling is thus changed and cooling now continues along bc until the point c is reached. At c, solidification has become complete, and from this point on the cooling is very rapid until the original curve is obtained again.

The temperature of b is the temperature at which solidification commences and therefore represents a point on the liquidus, or freezing point curve of the equilibrium diagram. Similarly, the point c gives the temperature of complete solidification and therefore marks a point on the solidus. There is some difficulty in determining this latter point since it is easily distorted in one way or another. If insufficient time is given for the complete alteration of solid solution this point will tend to be too low. To overcome this, Tammann proposed the following procedure. He suggested carrying out with the same specimen cooling curves with different rates of cooling and thus a value of c would be obtained

for each case. The temperatures of these points are then plotted against the rates of cooling used and the resultant curve extrapolated to infinite rate of cooling. The value thus obtained would be the ideal value of  $c$  and therefore a true point on the solidus curve.

In actual practice the curve takes the form shown in Fig. 9. The point  $b$  is interpreted as before, i.e., the beginning of solidification, and cooling then continues along  $bc$ . This is not, however, a straight line as in the ideal diagram but instead is rounded off somewhat from  $c_1$  to  $c_2$  where there was a sharp point  $c$  before. The point of complete solidification is now represented by the point  $c_2$ . From this point the cooling follows a straight line to  $d$  and so by extrapolating this line and the straight portion  $bc_1$  until they intersect, the ideal point  $c$  is obtained.

In the cases where supercooling or unequal cooling occur, the curve is like that shown in Fig. 10. There is no longer a straight curve from  $b$  to  $c_1$  but instead there is a dip on the curve at the upper end as shown. To obtain the ideal point  $b$ , the straight portion of the curve  $b_2c_2$  is extrapolated back to intersect the curve from  $a$ , which represents the regular cooling of the mass. The point  $c$  is obtained in the manner described above.

Fig. 11 shows the form of the curve where there is a eutectic on the equilibrium diagram. At  $b$  the equilibrium line is crossed, i.e., solidification commences, and then cooling occurs as before along the curve  $bc$ . The horizontal  $cd$  represents the separation of the eutectic mixture, during which the temperature remains constant. The point  $d$  is obtained by the production of the straight lines  $cd$  and  $de$  to intersect; then the line  $cd$  gives the theoretical or ideal halt.

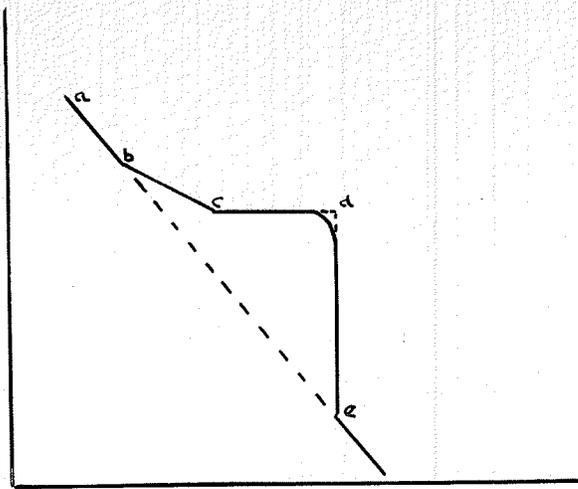


Fig. 11

Supercooling is the most common cause for the deviations found in actual practice but this phenomenon is very rare in metallography. A supercooling effect will occur if the second component does not appear at the eutectic, for the mother liquor will become unduly rich in this component and the temperature will fall below that of the true eutectic. The temperature will rise back to the eutectic temperature as soon as this component does appear, but, since it was in excess in the liquid, some of it will remain liquid after the eutectic solidification has become complete. This will continue to solidify and therefore the shoulder of the curve at d will be exaggerated.

#### Other Methods of Investigation

In addition to and, very frequently, in conjunction with the method of thermal analysis in metallographic investigation, the microscopical examination of polished surfaces of sections of alloys is used.

Certain characteristic patterns are exhibited on the surfaces of alloys which have been etched by some reagent and these depend upon the position of the freezing point of the alloy on the equilibrium curve. The type of microscopic structure which alloys will display can often be predicted if we have a knowledge of the

complete freezing point curve of the metals which form the alloys.

If we examine an alloy which has a freezing point near a summit on the freezing point curve, we find that the whole section is comprised of one substance which may or may not show very fine boundary lines marking out the separate crystals. These lines are most usually seen as three intersecting lines at the points where the crystals meet.

When either one or the other component is added to an alloy and the freezing point curve is followed down from a summit, these lines between the polygonal sections of the crystals become more and more distinct. They form a sort of tessellated pattern with an irregular polygon, generally without re-entrant angles, as the unit. Very often these polygons approach a hexagon or have somewhat rounded angles, forming what might be referred to as a blob. It is due rather to the limitation of space in which the crystals grow, than to any peculiarity of crystal structure that the hexagonal shape is assumed. As more of the component is added and we pass further down the curve, the spaces between the polygons widen and are filled with a substance which is different from that of which the polygons themselves are composed. This material between the polygons gradually increases in amount until it forms a continuous network in which the polygons, or blobs, form patterns. This pattern is sometimes one of rectangular crosses but more often consists of rows of blobs from which other rows branch, and these blobs are often oval or elongated. These rows of blobs become smaller in area as a minimum freezing point is approached and, when the substance between them is examined under a high power, it is seen to consist of a fine pattern of two substances, one of which is the same substance as the blobs. At the minimum freezing point or eutectic,

the whole alloy consists of this finer pattern which is characteristic of a eutectic alloy. When still more of one component is added and the freezing point caused to rise, we get a similar pattern to that obtained before, i.e., large blobs surrounded by a finer pattern, but this time, the blobs are seen to consist of the second substance which comprises the network. That is, the two constituents of the alloy have changed places in the structure.

To explain this characteristic structure in alloys, we consider the solid alloy as an interwoven mass of branching crystals immersed in a mother substance which did not solidify until the crystals had formed. This picture may be made somewhat clearer if we consider the following analogy. Imagine a thicket of fir trees whose branches are at right angles to their stems and whose stems are not all vertical. If a plane were taken through such a thicket at an angle to the vertical, the resulting section would show patterns similar to those described above. If the stems lay parallel to the plane of section and in it, the pattern would be one of lines at right angles to each other. If the stems were not actually in the plane we should get rows of dots and if the stems were at an angle to the plane of section, the dots would be elongated. These considerations and the fact that the rows of dots are straight, indicate that the large pattern of blobs and the related polygons are the pure substance which crystallized first and without constraint, since it was surrounded by liquid, and, therefore, they may be referred to as primary crystals. The surrounding material is the mother liquor which did not crystallize until after the first crystals had formed and so may be said to contain secondary and tertiary crystals. The marked absence of crystal form in these primary crystallized blobs is probably due to

the fact that they are what Lehmann calls "crystal skeleton". If the interstices of such crystals become filled with subordinate crystallization of the same substance, the resultant crystal will be somewhat rounded in shape. Prolonged etching may partially reveal a structure which may be that of the original crystal skeleton.

Another method which is becoming increasingly important in the investigation of metallic alloys is that of the study of alloys by means of X-rays. A great deal of valuable information as to the structure of matter in the solid state has been found by this method of crystal analysis. Von Laue was the first to discover the application of X-rays to the study of crystal structure and the present methods of investigation have all been developed from his classical experiment of the diffraction of X-rays by the crystal lattice. The reflection method, developed by W.H. and W.L. Bragg, and the powder method, due to Debye and Scherrer, are both used to determine the arrangement of structural units in the crystal lattice and also the absolute dimensions of the lattice itself. The X-ray method is of prime importance in the study of the solid phases, since changes in the solid state are demonstrated without doubt, even though the solid phase may be opaque and microcrystalline in structure. The identification of these changes, before the X-ray method was developed, was based on the fact that many of the physical properties change discontinuously, or change differently with respect to temperature, at the transition point. However, although in many cases these proved satisfactory, in other cases the method failed, due to the fact that the magnitude of the discontinuous change was too small to be recognized or because the system remained metastable. This

latter behavior is very frequently found in the case of allotropic modifications of metals.

But, as long as they have different space lattices, crystalline solids are considered to exist as separate phases, no matter how small the difference between their physical properties may be. This difference in space lattice is the most fundamental of all properties and, in substances whose crystal forms are frequently opaque and distorted, this property becomes very important in the identification of the separate solid phases.

These three methods of investigation, the thermal, the microscopical and the X-ray, are of primary importance in the study of metallography. If they are suitably applied and combined, these three methods will reveal the principal facts concerning the equilibrium of two components. Other methods may be valuable in certain instances and sometimes may be indispensable but they must be regarded as subsidiary to these three in the range of their applicability. The following are the most important of these subsidiary methods:

- (1) The electrical conductivity
- (2) The magnetic susceptibility
- (3) The electrode potential
- (4) The heat of mixture of the molten metals
- (5) The intensity of reflection of light
- (6) The atomic heats of the components and the alloy
- (7) The specific volume of alloy and components.

PREVIOUS INVESTIGATIONS

### Previous Investigations

The first reference to the alloys of aluminium and lead was found in a paper by A. Wright<sup>3</sup>, who stated that aluminium and lead form two layers when melted together. Analytical determinations of the two layers after they had been kept at a temperature of from 750 - 850°C for about eight hours showed that the aluminium-rich upper layer contained 1.91% lead and the lower lead-rich layer contained 0.07% aluminium. Somewhat later, Pecheux<sup>4</sup> claimed to have obtained three layers with these metals. He melted the metals, mixed them by stirring and then poured them into a mold. He stated that in alloys with more than 10% lead there were three layers formed, an alloy of lead and aluminium between layers of pure lead and pure aluminium. Analysis of this middle layer gave from 3 - 10% lead. Alloys of 2, 5 and 7% lead were stated to have given three successful alloys without liquation, whose densities decreased with the decrease in the amount of lead. Their fusion points were near that of aluminium and rose from that of the alloy with 7% to that of the one with 2% lead. His work, however, seems to be discounted by later discoveries including the results obtained by this writer. Gwyer<sup>5</sup>, also, conducted an investigation of the alloys of lead and aluminium and found that there were two halts on the cooling curves, one at the melting point of pure aluminium and the other at the melting point of pure lead, corresponding to the formation of two almost completely insoluble liquid layers. He states, however, that alloys with 1, 2, 3 and 5% lead showed primary separated crystals of aluminium surrounded with secondarily

formed lead, indicating that crystallization had begun with an emulsion of lead in aluminium. That is, in these alloys the formation of two layers had not taken place before the beginning of crystallization. This seems incompatible with his identification of the first halt point with the freezing point of pure aluminium. Two layers had, however, formed in alloys containing from 5 - 99.5% lead since the cold regulus showed two layers, of pure lead and aluminium with a slight lead content which was detectable microscopically. More recently, Claus<sup>6</sup> has stated that aluminium and lead are slightly soluble in each other in the liquid state, and also that up to about 5% lead is taken up by the aluminium in, however, colloidal, not true solution. The latest investigation is that of Hansen and Blumenthal<sup>7</sup>, who investigated the system by taking cooling curves. They found a depression of  $1.5^{\circ} \pm 0.5^{\circ}$  in the freezing point of aluminium produced in alloys with 3, 5, 7 and 24% lead. They noticed no similar effect produced on the freezing point of lead by the addition of aluminium.

**EXPERIMENTAL**

### Experimental

(1) The apparatus and its calibration:

The complete set up of the apparatus is shown in the accompanying Plates I and II and Fig. 13.

The furnace used for the melting of the alloys, and in which the cooling curves were taken, was of the electrical resistance type; it was capable of maintaining a temperature of 950°C for a long period of time, while a temperature of 1000°C could be reached. In the determinations of the cooling curves, the furnace was cooled gradually, in accordance with Plato's method of cooling, by means of two rheostats connected in series with it; these were calibrated so that when the slider was moved along one division per minute, the furnace cooled at the rate of about five degrees per minute. Through the cover of the furnace two holes were made to accommodate the thermocouples; these holes were made large enough to permit of free movement of the thermocouple casings by means of which the alloys were stirred.

The thermocouples used in the temperature measurements in the thermal analysis were of platinum : platinum-rhodium (10% rhodium). The wires were kept separate by inserting them in a double-bored sillimanite tubing which, in turn, was enclosed in another sillimanite tube to protect the junctions from the action of the molten metals. One thermocouple was inserted in the molten alloy and connected through a sensitive galvanometer to a potentiometer. The temperatures of the alloys were thus measured by means of readings on the potentiometer. However, the temperature, as obtained from the reading on the potentiometer

Diagram of Circuit

- P - Potentiometer
- S - Standard cell
- G<sub>1</sub> - Fine galvanometer
- G<sub>2</sub> - Coarse galvanometer
- R - Resistance
- B<sub>1</sub> - Battery
- B<sub>2</sub> - "
- K<sub>1</sub> - Tapping key
- K<sub>2</sub> - Switch
- K<sub>3</sub> - Double switch
- K<sub>4</sub> - "

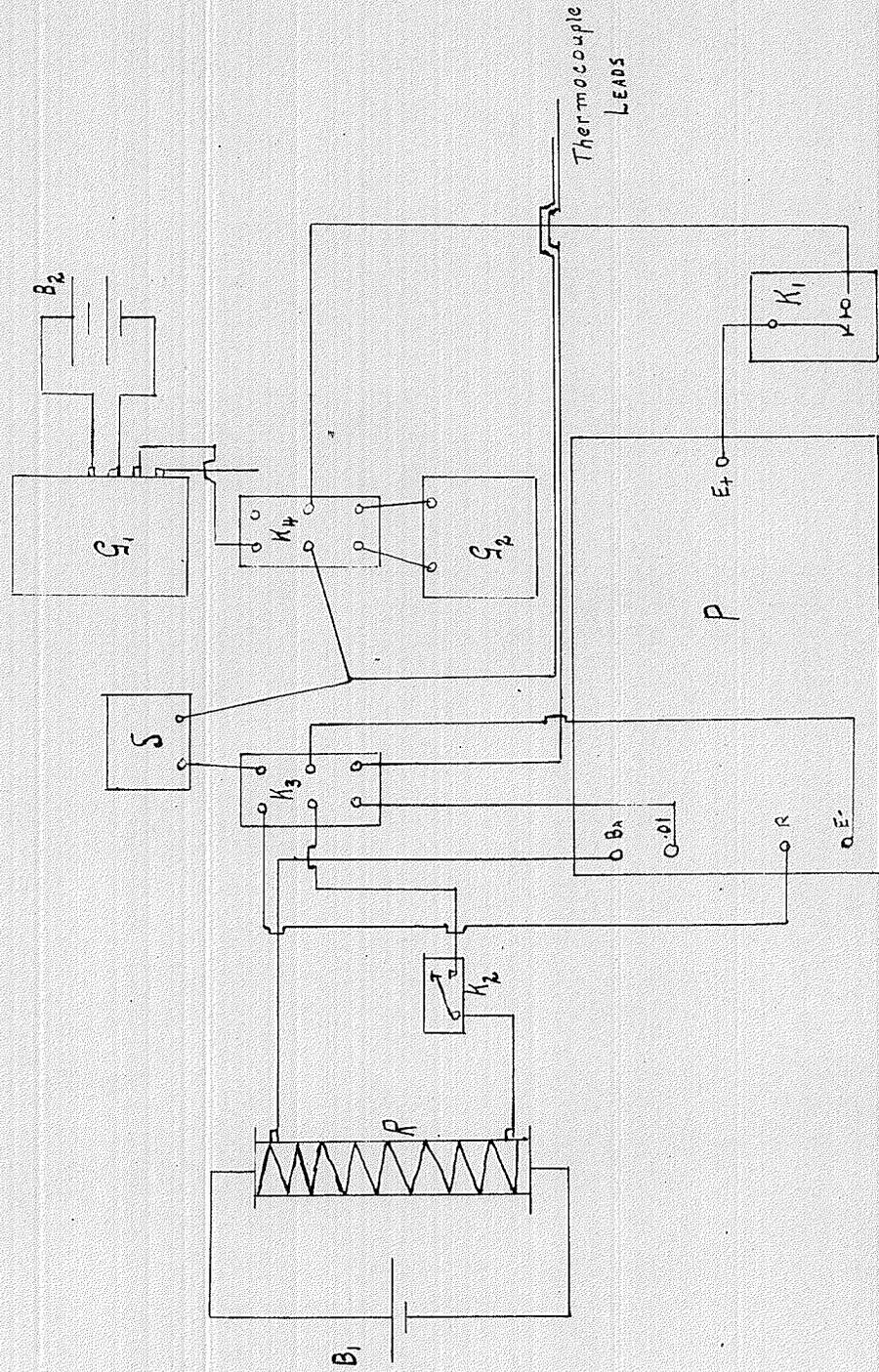
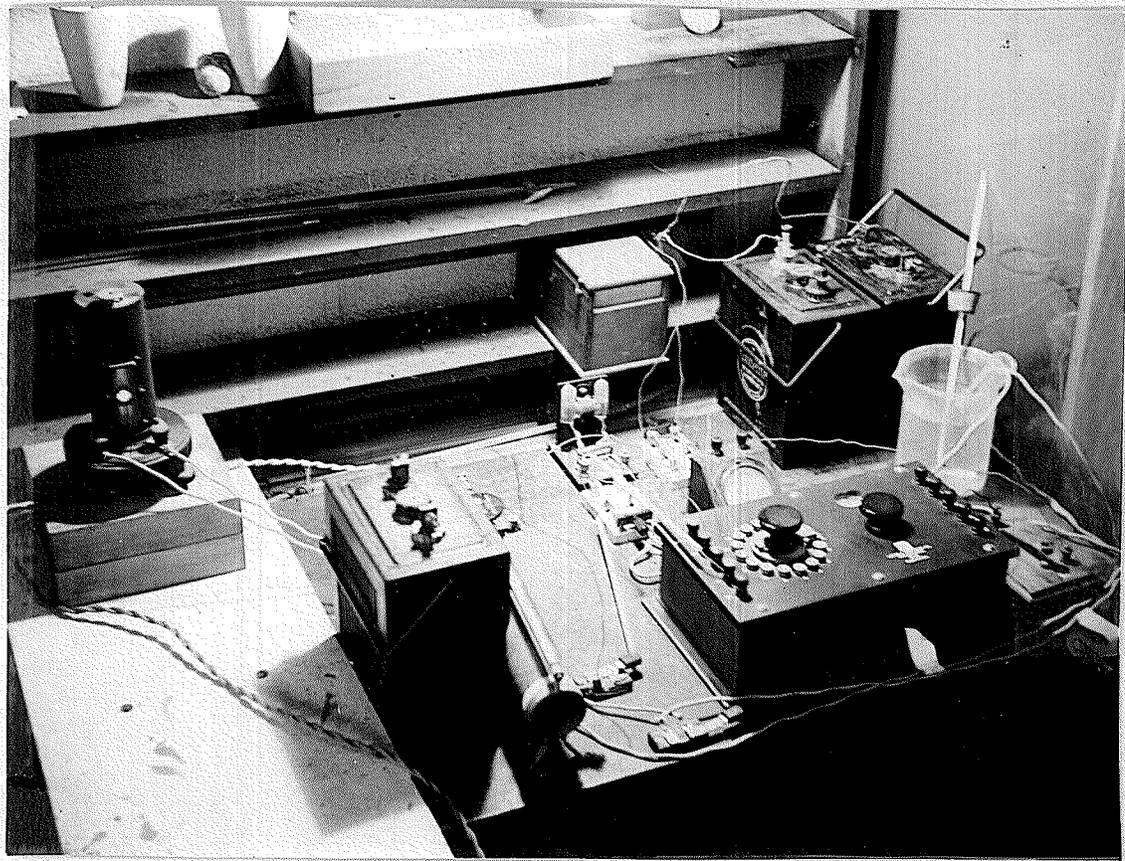


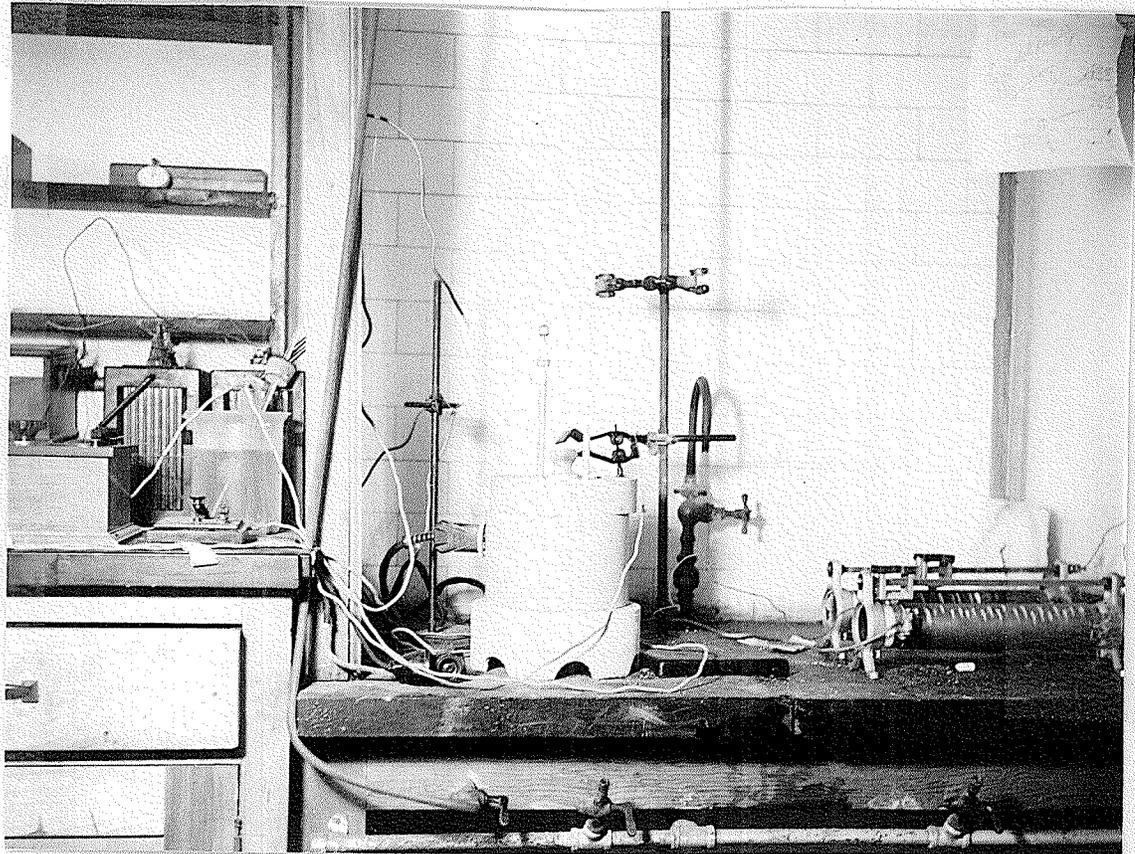
FIG. 13



Plate I



A.



B.

does not represent the actual temperature of the alloy, since the formulae derived for the e. m. f. of a thermocouple are based on the assumption that the cold junction, i. e., the points at which the wires of the couple make contact with the leads, are at  $0^{\circ}\text{C}$ . Thus, it is necessary to add to the temperature obtained from the potentiometer readings, the temperature that the thermocouple leads are actually at, in order to obtain the true temperature of the alloy. To get the temperature of the leads, one was passed through a test tube which was contained in a beaker of water at room temperature; a mercury thermometer in this beaker gave the temperature of the cold junction which must be added. The potentiometer used was capable of measuring  $10^{-6}$  volts and thus the sensitivity was found to be equivalent to a change in temperature of  $0.1^{\circ}\text{C}$ . The second thermocouple was placed in a neutral body in the furnace and was connected differentially with the first thermocouple through a delicate reflecting galvanometer. This is a separate circuit from that through which the first thermocouple was connected with the potentiometer. The neutral body that was used consisted of a copper cylinder of approximately the same thermal capacity as the alloys; a hole was bored in its center, about two-thirds of its depth, in which the thermocouple was inserted. This neutral body was employed in accordance with a method proposed by Sykes<sup>2</sup> in determining the temperature difference between the alloy and the enclosure. When both the alloy and the neutral body are cooling at a normal rate, the temperature difference between them remains practically constant or, in any instance, changes at a constant rate. However, when some thermal effect takes place in the alloy,

its rate of cooling is changed and, since the neutral body cools at the same rate as before, there will be a sharp change in the temperature difference between them. This shows up in the reflecting galvanometer as a sudden, sharply-defined deviation from the original temperature difference. Thermal effects can be measured in this way with much greater sensitivity than by taking only the direct cooling curve of the alloy.

To calibrate the thermocouple, several pure metals whose melting points were known were used, namely, tin -  $231.9^{\circ}\text{C}$ ; lead -  $327.3^{\circ}$ ; zinc -  $419.5^{\circ}\text{C}$ ; aluminium -  $658.7^{\circ}\text{C}$ . A calibration curve was plotted of these temperatures against the potentiometric readings obtained for them. The calibration was checked at intervals throughout the investigation by means of pure lead and pure aluminium. The differentially connected thermocouples were calibrated in the following manner. The couples were each placed in a bath of water, one of which was kept at room temperature. The other bath was gradually heated and, at intervals of one minute, readings were taken of the temperature of each bath and of the displacement on the scale of the reflecting galvanometer. In this manner it was found that a difference in temperature of  $1^{\circ}\text{C}$  between the thermocouple junctions was represented by a displacement of 3.6 mm. in the eyepiece.

## (2) General Method of Procedure:

The lead used in the investigation was pure assay lead. The aluminium which was used in the first part of the work was commercial aluminium with a purity of 99.2%. An analysis of this aluminium gave the following results:

Si .....	0.25%
Fe .....	0.58%
Al .....	remainder

However, after the investigation had been nearly completed, there was obtained some aluminium with a purity of 99.95%, and the salient points of the diagram were checked with it. The analysis of this aluminium was given as follows:

Si .....	0.007%
Fe .....	0.01%
Cu .....	0.029%
Ti .....	0.001%
Al .....	balance

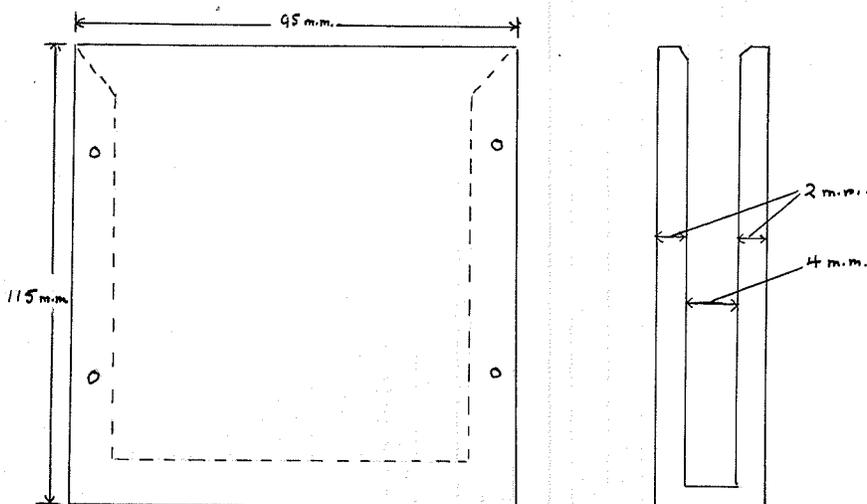
The total weight of the alloys prepared was in most cases fifty grams, although in some cases, in particular those in which equal volumes of lead and aluminium were mixed, a greater weight was taken. The alloys were prepared by first melting the aluminium in a crucible and then adding the appropriate amount of lead and stirring. The most satisfactory type of crucible was found to be an alundum crucible; glazed porcelain crucibles were also employed, but these were found to crack readily when the alloys were cooled. It was also found difficult to remove the alloys from these porcelain crucibles since the metals seemed to have a corrosive effect on them which caused a close adherence of the alloy and crucible. The alundum crucibles did not crack nearly so readily, nor did the metals seem to attack them as strongly. After the alloys were melted, the thermocouple was inserted and the temperature of the furnace was raised above the melting point of the alloy and kept constant at this point for a period of time. The furnace was then cooled by the method described previously

and readings were taken simultaneously on the potentiometer and reflecting galvanometer every minute. The direct cooling curve for the alloy and the curve for the temperature difference between the alloy and the enclosure were then plotted on the same graph. The instant at which the solidification of the alloy begins, shows up as a sudden break on the temperature difference curve; the temperature of the alloy at this instant is obtained from the direct cooling curve and this temperature taken as the freezing point of the alloy.

The battery gradually ran down in the course of the determinations and so it was found necessary to balance it against a standard cell before each determination. This was accomplished by means of a variable resistance connected to the battery.

In order to define the mutual solubility curve of lead and aluminium, the compositions of the two layers at temperatures above the melting point of aluminium had to be found. To accomplish this, mixtures of equal volumes of lead and aluminium were raised to temperatures at which the upper layer was molten, and then quenched, and each layer analysed. The quenching of the alloys was done by plunging the crucibles containing them into a large beaker of ice water. The transference of the crucible from the furnace to the beaker had to be made as rapidly as possible, so that the alloy would not cool off too much before quenching. This method of quenching was not found very satisfactory, however, since the liberation of steam during the quenching was quite violent and sometimes caused a certain mixing of the two layers. A very much better method of quenching was found in that described by Ruer and Birens. This consisted of pouring

the molten alloys into a thin steel mold. This mold, which is shown diagrammatically below, consisted of three thin steel plates bolted together with the center one cut away to form a narrow mold.



These plates are held together by nuts and bolts which can be loosened in order to facilitate the removal of the cast alloy. In the quenching carried out in this investigation, the mold was covered with a wet cloth which served to hasten the cooling. As before, the alloys were removed from the furnace and poured into the mold as quickly as possible.

Each alloy prepared, after cooling curves had been taken on it, was cut, analysed and examined microscopically as described below.

### (3) Chemical Analysis:

Samples of from 0.5 to 1.0 grams in weight were taken from the alloys by boring and were dissolved in nitric acid of about 50% strength. The aluminium was first precipitated from the solution as basic acetate, filtered off, redissolved in hot dilute nitric acid and finally precipitated as hydroxide.

This precipitate was ignited and weighed as  $\text{Al}_2\text{O}_3$  and the percentage of aluminium determined from it. The lead was precipitated as chromate from the combined filtrates which were made strongly acid with acetic acid and filtered through a Gooch crucible. The precipitate was dried at  $120^\circ\text{C}$  for two hours and then weighed as  $\text{PbCrO}_4$  and the percentage of lead calculated from it.

(4) Microscopic Examination:

The alloys to be examined were cut through vertically by means of a hacksaw. The roughness left by the saw was removed with files, the surface being made as smooth as possible with them. The alloy was then taken on to a coarse emery paper and polished in one direction until the scratches left by the file had been removed. In the polishing, the emery paper was placed on a glass tile for support and the specimen was rubbed backwards and forwards with a slight pressure, care being taken to keep the specimen flat on the surface. The polishing was then continued on emery papers of successively finer grades, the specimen being turned through an angle of  $90^\circ$  so that the new scratches crossed the old ones at right angles. The specimen was polished on each paper until the scratches left by the previous one had been removed. When the alloy was removed from the last paper, no scratches were visible to the naked eye. For the final polishing, the alloy was taken on to a revolving wheel over which was stretched a felt cloth. The polishing powder used was levigated alumina which was applied to the wheel

as a suspension in water. The final surface obtained showed no scratches when examined under the microscope.

For examination under the microscope, the specimens were mounted with plasticine on glass slides by means of a mounting stand. The microscope used in the examination of the specimens was of the ordinary metallographic type.

In order to bring out the structure of the alloys more clearly, various etching reagents were used. The etching reagents tried in the course of the investigation were the following: 10% solution of nitric acid, 20% solution of sodium hydroxide, bromine water, 20% solution of sodium carbonate. The most effective of these was found to be the nitric acid solution. In the process of etching, the specimens were placed in the solution with the polished surface uppermost and allowed to remain there for from five to ten minutes, depending on the aluminium content of the alloy; those with high aluminium content required the longest period of treatment. The specimens were then removed from the etching solution, rinsed off first in distilled water and then in alcohol, and finally dried.

Photomicrographs were taken of the etched surfaces of various alloys by means of a Bausch and Lomb photomicrographic unit, consisting of a simple box camera mounted on a vertical support. To prevent streaking of the film by stray light from the illuminating source, a light-tight connector was placed between the eyepiece of the microscope and the aperture of the camera. The section to be photographed was located, the camera swung into place over the microscope, and the final focussing obtained by means of a piece of frosted film placed in the back

of the camera. The sensitized film was then substituted and the exposure made.

(5) Hardness Determinations:

The hardness of the alloys was determined by means of a Brinell hardness-testing machine. The specimen was placed on a plate, which was adjusted until the surface was horizontal, and an indentation was made by means of a steel ball sustained under a given load for a given period of time. In these determinations the steel ball used had a diameter of 10 mm. and was kept under a load of 100 kilograms for 30 seconds. The usual load employed in testing the hardness of metals is 500 or 3000 kilograms, but with alloys having a high percentage of lead this load was found to be too great. Measurements of the indentation made by the steel ball were taken by means of a telescope having a scale in the eyepiece. Two measurements at right angles were taken on each indentation and the mean of these was considered to be the true diameter. Three determinations were made on each alloy tested. The degree of hardness of the alloy was given by the Brinell number which is calculated from the following formula:

$$H = \frac{P}{\frac{\pi D}{2} (D^2 - \sqrt{D^2 - d^2})}$$

where,

H = Brinell number

P = Load applied (in kilograms)

D = Diameter of the steel ball (in mm.)

d = Diameter of the indentation (in mm.)

## RESULTS AND CONCLUSIONS

### Discussion of Results

The thermal analysis of the alloys of aluminium and lead showed that, on the cooling curves taken for mixtures containing from 5 - 80% aluminium by weight, two distinct halts could always be observed. With alloys containing less aluminium or more aluminium than this, there was only one halt, the temperature of this being dependent on the particular metal forming the main constituent. The temperature of the higher halt was found to be slightly below the melting point of pure aluminium, and that of the lower halt to be just below the melting point of pure lead. The temperatures of the halts which were found for the different alloys are given in the following table:

Composit. of alloy Weight % Al	Temp. of the lower halt	Temp. of the upper halt
0	327.3°	-
5	325.75°	652.15°
10	322.75°	657.1°
20	323.9°	654.0°
40	323.5°	654.75°
80	-	654.65°
99	-	653.9°
100	-	658.7°

The depressions of the freezing points of both pure metals are very slight and, moreover, there is some variation in the

halt temperatures. Therefore, a check was made on the two halt points by substituting for the neutral body, crucibles of aluminium and lead successively and conducting the thermal analysis as before on an alloy containing 50% aluminium, i.e., cooling curves were taken. Here, there is also a halt occurring in the cooling curve of the neutral body and the temperature difference between the alloy and the neutral body will remain constant while the neutral body is solidifying. This temperature difference therefore gives the amount of the depression of the freezing point of the pure metal. The higher halt was checked by substituting pure aluminium for the neutral body, and the lower halt by substitution of pure lead. In this manner, the temperature of the higher halt was found to be  $657.1^{\circ}\text{C}$ , taking the freezing point of the pure aluminium as  $658.7^{\circ}\text{C}$ , and that of the lower halt,  $325.1^{\circ}\text{C}$ , taking the freezing point of pure lead as  $327.3^{\circ}\text{C}$ .

The results of the analyses of the various alloys are given in the following table:

Table II

Comp. of alloy	%age Pb in upper layer	%age Al in lower layer
% Al		
5	-	0.187
10	9.96	0.262
20	8.95	0.078
40	0.88	-
80	3.88	-

The analyses of the lower layers gives the composition

of the eutectic; this procedure would not be permissible, however, if the equilibrium curve had any appreciable curvature in this region. Thus, the composition resulted as 0.15% aluminium and 99.85% lead.

The analyses of the upper layers of the alloys showed that the amount of lead contained in them depended on the rapidity with which the alloy had been cooled, as much as 9.96% being found in one. The possibility of a peritectic point, with compound formation, could not be excluded, however, and so one alloy was kept at a temperature of 500°C for twelve hours, at which temperature the upper layer of the alloy was solid and the lower, liquid. Analysis of the upper layer of this alloy showed that the lead content had fallen to 3.88%. The process was repeated with another alloy, with the time of heat treatment being twenty hours at the same temperature as before, and the lead content was found to have been reduced to 0.88%. It was concluded, therefore, that a lead content of more than 1% did not represent an equilibrium condition but was mechanically held in the form of a colloidal dispersion. The density of such a dispersion containing 9.96% lead was determined to be,  $d_{40}^{25.1} = 2.88$ , while the mixture rule requires 2.90.

The composition of the point D on the diagram could not be determined by direct analysis and the branch DE is too short to permit of accurate determination by thermal analysis, but, since the temperature of D was known accurately, the point was therefore located by the intersection of the mutual solubility curve with the temperature horizontal through D. To determine the mutual solubility curve, mixtures of equal volumes of lead

and aluminium were quenched from definite temperatures above the melting point of pure aluminium and then analysed in order to determine the compositions of these points. The mixtures were raised, without previous heating, to the desired temperatures and kept there for from one to two hours. They were then quenched and each layer analysed. The mutual solubility curve was plotted from the values obtained in this way and is shown in the equilibrium diagram (Fig. 12). On the lead side of the diagram the curve ascends very steeply but, on the aluminium side, the slope of the curve is somewhat gentler, ascending from a percentage of lead of 1.16% at 672°C to a percentage of 1.7% at 800°C. The projection of this mutual solubility curve through the temperature horizontal of D gives the composition of the point D, which was found to be 1.10% lead.

The question of whether the phase separating along the branch DE of the curve was pure aluminium, or a solid solution of lead in aluminium, was settled by heating an alloy containing 0.7% lead for 48 hours at 500°C. Analysis of this alloy then showed that it contained only 0.18% lead. Therefore, the upper limit to the solubility of solid lead in solid aluminium must have this value.

The results that are detailed above were obtained by the use of the commercial aluminium which is only 99.2% pure. But after this work had been completed, some aluminium with a purity of 99.95% was obtained from the Aluminium Company of America. It was thought that the impurities in the commercial aluminium might have had some effect on the results obtained and so the salient points on the diagram were checked using the purer aluminium.

# Equilibrium Diagram of Al - Pb

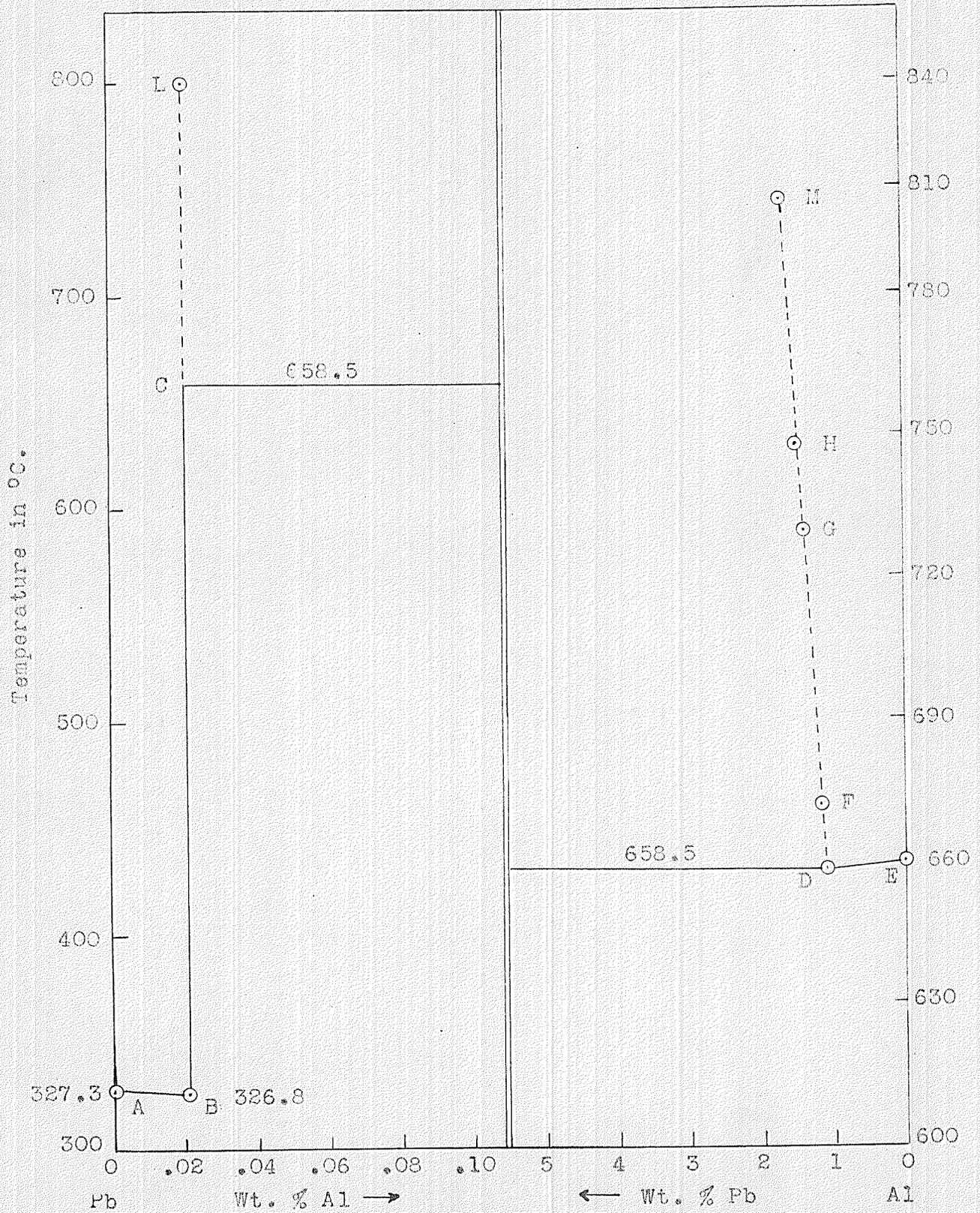


Fig. 12

In checking the depression caused by aluminium in the freezing point of lead, a mercurial thermometer was used in the measurement of the temperatures. A number of methods of finding the freezing point depression were tried, including the use of Rast's electrically heated melting point determination apparatus. In the investigation by this method, capillary tubes into which had been introduced pure lead and lead with a few percent of aluminium were placed on either side of the thermometer in the apparatus and the temperature was raised very slowly. The tubes were observed very carefully all the time in order to see whether the addition of aluminium caused a depression in the freezing point of lead and how much this depression was. The method was unsuccessful, however, for it was found impossible to melt either of the metals within the temperature range of the thermometer. The method that was found the most satisfactory was that of inserting the thermometer directly into the molten metal and taking a cooling curve. The thermometer bulb was protected by enclosing it in a glass tube; this tube was filled with mercury in order to ensure good thermal contact. The metal was contained in large pyrex test tubes, melted over a burner, and then put into a hot oil bath which served to slow the rate of cooling somewhat. Readings of the temperature were taken every minute until the metal had solidified and the cooling curve was plotted from them. The horizontal portion of the curve was taken as the freezing point of the metal. Cooling curves were first taken on a sample of pure lead, then sufficient aluminium was added to give an excess over the amount required in the eutectic and other curves were taken, and finally, the alloy was analysed. By this method it was found that a depression of

$0.5^{\circ} \pm 0.1^{\circ}$  was produced. The composition of the eutectic was found to be 0.025% aluminium, 99.975% lead. The difference in the percentage of aluminium between these results and those obtained before is, in all probability, due to the relatively large percentage of iron which occurred as impurity in the commercial aluminium used in the first case. The lower layer of lead would form a sort of sink in which all this iron would collect and the results of the analysis for aluminium would include this iron and would therefore be much greater than it should be.

To check the mutual solubility curve on the lead side of the diagram, an alloy containing about 0.5% aluminium was heated to  $800^{\circ}\text{C}$ , kept at that temperature for a few minutes, and then quenched. Analysis then showed the composition to be 0.017% aluminium. This value represents a somewhat lower value than that obtained for the eutectic composition, but the difference represents an error which is beyond the limits of experimental accuracy. Therefore, the two values were averaged and the mean value plotted for both points on the equilibrium diagram.

A check was also made on points on the aluminium side of the diagram. The melting point of the pure aluminium was determined and found to be slightly higher than that of the commercial aluminium. Thus, the value of  $660^{\circ}\text{C}$ , which is given by Hansen as the melting point of aluminium, was taken rather than the value  $658.7^{\circ}\text{C}$  which was stated before. 3% lead was added to the aluminium and a cooling curve was taken on this alloy, using as the neutral body a crucible containing pure aluminium, as was done before. In this manner, the depression caused by lead in the freezing point of aluminium was found to be  $1.5^{\circ} \pm 0.1^{\circ}$ . Therefore the temperature of the horizontal through D in the

equilibrium diagram now becomes  $658.5^{\circ}\text{C} \pm 0.1^{\circ}$ .

To check the solubility curve on this side of the diagram, an alloy of aluminium containing an excess of lead was heated at a temperature of  $748^{\circ}\text{C}$  for about sixteen hours and then cooled and analysed. The results of the analysis showed that the difference in purity of the aluminium used had little or no effect on these points. Thus, the composition of the point D remained as 1.10% lead, 98.9% aluminium.

#### Summary of Equilibrium Data:

The equilibrium diagram which is shown in Fig. 12 was constructed from the following data:

<u>Point (see diagram)</u>	<u>Composition</u>	<u>Temperature</u>
A	100% Pb	$327.3^{\circ}\text{C}$
B (eutectic)	0.021% Al	$326.8^{\circ}$
D (interpolated)	1.10% Pb	$658.5^{\circ}$
E	100% Al	$660.0^{\circ}$
F	1.16% Pb	$672^{\circ}$
G	1.40% Pb	$730^{\circ}$
H	1.5% Pb	$748^{\circ}$
L	0.021% Al	$800^{\circ}$
M	1.70% Pb	$800^{\circ}$

It was thought that the Raoult - van't Hoff relation might apply here, since the mutual solubilities of the aluminium and lead are so small; therefore, approximate agreement between the calculated freezing point depressions and the values found experimentally might be expected.

The van't Hoff formula states that,

$$K = \frac{0.02 \times T^2}{l}$$

where K is the freezing point constant, T, the absolute temperature of the freezing point and l, the heat of fusion.

Therefore, we have for the two metals,

$$\begin{aligned} K_{Pb} &= \frac{.02 \times (327.3 + 273)^2}{5.86} \\ &= \underline{\underline{1230.}} \end{aligned}$$

$$\begin{aligned} K_{Al} &= \frac{.02 \times (660 + 273)^2}{76.8} \\ &= \underline{\underline{227.}} \end{aligned}$$

Assuming that the dissolved metals are in the atomic condition we have the following results:

	$T_{obs.}$	$T_{calc.}$
Pb as solvent	0.5°	0.9°
Al as solvent	1.5°	1.2°

Thus it is apparent that the calculated values agree closely with the depressions actually found.

The microscopical examination of the alloys did not reveal anything of very great importance. The pure metals themselves, however, presented characteristic appearances. When etched with nitric acid, lead showed a crystalline surface; the photomicrograph of pure lead (Plate II) does not show this

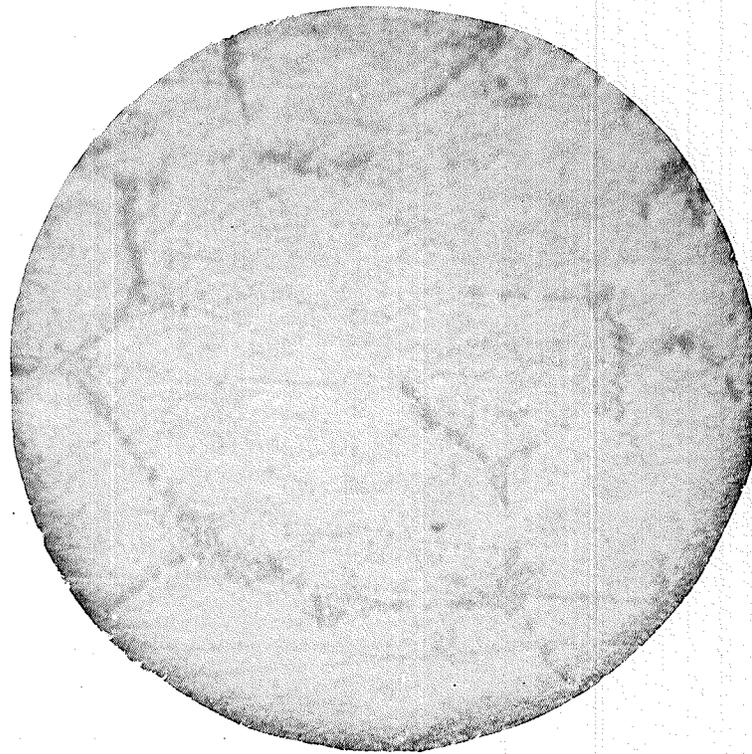
very clearly since it was found impossible to get the whole surface in focus in the photograph. The surface of pure aluminium shows a characteristic structure consisting of grains with a roughly hexagonal or polygonal outline. The polygonal outlines evidently represent a fairly coarsely-crystalline state. The eutectic structure was not distinguishable since the percentage of aluminium in it is so very small. In the upper layers of alloys which contained a dispersion of lead, the characteristic structure of aluminium was still visible but there seemed to be some heterogeneity along the grain boundaries which is, presumably, lead. All the photomicrographs were taken of polished surfaces which had been etched with a nitric acid solution, with the exception of Plate IV, A; the etching reagent used in this case was a 20% solution of sodium carbonate.

The Brinell numbers that were found for the various alloys tested are given in the table below:

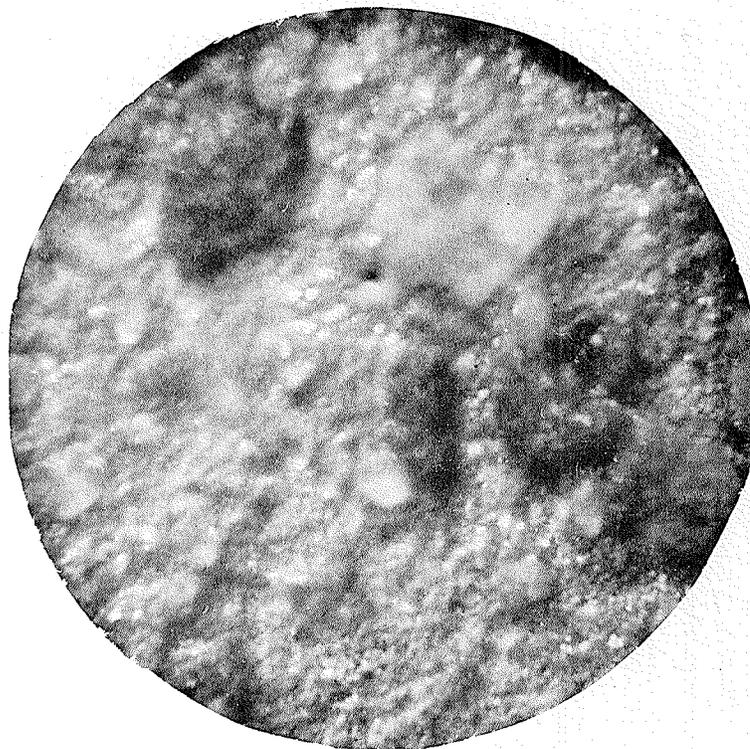
Table III

% age lead in alloy	Diam. of indentation	Brinell No.
0 (commercial Al 99.2%)	2.8 mm.	15.9
0 (99.90% Al)	3.05 mm.	13.3
0 (99.95% Al)	3.45 mm.	10.36
1.67% (in pure Al)	2.99 mm.	13.8
0.7% (in pure Al)	2.72 mm.	16.7
9.96% (in commercial Al)	3.01 mm.	13.7
0.18% (in commercial Al)	2.77 mm.	16.3
100%	5.25 mm.	4.24

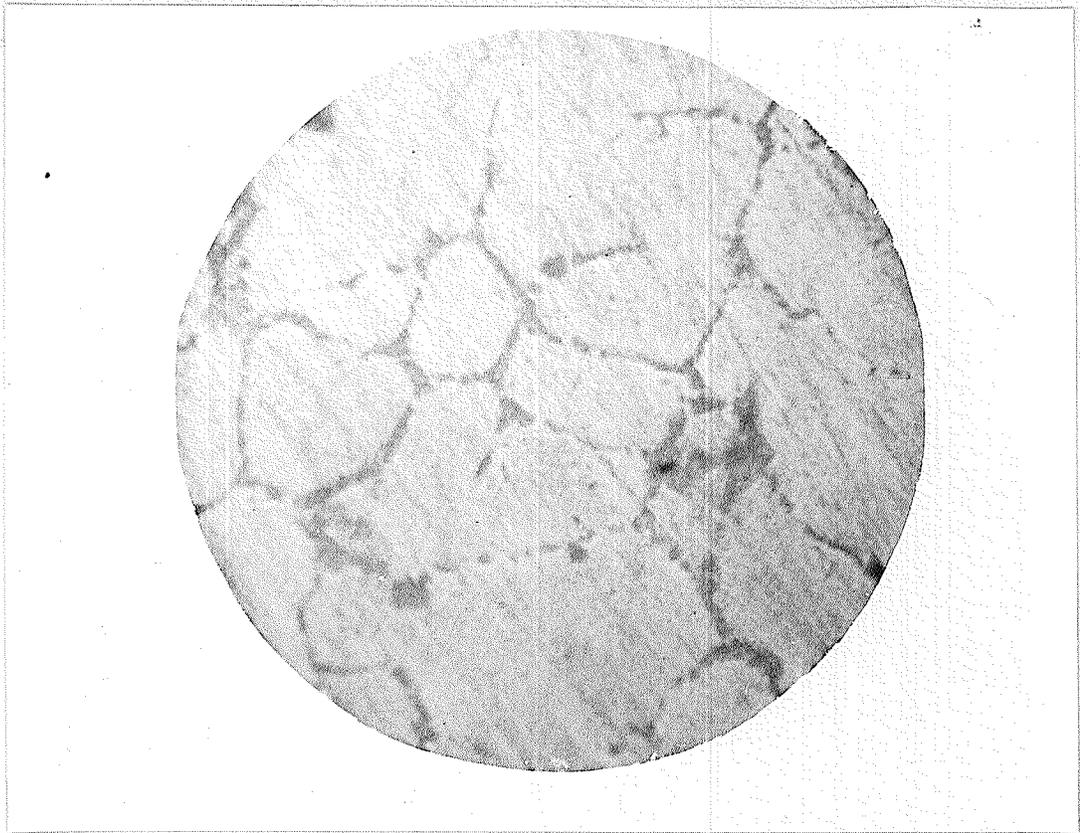
From the values given above, it appears that the commercial aluminium is considerably harder than the pure aluminium. Addition of lead seems first to make the aluminium hard and then to cause a softening effect. This is due very likely to the manner in which the lead is taken up by the aluminium.



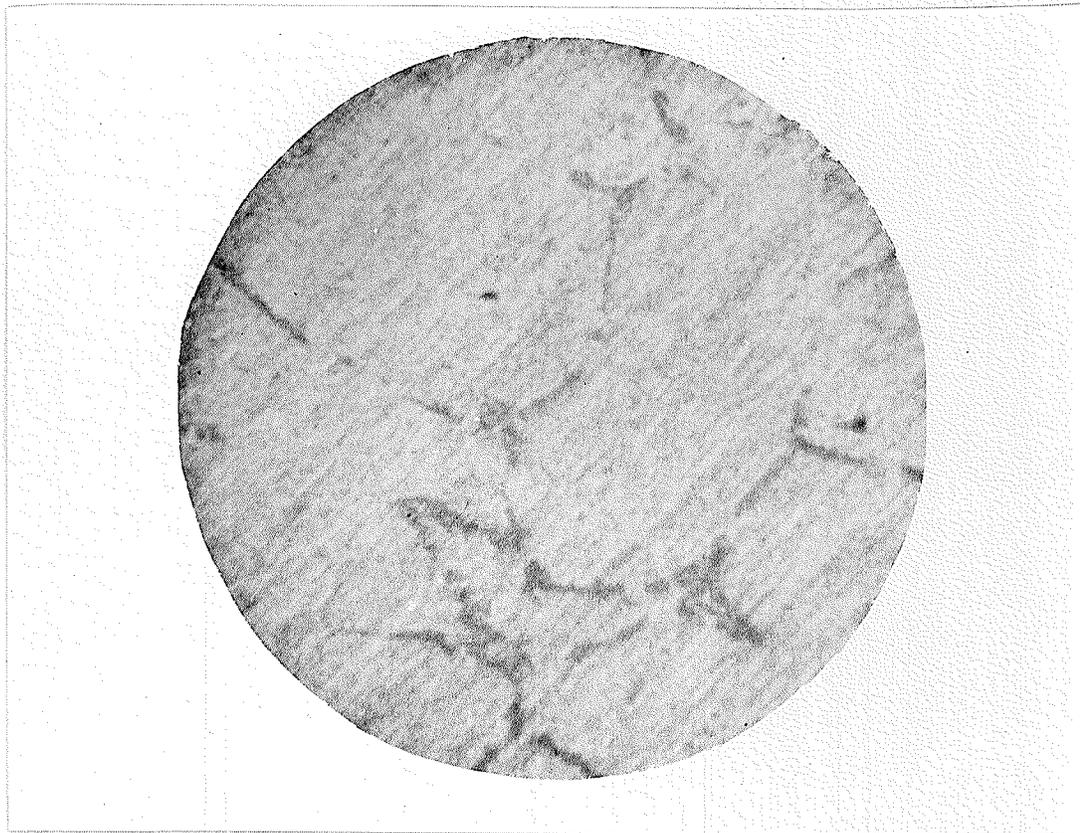
A. Pure aluminium x200



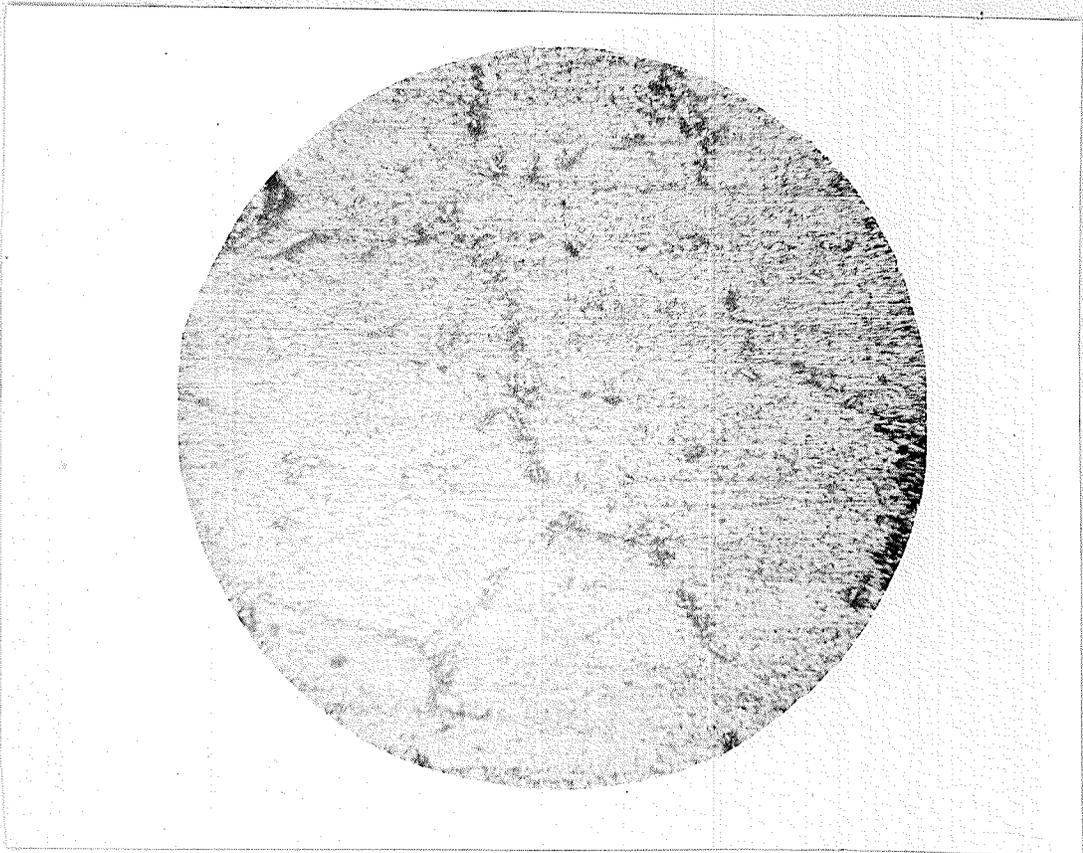
B. Pure lead x200



A. Aluminium with dispersed lead x200



B. Aluminium with 1% lead x200



A. Heat-treated Al-rich layer x200



B. Eutectic x200

### Conclusions

An investigation of the alloys of aluminium and lead has been carried out and the following are the main points that were established:

(1) The equilibrium diagram of the system aluminium - lead exhibits two invariant points. One of these points is a eutectic at a temperature of  $326.8^{\circ}\text{C}$ , corresponding to 0.021% aluminium. The other is the equilibrium point of the two liquid layers and solid aluminium, and occurs at a temperature of  $658.5^{\circ}\text{C}$  and a composition of 98.9% aluminium.

(2) The mutual solubility of liquid lead and liquid aluminium is small below  $800^{\circ}$ , but, presumably, it increases more rapidly above this temperature.

(3) Liquid aluminium can take up as much as 10% lead in the form of an emulsion, or possibly colloidal suspension.

(4) Aluminium and lead are mutually insoluble in the solid state.

(5) The addition of lead to aluminium first hardens the aluminium and then causes a softening effect.

In conclusion, the writer wishes to express his appreciation to the Departments of Geology, Engineering and Zoology for the courtesy shown him in allowing him the use of certain apparatus.

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