

A STUDY OF THE ALLOYS OF  
SILVER - ALUMINIUM - LEAD

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Being a thesis presented to  
the Committee on Post-Graduate  
Studies in partial fulfillment  
of the requirements for the  
degree of Master of Science.

April, 1940.

University of Manitoba

To DR. A. N. CAMPBELL  
for his invaluable guidance and  
advice throughout the course of  
this research, the thanks of the  
writer are most gratefully offered.

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## INTRODUCTION

## Historical Introduction

The study of metallic alloys is becoming increasingly more important due to the varied demands of industry for alloys possessing definite properties. There are few metals which possess, in the pure state, properties which make them suitable for industrial use but when these are alloyed with one or more other metals, the majority of them have numerous applications. Many metals which can be employed alone are frequently alloyed with another metal in order to modify any undesirable characteristics. Thus gold and silver, which are quite expensive, are alloyed with copper in order to reduce the price of objects in which these two metals are used and at the same time the resulting alloy is harder, thus giving a longer life to the object. Again, there are not very many elementary metals but by alloying them with one another an infinite number of new metals may be produced which will give the qualities required for any specified application.

The earliest studies of metallic alloys are of little value now but their importance lies in the fact that they established that the chemical constitution of an alloy determines the chemical, physical and mechanical properties. This means that the useful qualities of an alloy depend on the nature and proportion of the compounds which they form together as well as their various isomorphous mixtures and allotropic states.

The study of this relation of the internal structure to the physical, chemical and mechanical properties is known as metallography. Since the internal structure of the solid

metal or alloy is determined by the physical and chemical conditions under which it is formed, it is evident that metallography is a branch of physical chemistry and is a study of the equilibrium of heterogeneous condensed systems. It differs from physical chemistry, however, in that it takes into account the arrangement of the component particles in space, whereas the latter deals only with the nature and relative quantities of the phases in a system and with the transformation of energy accompanying chemical changes.

Metals and alloys are considered as a class apart from other mixtures and solutions which obey the same physico-chemical laws. This is due mainly to the extensive use and great importance of metals in industry. The earliest and many of the most important metallographic investigations have been under taken in an effort to meet the needs of practical metallurgy, especially in the iron and steel industry. Chemical analysis has long been used as a method of control of the metallurgical industries but it has only been in recent years that the study of structure has proved itself as an indispensable auxiliary method, the applications of which are becoming more important and more extensive every year.

The methods and results of metallography are not merely confined to metallic systems but may also be used in the investigation of non-metallic systems since the relations in the two types of systems are almost identical. This fact enables the geologist or mineralogist to study the formation and metamorphosis of igneous rocks by the methods of metallography. Similar study has given much information about the rather obscure region of cements and slags. Thus it is

evident that metallography is not confined solely to metallic systems but is capable of much further extension.

The word "metallography" was originally used to signify the description of metals and their properties but, in this sense, it is now obsolete. It is now generally accepted as designating the study of metals and alloys by microscopical or any other means.

The earliest use of the microscope in the examination of metals and alloys was the work of Robert Hooke who, in 1665, described the appearance of lead crystallizing from its alloy with silver. At first, the method of investigation consisted in merely examining the fractured surface with a microscope. Later, Widmanstätten showed that certain surfaces developed a distinct and characteristic structure when oxidized by heating in air. This method was then replaced when it was found that much better results could be obtained if the surface was etched with nitric acid. As early as 1864 the method of preparing and examining microscopic sections had been perfected to such a degree that publications of H. C. Sorby contain photomicrographs which have hardly been surpassed in excellence by later workers.

For a long time it was not known whether to regard alloys as chemical compounds or as mechanical mixtures but it was shown by Levol, who carried out some of the earliest researches on alloys, that only a few alloys remain homogeneous throughout the process of crystallization, all the rest being capable of separation into more fusible and less fusible parts.



Soon after this, Matthiessen began investigating the physical properties of alloys and he concluded that alloys may be regarded as solidified solutions which may or may not contain compounds according to the circumstances under which the alloy was formed. His work was based on the fact that if a compound is present, the physical properties will change in a discontinuous manner, and a study of this change will determine the composition of the compound. He therefore studied alloys containing the same component metals in varying quantities and sought for any discontinuous changes in their physical properties. This work was the beginning of the application of the methods of physical chemistry to the study of alloys.

The next advance in the study of alloys was made after Raoult put forth the law regarding the depression of the freezing point of solutions. It had been observed before this time that many alloys had a lower freezing point than either of the pure components so that a study of alloys from this point of view was immediately suggested.

When Gibbs propounded his theory of phases, it was suggested that this might be applied to the study of alloys. The first important application was made by Roozeboom who used the results obtained by Roberts-Austen in the thermal analysis of iron and steel and from this he constructed a complete diagram for the thermal equilibrium of iron and carbon.

Roozeboom also contributed very materially to the advance of metallography when, in 1899, he reviewed from the theoretical standpoint of the phase rule, the possible types of solid solutions or mixed crystals in binary systems.

At first, his teaching was only applied to the study of iron but was gradually extended to the study of all alloys.

Heycock and Neville carried out many important studies on alloys at about this time and they introduced the method of quenching from determined temperatures as a method of research.

In 1903, G. Tammann began a survey of a large number of binary metallic systems in an attempt to establish regularities between alloys of different metals. His work, in itself, is not very important for his materials were often impure and his experimental methods were not very accurate so that most of the diagrams that he put forward have had to be revised. The importance of his work lies in the fact that it stimulated interest in the study of metallic alloys and this in turn soon produced much valuable material on the nature and properties of metals and alloys.

## Theoretical Consideration

### (a) General Phase Rule

It was realized as early as the last quarter of the eighteenth century that chemical reactions, in general, do not proceed to completion in one direction but that, at some intermediate stage, they reach a state of equilibrium. Many attempts were made to account for the various known cases of equilibria by the general laws known at that time. These were not satisfactory due to the fact that in all of them some hypothetical assumptions were made as to the nature and constitution of matter. Wenzel and Berthollet both knew that the mass of the substances exerted a considerable influence on the equilibrium of a system but it remained for Guldberg and Waage to establish the Law of Mass Action by means of their mathematical treatment. This law served fairly satisfactorily when dealing with most cases of homogeneous equilibrium but several assumptions were necessary in order that it might be applied to systems in which there was heterogeneous equilibrium. This law failed, as was to be expected, when it was applied to systems where nothing was known of the different molecular aggregates or of the molecular complexity in the system. This must be the case since this law was derived on the basis of the kinetic and molecular theories and both of these theories contain certain assumptions as to the nature and condition of the substances taking part in the equilibrium.

It was not until ten years after the law of mass action had been put forward by Guldberg and Waage that a satisfactory means of dealing with equilibria was developed by Willard Gibbs. His theory was entirely free from any

assumptions as to the nature and constitution of the participating substances. He showed how all cases of equilibrium could be grouped into classes and explained how systems which were apparently similar behaved differently while systems which were apparently different behaved in the same manner.

Horstmann had previously attempted to derive a law governing equilibria using the laws of thermodynamics as a basis. When Gibbs began his work on this subject, he used the same idea and deduced his theory of equilibria thermodynamically. Gibbs considered that in a system in equilibrium only three factors, temperature, pressure and the concentration of the components of the system, could be varied independently. His theory is now known as the Phase Rule and it defines the condition of equilibrium as the relation between the number of phases and components of the system.

The phases of a system may be defined as the different homogeneous but physically distinct portions of the system which are marked off in space and separated from the other portions of the system by bounding surfaces. Thus, the substance water may exist in three phases, ice, water and vapor. A phase need not be chemically simple although it must be physically and chemically homogeneous. Thus, a gaseous mixture constitutes only one phase due to the fact that all gases are perfectly miscible. A liquid mixture may or may not constitute a single phase since some liquids are only partially miscible; a solution forms only a single phase. When we consider heterogeneous mixtures, there are as many phases present as there are substances in the mixture.

The components of a system are defined as "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>1</sup> Once again, taking the system ice - water - vapor, it is evident that, while there are three phases present, there is only one component - water. If we consider a case such as that when calcium carbonate dissociates into calcium oxide and carbon dioxide, it is seen that, when equilibrium is established, there are three different substances present. Although these three substances are necessary before equilibrium can be set up, the system is not one of three components because these three are not all mutually independent, i.e. if two of these are taken, the relation existing between them is such that the composition of the third is defined. Thus, this is a system of two components. The choice of components is quite arbitrary since it is not the nature of the components which is important but only the number. The choice is, therefore, determined by the simplicity, suitability or generality of application of those taken.

The third quantity needed in the enunciation of the Phase Rule is the number of degrees of freedom. This may be defined as "the number of the variable factors, pressure, temperature and concentration of the components, which must be arbitrarily fixed in order that the condition of the system may be perfectly defined".<sup>2</sup> Again taking the system ice - water - vapor as an example, it will be seen that where these can coexist, the state of the system is perfectly defined with regard to temperature and pressure and any

alteration of the arbitrary variables will cause one of the phases to disappear. This system is, therefore, described as having no degrees of freedom. If we now consider the system water - vapor, it is evident that if the temperature is fixed, the pressure under which the system will be in equilibrium is also determined; this system has one factor which may be arbitrarily fixed and, therefore, has one degree of freedom. Finally, with a gaseous system, the pressure and temperature may be altered without causing any change in the volume of the system and is therefore said to have two degrees of freedom.

By means of the three definitions given above, Gibbs has defined the condition of equilibrium as a relation between the number of co-existing phases and components. His Phase Rule may be stated as follows: "a system consisting of  $n$  components in  $n - 2$  phases can exist 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>3</sup> This rule may be presented in the form of the following equation:

$$F = n - r + 2$$

where  $n$  denotes the number of components;  $r$ , the number of phases; and  $F$ , the degree of freedom of the system.

From the equation, it is evident that as the number of phases increases, the number of degrees of freedom diminishes, i.e. the system becomes more and more defined.

In metallography, most of the cases with which we have to deal may be somewhat simplified due to the fact that

it is frequently possible to omit the vapor phase when determining the freezing point diagram of metals, since the volatility of most metals is extremely small at their melting point. In most investigations, the pressure under which equilibrium is reached is constant and is that of the atmosphere since the vessels in which the fusion is carried out are open to the air or else are connected with other vessels in which the pressure is atmospheric. Thus, while the effect of pressure on the freezing point is of great scientific interest, it may be omitted in all but a few exceptional cases when dealing with metallic alloys.

In the case of metallic alloys, therefore, when we omit the vapor phase and do not consider any changes in pressure, the net effect is to reduce the number of variables to two, temperature and concentration. Then we may represent the condition of equilibrium by means of the following formula:

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

and it is in this form that the Phase Rule is most usefully employed in the consideration of alloys.

#### (b) Binary Systems

##### (i) General

All of the known types of solid substances may be grouped into two classes, amorphous and crystalline substances. By the microscopic examination of the fracture of alloys, it has been established that the alloys belong to the latter class. Where the alloy takes on a structure similar to that of glass, the microscope will not reveal this fact but in these cases it may be shown by other properties that this is

equally true here. one of the simplest means of determining this is by their behaviour on cooling from the molten state. Amorphous bodies, which have been fused and allowed to cool, do not solidify at a constant temperature but pass through a series of intermediate stages known as the "muddy" state. The continuity of the temperature fall between the different states is readily shown by means of a thermometer immersed in the mass. The solidification of a crystalline body takes place in an entirely different manner. The temperature fall is steady until solidification begins, at which point there is a sudden temperature arrest owing to the liberation of the latent heat of crystallization. Then, after all has solidified, the temperature again falls steadily. All alloys which have been fused and allowed to cool exhibit this temperature arrest, proving that they are all crystalline substances.

Due to the crystalline structure of alloys, it is to be expected that the action of heat will produce results similar to those shown by other crystalline mixtures, such as mixtures of salts obtained by fusion or even ordinary solutions. A large number of experiments have shown that this is true.

If we take an ordinary solution of a salt in water and determine its freezing point, it will be found that the addition of the salt has caused a lowering of the freezing point of the solvent. Also, the temperature of solidification of fused mixtures of salts, in the majority of cases, is found to be lower than the melting point of the salt to which small quantities of the other have been added. This same behaviour is noted with metals. For example, the



addition of small quantities of silver, copper, nickel or lead will lower the melting points of antimony and tin. In some cases, the effect is an elevation of the temperature of solidification rather than a lowering, as seen when silver is added to cadmium or zinc. This fact is not a dissimilarity between the behaviour of crystalline mixtures and alloys, however, for this phenomenon has also been observed in certain fused mixtures of salts, e.g. potassium sulphate added to potassium chromate.

When an elementary substance or a definite compound is fused and allowed to cool, it solidifies completely at one definite temperature. With salt solutions and fused mixtures of salts, the solidification begins at a certain temperature, continues only if the temperature falls and finally all becomes solid at some definite temperature. The point at which the solidification commences depends on the composition of the solution or mixture but the temperature at which solidification becomes complete does not. In many binary alloys the temperature at which solidification becomes complete does not possess a single value for all the alloys of the two components but they may all be divided into a small number of groups such that all the alloys in any one group will finally solidify at the same temperature. The number of these groups is not often more than three.

The point at which solid just begins to separate from the fused mass is considered as the point of fusion or of solidification of the mixture since this point is easily determined. This point is the crystallization point of aqueous mixtures. When the fusion points have been determined for a number of mixtures, these temperatures are

then plotted against the corresponding compositions of the mixtures and the resulting curve is known as the fusion curve. Curves which relate compositions of saturated solutions to corresponding temperatures are called solubility curves.

For a long time the identity between these two types of curves was overlooked and, as pointed out by Le Chatelier, was probably due to the fact that for solubility curves the temperatures were plotted as abscissae while in fusion curves they were plotted as ordinates, thus giving the curves a different orientation.

In a graphical representation, the arbitrary variable is usually plotted as the abscissae and the function of this variable, as determined by experiment, is plotted as the ordinate. When studying the solubility of a substance, one starts with the temperature specified and then determines the composition of the liquid in equilibrium in contact with an excess of the salt. When investigating the fusibility, a mixture of a definite composition is taken and the temperature at which it just begins to solidify is determined. The analogy of the two kinds of phenomena is evident if we notice that the state of saturation of a liquid is independent of the quantity of the solid substance in contact with it, and that at the initial point of solidification, the liquid may be considered as being saturated with the solid substance which is depositing from the solution.

When the curve for the mutual solubility of two substances is plotted, it is well known that it consists of a number of distinct branches meeting at a sharp angle. There are as many of these branches as there are solid

substances depositing in a different chemical state from the liquid mixture. These distinct branches cut two by two and correspond to each of the substances present, to each of their allotropic forms and to each of the compounds which may be formed by them. Apart from the exceptional cases of supersaturation, the branches of the curve can only be observed experimentally in the region limited by successive points of intersection so that the complete solubility curve is unique but presents a certain number of angular points.

Loewel was the first to recognize by experiment the existence of multiple branches in the solubility curves of sodium sulphate, sodium carbonate and magnesium sulphate. Later, Roozeboom aimed at analogous conclusions when studying solutions of calcium chloride, and finally, Le Chatelier has shown that this is a necessary consequence of the fundamental laws of energy and there can be, therefore, no exception.

#### (ii) Thermal Analysis

There are today many different methods of metallographic investigation but one of the earliest methods, thermal analysis, still remains the most important of all and must be regarded as the foundation for any metallographic study. The other methods may give much valuable information regarding the alloy but without some knowledge of the diagram of thermal equilibrium it is rarely possible to interpret this information correctly. When the thermal equilibrium diagram is known, it shows what phases may be expected to be present in an alloy of given composition under given conditions of cooling.

In metallography, the essential problem is a knowledge of the phases present in the cold alloy and this may be obtained by thermal analysis and a knowledge of the freezing point curve. Another important point in thermal analysis is the information which it gives about changes taking place in the alloy after it has entirely solidified. Thus, an allotropic modification or similar change in the solid phase will show up in the thermal analysis, proving that the thermal effect accompanying the change is sufficiently marked. Due to the great amount of information which may be obtained by thermal analysis, it must necessarily be given the first place in any metallographic study.

The fundamental principle of the method of thermal analysis is that whenever there is a phase change, there is always a heat effect accompanying it. Thermal analysis is not always applicable if the heat effect is very small or if supercooling is very great, as in many organic compounds. The latter difficulty is rarely encountered in metallography since supercooling is almost unknown in metallic alloys. If the heat effect is very slight, some other method of investigation must be employed to determine the nature of the change.

The procedure in thermal analysis consists mainly of taking cooling curves or, in some instances, heating curves. The alloy to be examined is heated considerably beyond the phase change and the enclosure is then allowed to cool in such a manner that the loss of heat due to radiation, convection and conduction is uniform. Some instrument for measuring temperature is immersed in the alloy and the temperature noted at fixed intervals of time for any abnormal

behaviour.

If a pure substance is heated until it is molten and then allowed to cool slowly, the curve obtained by plotting temperature against time will be a continuous one at first. When the first particles of solid begin to separate out (if there is no supercooling) the temperature fall will be arrested and it will remain constant until the substance is completely solid, after which it will again fall steadily.

If, however, we take a solution and allow it to cool slowly, the temperature will again fall smoothly until solid particles begin to separate out. As the solid forms, there will be a certain amount of heat given out and the rate of cooling will alter, thus causing the cooling curve to show a change of direction at the freezing point. As more solid separates, the composition of the liquid phase will change due to the fact that it is being impoverished in the constituent which is separating as solid. The temperature, therefore, will not remain constant but will gradually fall until the eutectic temperature is reached. Here, the two components separate side by side and since a new solid phase is appearing, the system is now invariant. The temperature must remain constant at this point until all has solidified, after which it again falls uniformly.

This temperature is known as the eutectic temperature and is shown by all alloys, except in a few special cases. The length of time during which the temperature is constant at the eutectic is known as the eutectic halt and this depends on the amount of solution which remains unsolidified when the eutectic temperature is reached. If we start with equal amounts of solutions having different initial compositions,

the eutectic halt will be the greatest for the solution which has the exact composition of the eutectic point. This method also gives a means of checking the composition of the eutectic point for if the eutectic halt times are plotted against the compositions of the original mixtures, two curves will be obtained which will intersect at a point and this point will be the maximum halt time and will, therefore, represent the composition of the eutectic.

Thus, by observing any abnormal behaviour of the temperature, i.e. points where there is a break in the temperature - time curve, it is possible to map out the equilibrium diagram of the system. Also from the cooling curve, we may obtain valuable information regarding changes in the completely solidified alloy for here too, if the thermal effect is large enough, there will be a break on the curve. This is the method known as thermal analysis.

Where the thermal effects are small, the sensitivity may be increased by using the method outlined by Sykes<sup>16</sup>. This consists in determining the temperature difference between the specimen and the enclosure by means of two thermocouples connected differentially and then plotting this against time. A transformation shows up much more distinctly on a curve of this type than on the direct cooling curve.

(iii) Types of curves obtained.

(1) Components separate out in the pure state.

Where solid solutions are not present, the simplest type of diagram for a two component system is that shown in Fig. 1. The points A and B represent the melting

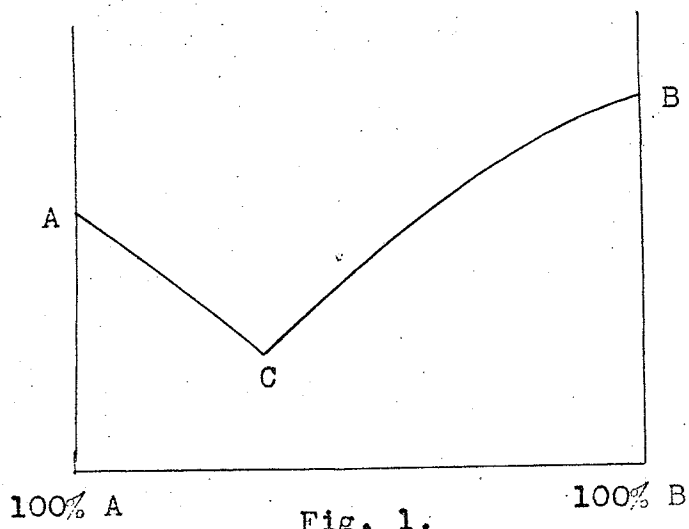


Fig. 1.

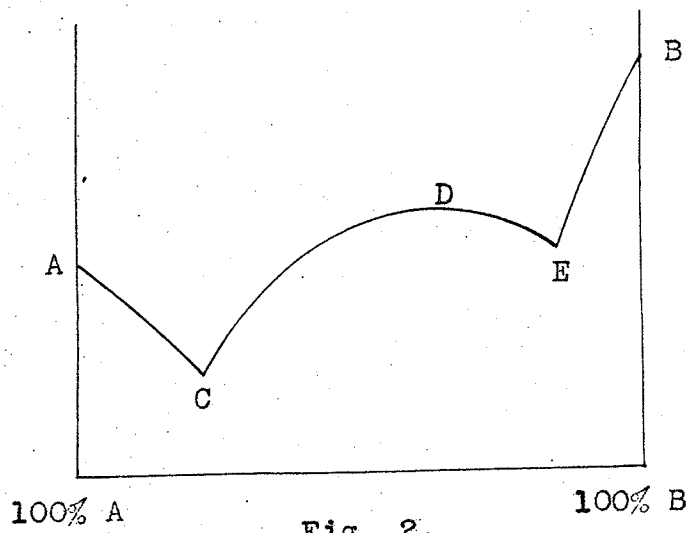


Fig. 2.

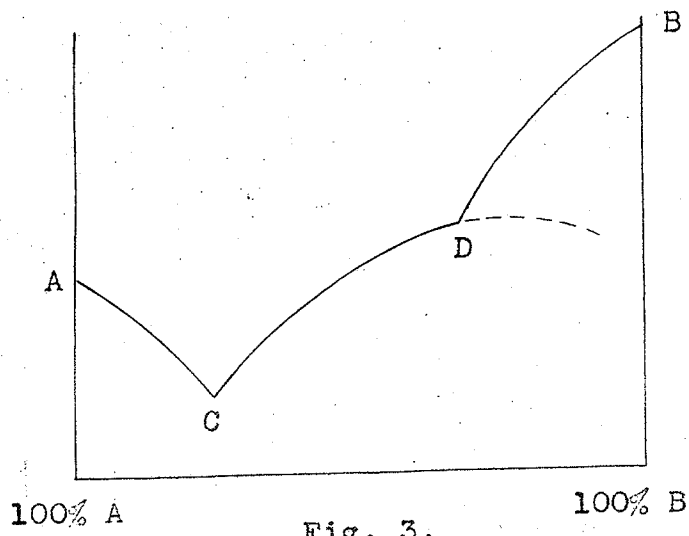


Fig. 3.

points of the pure components. When a solid substance is dissolved in a liquid, the freezing point of the liquid is lowered so that if solid B is dissolved in molten A, the freezing point of the solution will be lower than that of pure A. As more and more B is dissolved, the temperature of solidification will become steadily lower, as shown by the curve AC. The same holds true when A is dissolved in B so that we get the curve BC, where the solution is in equilibrium with solid B at different temperatures. These curves must finally intersect at a point, C, which is known as the eutectic point and at this point both solids are in equilibrium with a liquid having the composition of the point C. If any further separation takes place, it must do so by A and B separating side by side. This must be so, for if crystals of B separate, equilibrium can only be restored by the separation of crystals of A, and conversely. This explains the extraordinarily great homogeneity of most eutectic mixtures. Also, the temperature must remain constant at this point until the entire mass has solidified. This constancy of temperature and homogeneity of structure has caused many early workers to believe that these eutectic mixtures were true compounds.

(2) Compounds are formed with congruent melting points

The two components may form a stable compound possessing a congruent melting point, i.e. it can exist as a solid compound in equilibrium with a liquid having the same composition. In this case a third curve must be added to those described in the previous section. Since it has a congruent melting point, this will be lowered by the addition of either of the two pure components to the liquid



compound. Thus, it is evident that the melting point of the compound must be a maximum point on the equilibrium diagram, and the curve is of the type shown in Fig. 2. Again, A and B are the melting points of the pure components; D is the melting point of the compound  $A_xB_y$ . AC represents the compositions of liquid mixtures of A and B in equilibrium at different temperatures with solid A; BE, liquid mixtures in equilibrium with solid B; CDE, liquid mixtures in equilibrium with the compound as the solid phase. C and E are eutectic points; at C, the solid phases separating side by side are the pure component A and the compound  $A_xB_y$ ; At E, the solid phases are B and the compound  $A_xB_y$ . The point D may be higher than that of either of the pure components, it may be lower or it may occupy an intermediate position. Frequently, more than one compound having a congruent melting point may be formed, and in these cases there is a curve of the type CDE for each compound formed, the maximum of the curve in each case being the composition of the compound.

It might be thought that since D is a congruent melting point and since this will be lowered by the addition of a second substance, the two branches of the curve should intersect at a point and not pass continuously into one another. If no dissociation took place, even in the vapor phase, this would be the case, but when dissociation of the compound into its components takes place in the liquid phase, we obtain a mixture of molecules in the liquid phase and this mixture varies continuously with changes in temperature. Therefore, if the solid phase remains the same, the equilibrium curve must be continuous, as shown by the curve CDE. The smaller the degree of dissociation, the sharper will be

the bend of the curve; similarly, the greater the degree of dissociation, the flatter will the curve become. It is possible, with some degree of approximation, to calculate the degree of dissociation of the compound in the liquid phase from the extent of the flattening of the curve.

(3) Compounds formed with incongruent melting points.

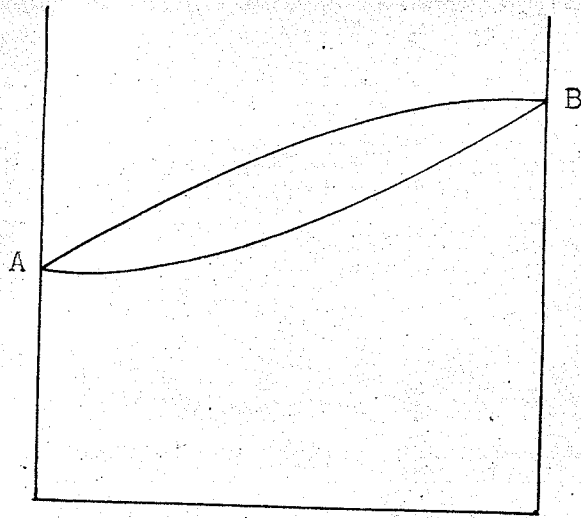
The two components may also form a compound which undergoes decomposition with the formation of another solid phase at a temperature below its congruent melting point. Compounds of this type are said to have an incongruent melting point and the equilibrium curve is of the type shown in Fig. 3. In a case of this type, the compound can only exist in contact with a solution containing an excess of one of the components. If the line CD is continued metastably, as shown by the dotted line, the summit of the curve would correspond to the composition of the compound and would give the congruent melting point of the compound. This congruent melting point, however, is never realized because the compound is not stable at this temperature, decomposing at the point D. Therefore, the point D represents the limit of existence of the compound under the particular pressure which is assumed. Again, if a series of compounds can be formed, all of which have an incongruent melting point, we will obtain a series of curves such as CD on which there is no temperature maximum. In an equilibrium diagram of this kind there will be only one eutectic point. Each compound has a definite limit of existence which is marked by a break in the curve, such as that at D. Points such as D are known as peritectic points.

Where the compound has an incongruent melting point,

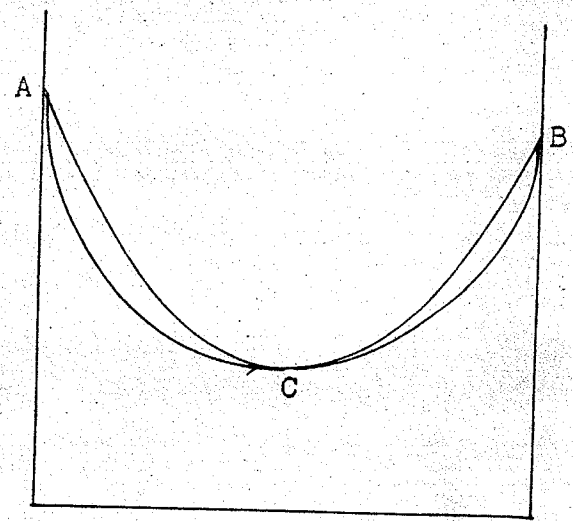
there is no temperature maximum on the equilibrium curve and it is, therefore, not possible to find the composition of the compound from a knowledge of the equilibrium curve alone. If the composition of the compound is not too far removed from the peritectic point, it is sometimes possible to determine it by merely extrapolating the curve CD; the maximum of this extrapolated portion is then the desired composition. This method is only approximate and fails in the majority of cases so that it is necessary to determine the composition by the method due to Tammann. At this point, there will be a temperature halt on the cooling curve similar to that obtained at the eutectic. The duration of this compound halt is plotted against the composition of the original mixture and the intersection of the two curves gives the composition for which the compound halt is a maximum, i.e. gives the composition of the compound. Another advantage of this method is that it provides a check on the position of the peritectic point for the compound halt will be zero at this point.

#### (iv) Formation of solid solutions

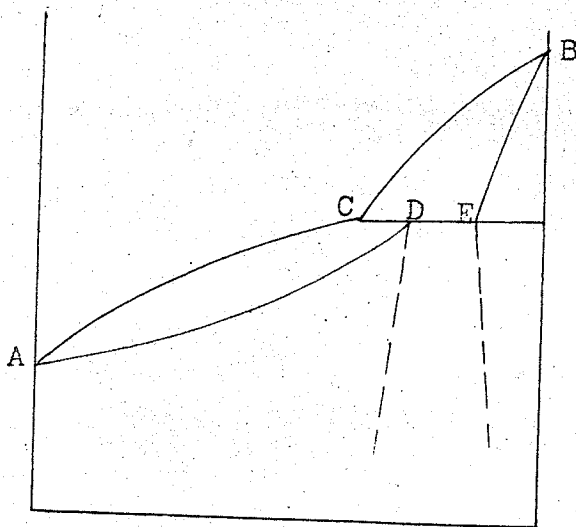
When solid solutions may be formed, we then have two phases in which the components are not generally present in the same concentration and the equilibrium diagram must then consist of two curves for each system, one relating to the liquid phase and one relating to the solid. The freezing point of the mixtures is the temperature at which the first trace of solid appears when the liquid solution is cooled; the melting point is the temperature at which the solid solution just begins to liquefy when heated. If we then



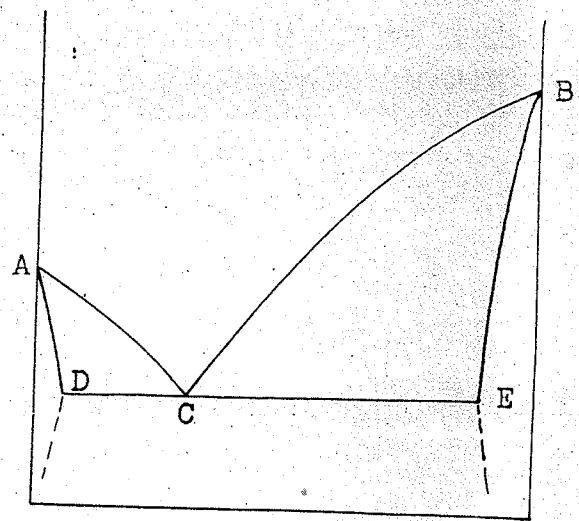
Type I



Type II



Type III



Type IV

Fig. 4.

plot the temperature - concentration curve, the freezing point curve will be the curve applying to the liquid phase while the melting point curve will apply to the solid phase. These curves are commonly known as the liquidus and solidus curves respectively.

In 1899, Bakhuis Roozeboom, working from the theory of thermodynamic potential, showed that the types of solid solution may be divided into two sections, depending on whether there is complete or partial miscibility.

- (1) The two components can form an unbroken series of solid solutions.

As with a liquid solution, a solid solution constitutes only a single phase so that when the two components are completely miscible in the solid state, there can only be one solid phase present which is a solid solution of varying composition. Also, when the two components are completely miscible in the solid state, they will be completely miscible in the liquid state so that there can be only one liquid phase. Since there can never be more than three phases present, the system can never become invariant so that when the two components form a continuous series of solid solutions, the equilibrium curve must also be continuous. There are two types of these systems known in metallography and they are:

- (a) The freezing points of all mixtures lie between the freezing points of the pure components.

Fig. 4, Type I.

As shown above, the freezing point curve must be continuous and in this case it is a line joining the melting

points of the two pure components. The melting point curve is also continuous and the melting points of the different solid solutions lie below those of the pure components. If we take a liquid mixture and allow it to cool until it strikes the liquidus, we can get the composition of the solid phase separating by drawing a horizontal line through the point where the liquidus is touched. The point where this line strikes the solidus then gives the composition of the solid phase.

The relative proportions of the liquidus and solidus 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>17</sup>

(b) The freezing point curve passes through a minimum.

Fig. 4, Type II.

This case is somewhat similar to the case where a simple eutectic is formed for here also there is a minimum freezing point. The difference lies in the fact that in the former case we have two curves intersecting at a point, while in the latter there is only one continuous curve. At the minimum point, the compositions of the liquid and solid phases are identical while on one side of the minimum point the liquid phase contains relatively more of the one component than does the solid phase while on the other side, it contains relatively less. Therefore, at the minimum point, liquefaction and solidification will take place completely

at this one temperature.

- (2) The two components do not form a continuous series of solid solutions.

This case corresponds to that of partial miscibility of liquids. The solid component A can dissolve the solid component B until a certain concentration has been reached. After this point, a new solid solution makes its appearance and it is a solution of A in B. At the point where this new solid solution just appears, we have four phases in equilibrium, solid solution of B in A, solid solution of A in B, liquid solution and vapor; this point is, therefore, an invariant point. When we now plot the temperature - concentration curve, it will no longer be continuous but will exhibit a break or discontinuity at the point at which the invariant system is formed. There are two general types of curves found in systems such as this.

- (a) The freezing point curve exhibits a transition point. Fig. 4, Type III.

When the component B is added to A, the melting point of A is raised, as seen in the figure. Using the rule previously given, it will be seen that the concentration of B in the liquid solution will be less than in the solid solution; this fact is shown in the figure by the curve AD. If, however, we add component A to the component B, we find that the melting point of B is lowered and the curves BC and BE are then obtained for the liquid and solid phases respectively. At the temperature of the line CDE, the liquid solution having a composition represented by the point C, is in equilibrium with a saturated solid solution of B in A.

represented by the point D, and a saturated solid solution of A in B represented by the point E. The solid phase, therefore, exhibits a discontinuity at this point. Since there is a change in the solid phase, there must also be a break in the freezing point curve at this point.

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

In this case the freezing point of each of the components is lowered by the addition of the other, until finally a point is reached at which the liquid solution solidifies to a mixture of two solid solutions.

At the eutectic point, the liquid solution is in equilibrium with two different solid solutions, the compositions of which are represented by the points D and E. If we take a fused mixture containing the components A and B in the proportions in which they are present at the point C and allow it to cool, it will solidify completely at the temperature given by the point C. The solidified mass will be a conglomerate of two different solid solutions.

The two solid solutions will be a saturated solution of Bin A, represented by the point D, and a saturated solid solution of A in B, represented by the point E. When two liquids which are only partially miscible are heated, the mutual solubility will change; this is also the case with metals which are partially miscible in the solid state. Therefore, in a case where there are two solid solutions formed, these need not remain the same as when they were deposited from solution but may, at some lower temperature lose their homogeneity. This fact is one which is quite important in the formation of alloys.



(v) Methods of cooling

In metallography, the usual procedure in thermal analysis is to take cooling curves of a fused sample of the substance under investigation. In taking the cooling curves, there are two general methods of cooling the fused mass; these are the method of free cooling and the method of gradual cooling, the latter method being due to Plato.

(a) Method of free cooling

The mass is placed in a furnace fitted with a thermocouple and the temperature is raised until the mass is entirely molten. The heating is then cut off completely and the melt allowed to cool; temperature readings are taken at regular intervals of time.

The advantage of this method is that it is quite rapid since the furnace will cool off in a comparatively short time. When we plot temperature against time, we find that the cooling takes place in accordance with Newton's law of cooling, and the resulting curve is of the type shown in Fig. 5. This curve is the simplest one possible, i.e. there is no solidification or other phenomena taking place.

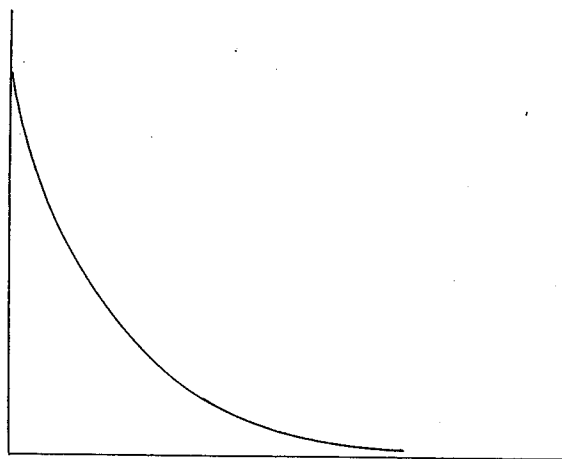


Fig. 5

(b) Method of Plato

This is the method of gradual cooling. The specimen is again placed in the furnace and the temperature is raised until all is molten but instead of the current being cut off completely, it is gradually reduced by means of a rheostat attached to the furnace. The slider on the rheostat is moved along a certain interval at constant periods of time and the temperature is taken each time. If solidification or other phenomena do not occur, the curve will be as shown in Fig. 6, when temperature is plotted against time.

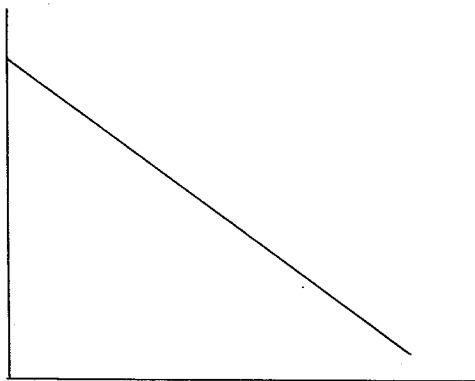


Fig. 6

The method of gradual cooling is the one most frequently used in taking cooling curves for, on a curve such as this, it is much easier to detect the point at which any change is taking place in the melt. When there is a change, this shows up as a change in the direction of the line.

In many cases, the heat evolved is quite small and if the method of free cooling were used, this might be completely overlooked since it is much more difficult to detect a change of direction in a curved line than it is in a straight line.

Using the method of gradual cooling, we may expect the following types of curves:

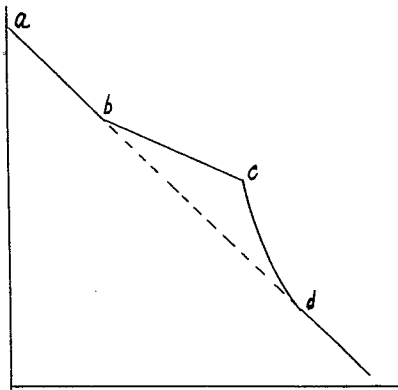


Fig. 7

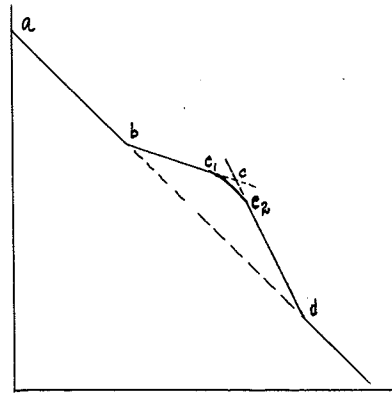


Fig. 8

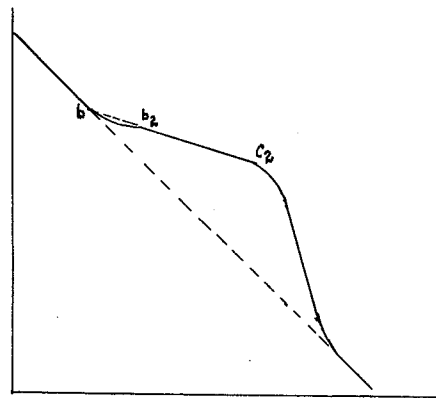


Fig. 9

The curve given in Fig. 7 is the curve which would be obtained if the cooling took place in an ideal manner. The cooling starts at the point *a* and continues uniformly until the point *b* is reached, at which point the first trace of solid appears. Since the composition of the liquid is changing, the rate of cooling is altered and, therefore, the slope of the line *bc* is different from that of *ab*. Cooling is continued until the point *c* is reached, where all has been converted into solid. After this point, the cooling is very rapid until the original curve is again obtained.

The temperature of *b* is the temperature at which solidification commences and is, therefore, a point on the

liquidus curve of the equilibrium diagram. The point  $c$  gives the temperature at which solidification is complete and thus gives a point on the solidus curve. If sufficient time is allowed, the composition of the solid solution will alter in sympathy with the melt but usually the cooling is too rapid for this to take place. This tends to make the point  $c$  too low and it is often difficult to determine  $c$  accurately. Tammann devised a method of overcoming this by carrying out cooling curves with different rates of cooling. In each case a value for  $c$  is obtained from the cooling curve and the temperature of this point is then plotted against the rate of cooling used in the experiment. By extrapolating this curve to infinite rate of cooling, the ideal value of  $c$ , and therefore a true plot on the solidus, is obtained. This method is rather tedious, however, and the usual method of obtaining  $c$  is given below.

In actual practice we obtain a curve of the type shown in Fig. 8. Again, solid begins to appear at  $b$  and theoretically the curve  $bc$  should be a straight line, but instead there is a shoulder formed from  $c_1$  to  $c_2$ . The latter point corresponds to the point  $c$  on the ideal diagram and the mass is completely solid at this point. After this point, the cooling follows a straight line along  $c_2d$  until the original curve is once more obtained. The true value of the point  $c$  is readily obtained by extrapolating  $bc_1$  and  $c_2d$  until they intersect.

In some cases there may be unequal cooling or slight supercooling so that instead of the point  $b$  being sharply defined, there may even be an arc at the upper end, giving a curve of the type shown in Fig. 9. The true value of  $b$

is obtained by extrapolating the straight portion of the curve,  $b_2c_2$ , until it intersects the first portion of the curve.

If there is a eutectic in the equilibrium diagram, we then obtain a curve such as that given in Fig. 10.

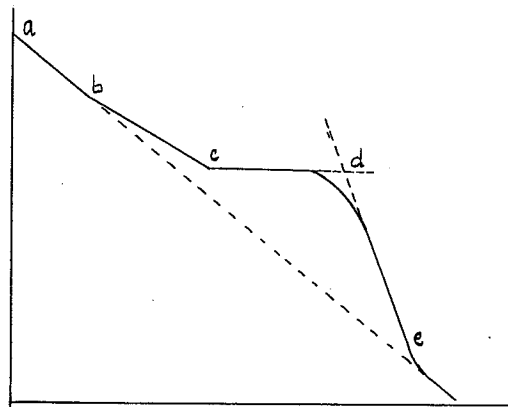


Fig. 10

The point b represents the point at which the mixture first strikes the equilibrium curve. Cooling continues along bc until the eutectic temperature is reached, at which temperature the entire mass solidifies completely, as seen by the horizontal cd. In order to obtain the point d, the straight lines cd and de are continued until they intersect; then cd gives the theoretical eutectic halt.

In actual practice, the chief deviation is due to supercooling. When this occurs, one of the components does not appear when the eutectic temperature is reached and the mother liquor becomes unduly rich in this component. The temperature falls below the true eutectic temperature but rises back to the horizontal when the second component begins to solidify. However, due to the liquid being enriched in one component, a little of this is left behind as liquid after the eutectic solidification has been completed. This

continues to solidify and causes the shoulder at  $d$  to be exaggerated. This difficulty is rarely encountered in metallography since the supercooling of metals is relatively slight.

(vi) Other methods of investigation

The method most commonly employed in conjunction with thermal analysis in the study of metallic alloys is that of microscopical examination of the polished surface of a section of the alloy.

The types of pattern visible on the etched surface depends on the position of the freezing point on the equilibrium curve. If the freezing point curve of two metals is known, it is possible to predict the microscopical structure of the alloys formed by them.

When the freezing point of an alloy lies near the summit of the curve, the whole surface of the section is filled with one substance, although it is sometimes possible to detect fine boundary lines marking out the separate crystals. These lines are most often seen at the angles where the crystals meet, in which case the boundary line consists of three branches meeting at a point.

When, by the addition of either metal, the summit of the curve is passed, the lines between the polygonal sections of the crystals become distinct so that the pattern is that of a tessellated pavement, the unit being that of an irregular polygon, often approximating to a regular hexagon and often with somewhat rounded angles so that it may be called a blob. It does not seem necessary to attribute the hexagonal shapes to any peculiarity of crystalline structure but rather to the limitations of space in which the closely

packed crystals have formed. As the composition descends from the summit of the curve, the spaces between the polygons widen and are seen to be full of a substance different from that of the polygons themselves. When the composition descends still further, the interpolygonal matter becomes a continuous network and the isolated polygons or blobs arrange themselves into patterns. The individual blobs are often oval or elongated into bars and are usually placed in rows with other rows branching from them. The pattern is sometimes mainly one of rectangular crosses.

As the composition of the specimen approaches that of a eutectic mixture, the rows of blobs become smaller in area and the mother substance around them is sometimes seen to consist of a much smaller pattern of two substances, one being the material of the blobs. Finally, at the eutectic, the large blobs disappear entirely and the whole alloy consists of the small pattern; this structure is typical of all eutectic alloys. If we continue adding the same metal, thus causing the freezing point to rise again, the large blobs once more appear surrounded by the minute pattern. In this case, while the fine pattern is the same as before, the blobs now consist of the second substance of the network.

If we consider only the plane surface of a section of an alloy, the rows of blobs, each blob isolated from the next yet obviously connected with it by some law, are puzzling. But if we think of the solid alloy as consisting of a mass of crystals with other crystals branching from them, the whole system immersed in a mother substance which solidified after the formation of the crystals, we see at once that a section of the mass would present the appearance

described above. This may be picture as like a thicket of fir trees in which the branches are at right angles to the stems and in which the stems are not all vertical. If a section were made of this thicket by a plane inclined to the vertical, we should get patterns like those described. If a stem lay in the plane of section, we should get lines at right angles to each other. If the stem were parallel to the plane but not init, we would get parallel rows of dots. With the stem oblique to the section, the dots would appear elongated.

These considerations, along with the straightness of the lines of dots, show that the large patterns of blobs and the polygons with which they are related are the pure substance which crystallized first and without restraint since it was surrounded by liquid, whereas the surrounding matter is the mother substance which was liquid during the first stage of crystallization. It is probable that the marked absence of crystal form in the blobs is due to these blobs being crystal skeletons; a snow crystal is the most familiar type of crystal skeleton. If we imagine the interstices between the fernlike pattern of such a crystal to be filled with subordinate crystallization of the same body, the original outline will be lost and the final outline will be rounded. Prolonged etching may partially reveal the structure of the original skeleton.

Another method of investigation in the study of metallic alloys which is becoming quite important is that of X-ray examination. Our knowledge of the structure of matter in the solid state has been advanced greatly due to the



application of this method to crystal analysis. It was shown by von Laue that the crystal lattice could be determined by the diffraction of X-rays and since that time the method has been developed to such an extent that the absolute dimensions of the crystal lattice, as well as the arrangement of the structural units in it, can be determined. The importance of the X-ray method is that changes in the solid state can be determined even when the solid phase is opaque or microcrystalline in structure. The methods used prior to X-rays was based on the fact that the physical properties of a solid body change discontinuously with temperature at a transition point. The various methods used to detect these changes in properties provided much valuable information but they failed in many cases because the magnitude of the discontinuous change was very small or because the system remained obstinately metastable, as in the case of the allotropic modifications in many metals. The advantage of the X-ray method is that no matter how small the difference between the physical properties of two solid phases may be, their existence as two separate phases requires that they possess a different crystal lattice. This property is the most fundamental of all. Where the crystal forms are opaque or distorted, the importance of this method will at once be obvious.

These three methods of investigation, the thermal, the microscopical and the X-ray, are of primary importance in the study of metallic alloys. When they are suitably applied and combined, they will reveal the principal facts

concerning the equilibrium of the components. All other methods, although valuable in themselves, and sometimes indispensable, must be regarded as subsidiary to these three in the range of their applicability. As subsidiary aids may be mentioned the following:

- (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.

#### (c) Ternary Systems

The methods of investigating three metals in an alloy are the same as when the simpler alloys of two metals are dealt with, but the experimental difficulties, and the complexity of the conditions which may present themselves, are naturally much greater. For this reason, in spite of the number of alloys of technical importance containing three metals, few ternary systems have been completely investigated.

##### (i) Graphical representation

The thermal equilibrium of a ternary system can only be represented graphically by a model in three dimensions or by phase projections of such a model. The method employed in metallography is that due to Willard Gibbs, but more generally associated with Stokes, who independently devised the same scheme.

The percentage compositions of the alloys are represented by an equilateral triangle, the height of which is 100. The three points A, B and C, at the corners of the triangle, represent the pure metals; a point on the line AB represents a binary alloy of A and B, and similarly for the pairs AC and BC; and any point within the triangle corresponds to an alloy of the three metals.

However, the very similar arrangement due to Roozeboom is usually preferred. The vertices represent the pure metals as before, the sides of the triangle are each divided into 100 parts, and the co-ordinates of a point representing a ternary alloy are measured in directions parallel with the sides; the sum of these distances is always 100.

For a complete representation of the system, the ordinates of temperature must now be erected as perpendiculars to the plane of the triangle, and their summits joined to form a surface or a system of surfaces, so that the space model finally obtained is a triangular prism.

In employing the triangular diagram, it will be of use to note a property of the equilateral triangle. A line drawn from one corner of the triangle to the opposite side represents the composition of all mixtures in which the relative amounts of two of the components remain unchanged. Thus, as Fig. 11 shows, if the component C is added to the mixture x, in which A and B are present in the proportions of a:b, a mixture x', which is thereby obtained, also contains A and B in the ratio a:b. The two triangles ACx and BCx are similar to the two triangles HCx' and KCx';

and therefore,  $Ax:Bx = Hx':Kx'$ . But  $Ax = Dx$  and  $Bx = Ex$ ; further,  $Hx' = Fx'$  and  $Kx' = Gx'$ . Therefore,  $Dx:Ex = Fx':Gx' = b:a$ . Therefore, at all points on the line  $Cx$ , the ratio of A to B is the same.

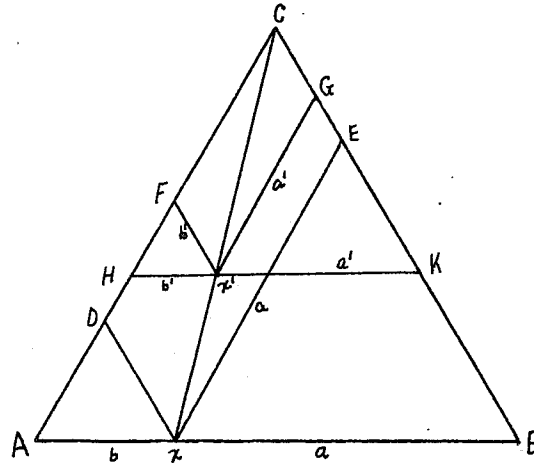


Fig. 11

### (ii) The ternary eutectic point

The ternary system may be represented as a triangular prism which has for its three faces the three binary systems obtained by taking the metals in pairs. The freezing point surfaces, which start from the angles of the prism, intersect along three lines, forming three valleys. The eutectic temperature of a binary system may be regarded as the simultaneous freezing point of the two component metals, and the addition of a third metal lowers this freezing point just as the addition of a second substance lowers the freezing point of a pure metal. The curves of intersection, or the bottoms of the valleys, therefore slope downwards from the outer faces to the interior of the prism. They finally intersect at a point, the ternary eutectic point, which necessarily represents the lowest temperature attainable with the three components given. The ternary eutectic point represents an invariant system; three solid

phases can exist in equilibrium with a ternary solution only when the latter has one fixed composition and when the temperature has a definite value. This eutectic point has, therefore, a perfectly definite position, depending only on the nature of the three components.

(iii) Ternary systems in which a region of partial miscibility occurs.

The formation of immiscible liquid phases is of importance in systems composed of three metals. When, to a mixture of two metals, a third metal is added, the mutual solubility of the two original metals is changed. The result is that the two layers approach more nearly to equality of composition as the quantity of the third metal is increased, until finally a point is reached at which the two liquid alloys become identical, and a single homogeneous liquid phase is formed. If a triangular diagram is constructed showing the composition of the liquid phases at some given temperature, a result such as that shown in Fig. 12 is obtained.

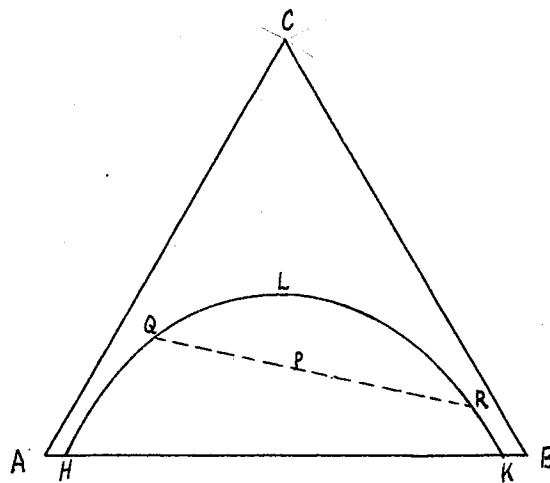


Fig. 12

A mixture, the original composition of which is expressed by a point falling within the curved boundary, as at P, separates into liquid layers, the composition of which are represented by Q and R; the alloys Q and R are then conjugate alloys. The line joining them must pass through P and was called by Stokes a tie line. As the proportion of the third metal is increased, the tie lines become shorter, finally vanishing at the point L. At this point the two liquid phases become identical in composition and the mixture becomes homogeneous. Thus all points in the triangle, lying outside the curve HQLRK, represent homogeneous liquid alloys; while points within this curve represent alloys which, at the given temperature, can only exist in the form of two liquid phases. The curve separating the two regions is the critical curve, and the points falling within it represent what are termed by Wright<sup>4</sup> as ideal alloys. That is, ideal alloys are those mixtures which divide into two or more different fluid alloys on standing molten for a sufficient time; real alloys, on the other hand, are those mixtures which remain homogeneous whilst molten, even on long standing.

The diagram in Fig. 12 is an isothermal diagram, i.e. it represents the state of things at a certain constant temperature. If similar triangular diagrams are constructed for a number of different temperatures, the area enclosed by the critical curve diminishes with increase of temperature in accordance with the increase of mutual solubility of the two liquid phases when heated. At a sufficiently high temperature it would vanish entirely, and all mixtures of

the three metals, whatever their relative proportions, would form a homogeneous liquid. In the space model of the ternary system the critical surface will thus be closed above and the highest point of the surface will be the critical point of the binary system which yields immiscible liquid phases.

It has been shown by Stokes that, in accordance with the doctrine of phases, the composition of the two conjugate alloys is independent of their relative quantity. This is a necessary consequence of the principle of equilibrium involved.

An equilibrium of this kind may be looked at from another point of view. Instead of the influence of a third metal in altering the mutual solubilities of two others, the proportion in which the third metal is distributed between the two others is considered. The ratio of the concentrations of this third metal in the upper and lower layers may be called the partition coefficient of the third metal between the other two. The concentration of this added metal is not usually the same and the tie lines are therefore not, in general, parallel to the base of the triangle; the critical curve is, therefore, more or less asymmetrical.)

In most cases the contour of the critical curve exhibits no marked sinuosity or irregularity, but in a few instances it shows a marked bulge outwards or notch inwards, which reaches its maximum development when the ratio between the third metal and one of the immiscible metals approaches toward that indicating some definite atomic compound.

In many cases, although no irregularity of outline of the critical curve is noticeable, yet the configuration of the tie lines exhibits some peculiarity leading to the idea that an atomic compound of some of the metals, which affects the relative distribution of the metals in the two conjugate alloys, is formed. Thus the convergence of the tie lines towards some central point may suggest the existence of an atomic compound. In the majority of cases, however, no change of direction in the slope of the tie lines is noticeable throughout the whole series, all sloping either to the right or to the left; there is no fixed law regulating the direction of slope. It would seem that, while the nature of the added metal obviously influences the direction of slope, it cannot be deduced that one given metal, acting as the third metal, always gives a slope to the right, and another one to the left, and so on.



PREVIOUS INVESTIGATION

Temperature in °C.

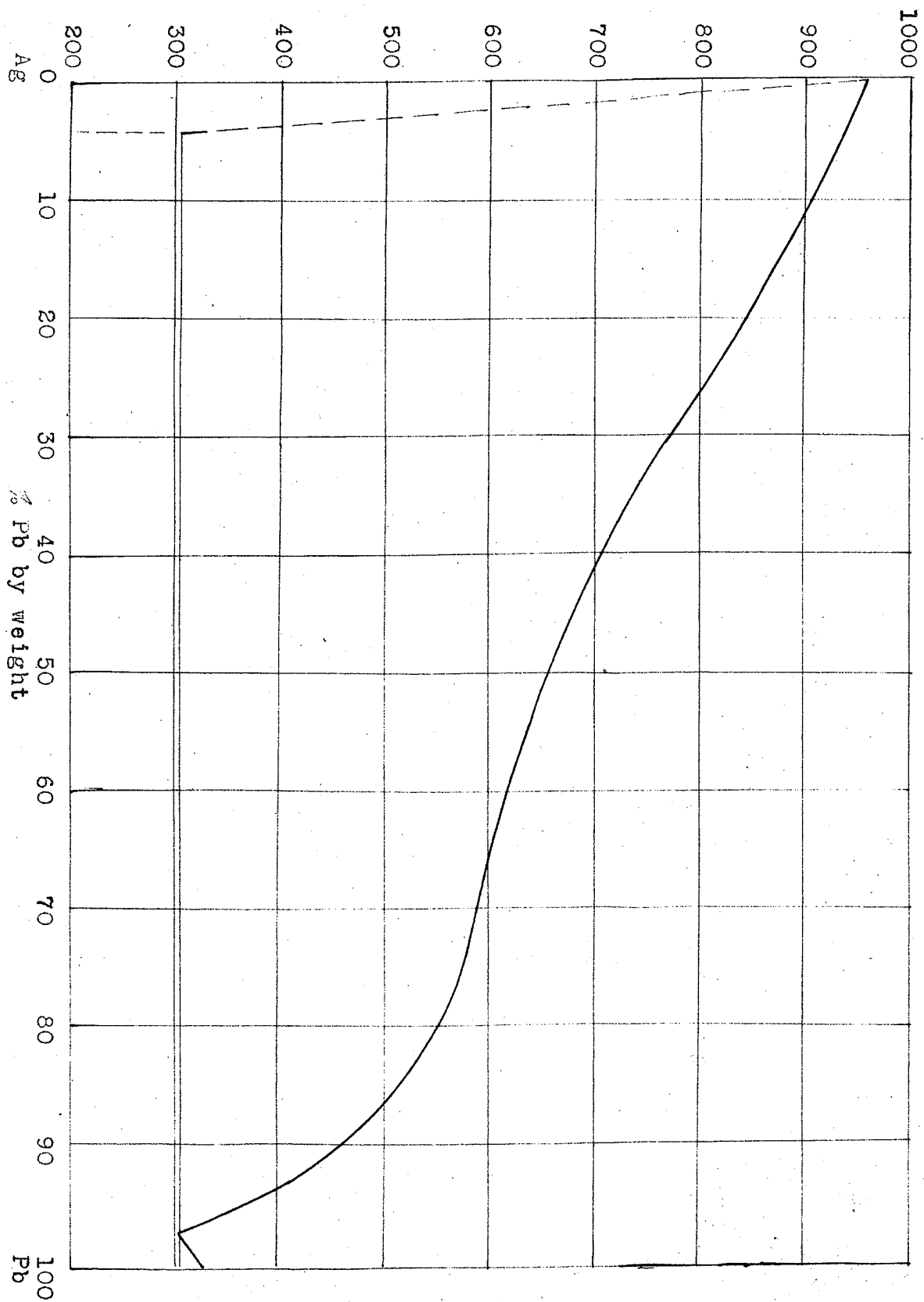
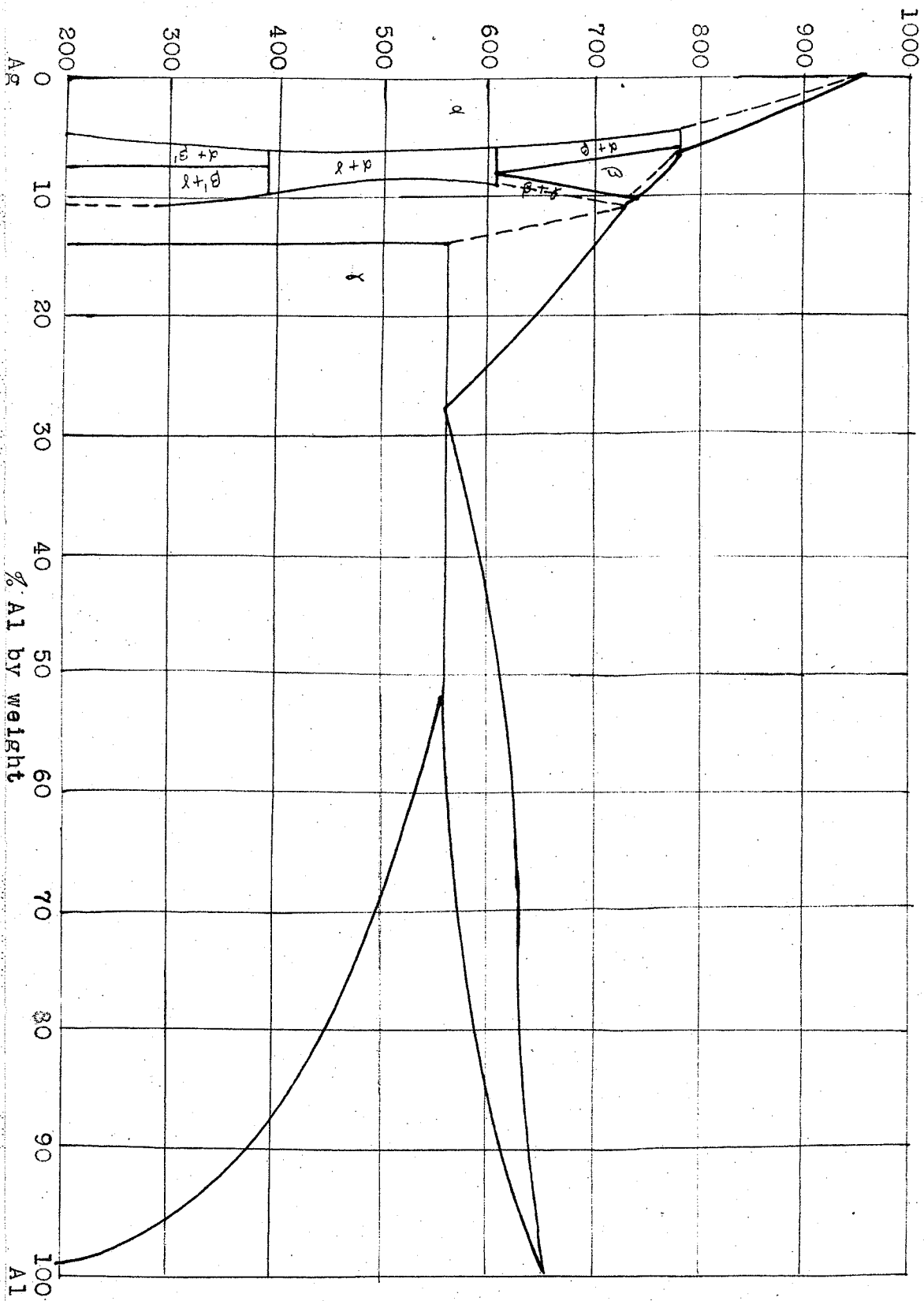


FIG. 13.

Temperature in °C.



### Previous Investigation

The results obtained by various workers for the three binary systems, Silver - Lead, Silver - Aluminium, and Aluminium - Lead, and the ternary system, Silver - Aluminium - Lead, are given below.

#### (i) Silver - Lead

G. J. Petrenko<sup>5</sup> determined the phase diagram for this system and found it to consist of two curves which intersect at a eutectic having a composition of 2.5% silver by weight and a temperature of  $303.3^{\circ}$ . This eutectic mixture was found to be harder than pure lead.

F. Yoldi (with D. L. de A. Jimenez)<sup>6</sup> found that cooling curves and photographs of the alloys of lead and silver gave no evidence of the formation of compounds. The eutectic mixture contained 2.3% silver and separated at  $300 - 305^{\circ}$ . The components are completely miscible in the liquid state. The Brinell hardness changes continuously for alloys containing 25 - 100% of silver.

Heycock and Neville<sup>7</sup> found that the eutectic temperature was  $304^{\circ}$  and the eutectic composition, 4% silver.

The equilibrium diagram has been constructed and is given in Fig. 13.

#### (ii) Silver - Aluminium

Petrenko<sup>8</sup> examined the system thermally and from the diagram obtained, concluded the existence of two compounds,  $AlAg_2$  (88.89 wt. % Ag) and  $AlAg_3$  (92.31 wt. % Ag). Gautier had previously worked out part of the diagram and had found a maximum corresponding to the compound with the composition  $AlAg_2$ . Petrenko was unable to confirm this

maximum and believes it more probable that the compound  $\text{AlAg}_2$  forms owing to a peritectic reaction at  $718^\circ$ , and the alloy with the composition  $\text{AlAg}_3$  corresponds to the end point of the peritectic horizontal at  $770^\circ$ . Also Al and  $\text{AlAg}_2$  form a eutectic at about 69% Ag and  $567^\circ$ .

W. Broniewski<sup>9</sup> observed the electrical conductivity, the temperature coefficient of the electrical resistances, the thermoelectric force and the potential of silver-aluminium alloys. The curve of the temperature coefficient and the thermoelectric force shows two marked maxima at 60.9% and 75.4% by volume of Ag, corresponding to the compounds  $\text{Al}_2\text{Ag}_3$  (85.71 wt. % Ag) and  $\text{AlAg}_3$ . The former compound does not agree with Petrenko's curve and since the latter's work has the greater justification, it is thought that the second compound is not  $\text{Al}_2\text{Ag}_3$  but is  $\text{AlAg}_2$ .

<sup>10</sup> M. Hansen investigated that part of the phase diagram of alloys with 0 - 60% Ag. The results obtained by thermal analysis show that the temperature lies almost throughout somewhat lower than that obtained by Petrenko, with similar alloys observed. By thermal analysis, he found the eutectic to lie at  $558^\circ$  and the microscopic investigation was in agreement with this, giving the eutectic as being between  $555^\circ$  and  $565^\circ$ . The solubility of silver ranges from about 0.75% at  $200^\circ$  to about 48% at the eutectic temperature. Under  $200^\circ$  the solubility probably becomes still lower, as can be shown by hardness tests, so that at room temperature the saturation limit lies under 0.5% Ag.

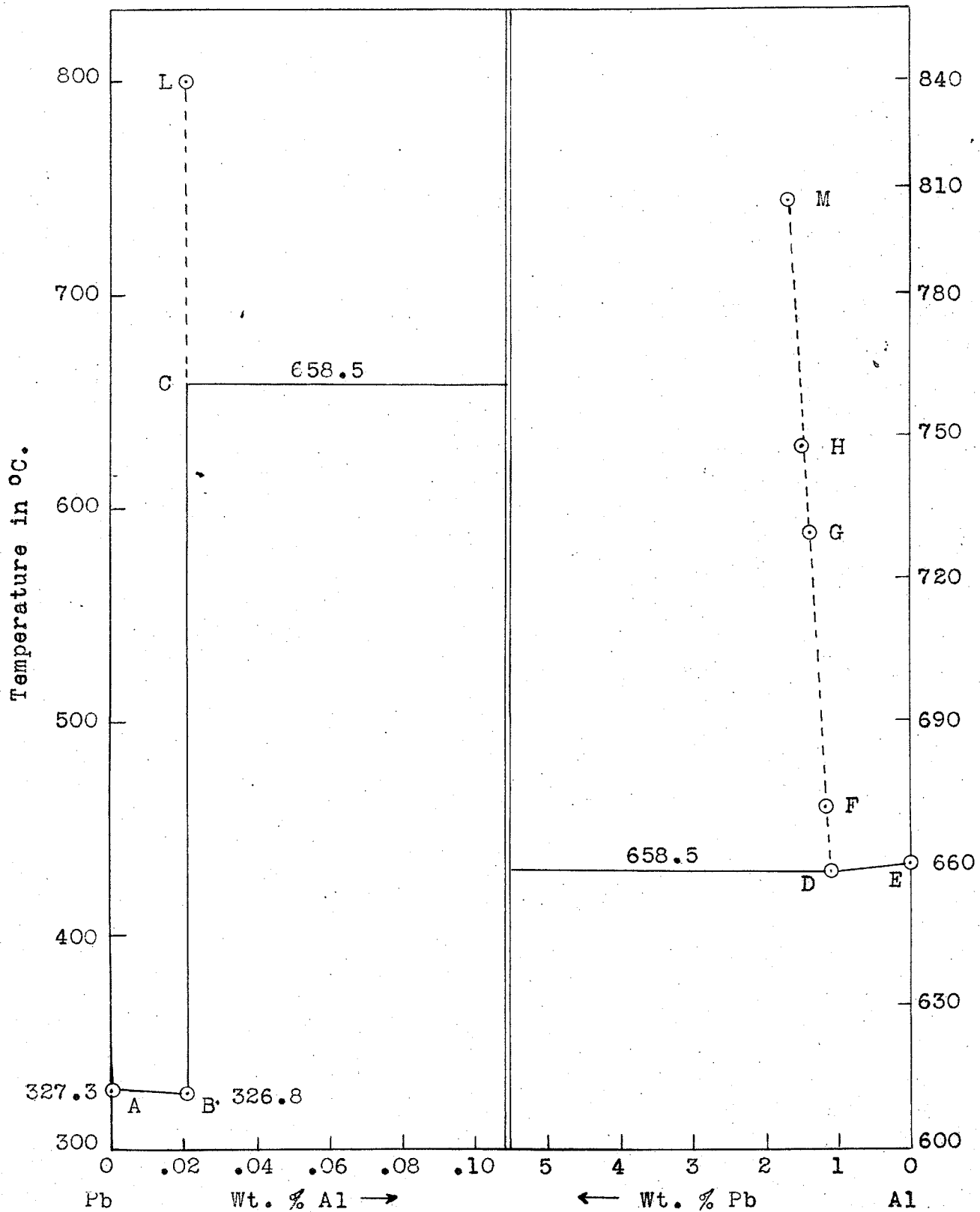
Shuzo Ueno<sup>11</sup> investigated the system by means of the intensity of reflection of light. The intensity of

reflection of the silver is rapidly diminished by the addition of the aluminium until it attains a minimum at the middle of the series of the solid solution, beyond which the intensity is again increased through the influence of the compound  $AlAg_3$  where it has a maximum. The curve then falls rapidly to the second compound  $AlAg_2$  where there is a break, and continues to fall gradually to a minimum at the eutectic. The curve of reflection runs generally in a smooth line, except the part of the two compounds, of which  $AlAg_3$  is characterised by a maximum and  $AlAg_2$  by a minimum.

Hoar and Rowntree<sup>12</sup> studied the equilibria of this system above  $600^\circ$  thermally and micrographically in the range 0 - 15% Al by weight. The liquidus is in general agreement with that found by Petrenko but the freezing points are all some 5 -  $10^\circ$  higher than those of Petrenko's corresponding alloys, which is probably due to the greater purity of their aluminium. There are two breaks in the curve, the first at 6.2% Al and  $779^\circ$ , the second at 10.8% Al and  $729^\circ$ ; no maxima or minima occur.

Ageew and Shoyket<sup>13</sup> studied the system up to 10% Al by means of X-rays. They found that the  $\beta$  phase, formed by the peritectic reaction at  $779^\circ$ , decomposes into a mixture of  $\alpha$  and  $\gamma$  below  $600^\circ$ . The  $\beta'$  phase ( $AlAg_3$ ) is only stable at temperatures below  $400^\circ$ , above this temperature it decomposes into a mixture of  $\alpha$  and  $\gamma$ .

The equilibrium diagram, as constructed from these investigations, is given in Fig. 14.



The System Aluminium - Lead

Fig. 15

(iii) Aluminium - Lead

Mr. R. W. Ashley<sup>14</sup>, working in this laboratory, investigated this system and found that the melting point of aluminium was lowered  $1.5^{\circ}$  by the addition of 1.10% of lead. There is also a eutectic containing 0.021% Al and this has a temperature of  $326.8^{\circ}$ . The solubility of lead in liquid aluminium rises from 1.10% at  $658.5^{\circ}$  to 1.70% at  $800^{\circ}$ ; the solubility of aluminium in lead is so slight that no appreciable increase was observed up to  $800^{\circ}$ .

(iv) Silver - Aluminium - Lead

C. R. A. Wright<sup>15</sup> obtained the critical curve for this system but no record was made of temperature other than the fact that the alloys were first heated to about  $870^{\circ}$ . There is no marked irregularity of contour visible nor any tendency towards convergence of the tie lines to a fixed point. The tie lines slope uniformly to the left, i.e. toward the lead angle of the diagram.

The diagram of the Aluminium - Lead system is given in Fig. 15.



**EXPERIMENTAL**

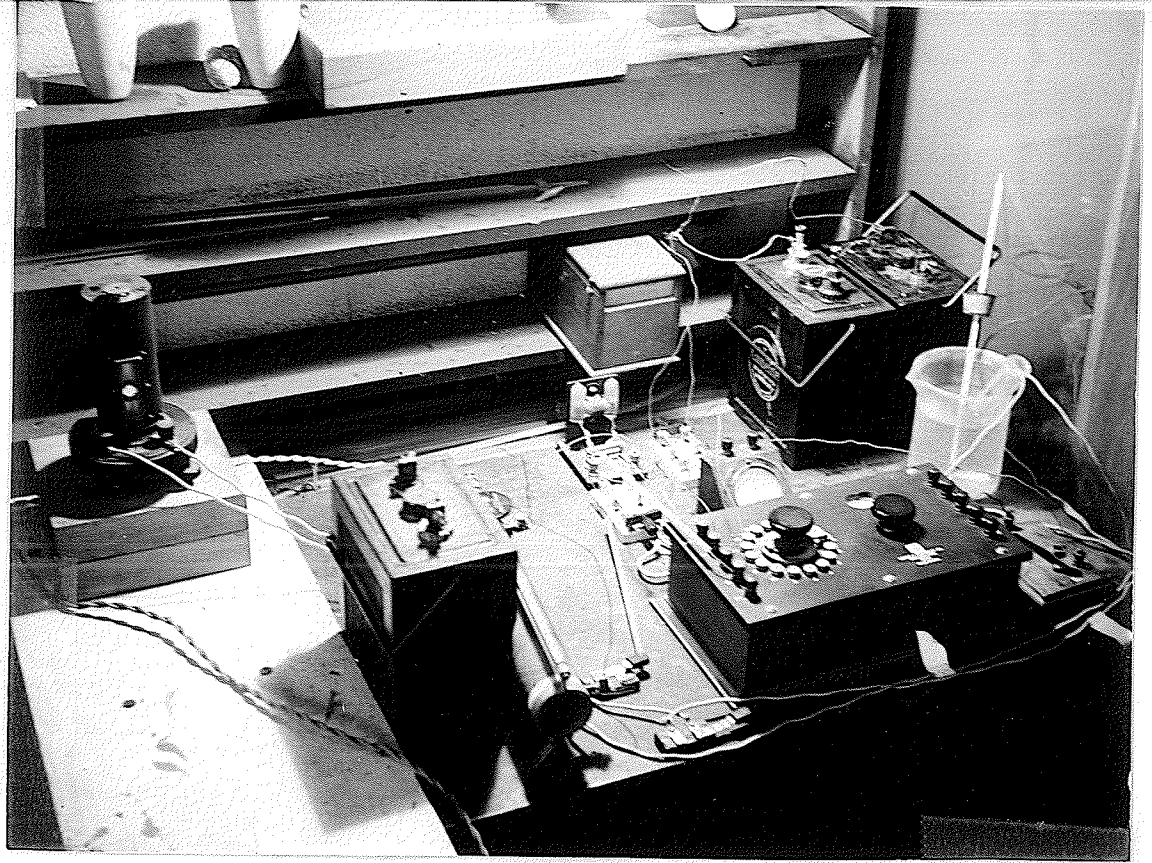


PLATE I

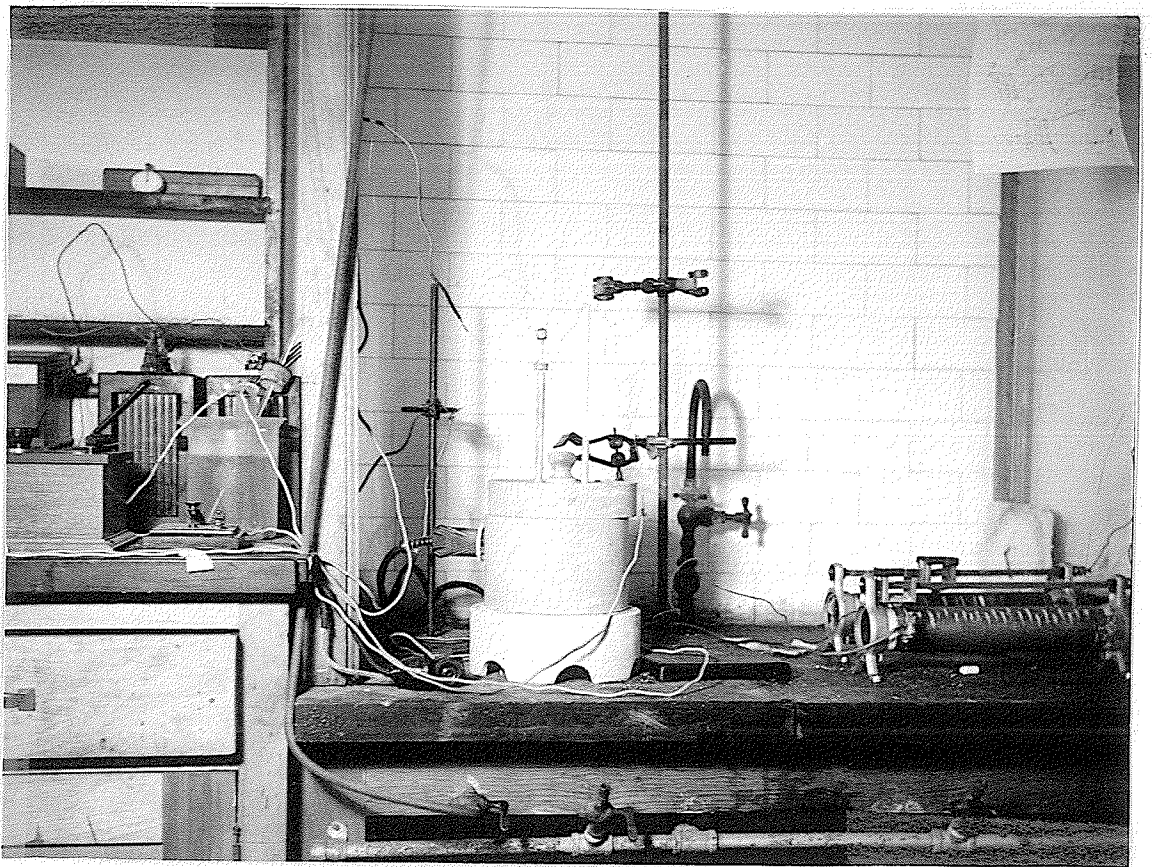
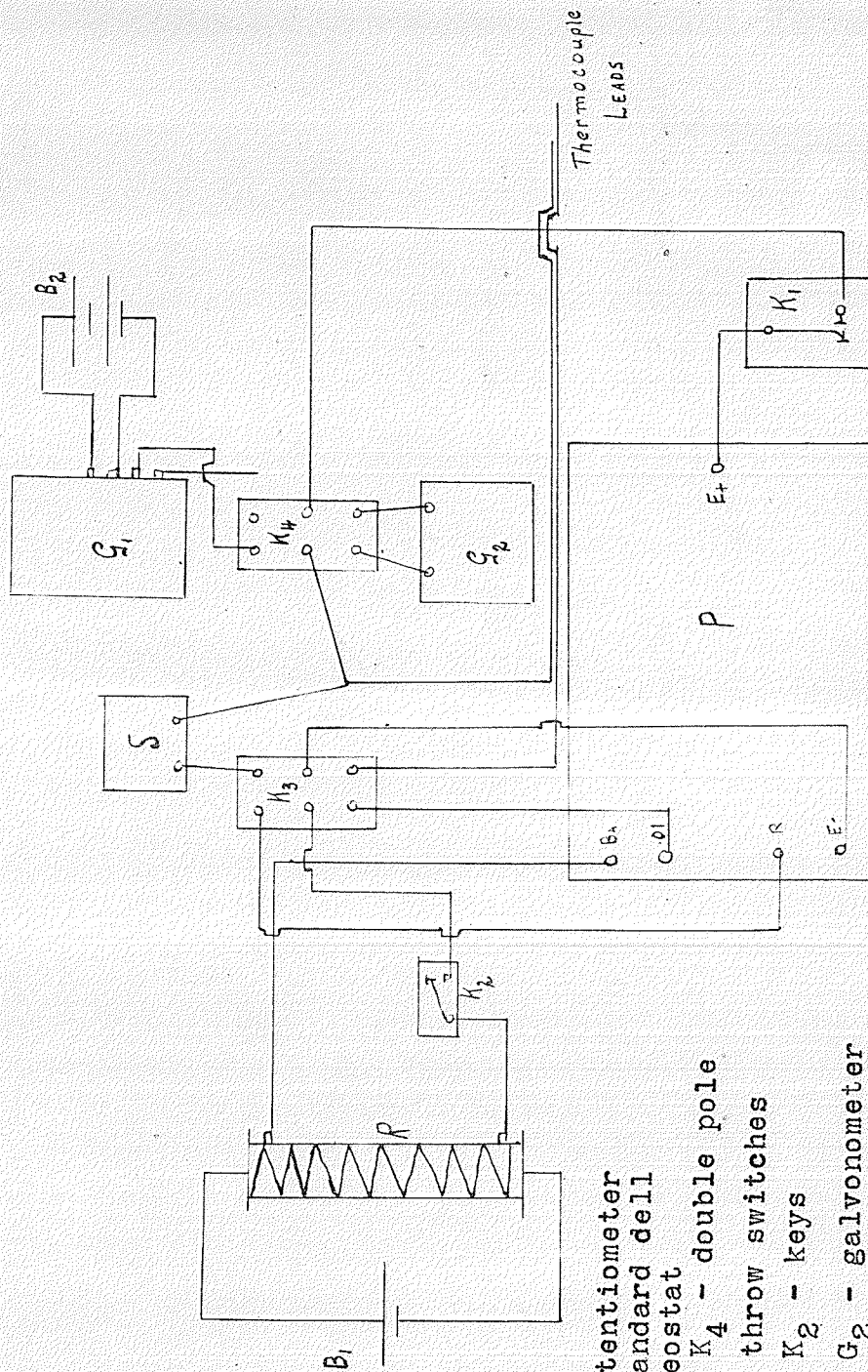


PLATE II



- P = Potentiometer
- S = Standard cell
- R = Rheostat
- K<sub>3</sub> and K<sub>4</sub> = double pole double throw switches
- K<sub>1</sub> and K<sub>2</sub> = keys
- G<sub>1</sub> and G<sub>2</sub> = galvanometer

Fig. 18

## Experimental

### (1) The apparatus and its calibration

The complete set-up of the apparatus used in this investigation is shown in Plates I and II, and Fig. 18.

The furnace in which the alloys were melted was of the electrical resistance type and was capable of maintaining a temperature of  $950^{\circ}$  for a long period of time, but temperatures slightly over  $1000^{\circ}$  could be reached. In order to cool the furnace gradually, in accordance with Plato's method of cooling, two rheostats were connected in series with it; these were graduated in such a way that, when the slider was moved along one division per minute, the rate of cooling of the furnace was about  $5^{\circ}$  per minute. Holes were made in the cover of the furnace to enable two thermocouples to be inserted; these were large enough to permit free movement of the thermocouple casings, so that the alloy could be stirred by means of these.

The thermocouples used in the measurement of the temperatures were of the Pt - Pt/Rh type. The wires were separated along their length by passing them through a small double-bored sillimanite tube which was in turn enclosed in another sillimanite tube in order to protect the junction from the action of the molten metals. One thermocouple was inserted directly in the molten alloy and was connected to a potentiometer through a sensitive galvanometer. Thus from the readings on the potentiometer, the temperature of the alloy was found. The sensitivity of the potentiometer was equivalent to a change of  $0.1^{\circ}$  in the temperature and, therefore, an accuracy of  $\pm 0.25^{\circ}$

may be claimed for the results obtained. The second thermocouple was placed in a neutral body and was connected differentially with the first thermocouple through a reflecting galvanometer. The neutral body consisted of a copper cylinder of approximately the same thermal capacity as the alloy and was used in order to determine the temperature difference between the specimen and the enclosure. This method was first proposed by Sykes and owes its applicability to the fact that, on cooling, the temperature difference between the specimen and the neutral body remains practically the same until some thermal effect takes place in the alloy. When this occurs, the rate of cooling of the alloy is changed while that of the neutral body remains the same as before, i.e. follows the cooling of the furnace. This is seen in the galvanometer as a sudden, sharply defined deviation from the original temperature difference.

The temperature obtained from the potentiometric measurements does not represent the true temperature of the alloy due to the fact that the formulae derived for the E.M.F. of a thermocouple are based on the assumptions that the cold junctions, that is, the points at which the wires of the couple make contact with the leads, are at  $0^{\circ}\text{C}$ . Therefore, it is necessary to pass the lead through a test tube which is contained in a beaker of water at room temperature. A mercury thermometer in this beaker gives the cold junction which must be added to the potentiometric measurement in order to obtain the true temperature of the alloy.

The thermocouple was calibrated by taking the

melting points of several pure metals. Those taken were tin,  $231.9^{\circ}$ ; lead,  $327.3^{\circ}$ ; zinc,  $419.5^{\circ}$ ; aluminium,  $658.7^{\circ}$ . A calibration curve was plotted from the potentiometric readings obtained. The calibration was checked at intervals throughout the investigation by means of pure lead and pure aluminium in order to make certain that the thermocouple was not contaminated.

The differentially connected thermocouples were calibrated in the following manner: one thermocouple was placed in a bath of water at room temperature while the other was placed in another bath which was gradually heated. Temperature readings and displacements on the scale were taken every minute and it was found that a difference of  $1^{\circ}$  in temperature was represented by a displacement of 3.6 mm.

(ii) Method of taking cooling curves

The silver and aluminium were put in a crucible and melted by means of a Meker burner; the lead was then added, the alloy thoroughly stirred and the crucible then transferred to the furnace. This method is open to the criticism that the alloy might take up some of the hot gases from the burner, although it is doubtful whether these would have any effect on the cooling curve of the alloy. It would have been preferable to melt the alloys right in the furnace but, unfortunately, when the silver content of the alloy was high, the furnace would not produce a temperature high enough to melt the silver. Consequently it was necessary to resort to the Meker.

The total weight of alloy taken was generally about 100 grams.

The thermocouples were inserted through the holes in the cover and the temperature of the furnace raised to a point where the alloy was entirely molten at which point it was kept constant for a short time. The slider on the rheostat was then moved along one division per minute and readings taken simultaneously on the potentiometer and the reflecting galvanometer every minute. These readings were then plotted on the same graph and from this the temperature of the thermal effect was determined.

Due to the battery gradually running down, it was found necessary to balance it against a standard cell by means of a rheostat before each determination.

The crucibles used in the first part of the work were made of alundum and they proved entirely satisfactory. When these were used up, there were no more obtainable so that Coors glazed crucibles had to be used. These were very unsatisfactory due to the fact that once the alloy had been cooled, if it were reheated, the crucible broke. Thus many alloys had to be discarded due to contamination picked up when the crucible broke while heating the alloy for a second determination. To prevent this, a small porcelain basin was put in the furnace and the crucible placed in this.

### (iii) Microscopical examination

The alloys to be examined were cut through vertically and the surface made as smooth as possible by means of files. The alloy was then taken on to a coarse emery paper and polished in one direction until the scratches made by the file had been removed. An emery paper of a

finer grade was then substituted and the polishing continued in a direction at right angles to that used with the previous paper until the scratches left by the coarse paper had been removed. This operation was continued, using progressively finer emery papers, until the surface appeared absolutely free from scratches to the naked eye. For the final polishing, the alloy was taken on a wheel covered with a felt cloth to which was applied a suspension of levigated alumina in water. This was continued until there were no scratches visible on the surface, even when examined under the microscope.

The specimens were mounted for examination by the microscope on glass slides with plasticine by means of a mounting stand.

The structure of the alloys was brought out more clearly by the use of various etching reagents. Those tried in the course of the investigation were: a 10% solution of nitric acid, a 20% solution of sodium hydroxide, bromine water, a 20% solution of sodium carbonate, and a dilute solution of a chromic acid - sulphuric acid mixture. Of these reagents, the most effective was found to be the 10% solution of nitric acid. The specimens were placed, with the polished surface up, in the solution and allowed to remain there for from five to ten minutes, depending on the concentration of aluminium in the alloy; those with high percentages of aluminium required the longest period of treatment. The specimens were then removed from the solution, rinsed off in distilled water, put in alcohol to remove the water and then they were dried.



After etching, photomicrographs were taken of each alloy. The equipment used for the photography was a Bausch and Lomb photomicrographic unit, consisting of a simple box camera mounted on a vertical supporting rod. 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 position over the microscope and the final focussing obtained by means of a piece of frosted film placed in the back of the camera. The sensitive film was then substituted and the exposure made.

#### (iv) Hardness determinations

The hardness of the alloys was determined by means of a Brinell hardness testing machine. The specimen is placed on a plate which is adjusted until the surface of the specimen is horizontal and an indentation is 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 kgms. for 30 seconds. The usual load used in testing the hardness of metals is 500 or 3000 kgms. , but with alloys having a high percentage of lead, this load was found to be too great. The indentations made by the steel ball were measured by 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. The degree of hardness of the alloy is given by the Brinell number which is calculated

from the following formula:

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

where, H is the Brinell number

P ----- load applied

D ----- diameter of the steel ball

d ----- diameter of the indentation.

#### (v) Analysis of the alloys

The aluminium used in the preparation of the alloys was 99.2% pure, containing 0.58% iron and 0.22% silicon. The lead contained 0.0001% silver and 0.0025% copper. The silver used was the highest purity fine silver.

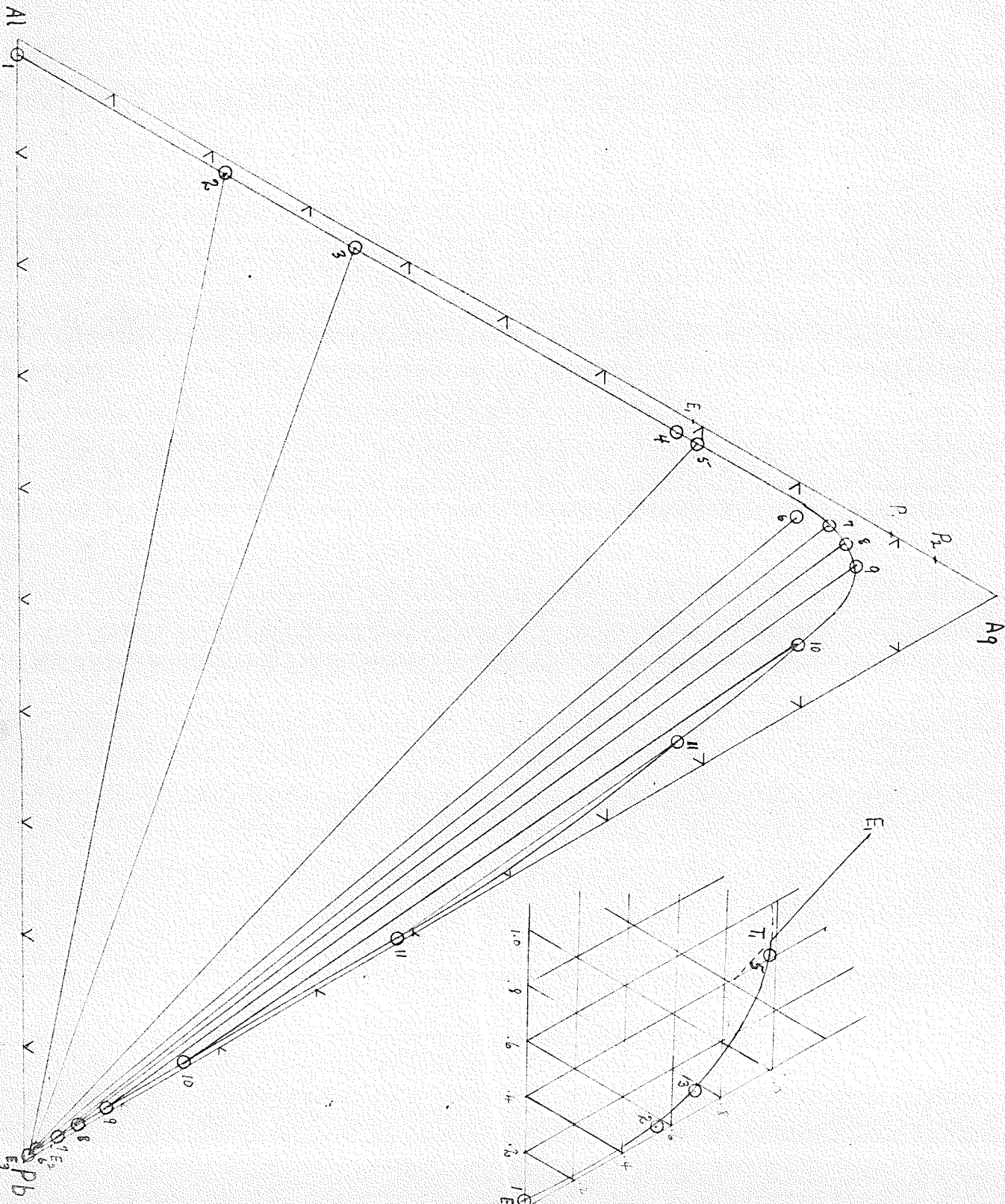
For analysis, the alloy was cut vertically and representative borings taken from the upper layer. Borings could not be obtained from the lower layer so that it was necessary to cut off shavings by means of a sharp knife. The samples were then weighed, dissolved in nitric acid and the solution made up to 250 cc. 25cc. of this solution were then taken and the silver content determined by titrating with potassium thiocyanate using ferric indicator. Another 25 cc. of the solution were taken, the silver precipitated as AgCl and this then filtered off. The aluminium was first precipitated as the basic acetate, dissolved and reprecipitated as hydroxide; the precipitate was then ignited and weighed as  $Al_2O_3$ . The filtrate from the aluminium was rendered distinctly acid with acetic acid and the lead precipitated by adding potassium chromate; this was filtered through a Gooch crucible, dried at  $120^\circ$  and weighed as lead

chromate.

In order to plot the results obtained, on triangular graph paper, the analyses were finally calculated to a total percentage of 100.

In alloys rich in aluminium and containing relatively small amounts of silver, the results obtained for the lead analysis were meaningless due to the fact that aluminium may hold as much as 10% lead in the form of a colloidal dispersion. Heat treating these alloys, i.e. allowing them to stand for a long time at a high temperature, greatly reduced the amount of lead present but the results were still not satisfactory. It was finally found necessary to resort to thermal analysis in these cases. For this method, an alloy of aluminium and silver was made up which had a definite known composition, the temperature of solidification was found and then lead was added in quantities of  $\frac{1}{2}\%$  at a time. The temperature of solidification was determined each time until a constant temperature was reached. Then, by plotting the temperature of solidification against the percentage of lead added, the true amount of lead in the alloy could be determined, the remainder being held colloiddally. As the percentage of silver in the alloy increased, and therefore the aluminium content decreased, this colloidal effect gradually diminished until, finally, above about 80% silver, the phenomenon seemed to have disappeared entirely and the chemical analysis could be taken as accurate.

R E S U L T S



Liquoid diagram for the system Ag - Al - Pb  
 FIG. 16

## Results

In order to obtain the liquidus curve for the system, silver - aluminium - lead, eleven alloys of varying compositions were taken. The metals are only partially miscible so that in all of these alloys there were two layers formed. Cooling curves were taken of each alloy, the specimen cut vertically and samples taken from each layer for analysis. The solidification temperatures and analyses found are given in Tables I - IV. The curve, as obtained from these data, is shown in Fig. 16. This curve is purely a liquidus and involves no transformations or changes in the solid state.

Table I

Analysis of the lighter alloys

Number of alloy	Wt. %		
	Ag	Al	Pb
1	0	98.90	1.10
2	21.25	77.60	1.15
3	34.51	64.13	1.36
4	67.50	30.71	1.73
5	69.20	29.03	1.73
6	79.64	17.21	3.11
7	82.86	14.76	2.38
8	84.56	12.40	3.04
9	85.58	9.69	4.71
10	79.73	5.79	14.48
11	67.29	3.38	29.33

Table II

## Temperature arrests in the lighter alloy

Number of alloy	1st trial	2nd alloy	Mean
1			658.5
2	611.6	613.4	612.5
3	594.7	593.1	593.9
4	548.3	548.9	548.6
5	582.4	580.8	581.6
	548.9	548.6	548.7
6	664.4	664.8	664.6
	547.5	548.6	548.1
7	699.0	696.3	697.7
8	723.2	723.4	723.3
9	728.1	729.0	728.5
10	738.4	734.1	736.3
11	727.5	725.3	726.4

Table III

## Analysis of the lower alloys

Number of alloy	Wt. % Ag	Wt. % Al	Wt. % Pb
1	0	.025	99.975
2	.54	.025	99.40
3	.70	.078	99.18
5	.97	.41	98.62
6	1.08	.38	98.54
7	3.39	.24	96.37
8	5.59	.32	94.09
9	8.31	.21	91.48
10	16.55	.17	83.33
11	38.42	.30	61.03

Table IV

## Temperature arrests in the lower alloys

Number of alloy	1st trial	2nd trial	Mean
1			326.8
2	324.4	323.6	324.0
3	320.8	320.8	320.8
5	322.7	325.2	323.9
6	306.5	307.0	306.7
7	305.2	304.0	304.6
8	306.3	306.1	306.2
9	303.8	304.5	304.2
10	397.5	400.2	398.9
	304.0	303.7	303.9
	596.8	596.0	596.4
11	303.0	306.0	304.5

In Table I, the lead content of the alloys 2 to 5 inclusive was determined by means of thermal analysis, as described previously. The high value for lead in alloy 6 is probably due to the fact that the colloidal phenomenon has not yet entirely disappeared. The values for the remaining alloys were obtained by chemical analysis. The figures for alloy 1, containing no silver, are those obtained by MR. R. W. Ashley<sup>14</sup>.

In the lighter alloy, the silver content increases until it reaches a maximum of 85.58% by weight, after which it falls again. With increasing silver content the lead content also rises. This increase is very slight at first, rising from 1.10% in the alloy which contains no silver



to 1.73% in the alloy containing silver and aluminium in the proportions in which they are present in the binary eutectic of the silver - aluminium system. From this point, the lead content rises very rapidly.

As the amount of silver increases from 0 - 69% by weight, the temperature falls until it finally reaches a minimum value of  $548.5^{\circ}$ . This is the temperature at which the  $\text{AlAg}_2$  - Al eutectic plus 1.73% lead strikes the miscibility curve. Beyond 69% silver, the temperature begins to rise rapidly and continues to rise even in alloys whose composition lies past the summit of the miscibility curve. It finally attains a maximum value of about  $736^{\circ}$  in the alloy containing about 80% silver and 14% lead. Thus the temperature maximum does not coincide with the maximum of the miscibility curve.

In the heavier alloy, the silver content rises very slowly until after the lighter alloy has passed to the right of the summit of the curve, after which the content of the alloy increases very rapidly. The aluminium content remains very small even in alloys with a silver content up to 40%.

Theoretically, two ternary eutectica should be present in the heavier alloy. This at once becomes evident if we consider an exaggerated diagram such as that given in Fig. 17.

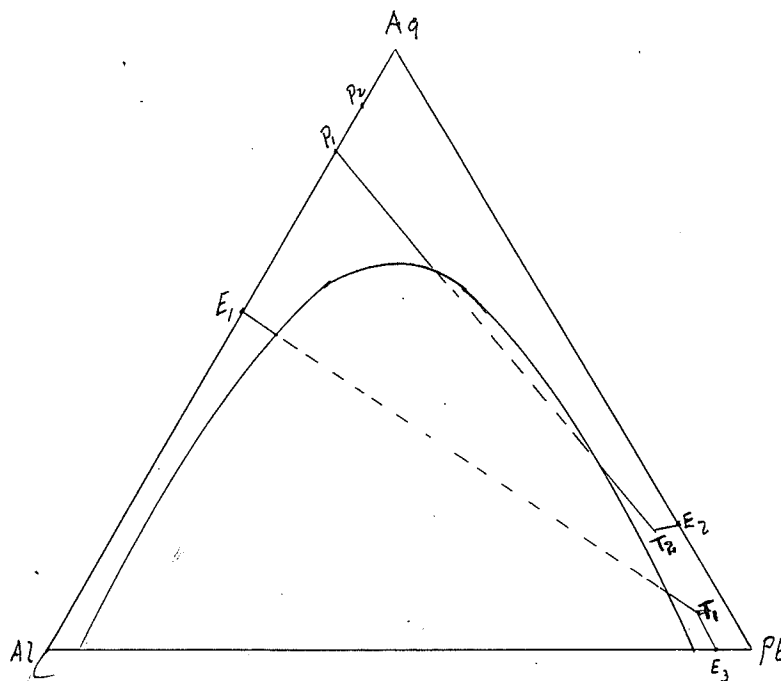


Fig. 17

where $P_1$	-----	"	"	"	"	"	"	"	"	the composition of the compound $AlAg_2$
$P_2$	-----	"	"	"	"	"	"	"	"	"
$E_1$	-----	"	"	"	"	"	"	"	"	binary eutectic $AlAg_2$ -Al
$E_2$	-----	"	"	"	"	"	"	"	"	of Ag - Pb
$E_3$	-----	"	"	"	"	"	"	"	"	of Al - Pb
$T_2$	-----	"	"	"	"	"	"	"	"	ternary eutectic of $AlAg_2$ - Ag - Pb
$T_1$	-----	"	"	"	"	"	"	"	"	ternary eutectic of $AlAg_2$ - Al - Pb

The formation of these eutectica are explained in the following manner. Along the line joining the point  $E_3$  with the silver vertex of the triangle, aluminium and lead separate side by side when the eutectic temperature has been reached; along the line joining the point  $E_1$  with the lead vertex, the separating substances are aluminium and the

compound  $\text{AlAg}_2$ . Thus, where these two lines intersect, the three phases,  $\text{AlAg}_2$ , Al and Pb, must separate side by side. From a consideration of the phase rule it is evident that the point where these lines intersect forms an invariant point, The ternary eutectic. Similarly, along the line joining the point  $P_1$  to the lead vertex, the solid phase separating is the compound  $\text{AlAg}_2$ . This intersects the line drawn from  $E_2$  to the aluminium vertex, along which silver and lead are separating together. Once again, at the point of intersection, the three phases,  $\text{AlAg}_2$ , Ag and Pb, are in equilibrium with the liquid phase and thus a second ternary eutectic is formed at this point.

These two eutectical were actually found but time did not permit an accurate determination of their compositions. In order to get this, the method of thermal analysis would have to be used. That is, for  $T_2$ , one would start with the binary eutectic mixture of silver and lead and add small quantities of aluminium, taking the temperature of solidification each time until a constant temperature is reached. Then, by plotting the percentage of Al added against the temperature, the composition of the eutectic could be determined. Similarly for  $T_1$ , start with the binary eutectic of aluminium and lead and add small quantities of silver. The compositions of these two eutectica have been obtained here by the graphical method. Thus, in the inset in Fig. 16, a line is drawn through the plots of the heavier alloys, 2, 3 and 5, and extended to meet the line from the  $\text{AlAg}_2$  - Al eutectic. In this way the composition

of the ternary eutectic,  $\text{AlAg}_2 - \text{Al} - \text{Pb}$ , is found to be 98.57% Pb, 0.97% Ag, and 0.46% Al. The eutectic temperature at this point is  $324.0^\circ$ .

For the second ternary eutectic, a line was drawn from the silver - lead eutectic to the aluminium vertex and another, from the point corresponding to the compound  $\text{AlAg}_2$ , to the lead vertex.. The intersection of these two lines is taken as the composition of the ternary eutectic,  $\text{AlAg}_2 - \text{Ag} - \text{Pb}$ , and this is: 97.2% Pb, 2.2% Ag and 0.6% Al. The eutectic temperature in this case is  $304.3^\circ\text{C}$ .

The temperature of  $596.8^\circ$  and  $398.9^\circ$ , obtained in alloy 10, are due to the fact that, in the Al - Ag system, a  $\beta$  phase forms owing to a peritectic reaction at  $779^\circ$ . This phase is, however, stable only above  $600^\circ$  and at  $610^\circ$  it decomposes into a mixture  $\alpha + \gamma$ . This mixture also has a region of limited existence and at a temperature of about  $400^\circ$ , the  $\beta'$  ( $\text{AlAg}_3$ ) phase is formed and this is the form which is stable at room temperature. From these temperatures, it would appear as if these transformation temperatures were lowered when lead is also present in the system.

From analysis, it is evident that the lighter alloys always contain more silver than the heavier alloys and, therefore, the tie lines slope uniformly to the right as seen in Fig. 16.

"There is no marked irregularity of contour on the curve nor any tendency towards convergence of the tie lines to a fixed point". These observations have been made by Wright<sup>15</sup> and are confirmed by the present work.

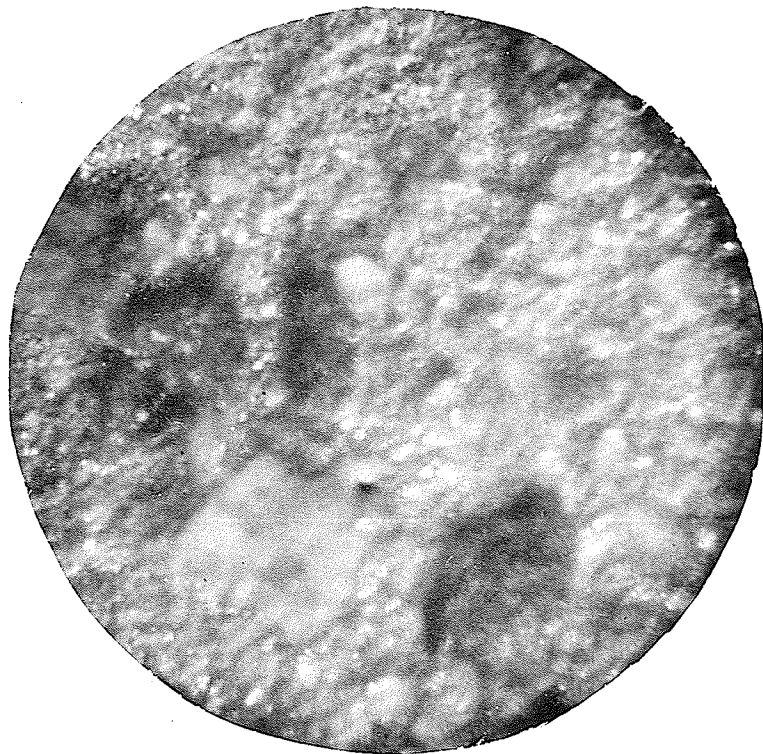
Due to lack of space in Fig. 16, the temperatures of the individual points have not been put in. These may, however, be found in Tables II and IV. The diagram given is not an isothermal one so, in order to visualize the shape of the complete curve, these temperatures must be related to their corresponding alloys.

Brinell hardness tests were made on a number of the alloys and the comparative results obtained are given in Table V.

Table V

Specimen	Brinell Number
Pure Lead	4.24
Pure Aluminium	15.92
Pure Silver	12.73
Eutectic, silver - aluminium	79.57
Eutectic, silver - aluminium saturated with lead	
Alloy 4	66.25
Lighter Alloy 3	58.34
Lighter Alloy 2	55.30
Lighter Alloy 6	63.66

From the table, it is evident that when silver is added to aluminium, the resultant alloy is very much harder than either of the two component metals. When lead is added, its presence seems to reduce the hardness. The alloys appear to reach a maximum hardness with the alloy in which aluminium and silver are present in their eutectic proportions and saturated with lead. With alloys beyond this composition, the increasing lead content reduces the hardness.



Pure Lead

x200

Plate III.



Pure Aluminium

x 200

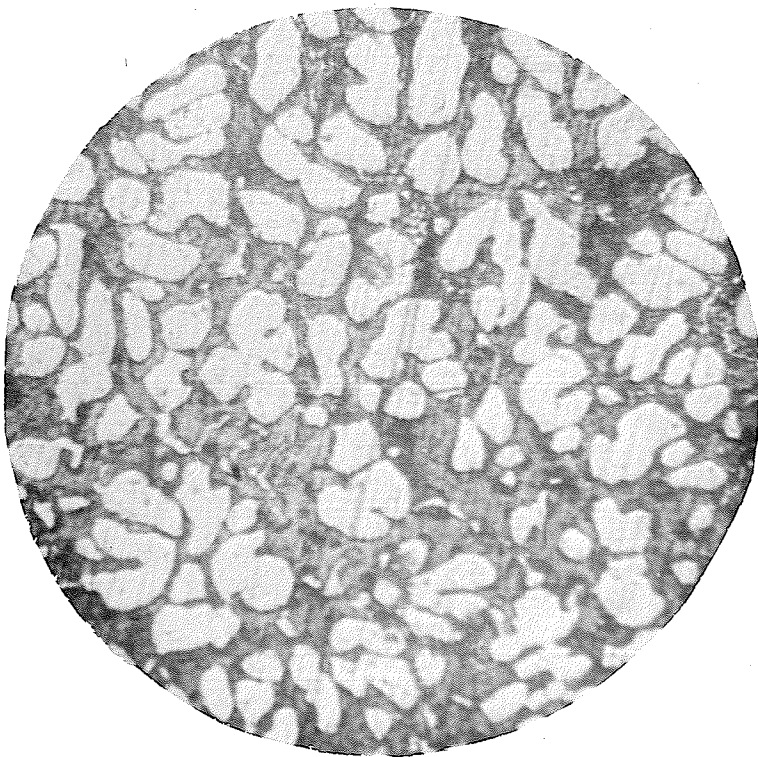
Plate IV.



Lighter Alloy 3

x400

Plate V.



$AlAg_2$  - Al Eutectic

x 200

Plate VI.



$AlAg_2$  - Al Eutectic + 4% Pb x 400

Plate VII.



## Micro Structure

The results obtained from the various microscopic examinations is given by the photomicrographs shown in Plates III to VII.

Plate III is a photomicrograph taken of pure lead. Large crystals, characteristic of the structure of lead, are easily seen on the surface of the specimen. The structure shown here is that obtained after etching for 5 minutes with a 10% solution of nitric acid. The magnification was 200 diameters.

Plate IV shows the crystal structure of pure aluminium. The separate crystals are marked out by fine boundary lines. These are evident at the angles where the crystals meet, consisting of three branches. It is quite possible that in absolutely pure aluminium this crystal structure would not be so clearly seen. Here, the impurities in the aluminium would be held between the crystals thus giving the crystal outline more sharply. This specimen was etched for 10 minutes with a 10% solution of nitric acid.

Plate V shows the appearance of the alloy containing 34.51% silver (lighter alloy 3). The large bright mass is a blob of the compound  $AlAg_2$ . This crystallized out first and the surrounding mass, which is aluminium, solidified afterwards. The compound takes a much better polish than the aluminium due to the fact that it is much harder and it does not stain on etching with nitric acid. A large number of skeleton crystals were also visible in this alloy. This was etched for 20 minutes with nitric acid.

Plate VI is the eutectic mixture  $AlAg_2$  - aluminium.

This structure is typical of eutectic mixtures, i.e. a small pattern of one substance surrounded by a second. Again the bright blobs are the compound  $AlAg_2$  surrounded by the darker mass which is aluminium. Etched for 5 minutes with a 10% solution of nitric acid.

In Plate VII, 4% lead has been added to the eutectic alloy seen in Plate VI. The structure is very similar to that of the eutectic mixture but the bright compound particles are much larger and between them is a dark field, aluminium, crossed by a number of parallel bright lines. This specimen was etched for 1 minute with a 20% solution of sodium hydroxide.

### Summary

(1) The area of partial miscibility for the ternary system, silver - aluminium - lead, has been determined by thermal analysis and has been found to extend to alloys containing a maximum of 85.58% silver and 4.71% lead by weight.

(2) The temperature corresponding to this area has been found to fall at first until the temperature of 548.5° is reached. This is the temperature of solidification of the alloy which contains silver and aluminium in their eutectic proportions and is saturated with lead. The temperature then increases to a maximum of about 736° in the alloy containing about 80% silver and 14% lead. This temperature maximum does not coincide with the maximum of the liquidus curve but lies well to the right of it.

(3) Two ternary eutectica were found. The first has the composition 98.57% Pb, 0.97% Ag and 0.46% Al. This lies at the temperature 324.0°. The second eutectic has the composition 97.2% Pb, 2.2% Ag and 0.6% Al. The eutectic temperature here is 304.3°C.

(4) The hardness of the alloys increases with added silver and lead until it attains a maximum at the alloy having the composition of the  $AlAg_2$  - Al eutectic plus 1.73% lead. After this point, the increasing quantity of lead present begins to reduce the hardness.

### Acknowledgement

I would like to express my appreciation to the Geology, Zoology and Engineering departments for their courtesy in allowing me the use of various pieces of apparatus during the course of this investigation.

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