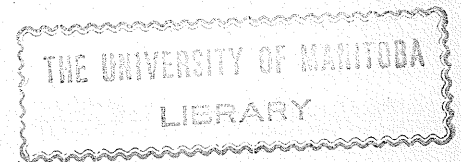


A STUDY OF THE ALLOYS OF  
SILVER - ALUMINIUM - LEAD

By  
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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.



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University of Manitoba

To DR. A. N. CAMPBELL  
in earnest appreciation of 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

There has been some difference of opinion as to the origin of the word "alloy", but according to Roberts-Austen it is derived from the Latin word alligo (ad ligo) "to bind to", and refers to the union or binding together of the metals constituting the alloy.

Perhaps the most satisfactory definition of an alloy is that given by the American Society for Testing Materials<sup>47</sup>, which defines an alloy as "a substance having metallic properties, consisting of two or more metallic elements, or of metallic and non-metallic elements, which are miscible with each other when molten, and have not separated into distinct layers when solid." However in the commercial sense the term "alloy" would also include the case where some separation into distinct layers had taken place.

From the earliest times alloys were produced accidentally by the simultaneous reduction of mixtures of metallic ores, but there is little doubt that the first metals to be intentionally alloyed were the precious metals, gold and silver, in order to facilitate working, or for the purpose of coinage. The word alloy is sometimes used to imply a sense of depreciation or a lowering of value. This is etymologically incorrect however, and probably has its roots in early fraudulent attempts to substitute base metals for precious ones in varying quantities.

The importance of the study of metallic and non-metallic alloys is evident when we consider the extent to which they are employed. Elementary metals are few in character but by the

judicious selection of metals, alloys of greatly varying characteristics may be produced. Industrially the importance of alloys cannot be over-emphasized. For example, pure iron is a commercial rarity, while steel, an iron-carbon alloy, which is probably the most important of the alloys, is omnipresent. Its uses are manifold-an industrial necessity. A few more striking examples may be called to mind, such as the high-speed cutting steels, modern guns and armour-plate, armour-piercing projectiles, non-corrodible alloys for the construction of vessels for chemical manufactures, new light alloys of remarkable strength and durability utilised in aircraft and many others too numerous and now accepted as too commonplace to be mentioned.

However it is not only in the evolution of new and strikingly important materials that the importance of the study of alloys lies, but in the light thrown on their structure, which gradually is revealing more and more knowledge regarding the solid state of matter. The early studies of alloy systems, while of very little practical value at present, are however important because of the fact that it was then realized that the chemical constitution of an alloy governs the chemical, physical, and mechanical properties of that alloy. Thus the properties of an alloy could easily be predetermined, depending on the nature and proportion of the compounds which are formed, as well as the isomorphous mixtures which occur.

Metals and alloys obey the same physico-chemical laws that govern mixtures and solutions. The fact that they are

considered as a class apart is due, no doubt, to their very great practical importance.

Desch<sup>48</sup> defines "metallography" as the study of the internal structure of metals and alloys, and of its relation to their composition, and to their physical, chemical and mechanical properties. It is a branch of physical chemistry, since this internal structure will undoubtedly depend on the physical and chemical conditions under which the alloy is formed and thus the study of structure resolves itself down to a study of equilibrium in heterogeneous condensed systems. However, where physical chemistry concerns itself generally with the nature and relative quantities of the phases in a system, and the energy transformations which accompany chemical changes, metallography also deals with a further variable--the arrangement of the component particles in space.

Observations on metals in some form or other go back as far as the uses of metals themselves, and metal objects of very great age have been found. In that vague sense the study of metallography could very well lay claim to great antiquity. However as a self-contained science it must be considered to be only of very recent origin. The great modern growth of interest in the study of the structure of alloys received its first great stimulus with the application of the microscope to the study of metals.

Robert Hooke in his "Micrographia" in 1665 described the appearance of lead crystallizing from its alloy with silver. This is probably the first recorded microscopic metallographic investigation. Réaumur, in 1722 began the technique of examining

fractured surfaces under the microscope and in a very carefully thought-out paper made some classical observations on the structure of steel and the hardening effect produced by quenching. Grignon, a French ironmaster, in 1775 described and illustrated crystals of iron found growing into the cavities of castings.

Examination of fractured surfaces very obviously has its limitations and very little progress was then made until Widmanstätten discovered that certain meteorites when cut and polished developed a characteristic structure on heating in air. Some time later he discovered that etching with nitric acid gave even better results and thus laid the foundations for the study of etch-reactions and identified the characteristic structure which still bears his name.

Henry Clifton Sorby<sup>49</sup> must however be entitled to the credit of being the founder of metallography, since he devised a systematic technique for the preparation and examination of micro-sections. Unfortunately the practical applications of his systematic work were not perceived at the time even though they were made at Sheffield, the centre of the British steel industry. Martens in Germany, and Osmond in France, neither of whom were aware of Sorby's earlier work independently confirmed it, and did much to contribute to the advancement of the badly neglected science. Among other early workers in this field should be mentioned Werth, Grevet and Charpy of France, Heyn, Wüst, Wedding, Stein in Germany, Andrews, Arnold, Roberts-Austen and Stead in England, and Howe and Sauveur in America.

Discussion for quite a while centred itself on the controversy as to whether alloys should be regarded as chemical compounds or merely mechanical mixtures. Levol systematically began the somewhat laborious process of examining series of alloys and showed that only very few remained homogeneous during the process of crystallisation, others being capable of separation into more fusible or less fusible parts. Several alloys proved to have a constant melting point e.g. the alloy of silver and copper in the proportion  $\text{Ag}_3\text{Cu}_2$  was found to possess this property. Levol therefore considered this to be a definite compound. However, more recent research has brought to light the fact that this is the eutectic mixture of the metals, which do not form an intermetallic compound. Nevertheless, research along this line marked a great advance in the study of alloys.

Matthiessen<sup>50</sup> was the first to apply the methods of physical chemistry to the study of alloys. He studied the physical properties of the alloys, such as density, conductivity, and thermo-electric power. This lead him to regard alloys as solidified solutions, containing, or not containing compounds depending on the metals chosen. He realized that the change in properties should be continuous and that the appearance of a compound would produce a discontinuity. This was the beginning of many such experiments.

The next great advance was the discovery of Raoult's Law of the Depression of Freezing Point. The application of this law to the study of alloys was suggested by the fact that alloys usually melt at a lower temperature than their components.



Thus began a whole series of investigations and the publication of freezing-point curves of many binary systems.

Jüptner and Le Chatelier suggested the application of Gibbs Theory of the Phases and the first important application of this was made by Roozeboom in a classical paper<sup>51</sup> in which he constructed a complete diagram of the results obtained in the thermal analysis of the iron-carbon system. Although many changes have been made in this diagram by numerous investigators, yet its original substance has remained. Because it is the basis of the iron-carbon diagram, accepting the existence of the three allotropic modifications, and because it was the first application of the Theory of the Phases to alloys it remains an important document in the metallographic and physical chemical annals.

Roozeboom<sup>52</sup> in 1899 made another great scientific contribution when he reviewed the possible types of solid solution, working from the theoretical standpoint of the phase rule. The first important application of this to alloys other than iron was made by Heycock and Neville<sup>53</sup> who presented data and photomicrographs which were ample evidence of the high degree of accuracy and technical perfection attained in such a short period of time.

The school of metallographers founded in Paris by Osmond and Le Chatelier contributed largely to the advancement of the study. In England the Alloys Research Committee under the inspiring leadership of Roberts-Austen from 1891 upwards did much to further scientific knowledge by the publication of an important series of reports. On the death of Roberts-Austen

this work was continued by W. Rosenhain with the assistance of J. E. Stead and J. O. Arnold.

No review of the history of metallography would be complete without due reference to the work of G. Tammann. Beginning in 1903 a long series of contributions came out of the Göttingen laboratory. A large number of binary systems were investigated with the object of establishing regularities between alloys of different metals. Though the data is not very accurate due to the crudity of the scientific methods used and the impurity of the materials, yet his work served as a very definite stimulus and did much to aid in the accumulation of scientific knowledge.

Today relatively few binary metallic systems remain uninvestigated and quite a few ternary systems have been studied. All of these are now serving to throw light on the internal structure and constitution of metals and alloys, and to aid in the evolution of general laws governing the solid state of matter.

THEORETICAL CONSIDERATION

(a) General Phase Rule.

The two great expressions describing in a qualitative manner all states and changes of equilibrium are the Phase Rule and the Theorem of Le Chatelier.

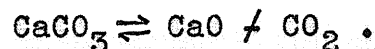
For many years prior to the enunciation of these two great precepts it was known that reactions do not take place completely in one direction but go to a certain point, at which an equilibrium is set up and under those conditions no further apparent change will occur. Wenzel in 1777 and Berthollet in 1799 both realized that this equilibrium might depend on the mass of the substances present. Guldberg and Waage<sup>54</sup>, by their statement of the Law of Mass Action made it possible to ascertain the conditions of equilibrium in homogeneous systems. However, due to the fact that this law was based on kinetic and molecular theories, it could not be applied to systems in which the number of different molecular aggregates or the degree of their molecular complexity was not known.

Ten years after the Law of Mass Action had been proposed, Gibbs<sup>55</sup> showed how, in a perfectly general manner, free from all hypothetical assumptions as to the molecular condition of the participating substances, all cases of equilibrium could be surveyed and grouped into classes, and how similarities in the behavior of apparently different kinds of systems, and differences in apparently similar systems, could be explained. As the basis of his theory, Gibbs adopted the laws of thermodynamics, a method of treatment which had at first been employed by Horstmann<sup>56</sup>. Furthermore, Gibbs considered that a system possessed three independent variables, namely temperature,

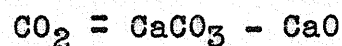
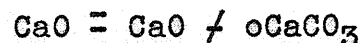
pressure, and the concentration of the components of the system, (the action of gravity and other forces being excluded). He then enunciated the theorem now known as the Phase Rule, by which he defined the conditions of equilibrium as a relationship between what are called the phases and the components of the system.

By "phases" we mean any homogeneous, physically distinct and mechanically separable portions of a heterogeneous system. In the case of water in equilibrium with its own vapor, there is the liquid and the vapor phase, two in number. If there is a salt dissolved in the water, there are still two phases, the liquid or solution phase and the vapor phase. If ice crystallizes, there is added a solid phase and the number becomes three. If, in addition the dissolved substance separates in the solid form or as a second liquid layer, there will be four phases present, the vapor, liquid and two solid phases, or the vapor, solid and two liquid phases as the case may be. Although the ice separates in many crystals, yet each is like every other in composition and taken together they constitute one phase. If the crystals were not alike, as is the case with rhombic and monoclinic sulphur, they would form as many phases as there were kinds of crystals, two in the example just cited, three if we have diamond, graphite and carbon. A mixture of gases will form only one phase since gases are miscible in all proportions. The familiar fact that the vapor pressure is unaffected by the amount of liquid present and that the solubility of a solid in a liquid is independent of the amount of solid in contact with the solution shows us that any equilibrium is independent of the amounts of the phase, or phases, present.

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. For example let us take ice, water, and steam in equilibrium. The system consists of three phases, namely solid, liquid, and vapor, but the number of components is only one, the chemical constituent  $H_2O$ . Hydrogen and oxygen, the constituents of water, cannot be regarded as components for only at a much higher temperature are they present in the form of a stable equilibrium. In a two-component system a choice of components is permitted. Take the case of the  $CaCO_3$ - $CaO$ - $CO_2$  equilibrium. At a given temperature, within certain limits, and after equilibrium has been established, there are three substances present: calcium carbonate, calcium oxide, carbon dioxide. While these substances are undoubtedly the constituents of the system between which the equilibrium exists, yet they are not all to be regarded as components. It can easily be seen that they are not mutually independent, but that by taking any two of these constituents the composition of the third is automatically defined by the following equation,



Thus taking the components  $CaCO_3$  and  $CaO$  the composition of each phase can be expressed as follows:-



Thus zero and negative quantities of the components are permitted, but it is usual to simplify matters by avoiding their use when making a choice of components.

In deducing the conditions for equilibrium in a heterogeneous system, i.e. in deducing the Phase Rule, Gibbs regarded every system as defined by the three independent factors or variables-temperature, pressure, and the concentrations of the components in each phase. Now in dealing with equilibrium from the standpoint of thermodynamics, there are certain "thermodynamic criteria of equilibrium" which must be considered. These criteria take the form of thermodynamic equations containing terms called thermodynamic potentials, characteristic of each component, the equilibrium being reached when these potentials reach certain values. By means of these equations it is possible to fix the values of a certain number of the variables of the system, in fact as many variables as there are equations. But the number of variables actually possessed by a system may be greater than the number of thermodynamic equations. The difference between the number of variables and the number of equations gives the number of variables which are left undefined by the equations. These variables, which are really variable at will, are called the degrees of freedom of the system. Findlay<sup>58</sup> defines the number of degrees of freedom of a system as the number of variable factors, temperature, pressure, and concentration of the components, which must be arbitrarily fixed in order that the condition of the system may be perfectly defined.

For example the case of liquid water in contact with water vapor is a two-phase, one-component system. We know from

experience that these two phases can coexist over a considerable range of temperature, without either disappearing or any new phase appearing. If we arbitrarily fix the temperature of the system at  $20^{\circ}\text{C}$ . the pressure will take up a certain equilibrium pressure, namely the pressure of saturated water vapor at  $20^{\circ}\text{C}$ . and the system will remain in this state infinitely. On altering the temperature to another value (within limits), other equilibrium positions will be taken up. Thus we have one arbitrary variable and the system is said to be univariant. If the temperature is lowered sufficiently, ice will make its appearance. This is only stable at a single point, the triple point. We cannot alter any variable without causing a phase to disappear. Thus the system is invariant. The number of thermodynamic equations is now equal to the number of variables and the degree of freedom is zero.

The original method of deducing the Phase Rule employed by Gibbs is by no means simple and many alternative methods have since been suggested by various authors. The following is due to Roberts<sup>59</sup>.

Consider the thermodynamic equilibrium of a system of  $C$  components and of  $P$  phases. Suppose that the pressure  $p$  and the temperature  $T$  are the same throughout the system, and that both remain constant. For simplicity it may be supposed that the system is contained in a cylinder with a movable piston, and that the pressure on the piston is kept constant while the whole is contained in a constant-temperature bath. Suppose that

$$M_1, M_2, M_3 \dots\dots\dots M_c$$



are the masses of the various components in the whole system. Further, suppose that the mass of component number 1 in phase number 1 is  $M_1'$  and that the mass of component number 1 in phase number 2 is  $M_1''$ , and so on up to  $M_1^r$ . In general the subscripts will refer to components and the superscripts to phases.

The total thermodynamic potential of the system  $\phi$  is given by the relation

$$\phi = \phi' + \phi'' + \phi''' + \dots + \phi^r$$

where  $\phi^1$  is the thermodynamic potential of phase number 1,  $\phi''$  that of phase number 2 and so on.

The thermodynamic potential of the first phase  $\phi^1$  is completely determined if we know the internal energy  $U^1$ , the entropy  $S^1$ , and the volume  $V^1$  of this phase, the relation between these quantities being

$$\phi^1 = U^1 - TS^1 + pV^1$$

and  $U^1$ ,  $S^1$ ,  $V^1$ , are completely determined if we know  $p$ ,  $T$ , and the masses  $M_1$ , etc. of the various components which are present in the phase. Exactly the same may be said about any of the other phases.

The condition for thermodynamic equilibrium is, that for an infinitesimal virtual displacement consistent with the external conditions (i.e.  $T$  and  $p$  to remain constant) the change in thermodynamic potential must be zero.

$$\begin{aligned} & \text{i.e. } \delta\phi = 0 \\ \text{or} & \quad \delta\phi' + \delta\phi'' + \delta\phi''' + \dots + \delta\phi^r = 0 \dots (1) \end{aligned}$$

Such an infinitesimal displacement is one in which the masses of the different components in the various phases change

(15)

$$\begin{aligned}
& + \frac{\partial \phi''}{\partial M_1''} \delta M_1'' + \frac{\partial \phi''}{\partial M_2''} \delta M_2'' + \dots + \frac{\partial \phi''}{\partial M_c''} \delta M_c'' \\
& \text{-----} \\
& + \frac{\partial \phi^p}{\partial M_1^p} \delta M_1^p + \frac{\partial \phi^p}{\partial M_2^p} \delta M_2^p + \dots + \frac{\partial \phi^p}{\partial M_c^p} \delta M_c^p = 0 \dots (3)
\end{aligned}$$

If all the  $\delta M$ 's were entirely arbitrary this equation could be satisfied only if all the coefficients of these variations were zero. This is, however, not the case since the total mass in each component remains constant.

$$\begin{aligned}
\therefore \delta M_1' + \delta M_1'' + \delta M_1''' + \dots + \delta M_1^p &= 0 \\
\delta M_2' + \delta M_2'' + \delta M_2''' + \dots + \delta M_2^p &= 0 \\
&\dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \\
\delta M_c' + \delta M_c'' + \delta M_c''' + \dots + \delta M_c^p &= 0
\end{aligned} \tag{4}$$

Under these conditions the necessary and sufficient condition for the vanishing of the left-hand side of equation (3) is

$$\begin{aligned}
\frac{\partial \phi'}{\partial M_1'} &= \frac{\partial \phi''}{\partial M_1''} = \dots = \frac{\partial \phi^p}{\partial M_1^p} \\
\frac{\partial \phi'}{\partial M_2'} &= \frac{\partial \phi''}{\partial M_2''} = \dots = \frac{\partial \phi^p}{\partial M_2^p} \dots \dots \dots (5) \\
\text{-----} \\
\frac{\partial \phi'}{\partial M_c'} &= \frac{\partial \phi''}{\partial M_c''} = \dots = \frac{\partial \phi^p}{\partial M_c^p}
\end{aligned}$$

Equation (5) gives the condition for the thermodynamic equilibrium of the system. It is important to remember that we have already shown that all the quantities occurring in equations (5) depend on the composition of the phases and not on their total mass.

It will be noticed that in all there are

$$C(P - 1)$$

equations which must be satisfied if the system is to be in thermodynamic equilibrium.

Let us now consider the number of independent variables on

(15)

$$+ \frac{\partial \phi''}{\partial M_1''} \delta M_1'' + \frac{\partial \phi''}{\partial M_2''} \delta M_2'' + \dots + \frac{\partial \phi''}{\partial M_c''} \delta M_c''$$

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$$+ \frac{\partial \phi^p}{\partial M_1^p} \delta M_1^p + \frac{\partial \phi^p}{\partial M_2^p} \delta M_2^p + \dots + \frac{\partial \phi^p}{\partial M_c^p} \delta M_c^p = 0 \dots (3)$$

If all the  $\delta M$ 's were entirely arbitrary this equation could be satisfied only if all the coefficients of these variations were zero. This is, however, not the case since the total mass in each component remains constant.

$$\begin{aligned} \therefore \delta M_1' + \delta M_1'' + \delta M_1''' + \dots + \delta M_1^p &= 0 \\ \delta M_2' + \delta M_2'' + \delta M_2''' + \dots + \delta M_2^p &= 0 \\ \dots & \\ \delta M_c' + \delta M_c'' + \delta M_c''' + \dots + \delta M_c^p &= 0 \end{aligned} \quad (4)$$

Under these conditions the necessary and sufficient condition for the vanishing of the left-hand side of equation (3) is

$$\begin{aligned} \frac{\partial \phi'}{\partial M_1'} &= \frac{\partial \phi''}{\partial M_1''} = \dots = \frac{\partial \phi^p}{\partial M_1^p} \\ \frac{\partial \phi'}{\partial M_2'} &= \frac{\partial \phi''}{\partial M_2''} = \dots = \frac{\partial \phi^p}{\partial M_2^p} \\ \dots & \\ \frac{\partial \phi'}{\partial M_c'} &= \frac{\partial \phi''}{\partial M_c''} = \dots = \frac{\partial \phi^p}{\partial M_c^p} \end{aligned} \quad (5)$$

Equation (5) gives the condition for the thermodynamic equilibrium of the system. It is important to remember that we have already shown that all the quantities occurring in equations (5) depend on the composition of the phases and not on their total mass.

It will be noticed that in all there are

$$C ( P - 1 )$$

equations which must be satisfied if the system is to be in thermodynamic equilibrium.

Let us now consider the number of independent variables on

which the quantities occurring in equations (5) depend. In the first place they depend on the compositions of the P phases. The composition of any one phase is determined if we know the masses of (C-1) of the components contained in unit mass of the phase. A knowledge of the masses of C components fixes the composition and the total mass. If the total mass is fixed, a knowledge of the masses of (C-1) components is sufficient to fix the composition. The compositions of the P phases therefore involve in all P(C-1) variables. In addition the quantities in equation (5) depend on the pressure p and the temperature T. The total number of variables involved is therefore

$$P ( C - 1 ) + 2.$$

The C(P-1) equations expressing the condition that the system is in thermodynamic equilibrium determine the values of C(P-1) of these variables. The remaining variables may be varied arbitrarily

$$\begin{aligned} \therefore F &= P(C-1) + 2 - C(P-1) \\ &= C - P + 2 \end{aligned}$$

where F = the number of Degrees of Freedom as previously defined.

A certain simplification may be introduced into most of the cases which are dealt with in metallography. Since the volatility of most metals at their melting-points is extremely small, it is commonly permissible to neglect the vapor phase when constructing the freezing-point diagram. In the same way the equilibrium may be assumed to be reached under a constant pressure, that of the atmosphere, since the work is generally carried out in the open laboratory. Pressure may therefore be omitted from the variables to be considered. The effect of omitting all consideration of

the vapor phase and of changes of pressure from the study of alloys is to reduce the number of variables to two, namely, temperature and composition. The conditions of equilibrium are then represented by the reduced formula

$$F^L = C - P + 1$$

While the Phase Rule gives the conditions for equilibrium in any given heterogeneous system, yet it gives no information regarding changes of equilibrium brought about by alteration of the external conditions of temperature and pressure. Le Chatelier's theorem by so doing greatly increased the scope and usefulness of the Phase Rule. In the words of Ostwald it may be stated as follows:-

If a system in equilibrium is subjected to a constraint by which the equilibrium is altered, a reaction takes place which opposes the constraint, i.e. one by which its effect is partially annulled.

The Phase Rule, while of extraordinarily great applicability has certain very definite limitations and these must always be borne in mind. The rule is based on thermodynamic principles and applies only to conditions of true equilibrium. The chief criterion of this true equilibrium is that the same conditions of equilibrium is reached from whichever side it is approached. Also such phenomena, such as surface-tension, force of gravity, etc. have not been taken into consideration in the deduction of the Phase Rule. The Phase Rule in its simplest form cannot include these, but they can be included by a revised mathematical treatment. The Phase Rule deals only with macroscopic amounts, microscopic amounts being dealt with on atomic principles.

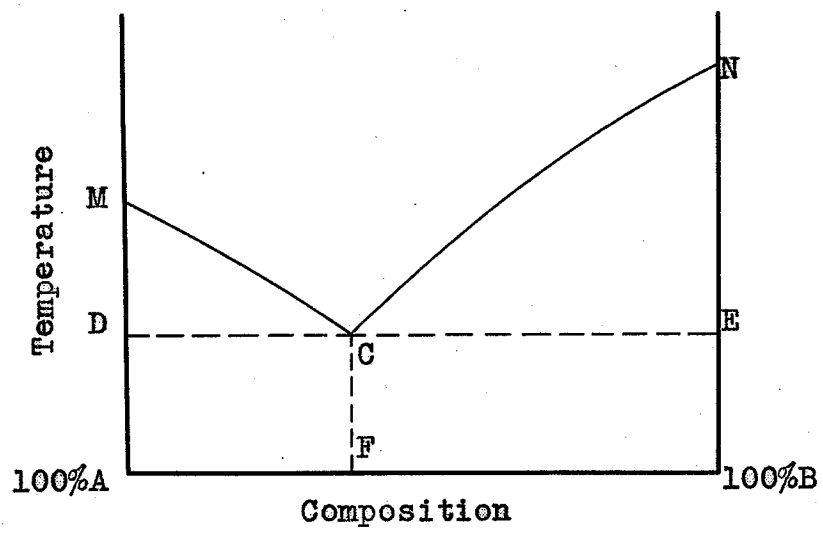


Fig. 1

### Binary Systems.

Although the Phase Rule may be stated mathematically, yet its understanding and practical application are best expressed graphically.

Since a two component system existing in one phase can constitute a ternariant system, a system with three degrees of freedom, then three variables, pressure, temperature and concentration must be taken into consideration. Thus for the graphic representation of all possible conditions of equilibrium a three co-ordinate system must be employed. Although reactions carried out under varying pressures are of the greatest scientific interest, yet most experiments are conducted at atmospheric pressure in the open laboratory. Thus two-component systems are usually represented as a plane section, parallel to the pressure axis. This is known as a temperature-concentration curve or a t-x diagram.

### Types of Equilibrium Diagrams.

#### I. The Components are Completely Miscible in the Liquid State.

##### (a). The Components separate out in the pure state.

The typical diagram for this system is shown in Fig. 1. M and N represent the melting points of the pure components. Since the freezing-point of a liquid is lowered by dissolving another substance in it, it follows that if a quantity of B is dissolved in A the temperature at which solid A will be in equilibrium with the solution will be lower than the freezing-point of pure A. The greater the concentration of B in A the lower will be the temperature at which A can exist in equilibrium

with it. Thus the curve MC represents the composition of solutions which are in equilibrium with the solid component A at different temperatures. The curve NC, by the same process of reasoning, will represent the composition of solutions in equilibrium with solid B. The two curves will then intersect at the point C. Another method of consideration would be the following. MC may be considered as a solubility curve, since it represents the temperatures at which solutions of B in A become saturated with respect to A. Thus NC will represent the temperatures at which solutions of A in B become saturated with respect to B. The point C is the point of intersection of these two solubility curves and at this point, the solution is simultaneously saturated with A and B. If crystals of A separate out, the solution will at once become supersaturated with respect to B, and equilibrium can be restored only by the separation of crystals of B. The metals A and B thus separate out side by side. The point C, as is clear from the diagram, lies at a lower temperature than the melting-point of either component and is the most fusible mixture which can be prepared out of the binary system in question. It is in consequence called a eutectic point, from the Greek word meaning "easily fusible".

At this point C we have four phases coexisting in equilibrium. This by Phase Rule considerations, would be an invariant point and constant temperature must necessarily result. Since the composition of the solution must also remain constant, then solid A and solid B must crystallise out from the eutectic solution in constant proportions.

This constancy of composition and of melting point was first



taken to symbolise compound formation. However many cases existed in what seemed to be open defiance of the Law of Simple Proportions. Also the eutectic composition would vary with pressure. It was soon realised that the eutectic was really a conglomerate of the two components.

A line DE is usually drawn parallel to the axis of concentration through the eutectic point C. This line represents the solidification of the eutectic mother-liquor and is called the eutectic horizontal. A vertical line from C to F separates those alloys which contain an excess of A over the eutectic proportions, from those which contain an excess of B. Thus above MCB all will be liquid. The area MDC will enclose solid A and melt. NCE will enclose solid B and melt. Below DCE everything is solid. DCAF will contain primary crystallisation of A plus eutectic mixture. CEBF will contain primary crystallisation of B plus eutectic mixture.

A completely molten mixture to the left of the eutectic point will behave as follows on cooling. A vertical line would at first be shown indicating a homogeneous liquid melt. However when the temperature has fallen low enough to strike the curve, solid A will separate out. The melt is thus enriched with respect to B, and with falling temperature the composition of the melt will move to the right. Thus, with falling temperature A separates out progressively along MC in the direction of C, the mother-liquor getting richer in B until the temperature and composition of the mother-liquor have achieved that of the eutectic point. At this point solid B makes its appearance and A and B separate side by side in the same proportions as they are now

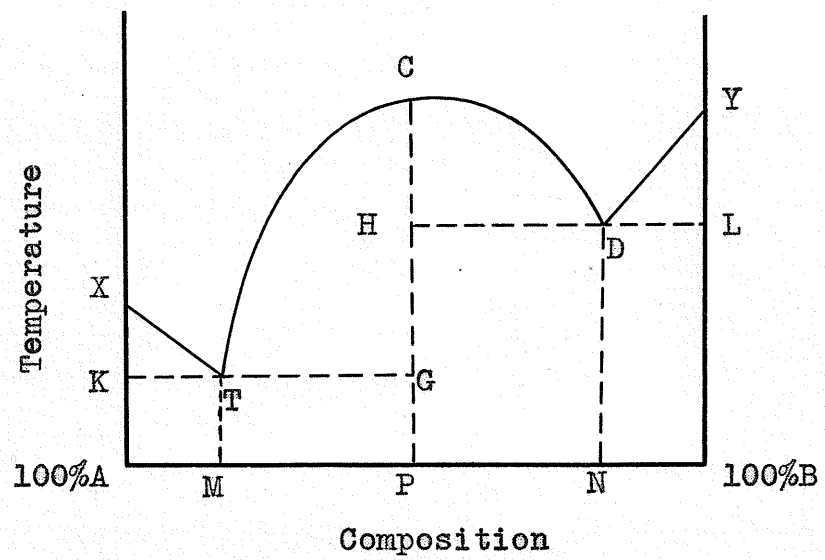


Fig. 2

present in the melt.

Similarly a molten mixture on the other side of the diagram would separate pure B, followed by eutectic crystallisation. If the eutectic mixture is cooled, it would freeze at the eutectic temperature yielding only eutectic crystallisation.

(b). Compounds are Formed with a Congruent Melting-Point.

A compound with congruent melting-point is one which is capable of existing in equilibrium with a liquid of the same composition. Such a compound will behave similarly to that of a pure metal, its freezing point being depressed by the addition of either of the components. The freezing-point curve therefore, shows a maximum corresponding with the composition of the compound as shown in Fig. 2. X, Y and C are the congruent melting-points of A, B, and the compound  $A_xB_y$  respectively. XT will give the composition of solutions of A and B in equilibrium at different temperatures with component A as the solid phase. YD gives the composition of solutions in equilibrium with component B as solid phase. TCD gives the compositions of the solutions in equilibrium with the compound as solid phase, CT and CD representing the depression of freezing-point of the compound with additions of pure A and B respectively. TCD is rounded indicating that dissociation has taken place in the molten state. The degree of dissociation can be calculated approximately<sup>60</sup> by the departure of the contour of the curve from the idealised state, i.e. two lines intersecting at a point.

A mixture to the left of T on cooling, will give the same results as in the case of the simple eutectic, with pure A crystallizing out until the eutectic is reached when A and B

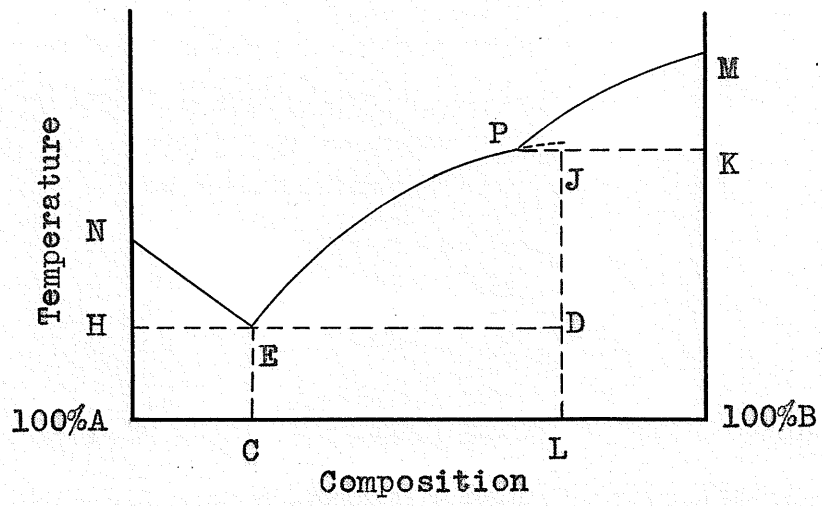


Fig. 3

crystallise out together in eutectic proportions. A mixture to the right of D will yield pure B followed by eutectic crystallisation. A mixture lying between B and C will yield compound as the primary crystallisation followed by eutectic crystallisation. Between C and D compound crystallisation would first occur, followed by the secondary eutectic. Thus, above XTCDY all is molten. Below KTGHDL all is solid. XKT will contain solid A and melt, YDL - solid B  $\neq$  melt, TGHDCCT - compound  $\neq$  melt, KTAM - A  $\neq$  eutectic, TMGP - compound  $\neq$  first eutectic, HGPND - compound  $\neq$  second eutectic, and DNBL - B  $\neq$  second eutectic.

The exact composition of the compound may be in doubt due to the rounded maximum. A fairly accurate method for the determination of this maximum is described in the section headed Thermal Analysis.

(c). Compounds are Formed with an Incongruent Melting-Point.

A compound is formed which cannot exist in equilibrium with a liquid of its own composition, but decomposes below its melting-point to form a liquid and a solid of different compositions than its own. The general form of the equilibrium diagram is shown in Fig. 3.

Pure A will separate along NE, the eutectic point being reached at E. The ascending branch EP corresponds with the crystallisation of a compound of the two metals A and B, but instead of reaching a maximum and again falling to a second eutectic point, as in the case of the formation of a compound with congruent melting-point, the freezing-point curve changes in direction at the point P and ascends to the solidification

temperature of pure B. Thus PM represents the composition of solutions in equilibrium with B as the solid phase. P is known as the peritectic point, and PK is the peritectic horizontal. P is not the real maximum of the curve, which is shown dotted in the diagram, but represents the temperature at which dissociation occurs.

A molten mixture, whose composition lies between E and P, will separate pure compound on to the eutectic, so that the eutectic obtained is eventually pure A plus compound. Below the eutectic horizontal all is solid. The composition of the compound lies to the right of P, and a hypothetical vertical line can be drawn corresponding to the compound composition. A mixture to the right of the peritectic point and to the left of the composition of the compound will separate pure B, since the temperature is above the peritectic point, i.e. above the temperature at which pure compound can exist. Cooling progresses down the curve, the melt getting richer in A, with pure B separating until the peritectic point is reached. At this point the compound comes into existence, and it does so by the chemical reaction of the B, which has separated, and the melt, to form the solid compound leaving melt in excess with the peritectic composition. On further cooling the composition of the melt will proceed down the curve with pure compound separating until the eutectic is reached. A mixture between J and M will act as the above mixture did until P is reached. Now however the melt contained more B than was necessary for the compound composition. Compound formation will occur at P between the separated B and the

melt. The interaction will now be complete leaving compound plus excess B.

In the area JKBL all will be solid, being a mixture of compound plus excess B. In the area HDLA, all will be solid, consisting of a mixture of compound plus excess A. To the left of EC, primary crystallisation of A plus eutectic structure will occur, to the right of EC, primary crystallisation of compound plus eutectic structure will be present. The semi-triangular areas are areas of liquid and solid in equilibrium, the solid being pure A, B, or compound.

#### Formation of Solid Solutions.

In many cases it has been observed that there crystallises from a solution, not the pure components or compounds of these, but a homogeneous crystalline mixture of the two components. To this homogeneous solid mixture Van't Hoff gave the name "solid solution". The German equivalent of solid solution is "Mischkristall" which unfortunately has been translated into English as Mixed Crystals. The term "Mischkristall" implies miscibility and in German is a satisfactory term to use, but the English equivalent implies a mechanical mixture of the two and thus is not correctly used. Two metals which are soluble in each other are said to be "isomorphous" and the alloys are referred to as "isomorphous solid solutions".

To represent the behavior of a system consisting of liquid and solid solutions two curves are necessary, which in certain cases lie very close together but are never identical. The liquidus curve is obtained by plotting the freezing points of

various liquid solutions against temperature. The freezing-point is defined as the temperature at which solid just begins to separate out from the liquid mixture. The solidus curve is obtained by plotting melting-points against temperature. The melting-point is taken as that temperature at which the solid solution just begins to liquefy. The relative position of the solidus and liquidus curves may be stated as follows:-

"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." 61

When solid solution occurs in a system, the two components may be either completely or only partially miscible in the solid state and therefore it is usual to divide the consideration of the types of solid solution into two sections. The following classification is due to Bakhuis Roozeboom<sup>52</sup>, who in a classical paper in 1899 reviewed the different types of solid solution.

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

Since the two components are miscible in all proportions with each other in the solid and liquid states, there can only be one solid and one liquid phase, and thus never more than three phases in equilibrium. The system can thus never become invariant, and the temperature-composition curve must be continuous.



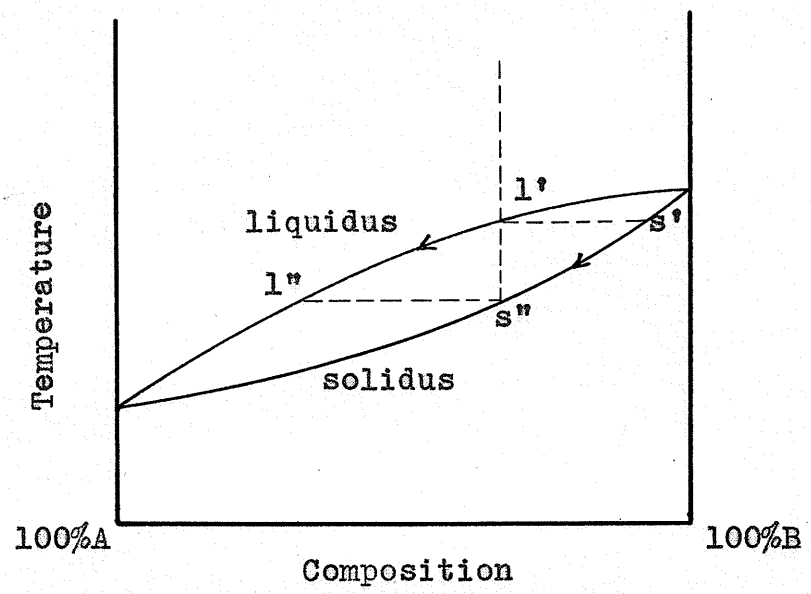


Fig. 4

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

This type (Fig. 4) consists of two smooth curves joining the melting-points of the pure components. The liquidus and solidus may be chosen by the aforementioned rule. Above the liquidus, everything is liquid. A mixture on cooling will strike the liquidus curve. A solid phase will now appear being a solid solution of A in B or B in A. The composition will not be the same as that of the liquid  $l'$ , but may be determined by drawing a projection, parallel to the concentration axis, to the point where it would strike the solidus. Thus a solid solution of composition  $S^1$  would separate out. If the mixture is cooled with great slowness the liquid composition will move down the liquidus, since it is impoverished in B. The solid solution will alter its composition in harmony with this by solid diffusion and interaction with the melt. As the process goes on, more and more melt will solidify, and the solidified mass keeps itself homogeneous by solid diffusion and interaction. The whole mass will solidify when the solid solution has the same composition as the melt had. The necessity for slow cooling can readily be seen, since solid diffusion takes place very slowly. With rapid cooling primary solidification will occur as above. Solid diffusion cannot now take place and another layer of solid will separate as a coating on the first. Thus stratification or Coring results.

(b). The freezing-point curve passes through a maximum.

This type has recently been shown to be thermodynamically

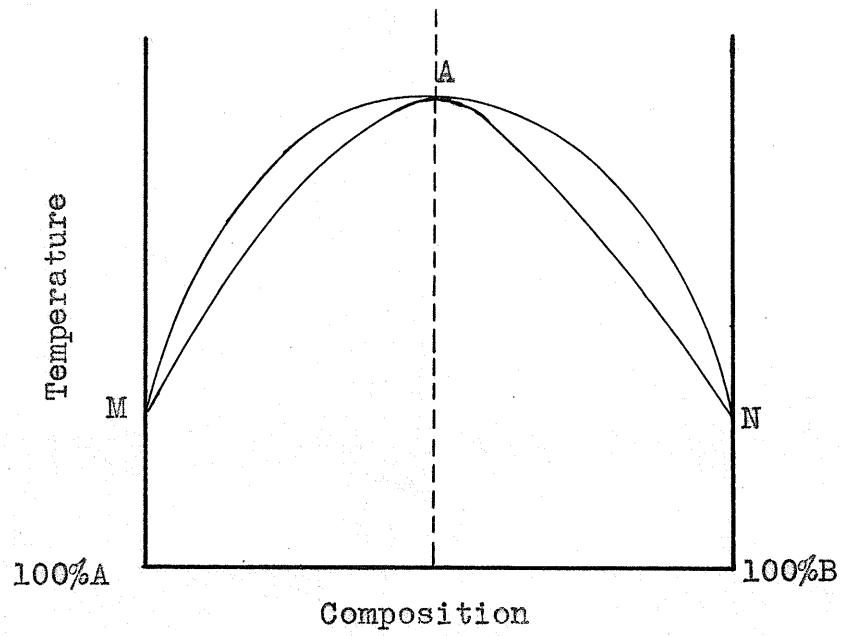


Fig. 5

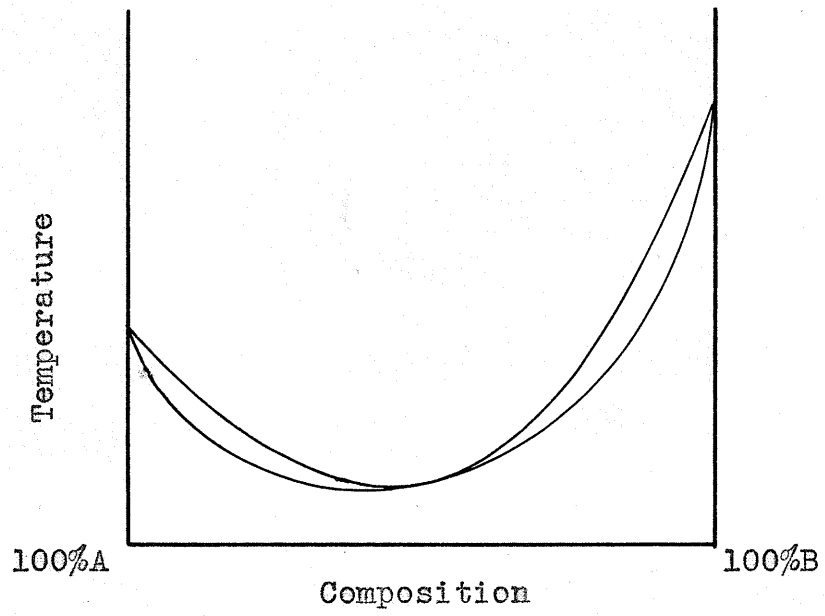


Fig. 6

unstable. As it occurs even in recent text-books some mention of it will be made here. As shown in Fig. 5 it consisted of two continuous curves intersecting at a maximum. Occurring very rarely it was found only with optical isomers, e.g. dextro and laevo carvoxime. However these unite to form an optically inert racemate which has unlimited solubility for both the dextro and laevo compounds. Thus we are not dealing with a case of dextro and laevo solubility, but actually with two separate cases of compound and isomer. This can readily be seen if a dotted line is drawn down the centre of the diagram as in Fig. 5. We now have two separate systems similar to that of Case (a).

(c). The freezing-point curve passes through a maximum.

This type is illustrated by Fig. 6. Two continuous curves pass through and intersect at a minimum. At this minimum the composition of solid and liquid is identical. Molten mixtures to the right and left of the minimum will yield homogeneous solid solutions, if the cooling is slow enough, as described in Case I. A composition corresponding to the minimum will solidify at the temperature corresponding to the minimum.

(2). The two components do not Form a Continuous Series of Solid Solutions.

This case is analogous to that of the partial miscibility of liquids. Each component will only dissolve a certain amount of the other. A mixture gap will thus occur and any mixture in the gap will be heterogeneous, yielding the two saturated end members of the series of solid solutions. Since two solid

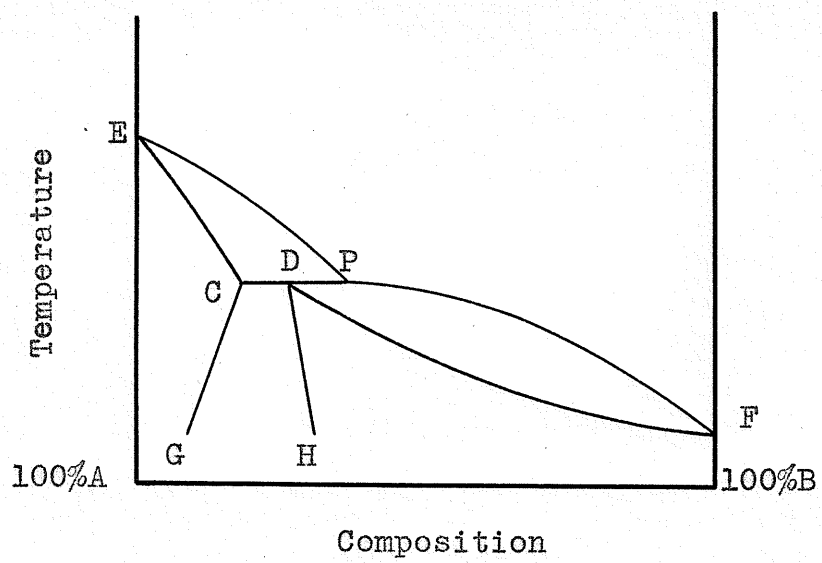


Fig. 7

phases can now coexist, an invariant point may occur. The temperature-concentration curves need no longer be continuous but will show a break or discontinuity at the point at which the invariant system is formed.

(a). The freezing-point curve exhibits a transition point.  
(Fig. 7).

By applying the criterion given previously, EP and PF represent the compositions of liquid solutions, while EC and DF represent the composition of solid solutions. CDP represents the equilibrium between the liquid solution and the two saturated end members of the series of solid solutions, represented by C and P.

(i). A mixture to the left of the mixture-gap.

The result is exactly the same as that described under Case I. Homogeneous solid solution of the same composition as the original melt will result, if the cooling is carried out slowly enough.

(ii). A mixture within the Solubility Gap.

When EP is reached, solid solution will separate out, whose composition is given by the corresponding horizontal. With slow cooling the liquidus composition will move down EP, and the corresponding solidus down EC until P, the peritectic point, is reached. All will however not be solid since C, which will separate, contains less B than the original mixture. D will now appear. Four phases are present and invariance results which is maintained by the simultaneous separation of C and D until all is solid. The result will be a heterogeneous solid

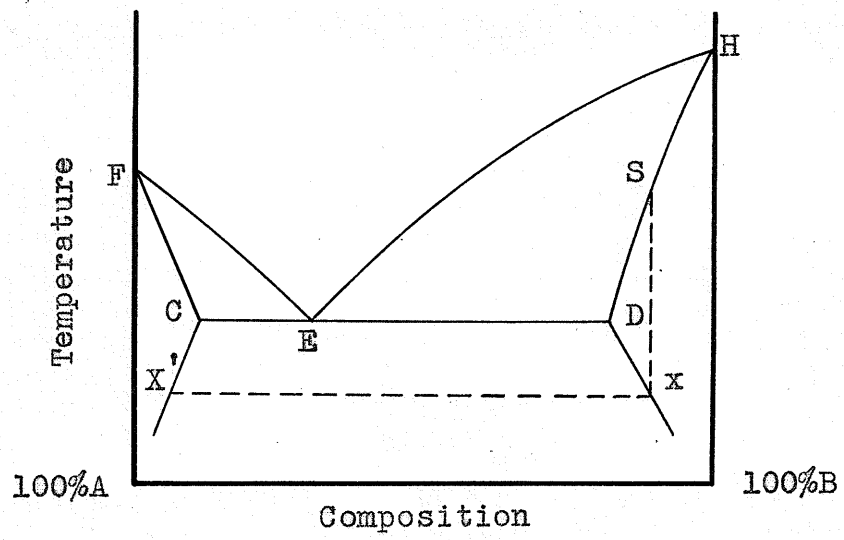


Fig. 8

consisting of the saturated end members of the series of solid solutions.

(iii). A mixture to the right of the mixture gap, but to the left of P.

With decreasing temperature, homogeneous solid solution of the EC series will result and this will continue, the liquidus falling down to P, and the solid solution to C. C and D now separate side by side. However, for algebraic reasons, separation of C and D is not enough to keep the liquid composition unchanged. C will dissolve out, and D increases in amount until finally all trace of C has disappeared, and D is the only remaining solid phase. Liquid will still remain however, since the original liquid mixture was richer in B than the solid solution D is. Solidification will now occur as in Case I. The solidus will keep in harmony with the liquidus by solid diffusion and interaction with the melt, if the cooling is slow enough, until the solid is the same composition as the melt, and all is solid.

(iv). A mixture to the right of P.

The result will be homogenous solid solutions of the same composition as the melt.

(b). The freezing-point curve exhibits a eutectic point.

(Fig. 8)

A true eutectic occurs here, but unlike the simple eutectic, the solid phases are not pure A and B, but the saturated end members of the two series of solid solutions.



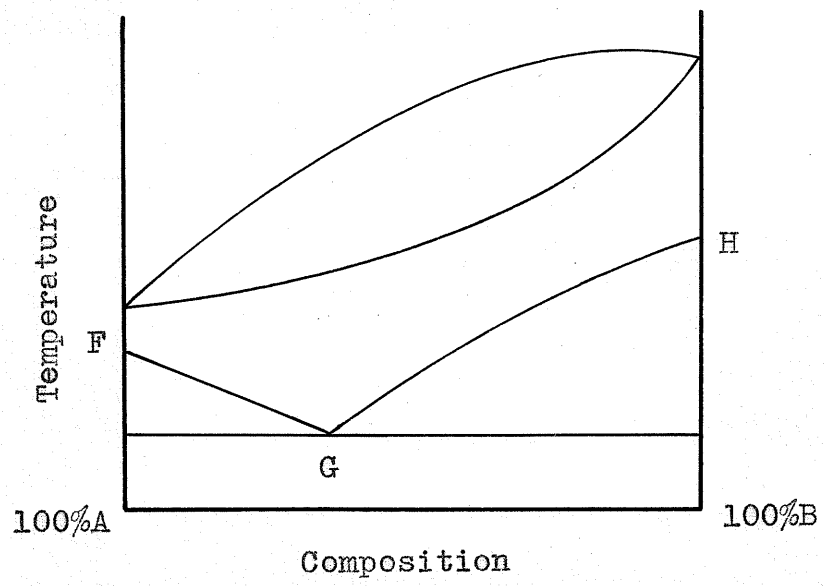


Fig. 9

(i). A mixture to the left of the mixture gap.

With cooling sufficiently slow to allow for solid diffusion to take place, a homogeneous solid solution of the A series will result.

(ii). A mixture to the right of the mixture gap.

This will eventually give a homogeneous solid solution of the B series.

(iii). A mixture in the gap.

To the right of the eutectic, separation of the solid solution of the B series will occur, the solid solution changing until arrival at the eutectic. A solid solution of the A series now makes its appearance, and the two solid solutions now separate out side by side until all is solid.

Curves representing solid solubility lines always run through the end of the mixture gap. Thus, a solution of the composition of S as shown in Fig. 8, will exist stably on further cooling, until the temperature falls low enough so that intersection of the solid solubility line occurs. Now if solid separation did not take place, supersaturation would occur. Thus "untmischung" takes place, solid solutions of the A and B series separate out, and if the cooling is slow enough the separation will be in harmony, A losing B, and B losing A.

Before leaving solid solutions it might not be amiss to introduce and explain a term which occurs in one of the binary systems connected with this investigation - the eutectoid. This is shown as the curve FGH in Fig. 9. The homogeneous solid solution resolves itself into two components. The temperature at

which each component crystallises from the solid solution is lowered by addition of the other, and we consequently obtain a solubility curve with two branches. The resemblance of this curve to the freezing-point curve of a eutectiferous series is at once apparent, and the analogy is a real one. Primary separation of the components takes place along the two branches, and when the temperature of intersection is reached, the remaining solid solution splits up into a conglomerate of the two components.

## II. The Components are not Completely Miscible in the Liquid State.

From our definition of alloys we saw that many alloys separated into two layers on solidification. It is also true that many alloys do not melt to form a homogeneous liquid, but form two immiscible layers within certain ranges of temperature and concentration. These are known as conjugate solutions. Solubility usually increases with temperature, although exceptions to this rule have been found. Thus two liquid layers may be formed on fusion, but as the temperature rises, the solubility of each of the components for the other must also rise. Thus a time will come when at a certain temperature the composition of the two liquid phases will become identical. This temperature is known as the critical solution temperature or the consolute temperature. This can readily be obtained with many substances, but in the majority of metallic systems its realization is very difficult, due to the fact that the critical temperature is higher than the boiling-points of the metals involved.

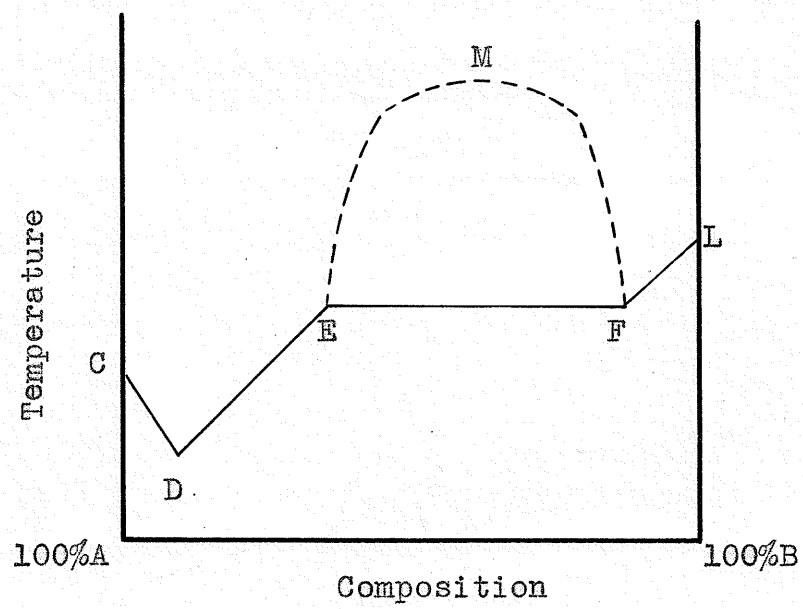


Fig. 10

With conjugate solutions present, four phases coexist. The system will be invariant. Thus the temperature and concentration must have definite values. If the two metals are completely immiscible in the liquid phase at a certain temperature, the freezing points of either metal will be entirely unaffected by the presence of the other. This of course is the limiting case, and probably non-existent, since no two substances are entirely insoluble in each other. This will be represented on the equilibrium diagram as two horizontal lines through the respective freezing points of the two metals. The usual form taken by the equilibrium diagram is that shown in Fig. 10. As is the usual case, the freezing point of each metal is lowered by the addition of the other. EMF is the miscibility curve. Everything within the area of this curve will break up into two layers. Thus a mixture to the right of F on cooling, will separate pure B once the curve FL is reached. The mixture composition will then proceed down the curve FL with falling temperature, until F, where the miscibility curve is reached. Only one liquid layer has previously existed. With further separation of B the composition would reach a point between F and E. This however is impossible, since EF is an area of heterogeneity and represents 2 layers in equilibrium. Thus a second layer with the composition of E now makes its appearance, and as previously indicated, invariance in temperature and composition results. With further separation of B the mean value of the alloy changes along the line EF. Since the composition of the layers remains constant, this is done by the changing of the relative amounts of the two layers, until

with sufficient separation of B at the point E the liquid alloy of composition F disappears. Now the system is univariant and with further crystallisation of B the eutectic is reached.

An alloy mixture in the region above EMF will break up into two layers, whose composition corresponds to E and F, when the miscibility curve is reached.

### Ternary Systems.

Three component systems are of very great industrial and general scientific importance. Yet due to the number of variables involved, relatively few ternary systems have been investigated. When we apply the Phase Rule to systems of three components, it is readily seen that five phases are necessary for invariance. Such a system will therefore exist at a quintuple point. Since the number of liquid phases can never exceed the number of components, and since there can be only one vapor phase, there must always be at least one solid phase at the quintuple point. As the number of phases decreases, the variability of the system increases from one to four.

Two component systems are represented on a t-x or temperature-concentration diagram. This however presents great difficulties when the number of components equals three. The problem has been solved in quite a number of ways. Most of the methods give a solid figure, the temperature being taken as the vertical axis, but it is possible to tell a great deal from the projections of the curves for the monovariant systems upon a plane, even though the temperature can no longer be read directly.

Schreinmakers<sup>62</sup> took for the X and Y axes the amounts of two of the components in a constant quantity of the third. Meyerhoffer<sup>63</sup> used a diagram which allowed one of the coordinates to be used to indicate the temperature. In a system composed of two salts and water, he measured the ratio of one salt to the other along one axis and the temperature along the other. This is serviceable in certain cases, but is very limited in

application, since it neglects the relative quantities of both salts in respect to the third component. The method proposed by van Rijn van Alkemade<sup>64</sup> seems to have no advantage over the diagram proposed by Schreinmakers. Gibbs<sup>65</sup> has suggested the use of a triangular diagram, the sum of the components being kept constant. If we take an equilateral triangle of unit height, the quantities of the different components are expressed as fractional parts of the whole, and the sum of their concentrations is therefore equal to unity and to the height of the triangle. A point within the triangle will represent the composition of a ternary mixture. Since, by geometrical reasoning, every point within the triangle has the property, that the sum of the perpendiculars from that point on the sides of the triangle is equal to unity (the height of the triangle), then the composition of the ternary mixture may be obtained in such a fashion. This type of diagram was used by Thurston<sup>66</sup> in some work on alloys. It is more generally associated with the name of Stokes<sup>67</sup>, who independently devised the same scheme, basing it on the method employed by Clerk Maxwell for the composition of colors. Roozeboom<sup>68</sup> has employed a modification of this diagram. He used the isosceles right-angled triangle, the equal sides being of unit length. The advantage of this arrangement is that the ordinary co-ordinate paper may be used. The diagram is open to the objection, that there is a different scale along the hypotenuse from that along the sides, so that one of the components seems to occupy an exceptional position. Roozeboom<sup>69</sup> proposed another form of triangular diagram which is distinctly



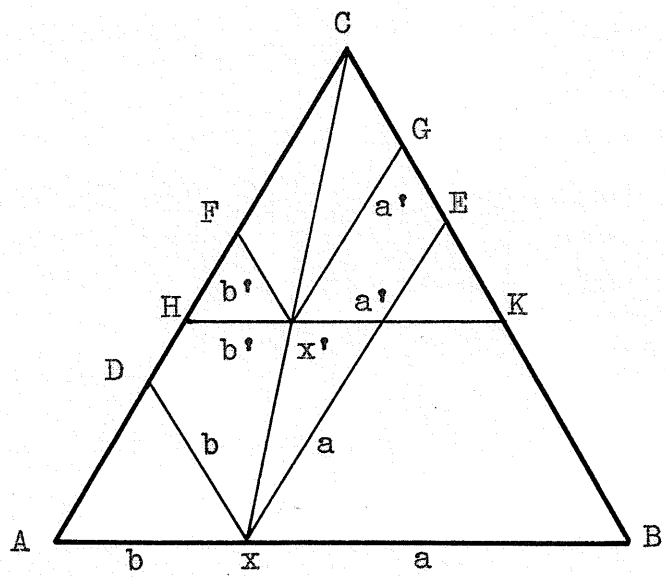


Fig. 11

superior to any of these already considered. It consists of an equilateral triangle with lines ruled parallel to each side instead of perpendicular. The sides of the triangle are divided into 100 parts, and the same scale is used for the binary systems in the side of the triangle as for the ternary systems in the interior. The co-ordinates of the point representing a ternary alloy are then measured parallel to the sides.

The triangular diagram is now usually employed, except in special cases, where some point is to be brought out not involving the variation of all three components. An important property of the equilateral triangle should be noted<sup>70</sup>. 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 a mixture x, in which A and B are present in the proportions of a:b, a mixture  $x^1$ , which is thereby obtained also contains A and B in the ratio a:b. For the two triangles ACx and BCx are similar to the two triangles HCx<sup>1</sup> and KCx<sup>1</sup>; and therefore,  $Ax : Bx = Hx^1 : Kx^1$ . But  $Ax = Dx$ , and  $Bx = Ex$ ; further,  $Hx^1 = Fx^1$  and  $Kx^1 = Gx^1$ . Therefore,  $Dx : Ex = Fx^1 : Gx^1 = b:a$ . At all points on the line Cx, therefore, the ratio of A to B is the same.

If it is desired to represent at the same time the change of another independent variable, e.g. temperature, this can be done by measuring the latter along axes drawn perpendicular to the corners of the triangle. In this way a right prism

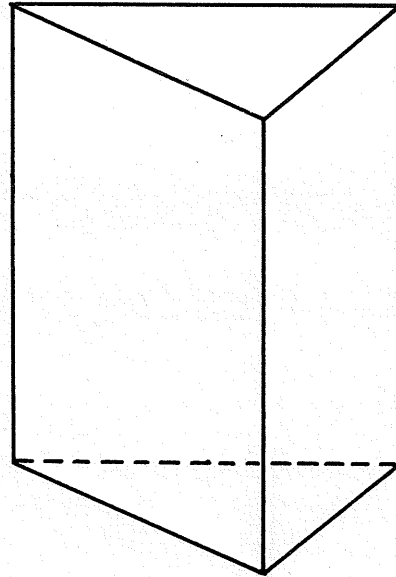


Fig. 12

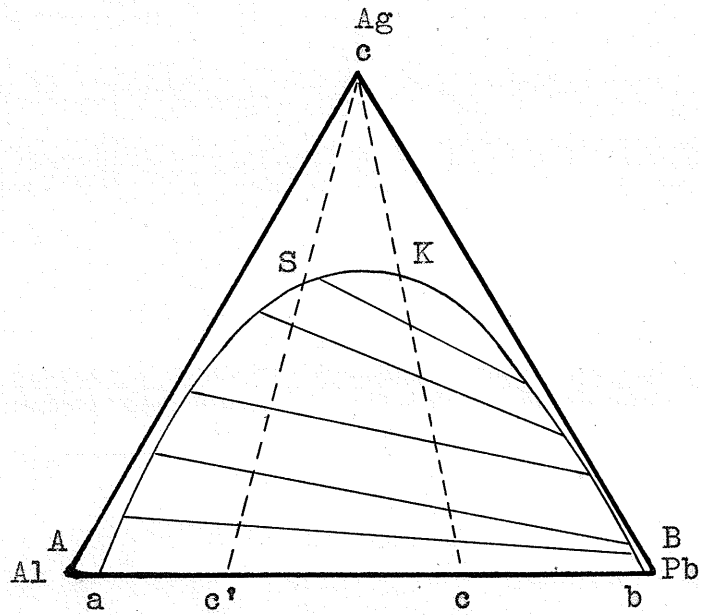


Fig. 13

(Fig. 12) is obtained, and each section of this cut parallel to the base will represent an isothermal surface.

#### Types of Systems Obtained.

There are numerous types of systems which may be obtained, increasing in complexity with the conditions of behavior of the component metals. However only two will be discussed here, since they bear a direct relationship to the diagram obtained in this research.

(i). The three components form only one pair of partially miscible liquids.

We have already discussed the case of two metals only partially miscible. When a third metal is added to these two, an increase or a diminution in the mutual solubility may occur. An increase in the mutual solubility is generally found when the third component dissolves readily in the other two; but when the third component dissolves only sparingly in the other two, its addition diminishes the mutual solubility of the latter.

A good example of this is the system under investigation. The results obtained by Campbell and Wallace<sup>46</sup> give a curve of the following type. (Fig. 13). Silver and aluminium, and silver and lead, are miscible in all proportions. But lead and aluminium are only partially miscible. Thus a mixture of lead and aluminium of the composition C would separate into two layers corresponding to a and b. When silver is added, it will distribute itself between the two liquid layers and two conjugate ternary solutions are thereby produced, which are in equilibrium with each other. Thus a series of pairs of ternary

solutions will be obtained by the addition of silver. But not only do the liquid phases become increasingly rich in silver, but the mutual solubility of the lead and the aluminium increases so that the lead layers become richer in aluminium and vice versa.

By the continued addition of silver, the composition of the successive conjugate solutions in equilibrium with each other becomes more nearly the same, and a point will be reached at which the two solutions become identical, and a critical point is thus reached. Increased addition of silver will now give single homogeneous solution.

This is expressed graphically by the so-called binodal curve  $aKb$ ,  $aK$  will represent the composition of solutions relatively rich in aluminium, while  $Kb$  the composition of solutions relatively rich in lead. The points on these two branches representing conjugate solutions in equilibrium are joined by what Stokes called "tie-lines". Since silver does not enter in equal amounts into the two layers, depending on its partition coefficient between the two, the tie-lines will not be parallel to  $ab$ , but are inclined at an angle. As the solutions become more nearly the same, the tie-lines shrink in length, and when the conjugate solutions become identical, shrink to a point. Since the tie-lines are not parallel to the side of the triangle, the critical point will not be at the summit of the curve, but somewhere below it, as shown by the point  $K$ .

It should be borne in mind that not all mixtures, on reaching homogeneity, will resemble the critical solution concentration.

This, in fact is only true for a mixture of composition C. A mixture of composition  $C^1$ , on cooling will act as follows. It was previously shown that the total composition of the different ternary systems, which will be obtained on the addition of silver, must be represented by a point on the line  $Cc^1$ . Each alloy formed, as long as it is in the binodal curve, will separate into two layers, whose composition may be obtained from the ends of the tie-lines. However the relative amounts of the two liquid layers formed differ more and more, until at S, a limiting position is reached, where one liquid layer will disappear and the other will remain.

The boundary curve of the heterogeneous system will depend on temperature, since with three phases present, the system is bivariant. The diagram in Fig. 13 is an isothermal section and similar triangular diagrams may be constructed for varying temperatures. If we make use of the right prism, with increasing temperature the critical point K will approach the partially miscible binary system, and the area of heterogeneity for the ternary system will shrink continuously until it approaches a single point - the critical point of the binary system.

In most cases the contour of the critical curve exhibits no marked irregularities, but in a few instances it shows a marked bulge outwards or notch inwards. This may indicate compound formation. Also the configuration of the tie-lines may lead to the conclusion that a compound is formed. For instance the tie-lines may all slope towards one central point. This is presumptive evidence of compound formation. In most cases,

however, the tie-lines exhibit no marked irregularities, but slope either to the left, or to the right. However no fixed law can be enunciated regarding the slope of the tie-line, since the same metal, when added to mixtures of different metals, may, or may not produce tie-lines with varying slopes, sloping either to the left, or to the right.

(ii). The ternary eutectic point.

Since the composition of the liquid phases vary with temperature, the right prism is again used for the graphic representation of the system. Each binary system will then be represented by the sides of the prism. Each binary system in the simplest case will exhibit a eutectic, since the addition of one metal to the other will lower the melting-point of that metal. If to each of the binary eutectica a small quantity of the third metal is added, the eutectic temperature of each will be lowered, and this depression is all the greater, the larger the addition of the third component. Thus we obtain three curves, sloping downwards and inwards, which indicate the varying composition of the ternary liquid phases. These curves will intersect at a point K which is the ternary eutectic. This point represents the lowest temperature attainable with the three components given. Each of the ternary eutectic curves is produced by the intersection of two surfaces, while at the ternary eutectic point, three surfaces intersect. The surfaces will be bivariant, since they represent a ternary solution in equilibrium with only one component in the solid state. The lines or curves of intersection of these represent equilibria with two solid phases, and are thus univariant, while the ternary eutectic point

will have three solid phases in equilibrium with a liquid and a vapor phase. The eutectic point, then, has a perfectly definite position, depending only on the nature of the three components.

Instead of employing the prism, the change in composition of the ternary solutions can be indicated by means of the projections of the curves of the intersections of the above surfaces, the particular temperature being written at the salient points.



### Methods of Determination of the Equilibrium Curve.

The methods employed for the experimental determination of the equilibrium curve will depend on the nature of the system to be investigated. Many methods have been used, with each method receiving many adaptations, depending on the conditions which presented themselves.

#### (I). Thermal Analysis.

The classical method of thermal analysis is still one of the most important methods, and must be regarded as the foundation of all the others. The basis of this method is that a phase change must necessarily result in an energy transformation. This energy transformation will usually manifest itself in a liberation or consumption of heat.

A distinction must however be drawn between crystalline and amorphous solids. Crystalline substances are bounded by plane surfaces, so oriented to one another, that the whole possesses some degree of symmetry. All other solid bodies must be classed as amorphous, and are to be regarded as nothing other than liquids of great viscosity. That amorphous solids differ from liquids only in degree, is demonstrated by the fact that on heating they lose, by imperceptible gradations, their rigidity and become as fluid as water. The absence of a definite transition point will make it difficult to attempt to distinguish such bodies as solid under one set of conditions and liquid under the next. While amorphous solids show a great continuity of state, this fortunately is not true of crystalline solids. Every

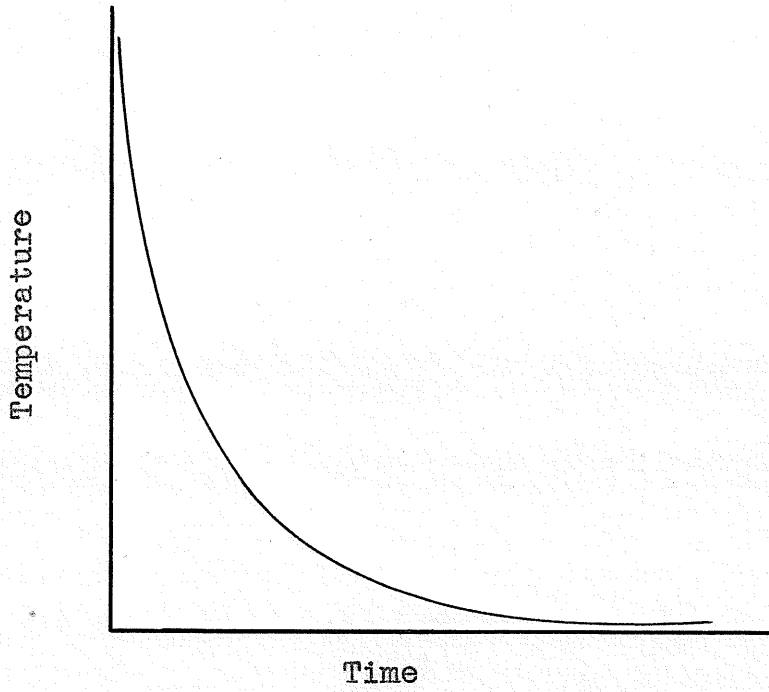


Fig. 14

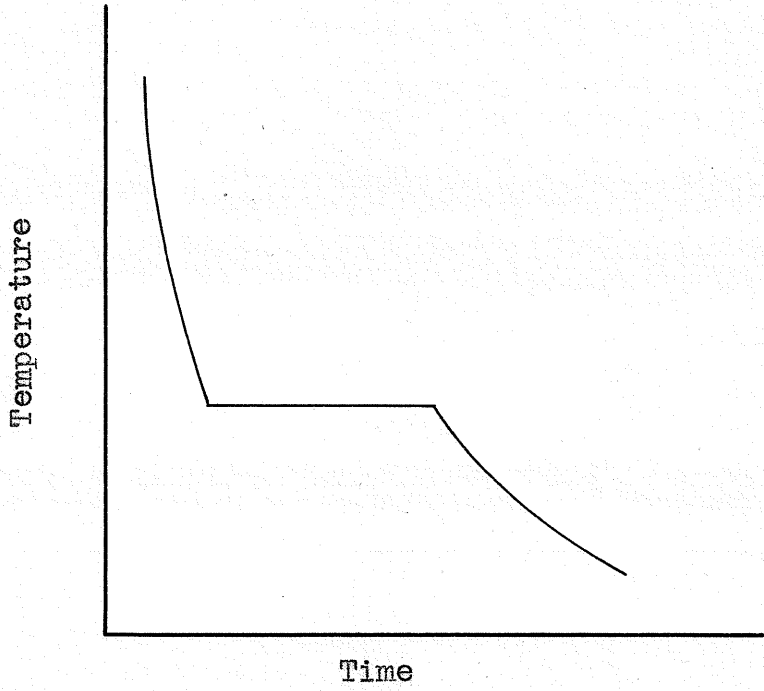


Fig. 15

crystalline solid has a definite transition point at which it undergoes an abrupt change into a liquid, with absorption of heat. Provided that this change is large enough to show on a cooling curve, it is detectable by thermal analysis.

When a pure substance cools without change of state, the curve connecting its temperature with time has a regular form, being exponential when the surroundings are at a constant temperature, according to Newton's Law of Cooling, as shown in Fig. 14. In all known cases heat is given out in freezing. If a molten pure metal is allowed to cool, solid particles will separate out at the freezing-point. This is provided, of course, that supercooling is absent, and in metals, with only very rare exceptions, supercooling does not occur. The solid particles will then liberate a certain quantity of heat. Any further loss of heat due to radiation, instead of reducing the temperature of the mass, causes further separation of solid, and this process continues, the temperature remaining constant, until the whole of the substance has passed from the liquid to the solid state, after which the temperature again falls in a regular manner. This type of behavior is illustrated in Fig. 15.

However suppose the substance under consideration is not pure, but a mixture of two substances which, to simplify matters, are perfectly miscible in the molten state forming a homogeneous solution, and each crystallises out in the pure state. Now we will get primary crystallisation, which will show up as delayed cooling on the curve. Since the composition of the solution alters with the separation of the solid phase, the temperature

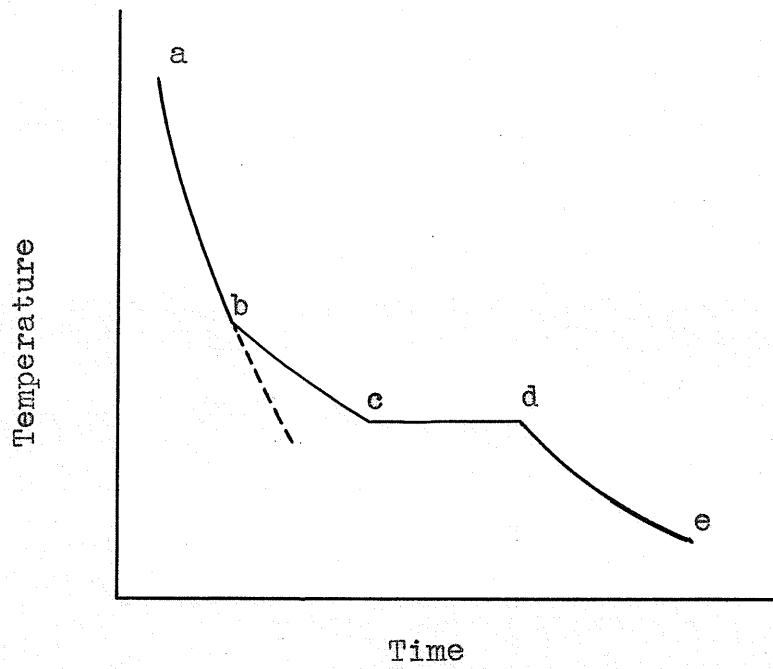


Fig. 16

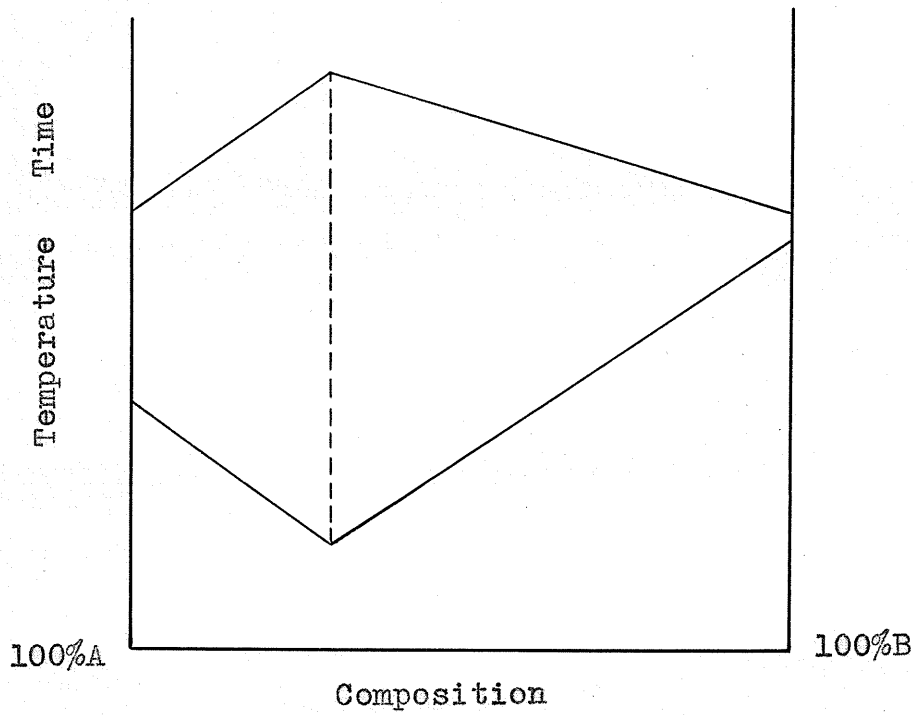


Fig. 17

will not remain constant, but will gradually fall until the eutectic point is reached. (Fig. 16). A second solid phase has now formed, invariance must result, and the temperature remains constant until complete solidification has occurred. The length of the plateau will depend on the amount of excess of any of the components over that of the eutectic composition. Thus as the eutectic composition is approached, the primary crystallisation will be shorter and the eutectic crystallisation greater. At the eutectic there will be no primary crystallisation, with an extended eutectic halt. This is the basis of Tammann's method<sup>71</sup> of finding the exact composition of the eutectic. Since the time taken for the eutectic mother-liquor to solidify may thus be taken as proportional to the amount of eutectic present, Tammann plotted eutectic halt times as ordinates, against the alloy composition as abscissae as shown in Fig. 17. The maximum time of solidification would then give the exact eutectic composition. This method gave useful service in the early days of thermal analysis, but is now rarely employed, due to the many possible sources of error in the experimental determinations.

Thus it is seen that by noting the temperatures at which halts occur on the cooling curves of different mixtures, it is possible to map out the equilibrium diagram of the system. The cooling curve, moreover, gives valuable information regarding the nature of the solid phases since, with sensitive apparatus, changes in the solid state are detectable.

In discussing the formation of compounds with congruent and incongruent melting-points, the difficulty of determining the exact composition of the compound was noted, due in the

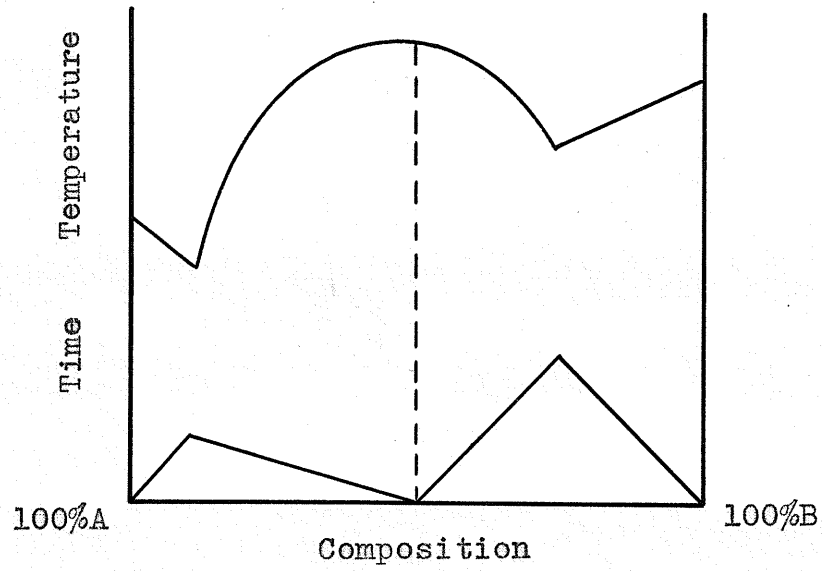


Fig. 18

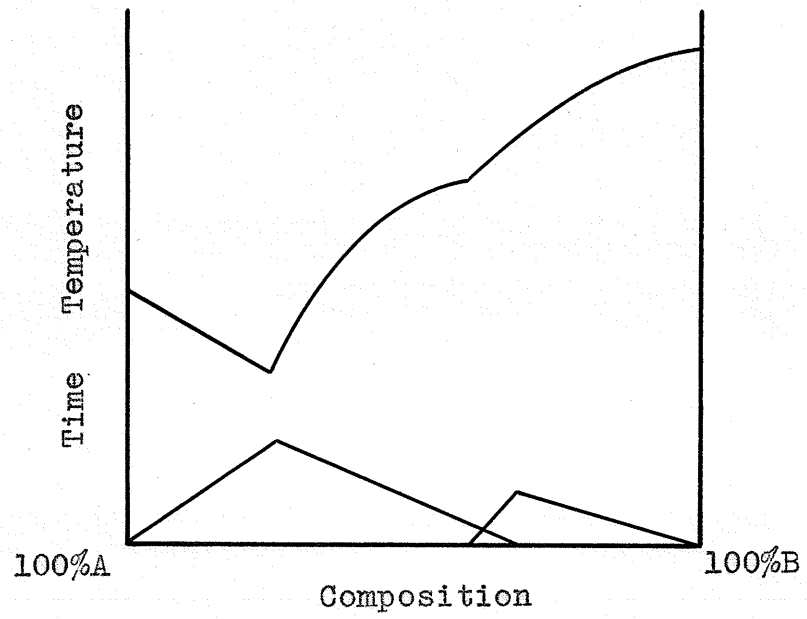


Fig. 19

first instance to dissociation in the molten state, and in the second to a dissociation of the solid compound. Tammann's method may be employed for the determination of these maxima. If the eutectic halt times are plotted, they would be zero for the pure components. They must also be zero for the compound composition. Thus the composition of the compound may be obtained, as shown in Fig. 18. If the eutectic and peritectic halts are plotted, as in Fig. 19, the hidden maximum may be obtained through the same process of reasoning since the peritectic halt should be a maximum, and the eutectic halt equal to zero at the Compound composition.

#### Types of Cooling Curves Employed.

##### (a). Free Cooling.

As previously indicated free cooling, i.e. the body allowed to cool naturally by radiation from a higher temperature to a lower one, would yield an exponential curve in accordance with Newton's Law of Cooling. The disadvantage of this type of curve is that a small change in slope can easily be missed due to the natural curvature. Also if the temperature is high, the cooling will be very rapid, and the heat effect may be missed.

##### (b). Graduated Cooling.

To overcome this difficulty Plato<sup>72</sup> suggested a system of gradual cooling. This would yield a rectilinear curve, and changes in slope would show up very easily on this. Since the methods of heating are now mainly of the electric type, the cooling could be carried out progressively and regularly by reducing the current. Plato did this by means of a wire

resistance wound on a porcelain cylinder and slowly rotated by a motor. Many methods have been employed by independent workers for this purpose, the methods ranging from very complicated pieces of machinery to simple rheostats.

(c). The Inverse-Rate Curve.

This was first adopted by Osmond<sup>73</sup> in 1887. For this purpose the observer notes the intervals of time which are occupied by the metal in rising or falling through successive equal differences of temperature. Thus one might take the times occupied by successive drops of 3°C. and plot these as abscissae against the actual temperature of the metal at each observation. In this way a curve is obtained whose ordinates are T (temperature) and whose abscissae are  $\frac{dt}{dT}$  where t is time. With a uniform rate of heating or cooling, this curve becomes a vertical straight line; an evolution of heat during cooling or an absorption of heat during heating causes the curve to deflect outwards and to form a hump or "peak". An example of this is shown in Fig. 20. This represents the cooling of an alloy whose components are completely miscible in the liquid state, insoluble in the solid state, and separate out in the pure form. As shown previously (Fig. 1) primary crystallisation will first take place. The solidification will set free a small quantity of heat and the curve shows a sudden outward bend. The temperature will then fall, with successive quantities of the metal crystallising out. Heat is being continuously liberated and the natural rate of cooling of the mass is thereby continuously retarded, being represented by ab in the curve. At B eutectic crystallisation



takes place with great heat liberation.

The advantage of this type of curve is that the method of plotting the observations is very economical of space, and thus allows the use of a very much more open scale, with the result that even minute thermal phenomena appear quite clearly. It can be shown that, if the rate of cooling is uniform, the area of the peak formed is proportional to the quantity of heat evolved.

(d). Differential Cooling Curve.

This method, proposed by Roberts-Austen<sup>74</sup>, consists of comparing the rate of cooling of the alloy under consideration, and a neutral body. The neutral body is one which is known not to undergo any structural changes in the temperature range under consideration. Thus it would cool ideally - that is, it would actually represent the temperature of the furnace, and would cool in the manner previously mentioned. The body is chosen to be of approximately the same thermal capacity as the alloy under consideration. The temperatures are usually measured by a differentially connected thermocouple, consisting of two thermojunctions arranged to oppose one another. One is placed in the neutral body and the other in the alloy under consideration. The one placed in the alloy, if used singly, will give the absolute temperature of the alloy. Thus on cooling two curves will result. One will give the absolute temperature of the alloy. The other will give the difference in temperature between the alloy and this neutral body. On cooling, the two should cool at approximately the same rate. Thus the difference curve should be at zero, or at the most would show a small fairly constant

displacement. When a thermal change in the alloy occurs, however, the temperature of the alloy will remain constant, or suffer delayed cooling, depending on the type of change, the neutral body will however go on cooling with the furnace. The result will be a temperature difference between the neutral body and the alloy. This will show up on the difference curve as a pronounced deflection.

Thus the sensitivity of the method has been greatly increased, since very small thermal changes, which would not show up on the ordinary cooling curve can readily be seen. Also the beginning of crystallisation can thus easily be determined. This method has been refined by Sykes<sup>75</sup>, working on the basis that the change in specific heats from one phase to another would be discontinuous.

## (2). X-ray Analysis.

The method of X-ray examination comes next in importance to that of thermal analysis. Metals crystallise in one of three simple lattices; the face-centred cubic, body-centred cubic, and close-packed hexagonal. Friedrich and Knipping, acting on the suggestion of von Laue, discovered that crystals act as three dimensional optical gratings for X-rays. This showed that the crystal consisted of a unit structure which kept recurring.

Apart from the obvious application of this to the science of crystallography, its importance lies in the fact that it enables a change in the solid phase to be demonstrated, even though that solid phase may be opaque and microcrystalline in

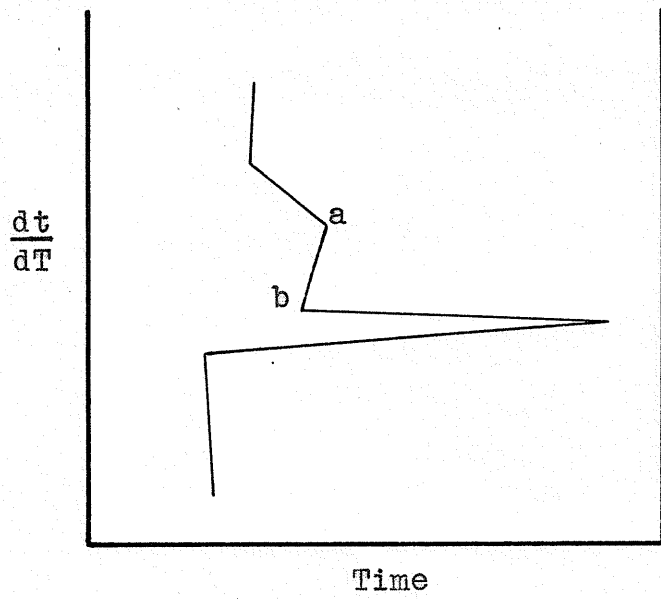


Fig. 20

structure. Previous methods failed to give desired results due to the fact that although a change had occurred, and this change resulted in a discontinuous change at the transition point, yet this change was either too small to be noted, or the system remained metastable.

However although the difference between the physical properties of two crystalline solids may be small, yet the X-ray method will give valuable information, regardless of whether a single phase region or a region containing two or more phases occurs. The gradual change of parameter of a solid solution with composition can be measured with precision, and a sudden break in the parameter-composition curve is a clear indication that a new region has been entered.

Two separate phases must possess different space lattices. This property is fundamental and thus the X-ray method has been widely used for fixing the phase boundaries on a complex system. The X-ray method is of special value in the examination of intermediate phases. Some systems, formerly regarded as simple, prove on detailed examination to include a number of such phases, some of which differ only very slightly in structure, so that they are easily overlooked when ordinary metallographic methods are used. This aspect of the problem has become more important since the introduction of the electronic rules, assigning certain probable constitutions to phases having a given lattice structure. Such phases are sometimes very complex, having a large number of atoms to the unit cell, so that they deviate appreciably from the simple cubic or hexagonal structure.

The general methods used are those of W. H. and W. L. Bragg (the reflection method), and that of Debye and Scherrer (the powder method). Many refinements have been adopted to these methods, such as X-ray photographs of hot alloys, thus serving to supplement the method of thermal analysis, and to throw more light on the structure of solids in general.

### (3) Microscopic Analysis.

Microscopic analysis is usually used in conjunction with thermal and X-ray analysis. Looked at in the ordinary way, metallic objects possess an appearance of complete homogeneity, but the existence of a structure at once becomes obvious when a piece of metal is broken. Thus it is not surprising that the first work on the application of the microscope to the examination of metals was carried out on fractures. This however proved to be a very limited field, since the irregularities of fractured surfaces make it impossible to use more than very moderate magnifications. Also the fracture itself is not necessarily a fair cross-section of the material, i.e. the fracture may, and in some cases does, pick out a path through a weak constituent.

The necessity of using cut sections having a plane surface was thus recognised, probably from the connection which was thought to exist between metals and igneous rocks. However the study of thin sections could not be employed, since the opacity of the metals would require extremely thin sections. Also it has been pointed out by Beilby that the operations of grinding and polishing alter the structure of the metal to a certain depth below the surface, and thus a very thin polished section of

metal, such as would have to be used, would not be representative of the general structure.

It is therefore necessary to examine prepared surfaces by means of reflected light. Care must be taken that the micro-section to be observed is representative of the metal under examination. If the alloy is sufficiently soft, it is cut by a hack-saw. If this cannot be done, the cutting should be performed in a manner which will not generate enough heat to be deleterious to the structure under consideration. The procedure for obtaining a smooth surface suitable for polishing will of course depend on the type of metal being used. Emery paper is usually used to remove saw-cuts and coarse scratches. The emery paper is placed on a hard support. The specimen, held between the fingers is now rubbed backwards and forwards with a slight pressure, using the coarsest emery paper. The process is continued until, on examination with a hand lens, no scratches are seen except the parallel series due to the emery paper. The process is now continued with finer papers. On passing from one paper to another, the specimen is turned through a right angle, so that the new scratches cross the old at right angles. The papers are mostly used dry, but for soft metals it is usually necessary to add a liquid, or to soak the paper in paraffin before using. The process of grinding is really one of cutting, the particles of emery cutting parabolic grooves in the metal.

The process of polishing was long thought to be merely a finer continuation of the above cutting processes. However the researches of Lord Rayleigh, Osmond and his collaborators, and Beilby<sup>76</sup> have shown that an essential difference exists between

the two. The effect of polishing is really to cause a surface flow of the substance being polished. Flow takes place, although only to a small depth, on the surface of even the hardest crystalline substances, and Beilby demonstrated the existence, on polished surfaces, of a thin layer of flowed, structureless material, strongly resembling in its behavior a high viscous fluid. Beilby regarded this flowed layer as having essentially the properties of an undercooled liquid, and he preferred the term "vitreous". The suggestion has been advanced that the process of flow is one of actual melting. The order of the pressures required to melt the metals, as calculated from their latent heat of fusion and their density, corresponds perfectly with the observed order of plasticity, and although the pressures seem enormous, they are only assumed to prevail in regions a few atoms thick, and for a short time.

In order to afford any insight into the structure of the metal, the polished surface of a specimen must be treated in some manner calculated to produce a surface pattern corresponding to the section of the internal structure presented by the polished surface. The polished surface, since it is not really representative of the alloy structure, must first be removed by the action of some suitable reagent. The usual practice is to etch the surface by means of some reagent which will attack the metal. The amorphous surface film is more readily attacked than the rest of the metal, and is thus rapidly and easily removed. The subsequent action of the agent will then depend on the nature of the metals involved. Usually a reagent is chosen such that its action on the alloy is a differential one, attacking one of the



components and not the others, thus showing up the true structure of the alloy.

While crystallisation of solid components from molten alloys, and of salts from their solutions, are similar processes, yet there is a great difference in the course of events in the two cases. Salts commonly separate from their solutions in the form of more or less perfect crystals, and on growing the crystals retain the same general form. Metals and alloys, on the other hand only exceptionally form such crystals. As a rule, a small crystalline nucleus grows almost exclusively in the direction of certain axes, giving rise to elongated and much branched forms, called "dendrites" or "crystal skeletons". None of the faces attain any great development. If the growth of the dendrite is confined in some directions, only a few of the possible skeletal axes are developed. The process of crystallisation from any given centre must ultimately reach a limit owing to the interference of adjoining crystals. The growth of the axes is thus arrested, and the further solidification of metal takes place interaxially, axes of higher order being formed until the spaces are filled with solid matter. Since in an actual crystallisation the centres of crystallisation are not uniformly distributed, and the orientation of the axes of neighbouring crystals is not the same, the solidified mass will be divided into irregular polyhedra, varying in size and shape. The typical structure of a solidified metal is therefore that of approximately polygonal grains, the boundaries of which are not crystal faces, but are due to interference during growth. Each grain is, to use the mineralogical term, an "allotriomorphic" crystal, the outline of which is determined by the presence of the



neighbouring grains.

The micro-structure of any alloy will depend on the type to which the system of the metals in question may belong, and on the position of the alloy in that system.

The microscopic appearance of solid solutions is often misleading, but is readily explained. If perfect equilibrium conditions are reached, the solid solution should, and does, resemble a pure metal - the homogeneous character of the molten solution is in that case so completely maintained that the microscope cannot detect the presence of any second constituent. If the cooling is too rapid to allow solid diffusion to take place, homogeneity will not be maintained and a two-phase alloy will be presumed to exist. If time is allowed for equilibrium to assert itself solid solubility lines are detectable in this manner. A series of alloys ranging a short way on either side of the supposed line are annealed for a long period - in some cases amounting to many weeks - at exactly known temperatures, and subsequently examined with the microscope. Up to a certain limit in composition they are found to be homogeneous, i.e. to consist of a single constituent. Beyond that composition no amount of prolonged heating will render them entirely homogeneous, i.e. traces of the second constituent still exist. The limit of solubility is thus fixed.

In the same way, quenching experiments often serve as the only true guide to the position of the solidus lines. This can be ascertained by quenching specimens of suitably chosen alloys from a series of temperatures lying slightly above and slightly below the temperature at which the solidus is likely to be met. The

specimens quenched from a temperature slightly above the solidus must contain, at the moment of quenching, a very small amount of molten metal, and during the rapid cooling which occurs in quenching, this liquid metal solidifies very quickly and thus produces minute regions of very fine structure. These "fusion spots" are readily noticed when the specimen is polished and etched.

A eutectiferous mixture will behave as follows. The pure metal will only show the irregular polygons. As some of the second component is added the spaces between the polygons gradually widen and are filled with a substance which is different from that of which the polygons themselves are composed. This material between the polygons gradually increases in amount until it forms a continuous network in which the polygons form patterns. As the eutectic is approached the polygons become smaller in size. If the substance between the spaces is examined under a higher power microscope, it is seen to consist of a fine pattern of two substances, one of which is the same as the polygons, in other words, the pure material. At the eutectic the entire field will be filled with this fine grain structure, typical of the eutectic structure. Further addition will now cause separation, in the form of polygons, of the second substance. Thus the two constituents of the alloy will have changed places in the structure.

#### Other Methods.

The three methods of investigation outlined above are the most important general methods used in the study of metallography. However the physical properties of an alloy very often give

definite clues as to the alloy structure. Thus certain other methods, though not of general applicability, may be used as guides in obtaining equilibrium diagrams. However obviously they are very limited in the range of their applicability. As subsidiary aids the following determinations may be mentioned:-

- (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 of the alloy.
- (7). the specific volumes of the alloy and components.

Lead-Aluminium.

Wright<sup>1</sup> who was the first to carry out investigations with these metals stated that aluminium and lead form two layers when melted together. Analytical determinations of the two layers after they had been kept at a temperature of from 750-850° C. for about eight hours showed that the aluminium-rich upper layer contained 1.91% lead and the lower lead-rich layer contained 0.07% aluminium.

Pécheux,<sup>2</sup> somewhat later claimed to have obtained three layers with these metals. He melted the metals, mixed them by stirring, and quenched them by pouring them into a steel mold. He stated that in alloys with more than 10% lead there were three layers formed, an alloy of lead and aluminium between layers of pure lead and pure aluminium. Analysis of this middle layer gave from 3-10% lead. Alloys of 2, 5, and 7% lead were stated by him to have given three successful alloys without liquation, whose densities decreased with the decrease in the amount of lead. Their fusion points were near that of aluminium and rose from that of the alloy with 7% to that of the one with 2% lead. Three layers, however in a two-component system would mean an invariant point. This has been discounted by the results obtained by later workers.

Gwyer,<sup>3</sup> conducted an extensive investigation of the alloys of lead and aluminium and found that there were two halt-points on the cooling curves, one at the melting point of pure aluminium and the other at the melting point of pure lead, corresponding to the formation of two almost completely insoluble liquid layers. He states however, that alloys with

1, 2, 3 and 5% lead showed primary separated crystals of aluminium surrounded with secondarily formed lead. This would indicate that crystallization had begun with an emulsion of lead in aluminium. That is, in these alloys the formation of two layers had not taken place before the beginning of crystallization. This seems incompatible with his identification of the first halt-point with the freezing-point of pure aluminium. Two layers had however formed in alloys containing from 5-99.5% lead since the cold regulus showed two layers of pure lead and aluminium with a slight lead content which was detectable microscopically.

More recently, Claus<sup>4</sup> has stated that aluminium and lead are slightly soluble in each other in the liquid state, and also that up to about 5% lead is taken up by the aluminium in colloidal, not true, solution.

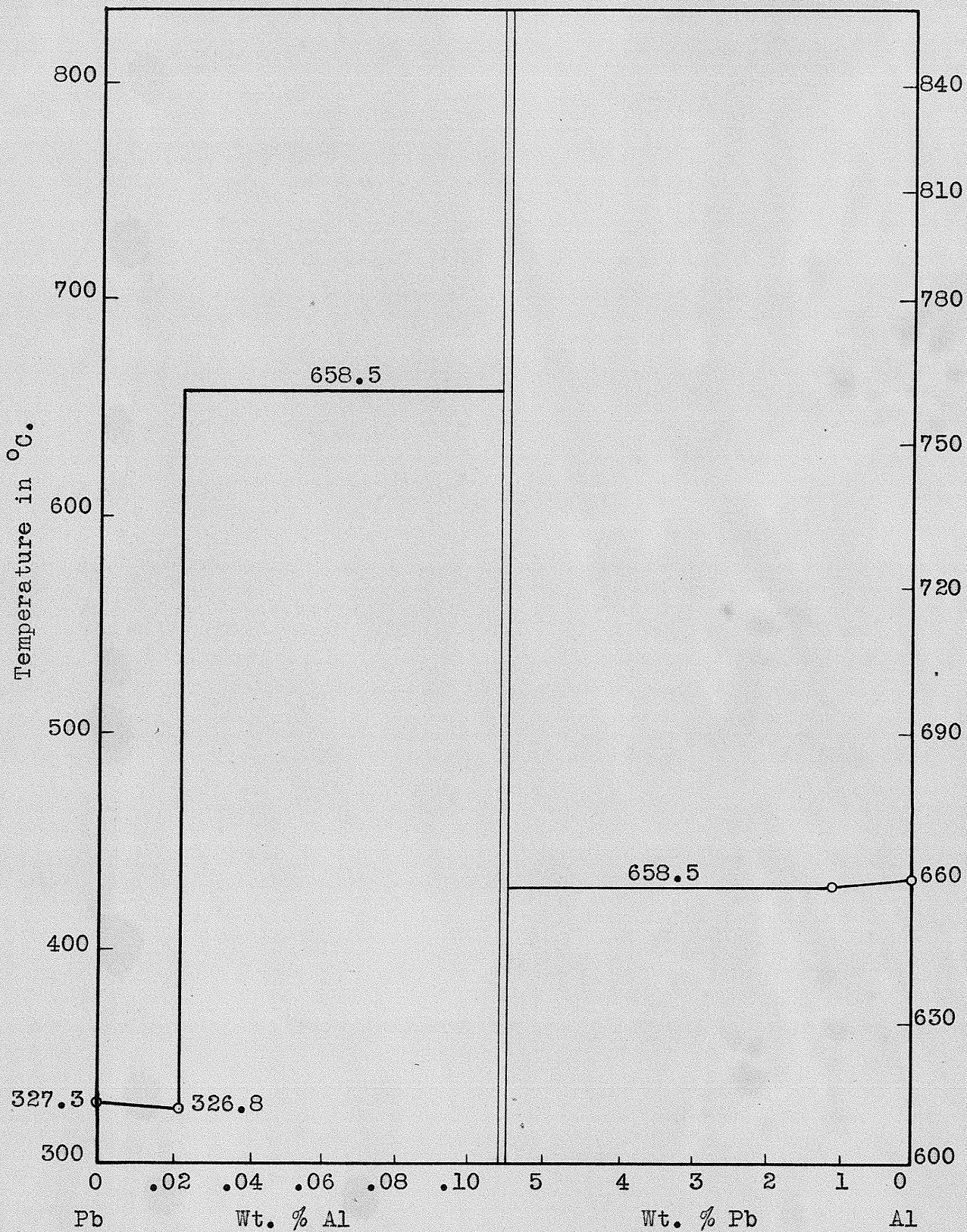
Hansen and Blumenthal<sup>5</sup> investigated the system by the cooling curve method. They record a depression of  $1.5^{\circ} \pm 0.5^{\circ}$  in the freezing point of aluminium produced in alloys with 3, 5, 7, and 24% lead. The aluminium used was 99.91% pure, and was found to be practically insoluble in molten lead.

Recently L. W. Kempf and K. R. Van Horn<sup>6</sup> investigated the solubility of lead in liquid aluminium and determined it to be about 1.52% at the freezing point of aluminium and to increase continuously with temperature to about 14.75% lead at  $1038^{\circ}$ . The freezing point of aluminium ( $660^{\circ}$ ) was lowered by the presence of lead to a minimum of  $658.5^{\circ}$ .

The most recent work is that carried out by A. N. Campbell and R. W. Ashley<sup>7</sup>. They determined the equilibrium diagram of

the system and showed that it exhibited two invariant points, the eutectic at  $326.8^{\circ} \pm 0.1^{\circ}$  C., corresponding to 0.021% aluminium, and the equilibrium-two liquid layers-solid aluminium at  $658.5^{\circ} \pm 0.1^{\circ}$  C-the freezing points of pure lead and pure aluminium being taken as  $327.3^{\circ}$  and  $660.0^{\circ}$  C., respectively. The composition of the aluminium-rich liquid at this point is 98.9% aluminium. The mutual solubility of liquid lead and aluminium is small below  $800^{\circ}$  C. In the solid state, lead and aluminium are mutually insoluble. Liquid aluminium can take up as much as 10% lead in the form of an emulsion or colloidal suspension. The aluminium used in this investigation was 99.953% pure.





The System Aluminium - Lead. (Campbell and Ashley)

Fig. 21

PREVIOUS INVESTIGATION



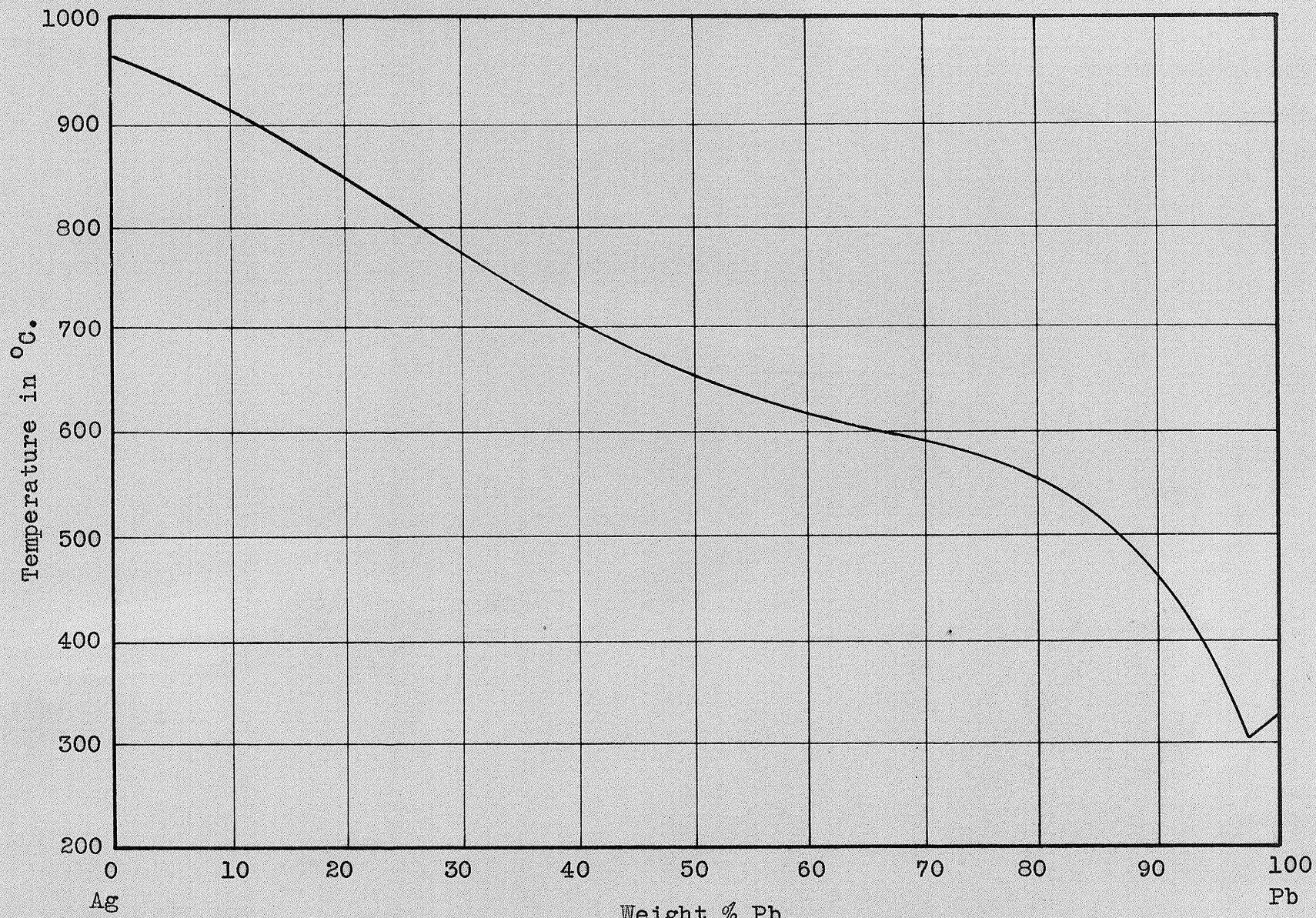


Fig. 22

The System Silver - Lead. (Petrenko)



### Silver-Lead

Heycock and Neville<sup>8</sup> found that the phase diagram consisted of two curves intersecting at a eutectic, having a composition of 4% silver by weight and a temperature of 304°.

G. J. Petrenko<sup>9</sup> determined the phase diagram for the system and found it to consist of two curves intersecting at a eutectic which had a composition of 2.5% silver by weight at a temperature of 303.3°. This eutectic mixture was found to be harder than pure lead.

F. Yoldi (with D. L. de A. Jimenez)<sup>10</sup> investigated the system with 1.50-10% silver by means of thermal and photomicrographic analysis. No compound formation was found. Primary and eutectic crystallization was found in the above region, excepting in the 2.19-2.51% silver region. This fixed the eutectic composition as 2.3% silver, separating at 300-305° C. The components were found to be completely miscible in the liquid state. The Brinell hardness changed continuously for alloys containing 25-100% of silver.

Haim H. Chiswick and Ralph Hultgren<sup>11</sup> examined the system by means of X-Rays. They confirmed the absence of intermediate phases. Powder patterns of samples of intermediate composition annealed for 4 weeks near the eutectic temperature showed the presence of two phases, which were identified as the terminal solid solutions. The solubility of lead in silver was found to be much less than the value estimated by Hansen.



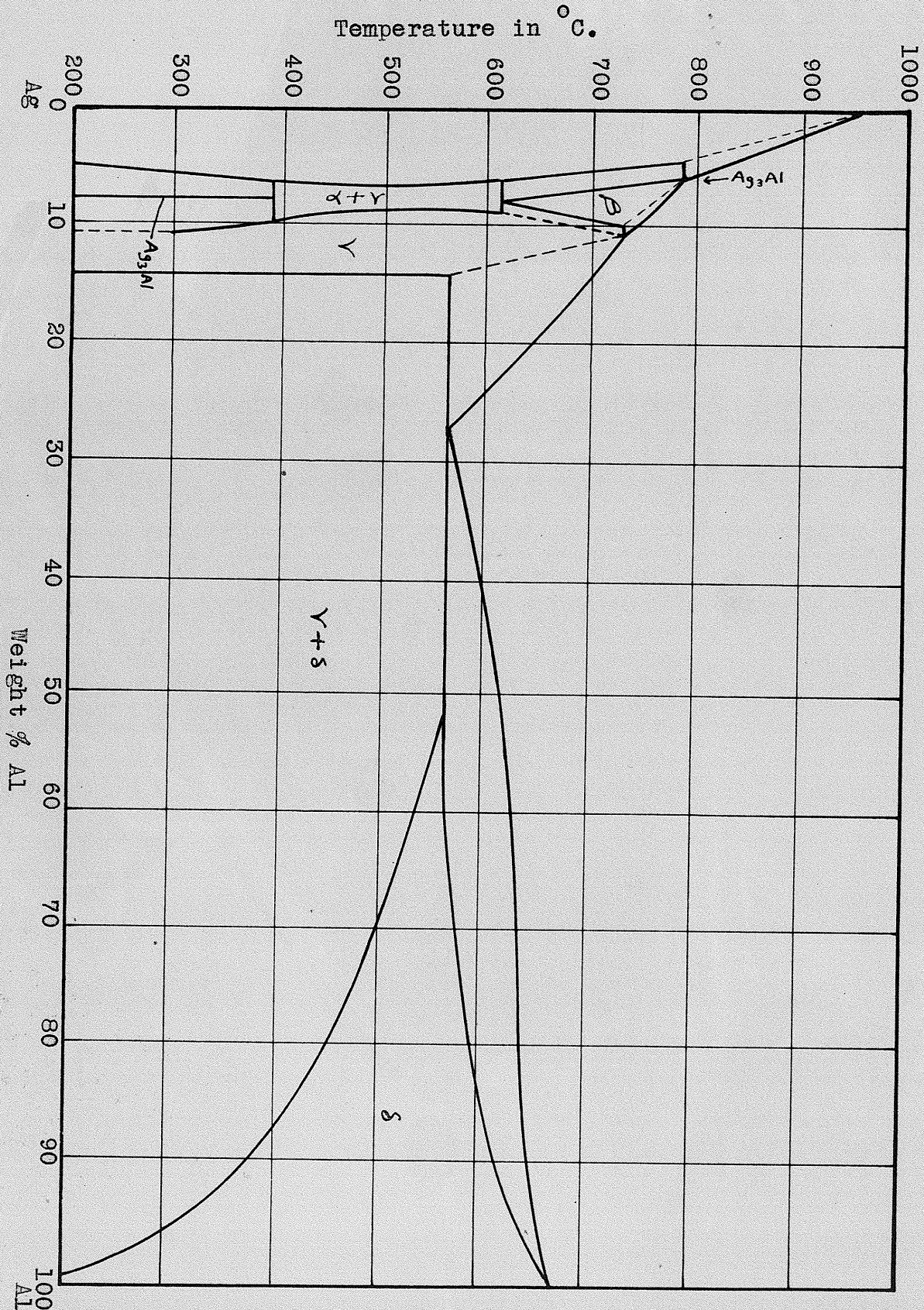


Fig. 23

Composite Diagram of the Silver-Aluminium System.

Silver-Aluminium

Wright<sup>12</sup> merely found that the metals were completely miscible in the molten state.

Gautier<sup>13</sup> determined the liquidus curve for the first time (11 alloys) and found a maximum for the composition  $\text{Ag}_2\text{Al}$ .

Heycock and Neville<sup>14</sup> found that the freezing point of silver was lowered to about  $923^\circ$  by the addition of 1.4% aluminium.

With the aid of thermal as well as microscopic analysis, the composition diagram (25 alloys) was completely plotted for the first time by Petrenko<sup>15</sup>. He decided on the existence of two compounds— $\text{Ag}_3\text{Al}$  (7.69% Al by weight) and  $\text{Ag}_2\text{Al}$  (11.11% Al by weight). He could not verify the maximum found by Gautier and stated that it was more probable that the compound  $\text{Ag}_2\text{Al}$  formed due to a peritectic reaction at  $718^\circ$  and the alloy with the composition  $\text{AlAg}_3$  corresponded to the end point of the peritectic horizontal at  $770^\circ$ . A eutectic also occurred at about 69% silver and  $567^\circ$ . He denied the existence of an Aluminium-rich solid solution.

Puschin<sup>16</sup> by the use of the drop of potential formulated the composition  $\text{AgAl}$  (20% aluminium by weight). This compound was found by later investigators to be non-existent.

W. Broniewski<sup>17</sup> determined the electric conductivity, the temperature coefficient of electric resistance, the thermo-electric power, and the potential of silver-aluminium alloys. The curves of the temperature coefficients and the thermo-electric power show two marked maxima at 60.9% and 75.4% by volume of silver, corresponding to the compounds  $\text{Al}_2\text{Ag}_3$  (85.71 wt. % silver) and  $\text{AlAg}_3$ . The former compound does not agree with Petrenko's results and since the latter's work has the greater justification,

$AlAg_2$  is taken as the second compound, not  $Al_2Ag_3$ . Broniewski confirmed the existence of the  $\delta$ -aluminium-rich solid solution which Petrenko had denied.

Beckman<sup>18</sup> determined the existence of the silver-rich  $\alpha$ -solid solution.

W. Kroll<sup>19</sup>, studying the solid portion of the system also confirmed the  $\alpha$ -solid solubility region and found that the solubility of silver in aluminium began at 20° C. with at least 1.5% silver by weight and at about 525° reached at least 9% silver by weight.

Hansen and Sachs<sup>20</sup> determined the existence of the silver-rich  $\alpha$ -solid solution.

M. Hansen<sup>21</sup> determined the composition diagram in the region of 0-60 wt. % silver. The liquidus curve and the eutectic temperature were determined by thermal analysis. The solidus curves and the silver solubility curves were determined micrographically. The solubility of silver ranges from 0.75% by weight at 200° to about 48% at the eutectic temperature. Below 200°, the solubility, as can be shown by hardness tests gets still smaller, so that at room temperature the saturation limit lies at less than 0.5% silver.

A. F. Westgren and A. J. Bradley<sup>22</sup> investigated the system by X-Ray analysis. They showed that the composition of the compound  $Ag_3Al = \delta$  phase, with an extremely narrow range of homogeneity and has the same structure as  $\beta$ -Mn, (cubic with 20 atoms in the elementary cube). With higher temperatures, around 610°  $\delta$  changes into  $\beta$  (with cubic space-centred lattice structure). They found that the second intermediary crystallization ( $\gamma$ )

is a solid solution of densest spherical packing, hexagonal structure lying between 8.5 and 14.3 atomic % aluminium. The possibility of a compound  $\text{Ag}_3\text{Al}_2$  (14.29 atomic % aluminium) existing, as suggested by Broniewski, was completely dissipated by Westgren and Bradley, who studied some of Broniewski's singular points and found them to be identical with the aluminium-saturated solid solution.

M. Tazaki<sup>23</sup> found the solubility of silver in aluminium at  $565^\circ$  (eutectic temperature) to be about 24% silver, and about 9% silver at  $400^\circ$ . The silver-rich part of the diagram with the exception of the eutectic points appears to be that of Petrenko's.

Enrico Crepaz<sup>24</sup> redetermined the whole system thermally and found a third peritectic point at  $698^\circ$  and besides  $\beta$ ,  $\beta'$  and  $\gamma$  postulated a fourth phase,  $\text{Ag}_3\text{Al}_2$ , which had previously not been found. The compound  $\text{Ag}_3\text{Al}_2$  formed a eutectic with a solid solution of silver in aluminium at  $567^\circ$  and a concentration of 26.5% Aluminium ( in the text 39.5% is given which must be a typographical error since the table and diagram clearly indicate 26.5% ). The solubility of silver in aluminium is given as 45% silver as derived from microscopic observation of specimens annealed at various temperatures for different lengths of time. At room temperature the solubility is less than 0.5% silver. The solubility of aluminium in silver at room temperature is 4.2%. The part of Crepaz's diagram which lies between 0 and 12% aluminium has been found to be theoretically unstable and has been supplanted by later work.

Shuzo Ueono<sup>25</sup> investigated the system by means of the intensity of reflection of light. The intensity of reflection



of 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 horizontal line, except the part of the two compounds of which  $AlAg_3$  is characterized by a maximum and  $AlAg_2$  by a minimum.

Hoar and Rowntree<sup>26</sup> studied the equilibria of this system above  $600^\circ C$ , in the region of 0-15% aluminium by weight. The liquidus temperatures determined were found throughout to lie 5-10° higher than those obtained by Petrenko, presumably due to the use of purer aluminium (99.5%). The first peritectic ( $\alpha + \text{melt} \rightleftharpoons \beta$ ) was found to lie at 5-6.2% aluminium by weight and  $779^\circ$ . The second peritectic ( $\beta + \text{melt} \rightleftharpoons \gamma$ ) lies at 10-10.8% aluminium and  $729^\circ$ . The  $\alpha/\alpha+\beta$  and the  $\alpha+\beta/\beta$  boundaries slope towards the axis with increase of temperature. Petrenko's indication of these as vertical is put down as due to his inability to determine the thermal changes, since the methods of micrography were used to accurately determine these boundaries.

R. T. Phelps and W. P. Davey<sup>27</sup> chose this system to investigate the nature of solid solution by means of X-rays. They found that saturation of aluminium in silver was reached at 5.4% aluminium by weight. Further addition of aluminium gave aggregates of  $Ag_3Al$  of sufficient size to show X-ray

diffraction patterns. They came to the conclusion that the aluminium in the solid solution was chemically combined with the adjacent silver, not a case of a direct substitution of aluminium atoms for silver in the silver lattice.

C. S. Barrett<sup>28</sup>, E. Jette and F. Foote<sup>29</sup>, S. Kokubo<sup>30</sup> and Ageew and Shoyket<sup>31</sup> investigated this system independently, could not confirm the findings of Phelps and Davey. They come to the conclusion, by very accurate measurement of lattice constants and density measurements that the solid solution is substitutional in character.

N. Ageew and D. Shoyket<sup>32</sup> studied the constitutional diagram of the system up to 10% aluminium by micrographic examination, X-ray analysis and hardness measurements. They found that the  $\beta'$  phase decomposed on heating at 400°C. into a mixture of  $\alpha$  and  $\gamma$ . The boundary of the  $\alpha$ -field was determined by precision measurements of the lattice parameter of the quenched alloys. The boundary of the  $\gamma$ -field was determined by micrographic examination and X-ray analysis. A two-phase region ( $\alpha + \gamma$ ) was found separating the  $\beta'$  and  $\beta$  phases between 400° and 600°C.

F. E. Tishtchenko<sup>33</sup> by the method of thermal analysis showed that at 771°  $AlAg_3$  was formed. This undergoes a transformation into  $\beta'$  at 606°. The modification of  $AlAg_3$  forms a solid solution with aluminium, reaching a maximum saturation of 10.2% aluminium at 722°. The solubility of aluminium in  $AlAg_3$  decreases with a fall in temperature.  $\beta'$ - $AlAg_3$  does not dissolve aluminium at 722°. A eutectic consisting of a combination of  $Al_2Ag_3$  and a solid solution of  $\beta$ - $AlAg_3$  with 10.2% aluminium separates. The compound  $Al_2Ag_3$  is stable in the interval 752-711°



while below  $711^{\circ}$  it can exist only in the metastable state. The stable state below  $711^{\circ}$  is a solid solution of  $\gamma$ " which is a solid solution of aluminium in  $\text{AlAg}_2$  reaching saturation at 14.33% aluminium. A complete transformation of the metastable  $\text{Al}_2\text{Ag}_3$  into the solid solution  $\gamma$ " occurs only on prolonged heating. In the interval  $711-400^{\circ}$  crystals of  $\gamma'$  (solid solution of silver in  $\text{AlAg}_2$ ) and  $\beta$  coexist. Below  $400^{\circ}$  the alloys with 7.7-11.1% aluminium exist as  $\beta'$  ( $\text{AlAg}_3$ ) and  $\gamma'$  ( $\text{AlAg}_2$ ).

Hansen<sup>34</sup> has the following to say regarding the above data. "It can almost certainly be considered that the experimenter has drawn false inferences by his explanation of his experimental results, since his conception is in direct contradiction to the results obtained by all the other investigators!"

Hume-Rothery, Mabbott and Evans<sup>35</sup> micrographically determined the solidus curves and the saturation boundary of the  $\alpha$ -solid solution. Aside from small quantitative differences the saturation boundaries of the  $\alpha$ -solid solution agree well with that as found by Ageew and Shoyket above.

Ichiji Obinata and Mosami Hagiya<sup>36</sup> studied the system in the range 0-11% aluminium by X-ray analysis at ordinary and high temperatures, by electric resistance methods and microscopic study. In the alloys containing 5.6 to 8.2% aluminium a eutectoid and a metatectoid reaction take place, the temperatures of which are  $615^{\circ}$  and  $420^{\circ}$  respectively. The metatectoid reaction,  $\alpha + \gamma \rightleftharpoons \text{Ag}_3\text{Al}$  can easily be suppressed by water-quenching of the alloy. The eutectoid reaction  $\beta \rightleftharpoons \alpha + \gamma$  is but little suppressed by the same treatment. The alloys quenched from the  $\beta$ -field consist of the  $\gamma$ -phase, supersaturated with silver,

showing roentgenographically the diffraction lines belonging to the hexagonal close-packed lattice. In the quenched hypo-eutectoid alloys anomalous increases in the electrical resistance was observed at  $200^{\circ}$  in heating. This was attributed to the formation of the compound  $\text{Ag}_3\text{Al}$ .

Ageew and Shoyket<sup>37</sup> repeated their previous work<sup>32</sup>, verified their previous results and found that the silver-aluminium eutectic mixture on cooling formed the  $\vartheta$  phase ( $\text{Ag}_3\text{Al}$ ).

Tishtchenko and Lukash<sup>38</sup> investigated the system up to 80% silver by the thermal and microstructure methods. The experiments confirmed the belief that in the liquid state the alloys contain  $\text{Ag}_3\text{Al}_2$ , which combines into complex compounds in the presence of excess aluminium and which plays an important role in the hardening process. Complex compounds are formed above  $750^{\circ}$ ; none below this temperature. The alloys containing 11.8-66.7% silver have a transformation at  $440^{\circ}$  with a maximum break at 46.5% of silver. This transformation corresponds to the recrystallisation temperature of the  $\delta$ -solid solution. The alloys with 66.7-85.7% silver also have small breaks which are explained by the same phenomena.  $\text{AgAl}_2$  is formed in alloys rich in aluminium at the eutectic temperature; it has no transformation in the solid state. The solubility curve of silver in aluminium, shows 46.5% silver at the eutectic crystallization temperature and shows alloys containing 11.8% of silver at  $440^{\circ}$ , and about 1% of silver at room temperature.  $\text{AgAl}_2$  (but not  $\text{Ag}_2\text{Al}$  as found by M. Hansen-Mitt. deutsch. Material prufungson'stalt, 5: 31, 1929 and 10 : 31, 1930) separates along the solubility curve.

Hajime Kato and Sadamu Nakamura<sup>39</sup> investigated the system by means of differential dilatometric analysis, microscopic examination and X-ray analysis in the range 3 to 11% aluminium and established the equilibrium diagram of the alloy rich in silver. Unfortunately this article is published in Japanese and is unavailable to us.

Hideo Zaziri<sup>40</sup> studied the system by means of thermal expansion, differential dilatation and microscopic structure. He concluded that the boundary line between  $\alpha+\gamma$  and  $\gamma$  differs somewhat from that given in previous papers. It lies virtually on the ordinate of about 7.7% aluminium. Specimens quenched from the  $\alpha+\gamma$  range and etched by a solution of 20 parts of water and 1 part of saturated  $\text{Cr}_2\text{O}_3$  in  $\text{H}_2\text{SO}_4$  distinctly show eutectic structures. The temper hardening of these alloys occurs in a range of 56-9.5% of aluminium in silver, and if these alloys are quenched at a temperature between 450 and 720° and tempered at 200-350°, Vickers hardness numbers of 300-365 are obtained. The hardening velocity of the alloys containing more than 7.7% aluminium, which corresponds to the constituent of  $\text{Ag}_3\text{Al}$ , differs from that of the alloys containing less aluminium; the former rapidly reach the maximum hardness after tempering, while the latter require at least several hours. The alloy quenched from a temperature above 600°, after tempering, has a hardness higher than that quenched from a lower temperature, presumably owing to the refining of grains due to a eutectic reaction. The hardening of the alloy is caused by the hard constituent of  $\beta'$  which is produced by the reaction between  $\alpha$  and  $\gamma$  due to tempering, while  $\alpha$  and  $\gamma$  are

obtained by quenching. An increase in hardness caused by the precipitation of supersaturated solid solution is not likely to occur.

G. I. Petrenko and F. A. Derkach<sup>41</sup> investigated the Widmanstaetten pattern in the system. To avoid oxidation the samples were covered with active C and sand. Those rich in aluminium were treated with HF. The Widmanstaetten pattern was observed in the region of 40-84% aluminium. The thermal conditions under which this structure appears depend on the degree of solution of the solid solution. In the samples with a concentration of 40-50% aluminium this pattern is formed at ordinary cooling after crystallisation from the liquid state and does not require any special heating to high temperatures. The solid solution of these concentrations is saturated with the  $\alpha$ -phase. Samples with a higher aluminium concentration give a Widmanstaetten pattern only after preliminary heating at a high temperature for a long time. Solid solutions of these concentrations are not completely saturated with the  $\alpha$ -phase.

F. E. Tishtchenko<sup>42</sup> investigated the region of the  $\beta$ -phase (5-8.3% aluminium) thermally, and confirmed the correctness of the diagram obtained by Hoar and Rowntree. He disclosed the constriction of the liquid and solid phase curves at 7.7-7.4% aluminium (by weight). The eutectic decomposition of the  $\beta$ -phase at 606° and the formation of  $AlAg_3$  at 456° were observed.

W. Hume-Rothery, G. V. Raynor, P. W. Reynolds, and H. K. Packer<sup>43</sup> in the most recent work on the subject, determined the equilibrium diagram for the system for 15 to 40 atomic %

aluminium. Unfortunately this paper could not be made available to us and as a result is not reproduced here.



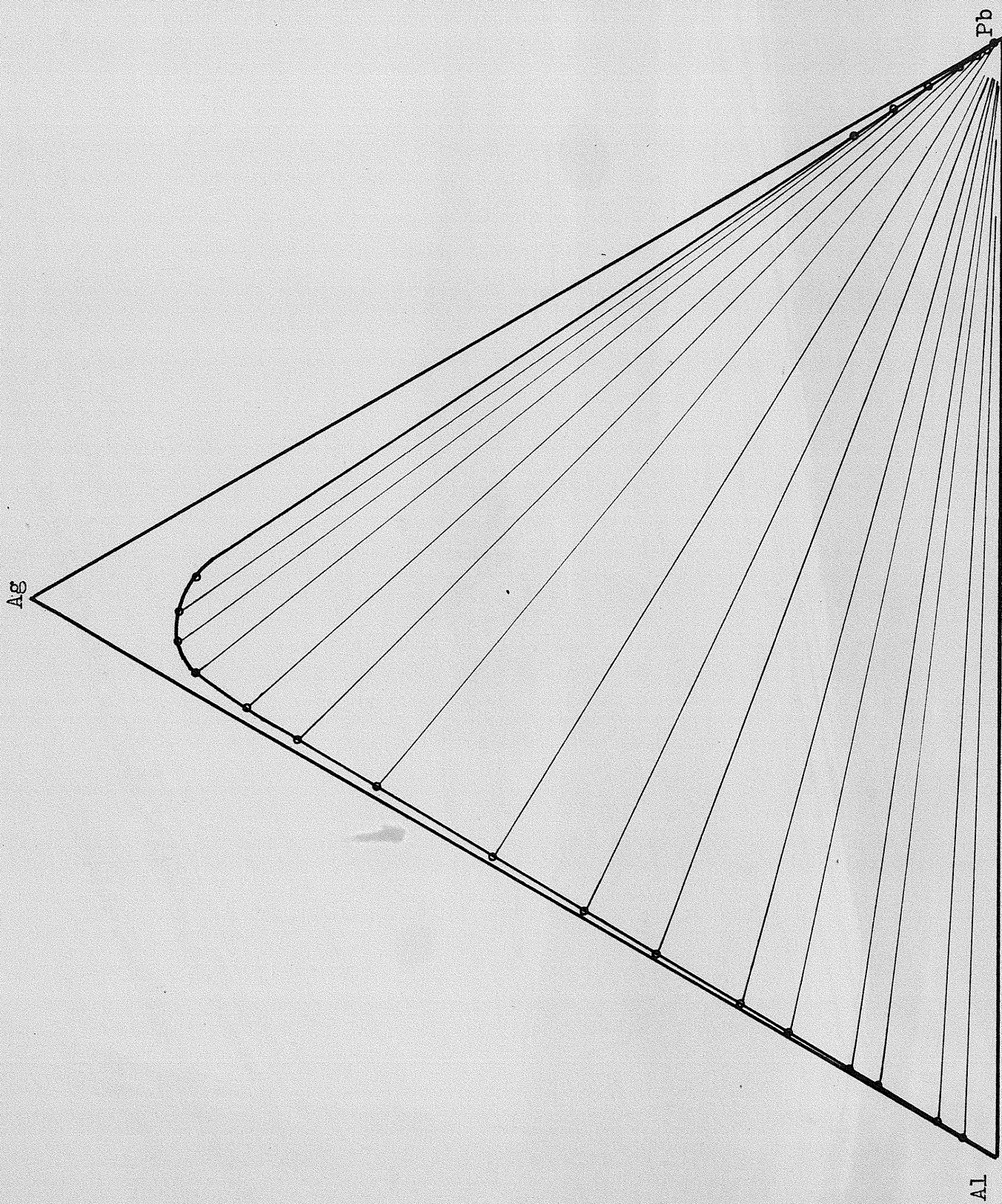


Fig. 24

The System Ag-Al-Pb at 1000°. (Lorenz and Erbe)

Silver-Aluminium-Lead

C. R. A. Wright<sup>44</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°. 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. towards the lead angle of the diagram.

Lorenz and Erbe<sup>45</sup> studied the ternary system to see if the distribution law could be applied. The miscibility curve was plotted for 1000°. They found that at 750°, with silver content of from 0-85% in the lighter phase and from 0-8% in the heavier phase, practically no solubility of lead in aluminium existed. This was done, however, only by acting on the assumption, that since part of the lead content of the alloys could be explained by the colloidal phenomenon, then all the lead present could be explained in this manner. That this is not so was recently shown by Campbell and Ashley<sup>7</sup>, also by Kempf and Van Horn<sup>6</sup>.

A. N. Campbell and W. G. Wallace<sup>46</sup> mapped the area of partial miscibility for the ternary system by thermal analysis and found it to extend to alloys containing a maximum of 85.58% silver and 4.71% lead by weight. The temperature corresponding to this area was found to fall at first until the temperature of 548.5° was reached. This was noted as 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



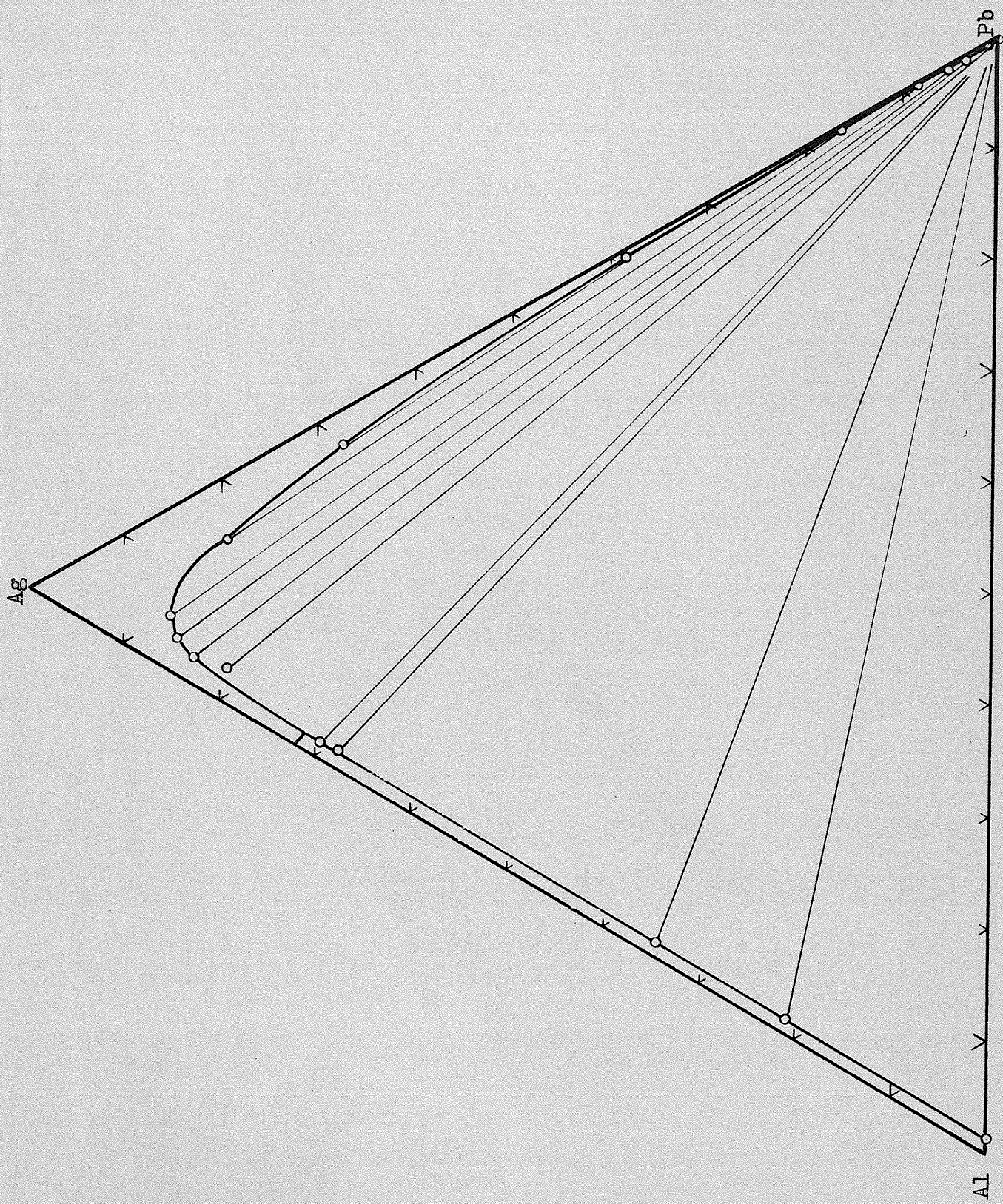


Fig. 25

The System Ag-Al-Pb. (Campbell and Wallace)



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. The hardness of the alloys increases with added silver and lead until it attains a maximum at the alloy having the composition  $\text{AlAg}_2$ -Al eutectic plus 1.73% lead. After this point the increasing quantity of lead present begins to reduce the hardness.

Discussion of Previous Investigation.

The bibliography supplied herewith for the previous investigation carried out on the three binary systems and the ternary, is believed by the writer to be the most complete in existence. It is much more complete than that found in Hansen's "Der Aufbau der Zweistoff Legierungen", and Janecke's "Kurtzgefasstes aller Legierungen", the two standard reference books usually employed.

Lead-Aluminium.

The work of Campbell and Ashley<sup>7</sup> seems to be the most recent and most exact. This supplements the work of Hansen and Blumenthal<sup>5</sup> and Kempf and Van Horn<sup>6</sup>. The only contradictory piece of research is that of Lorenz and Erbe<sup>45</sup> in their work on the ternary system. They obtained discordant results for the solubility of lead in aluminium for similar experiments. This they put down to the well known phenomenon of aluminium taking up a certain amount of lead in the form of a colloidal, but not true solution. To quote them, "When the excess of lead in any one layer of one trial must be explained by colloidal droplets of the heavier phase, so it cannot be seen why the whole lead content cannot be explained in such a fashion". This is given for experiments conducted isothermally at 750<sup>o</sup>, and as proof of the discordancy the authors quote analyses differing by 5%. At 1000<sup>o</sup>, however, although discordant results are still obtained, the authors choose to regard the lowest lead analysis as representing true solubility, and the excess lead in the higher analyses is taken as colloiddally dispersed lead.

However further inspection will show that even at 1000° the analyses differed by 3 and 4%. Why the authors chose to ignore this is not quite clear.

The colloidal effect while it is undoubtedly present, does not necessarily mean a negation of true solubility. This is realized by the above authors for their work at 1000°, yet is ignored for the work at 750°. The fact that a true solubility does exist was amply demonstrated by Campbell and Ashley. The diagram obtained by them is given in Fig. 21.

#### Silver-Lead.

The results obtained by different investigators for this system seem to be quite concordant. The diagram based on the work of Petrenko<sup>9</sup> is given in Fig. 22.

#### Silver-Aluminium.

This system is the most complex of the three. The first investigation was carried out by Wright<sup>12</sup> in 1892, and the complexity of the system and difficulty of investigation is evidenced by the fact that papers are still being published on the system, the most recent one being that of Hume-Rothery et al.<sup>43</sup> The system as it is now generally accepted, barring slight modifications, is based on the work of Hoar and Rowntree<sup>26</sup>, Ageew and Shoyket<sup>32</sup>, and M. Hansen<sup>21</sup>. The equilibrium diagram given in Fig. 23 is a composite diagram embodying all accepted data, as given by Hansen in "Der Aufbau der Zweistoff Legierungen".

#### Silver-Lead-Aluminium.

As previously shown very little work has been done on the

ternary system. The results obtained by Lorenz and Erbe<sup>45</sup> agree in general with the results obtained by Campbell and Wallace<sup>46</sup> excepting for the aluminium corner, which has been criticized above. The tie-lines slope in the same direction as found by Campbell and Wallace. A graphic representation of the work of Lorenze and Erbe is given in Fig. 24; while Fig. 25 shows the results of the work of Campbell and Wallace.

It now remained for us to complete the liquidus diagram by ascertaining the following:-

- (1). the temperature and composition of the ternary eutectic point.
- (2). the effect of the addition of lead on the first and second peritectic points of the Ag-Al system.
- (3). the areas of primary crystallisation of the various phases, noting homogeneity and heterogeneity.

The effect of lead on the solidus lines was also to be studied if the method of thermal analysis could throw any light on this.

EXPERIMENTAL

Experimental.Purity of Materials.

The silver used in this research was very pure, fine grain silver. The lead had the following impurities:-

$$\text{Ag} = 0.0001\%$$

$$\text{Cu} = 0.0025\%$$

The aluminium used was the very purest available, obtained through the courtesy of Dr. Frary and Mr. J.J. Bowman of the Aluminium Company of America, to whom the thanks of the writer are most gratefully offered. This following analysis was supplied.

$$\text{Si} = 0.007\%$$

$$\text{Fe} = 0.01\%$$

$$\text{Cu} = 0.29\%$$

$$\text{Ti} = 0.001\%$$

$$\text{Al} = \text{remainder}$$

Use of this very pure aluminium is extremely important, since in the binary system, lead-aluminium, investigated by Campbell and Ashley<sup>7</sup>, with 99.3% pure aluminium, and later with the above-mentioned aluminium, it was noticed that the use of the very pure aluminium had a decided effect on the composition and temperature of basic points in the system as found with the impure aluminium.

(1). The ternary eutectic point.

(a). Apparatus.

Since the temperatures involved were comparatively low, a mercurial thermometer was employed as the temperature-indicating device. The thermometer was graduated in  $0.5^{\circ}$  and with the aid of

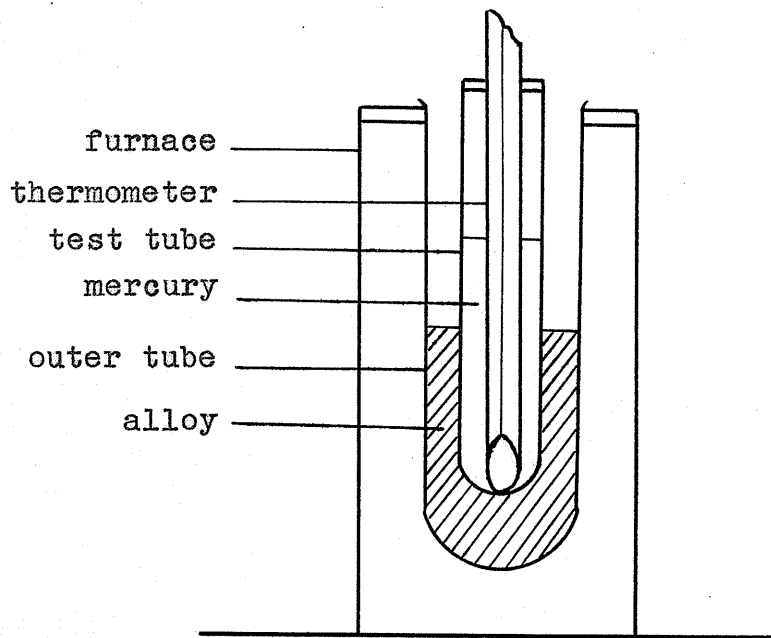


Fig. 26

a hand lens could be read to  $0.05^{\circ}$ . As a heating unit a cylindrical furnace was constructed. This consisted of a double layer of nichrome wire, connected in parallel, wound on a sillimanite tube. The layers were coated with a solution of  $\text{Na}_2\text{SiO}_3$  which on hardening served to keep the wires in position. The layers were separated by asbestos paper which also was coated with the sodium silicate solution. A temperature of  $450^{\circ}$  could be reached and maintained with this furnace if so desired. The graduated cooling was carried out by a bank of rheostats connected in series with the furnace. The alloy was contained in a hard glass test-tube. The thermometer was partially encased in a glass tube to protect it from the action of the molten alloy. Mercury was placed in the tube to ensure good thermal contact. The thermometer could then be used as a stirrer as well as a temperature indicator.

(b). General Procedure.

The apparatus was set up as shown in Fig. 26. 150 grams of lead were melted in the furnace in a large hard glass test tube. The thermometer and casing were now inserted, and the melt vigorously stirred with the thermometer acting as the stirrer. Using Plato's<sup>72</sup> method of graduated cooling, the freezing point of the pure lead was found. The bank of rheostats was calibrated in equal amounts, so that the introduction of a certain amount of resistance per minute would cool the furnace at the rate of  $2.5^{\circ}$  per minute. On solidification the contraction of the metal would cause the glass thermometer casing to break. To avoid this the metal was reheated immediately after solidification and the



thermometer was removed.

Enough aluminium was now added to saturate the lead and thus reach the binary eutectic, and the figures of Campbell and Ashley<sup>7</sup> were checked. The aluminium was added to the molten lead and plunged underneath the surface by means of the thermometer. A cooling curve was then taken. Small quantities of silver were now added to the binary eutectic, the temperature of solidification being noted each time. At the attainment of the eutectic an excess of silver was added to prove that the temperature of solidification would get no lower. Before analysis the alloy was heat-treated in the molten state for 24 hours to allow excess aluminium and silver to separate out by gravity, also to allow the aluminium to give up its colloiddally dispersed lead. The alloy was then analysed and the results are shown in Table I.

To show that the ternary eutectic was actually a condition of true equilibrium, it should be approached from both sides of the equilibrium. Accordingly the melting point of lead was once more determined, and then enough silver added to obtain the binary silver-lead eutectic. Aluminium was then added until a constant temperature of solidification was obtained. The alloy was then heat-treated for 24 hours and analysed. The results are shown in Table II.

(c). Method of Analysis.

The alloy was cut vertically and borings taken from various parts of the alloy. The borings were then mixed thoroughly to ensure uniformity. 10 grams of the alloy were now refluxed with 1:1 HNO<sub>3</sub> in a ground glass condenser until the borings had all

dissolved. The Pb was then precipitated as  $\text{PbSO}_4$ , by the addition of dilute  $\text{H}_2\text{SO}_4$  and the precipitate discarded. The filtrate, now free from lead, was made up to 500 c.c's.

The silver was precipitated as AgBr by adding excess KBr solution to 50 c.c's of the above solution in the darkroom under a red safe-light. A little  $\text{HNO}_3$  was added to prevent peptization of the AgBr and the precipitate allowed to settle overnight. It was then filtered through a sintered glass crucible, the precipitate was washed with water containing a little  $\text{HNO}_3$ , and then dried overnight at  $100^\circ\text{C}$ , and weighed as AgBr.

A new sample of 200 c.c's was now taken for the Al analysis. The Ag was removed by precipitation as AgCl with cold dilute HCl. The aluminium was then estimated by the 8-hydroxy-quinoline method, since this would give a very bulky precipitate and thus traces of Al could easily be estimated. The reagent was prepared by dissolving a sufficient amount of finely powdered 8-hydroxy-quinoline in 2N acetic acid to form a 5% solution. The sample was then made only slightly acid, warmed to  $50-60^\circ$  and treated with an excess of the reagent. A solution of 2N ammonium acetate was now added until a permanent precipitate was obtained, and then 20-25c.c's more of ammonium acetate was added to ensure complete precipitation of the Al. The precipitate was allowed to settle overnight and then filtered through a sintered glass crucible. The precipitate was then washed with cold water and dried at  $130^\circ$ . It had the composition  $(\text{C}_9\text{H}_6\text{ON})_3\text{Al}$  and contained 5.87% Al.

For the analysis of the Pb .5 grams of the alloy borings

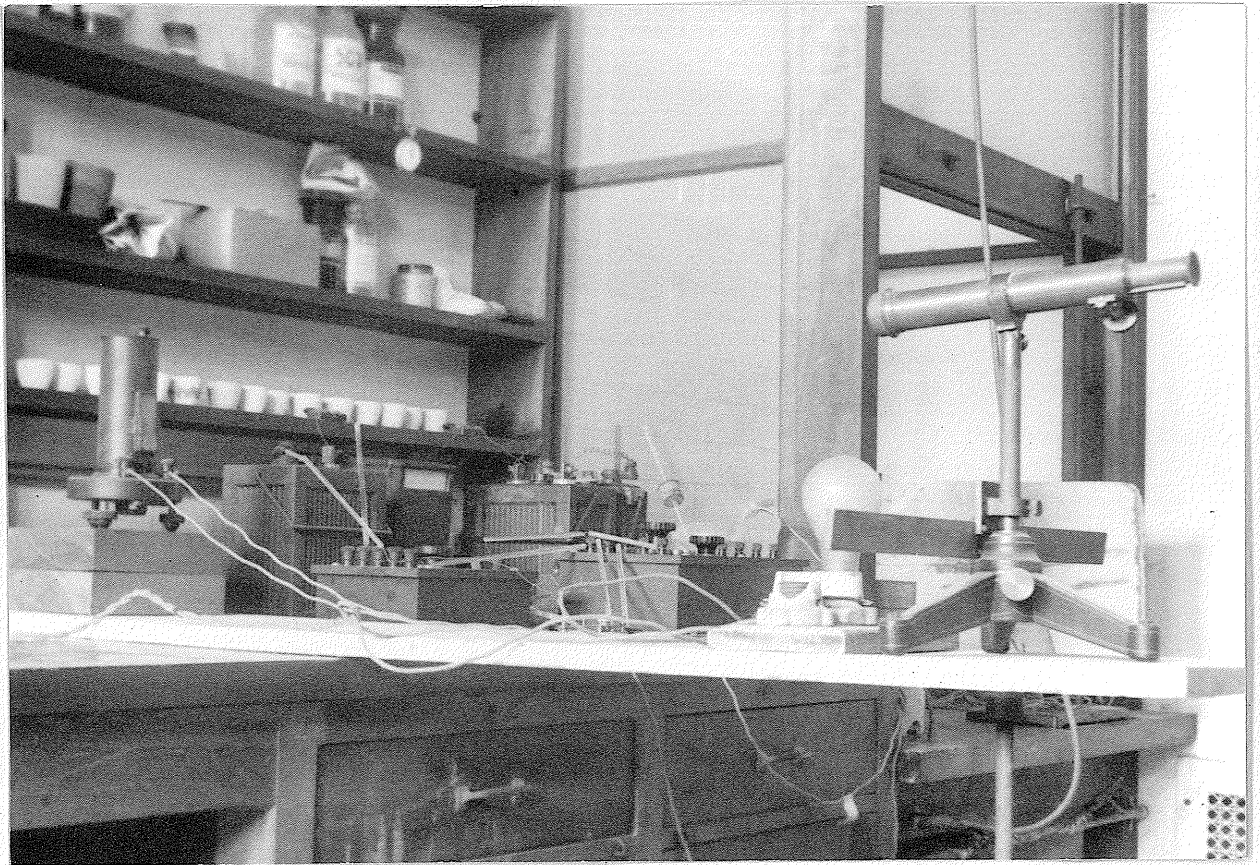


Plate I

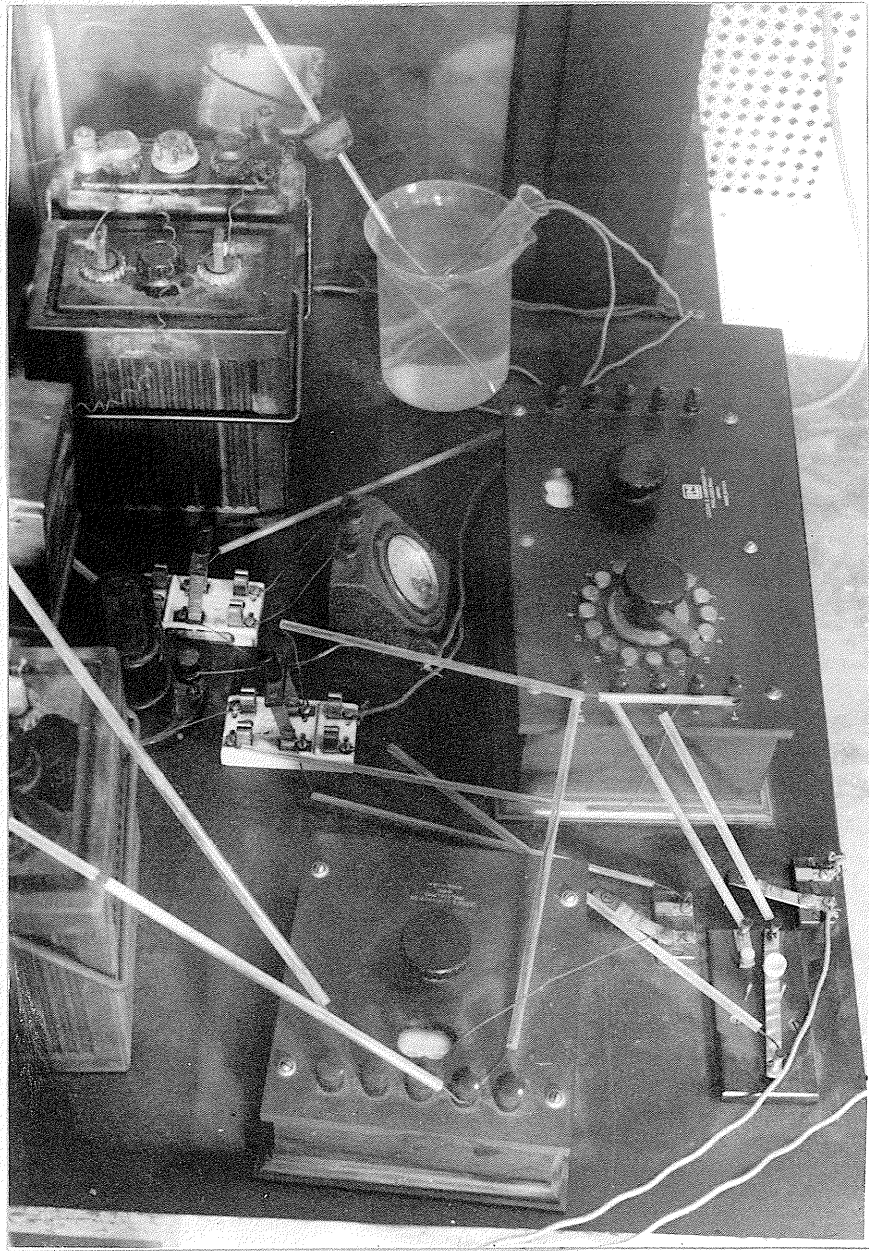


Plate II



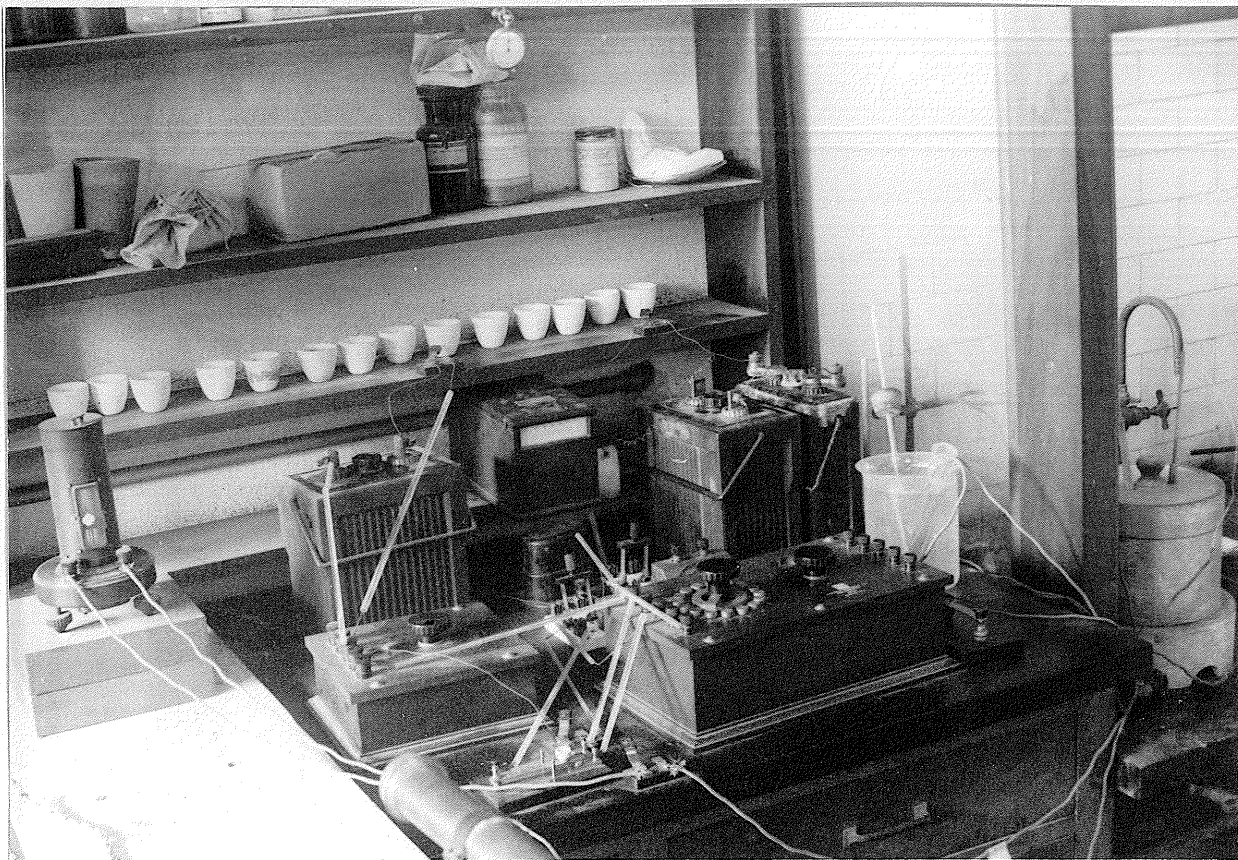


Plate III

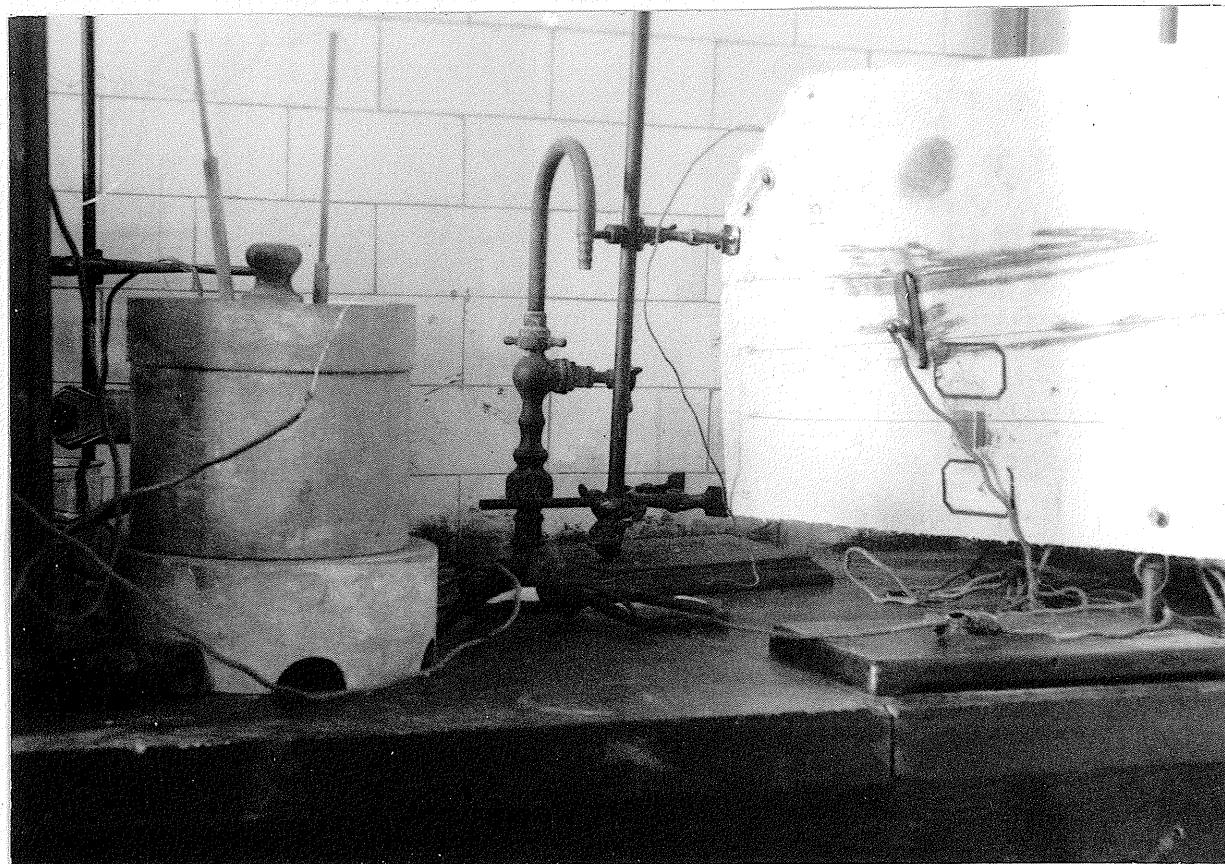


Plate IV

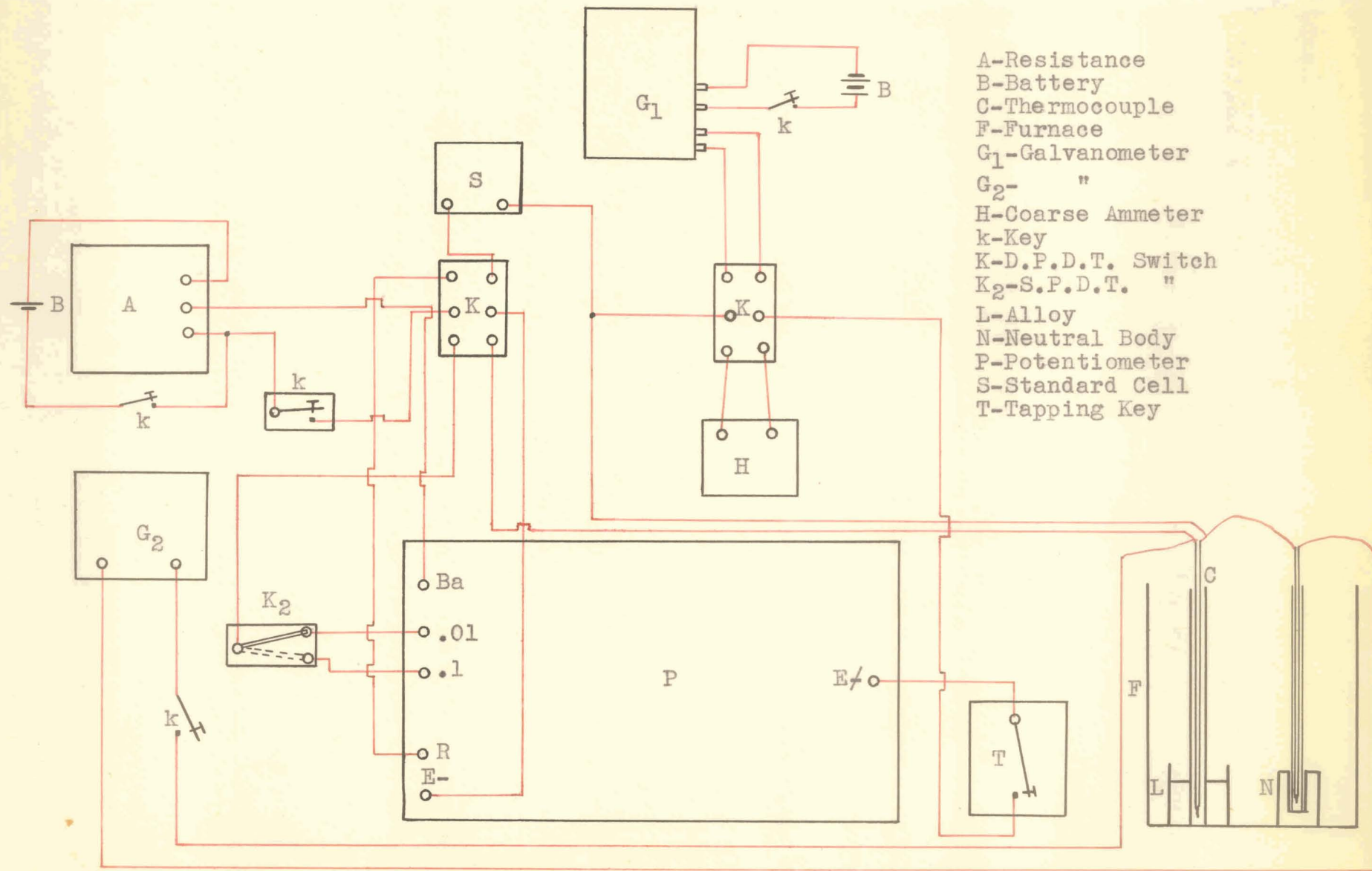


Fig. 27

Diagram of Apparatus for Thermal Analysis.

were dissolved in 1:1  $\text{HNO}_3$ . The Pb was then precipitated as  $\text{PbSO}_4$  in a casserole by the addition of 5 c.c.'s of conc.  $\text{H}_2\text{SO}_4$ . The solution was then boiled until dense white fumes arose, showing that the volatile acids and the water had been driven off. 25 c.c.'s of water were now added and the  $\text{PbSO}_4$  was filtered through a Gooch crucible. The precipitate was washed with alcohol until the washings no longer reacted acid to litmus. The Gooch was then dried at  $120^\circ$  and the precipitate weighed as  $\text{PbSO}_4$ .

(2). Differential Thermal Analysis.

(a). Apparatus.

The method used to obtain the data for points above the ternary eutectic were all done by the method of differential thermal analysis as suggested by Roberts-Austen<sup>74</sup>, using Plato's method of slow cooling<sup>72</sup>, as described previously.

The apparatus as assembled is shown in Plates I - IV inclusive, and diagrammatically in Fig. 27. Essentially it consisted of two circuits, a potentiometer circuit, and a reflecting galvanometer circuit. The temperature was measured by two thermocouples of the Pt-Pt/10% Rh type. The wires were separated down their length by passing them through a thin-walled double-bored sillimanite tube. This was in turn encased in an outer sillimanite tube to protect the thermocouple junction from the action of the molten metals. One thermocouple was inserted into the molten alloy and connected directly to a potentiometer through a sensitive galvanometer. Thus from the readings of the potentiometer the absolute temperature of the



alloy could be determined if the thermocouple was calibrated. The potentiometer could be read to one microvolt, which was equivalent to a change of  $0.1^{\circ}$  in the temperature.

The action of a thermocouple is based on the assumption that the E.M.F. generated is the result of a temperature difference between a hot junction and a cold junction, the cold junction being the point at which the wires of the couple make contact with the leads. If the cold junction is at  $0^{\circ}\text{C}$ . the potentiometric readings will thus indicate the true temperature of the alloy. Since it would be inconvenient to maintain a temperature of  $0^{\circ}\text{C}$ ., the leads were passed through a test tube immersed in a beaker of water at room temperature. Thus the temperature shown by the potentiometer would indicate the difference in temperature between the alloy and the beaker of water. The true temperature would thus be obtained by adding the temperature of the beaker of water to the difference of temperature. A mercurial thermometer graduated in  $0.1^{\circ}$  was used to indicate the temperature of the cold junction. The lead accumulator used was balanced against a standard cell before, and after, each experiment.

The other thermocouple was placed in a neutral body, which consisted of a cylinder of copper, of approximately the same thermal capacity as that of the alloy. A hole was bored in the centre of the cylinder to about two-thirds of its depth, the diameter of the hole just being sufficiently large to accommodate the thermocouple casing. This thermocouple was connected differentially with the first, connecting Pt to Pt and Pt/Rh

to Pt/Rh. This was then connected to a delicate reflecting galvanometer with a sensitivity of  $3 \times 10^{-9}$  amps. per mm. Thus the neutral body would cool with the furnace and the difference curve would show zero displacement, or at the most, a small constant displacement as long as the alloy cooled normally, with the furnace. When a thermal effect takes place in the alloy, the alloy will suffer delayed cooling, or will maintain a constant temperature until the change is complete. The copper cylinder will however go on cooling, and the difference curve will show a sudden sharp deviation.

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. The cover of the furnace had two holes through which the thermocouple casings could be inserted. The holes were large enough to permit free movement of the thermocouple casings so that the alloy could be stirred, yet they were not large enough to allow much heat to escape by radiation.

In order to cool the furnace gradually, a resistance was constructed as shown in Plate IV. This consisted of a long piece of nichrome wire strung out on a sheet of asbestos. The resistance wire was so divided, that by moving a movable contact one division per minute, the furnace would cool at the rate of  $2^{\circ}$  per minute. This slow cooling served to increase the sensitivity and thus show up small thermal effects.

The crucibles used to contain the alloy were made of alundum and were found by experience to be the most satisfactory

for the work required.

(b). Calibration.

The absolute thermocouple was calibrated from the freezing-points of the following very pure substances.

tin -  $231.9^{\circ}\text{C}$ .

lead -  $327.5^{\circ}\text{C}$ .

zinc -  $660.0^{\circ}\text{C}$ .

sodium chloride -  $801.0^{\circ}\text{C}$ .

silver -  $960.5^{\circ}\text{C}$ .

The silver-aluminium first peritectic point was also obtained very sharply, and this was then used as a point for calibration ( $779^{\circ}\text{C}$ .).

The potentiometric readings were plotted against the difference in temperature between the hot and the cold junction.

The differentially connected thermocouples were calibrated in the following manner. The couples were each placed in a bath of water, one of which was kept constant at room temperature. The other was gradually heated, and at one minute intervals simultaneous readings were taken of the displacement on the scale of the reflecting galvanometer and the temperature of the two baths. In this manner it was found that the reflecting galvanometer gave a displacement in the eyepiece of 1 mm. per  $0.3^{\circ}\text{C}$ .

The calibration of the absolute thermocouple was checked periodically to make sure that no contamination had been picked up by the thermocouple.

(c). Method of taking cooling curves.

The silver was melted in the alundum crucible, the crucible

being placed into the furnace when the furnace was at the required temperature, to cut down oxidation. When the silver was molten, the aluminium and lead were plunged beneath the surface and the alloy was stirred vigorously with the thermocouple casing. The total weight of alloy taken was usually 100 grams. To cut down oxidation, it was at first attempted to keep the alloy under a coating of molten KCl as was recommended by previous workers. This was found to be quite satisfactory if the alloy was already homogeneous. However if an addition had to be made, the KCl impeded the obtaining of a homogeneous mixture, and thus was discarded. The thermocouple casing was allowed to heat up with the alloy, since placing the cold casing into the alloy would cause the casing to snap. As soon as a test was completed, the alloy was reheated and the casing removed, since if it was left to cool to room temperature, on reheating the difference in coefficients of expansion would crack the casing.

When the alloy was entirely molten, it was stirred vigorously with the casing and kept at that temperature for a short period of time. The resistance was then gradually increased, moving the movable contact one division per minute. Readings on the potentiometer and galvanometer were taken alternately every half minute. Such an experiment usually lasted about 4 hours. These readings were then plotted on the same graph and from this the temperature of the thermal effects could be determined with great sensitivity.

(d). General Method of Procedure.

An alloy of the composition of the higher Ag-Al peritectic was made up, and a cooling curve taken to see whether, with our



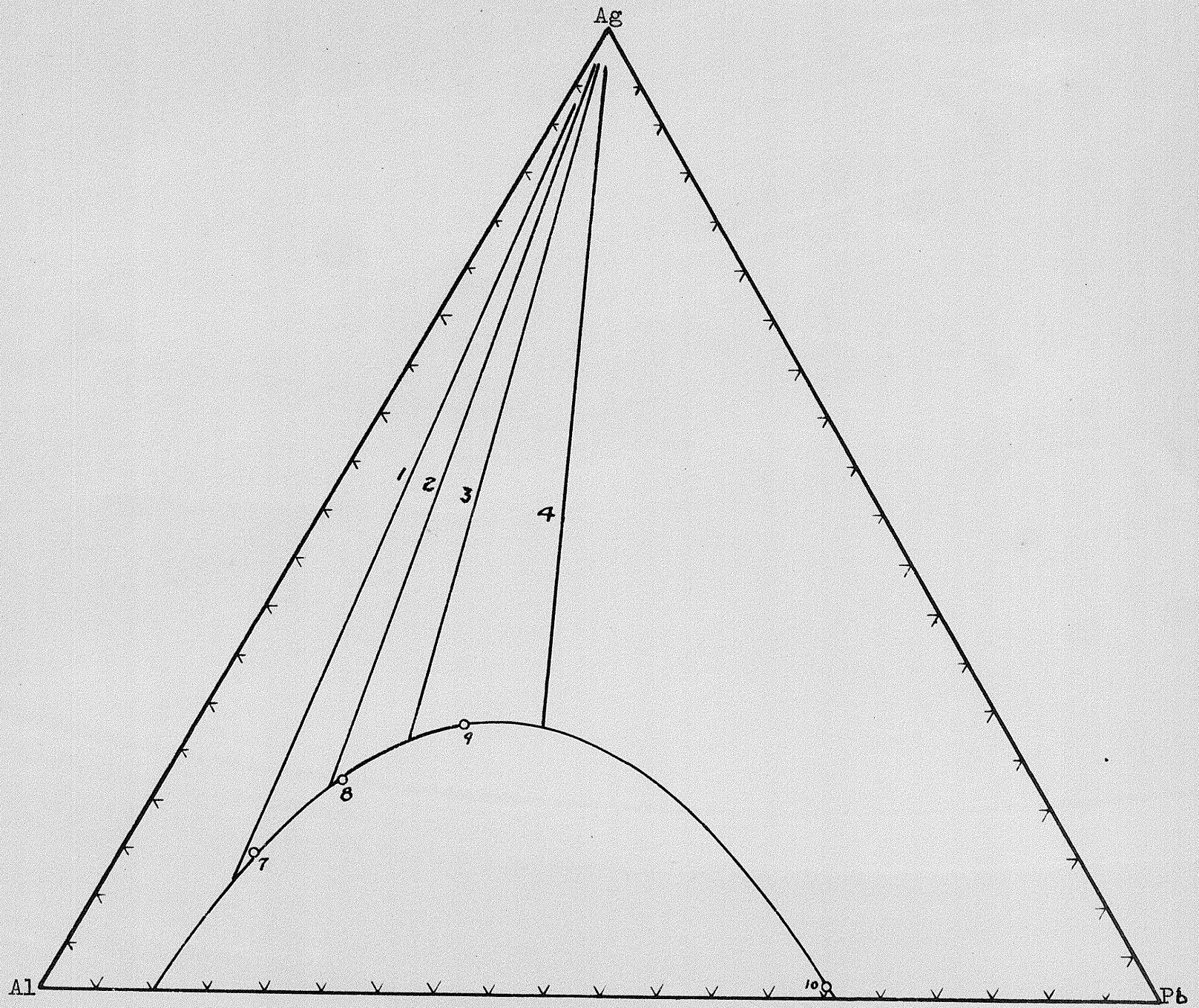


Fig. 28  
Sectioning Diagram

very sensitive apparatus, the changes in the solid state were detectable. It was soon seen that they were, and thus the effect of lead on the eutectoid and the compound separation could be studied thermally. Otherwise only micrographic and X-ray analysis could deal with this.

Accordingly an alloy of the composition of the first peritectic was made up and lead added to this in increasing quantities. The results obtained however were discordant. Only by supposing that a very high point existed on the partial miscibility curve could they be justified. Accordingly alloys no. 5,6,7,8,9, and 10, which had been prepared by Wallace, were examined thermally and his points were checked. The results are given in Table III. Although as can be seen certain changes were made, yet the temperatures obtained were not high enough to justify a high point on the miscibility curve. On analysis of our own alloy it was found that the composition had altered greatly due to oxidation, the Al gradually burning off, the net result being to bring the alloy composition close to the Ag-Pb binary system and thus raise the temperature of solidification. Attempts to find such a high point by the preparation of certain alloys also proved fruitless. Thus this method of investigation had to be dropped.

It was now resolved to map the diagram in detail by "sectioning" it, as shown in Fig. 28. The method employed was to start with an alloy of a certain known composition and analyze it thermally. The required composition for the next alloy was obtained by adding the required amounts of Pb and Al. After each line in the section had been completed the alloy

was analysed chemically and a small correction made for oxidation. The results for the four lines studied are shown in Tables IV to VII inclusive. The results obtained for each line were plotted graphically, each actually being a vertical plane through the solid diagram. The graphical results are shown in Figs. 29-32 inc. The end results were plotted on a magnified diagram and are given by Fig. 33.

(e). Analysis.

The alloy was heated till molten and then quenched in a steel mould. This was done to insure homogeneity for analysis, since if the alloy were allowed to cool slowly, segregation would result. Borings were then taken from various parts of the quenched alloy, mixed and remixed.

5 grams of the borings were refluxed with 1.1  $\text{HNO}_3$  in a ground-glass condenser until they had dissolved. The solution was then made up to 250 c.c.'s. 25 c.c.'s of this solution were then taken and the silver content determined by titration with KCNS using ferric indicator.

50 c.c.'s were then pipetted off from the original solution for the Pb analysis. The Ag was removed as  $\text{AgCl}$  by precipitation with cold dilute  $\text{HCl}$  and filtered. Sodium acetate was then added till the solution smelled strongly of acetic acid. Then excess  $\text{K}_2\text{CrO}_4$  was added until a permanent precipitate was obtained. This was filtered through a Gooch crucible, dried at  $120^\circ$  and weighed as lead chromate.

To the filtrate conc.  $\text{NH}_4\text{OH}$  was added, with constant stirring, until a permanent precipitate of the aluminium basic



acetate was obtained. This was boiled until it had coagulated, filtered, and ignited. The residue was weighed as  $\text{Al}_2\text{O}_3$ .

Since all the alloys considered here contained more than 80% Ag, the colloidal phenomenon previously mentioned could be ignored, since it does not occur in alloys with more than 80% Ag, and the Pb analyses could be taken as correct.

RESULTS

Results.

The data obtained by adding lead to the Pb-Al binary eutectic is given below in Table I.

Table I.		
Composition	Temperature of Primary Crystallisation	Eutectic Temp.
Pb	327.5°C.	-----
Pb 1 grm. Al	327.0	-----
" " 1/100%Ag	326.3	-----
" " 1/13%Ag	325.8	-----
" " 1/20%Ag	324.5	-----
" " 1/26%Ag	323.4	-----
" " 1/33%Ag	322.6	-----
" " 1/40%Ag	322.0	-----
" " 1/46%Ag	321.4	-----
" " 1/50%Ag	321.0	-----
" " 1/52%Ag	320.6	-----
" " 1/59%Ag	319.7	-----
" " 1/66%Ag	318.8	-----
" " 1/73%Ag	318.0	-----
" " 1/79%Ag	317.4	-----
" " 1/86%Ag	316.7	304.1°C.
" " 1/93%Ag	316.0	304.1
" " 1/100%Ag	315.7	304.2
" " 1/130%Ag	312.8	303.9
" " 1/150%Ag	310.4	304.2
" " 1/165%Ag	308.3	304.0
" " 1/185%Ag	307.9	304.1
" " 1/205%Ag	307.3	304.1

Continuation of Table I.

Composition	Temperature of Primary Crystallisation	Eutectic Temp.
Pb/1grm.Al/2.11%Ag	306.9	304.1
" " /2.18%Ag	306.1	304.1
" " /2.50%Ag	-----	304.2

On analysis, the ternary eutectic point was found to be almost identical with the binary Ag-Pb eutectic in composition, containing only traces of aluminium, less than 0.1%. The temperature is also almost identical, being found to be 304.1°C. The composition and temperature of the binary eutectic are given as 2.30% Ag and 300-305° by Yoldi and Jimenez.<sup>10</sup> Our results for the binary Ag-Pb eutectic gave 2.30% Ag and a temperature of 304.1°C.

Table II shows the effect of adding Al to the Pb-Ag binary eutectic.

Table II.

Composition	Temperature of Primary Crystallisation	Eutectic Temp.
Pb/2.5%Ag	-----	304.1
Pb/2.5%Ag/.07%Ag	-----	304.1
Pb/2.5%Ag/.13%Ag	-----	304.1

Analysis of the alloy showed it to be of the same composition as the above eutectic alloy.

Table III gives the results obtained from the thermal analysis of Wallace's alloys.

Table III.

<u>Alloy No.</u>	<u>Wallace's Results</u>	<u>Results Obtained</u>
5.	581.6	584.8
	548.7	550.0
6.	664.6	665.0
	548.1	550.0
7.	697.7	700.0
8.	723.3	708.5
9.	728.5	717.0
10.	736.3	736.0

Table IV corresponds to Line 1 in the sectioning diagram.  
Pb and Al were added to Ag in the ratio Al/Pb = 6.8/1.

Table IV(a)  
Analysis of alloys.

<u>No.</u>	<u>wt. % Pb</u>	<u>wt. % Al</u>	<u>wt. % Ag</u>
1.	.70	4.90	94.40
2.	.80	5.80	93.40
3.	1.00	6.60	92.40
4.	1.10	7.90	91.00
5.	1.30	9.00	89.70
6.	1.40	9.80	88.80
7.	1.50	10.60	87.90
8.	1.60	11.30	87.10
9.	1.76	12.00	86.24

Thermal effects noted in examination of the above alloys.

Table IV(b)

<u>Alloy No.</u>	<u>Temp. of Thermal Effect</u>	<u>Nature of Thermal Effect</u>
1.	815.2°C.	$\alpha$ -crystallisation
	769.2	First Peritectic
	601.8(very weak)	Eutectoid
	396.8( " " )	Compound Separation
2.	783.6	$\alpha$ -crystallisation
	764.8	First Peritectic
	597.7	Eutectoid
	402.7	Compound Separation
3.	773.8	$\beta$ -crystallisation (or peritectic)
	602.5	Eutectoid
	405.8	Compound Separation
4.	762.8	$\beta$ -crystallisation
	612.8(very weak)	Eutectoid
	411.4( " " )	Compound Separation
5.	751.0	$\varrho$ -crystallisation
	718.0(very weak)	Second Peritectic
6.	735.0	$\beta$ -crystallisation
	705.7	Second Peritectic
7.	712.3	Second Peritectic
8.	714.5	$\gamma$ -crystallisation
9.	712.3	$\gamma$ -crystallisation



Fig. 29

Equilibrium diagram of line 1,  
showing the effect of the addition  
of Pb and Al to Ag in the ratio of  
 $Al/Pb = 6.8/1$  (Table IV).

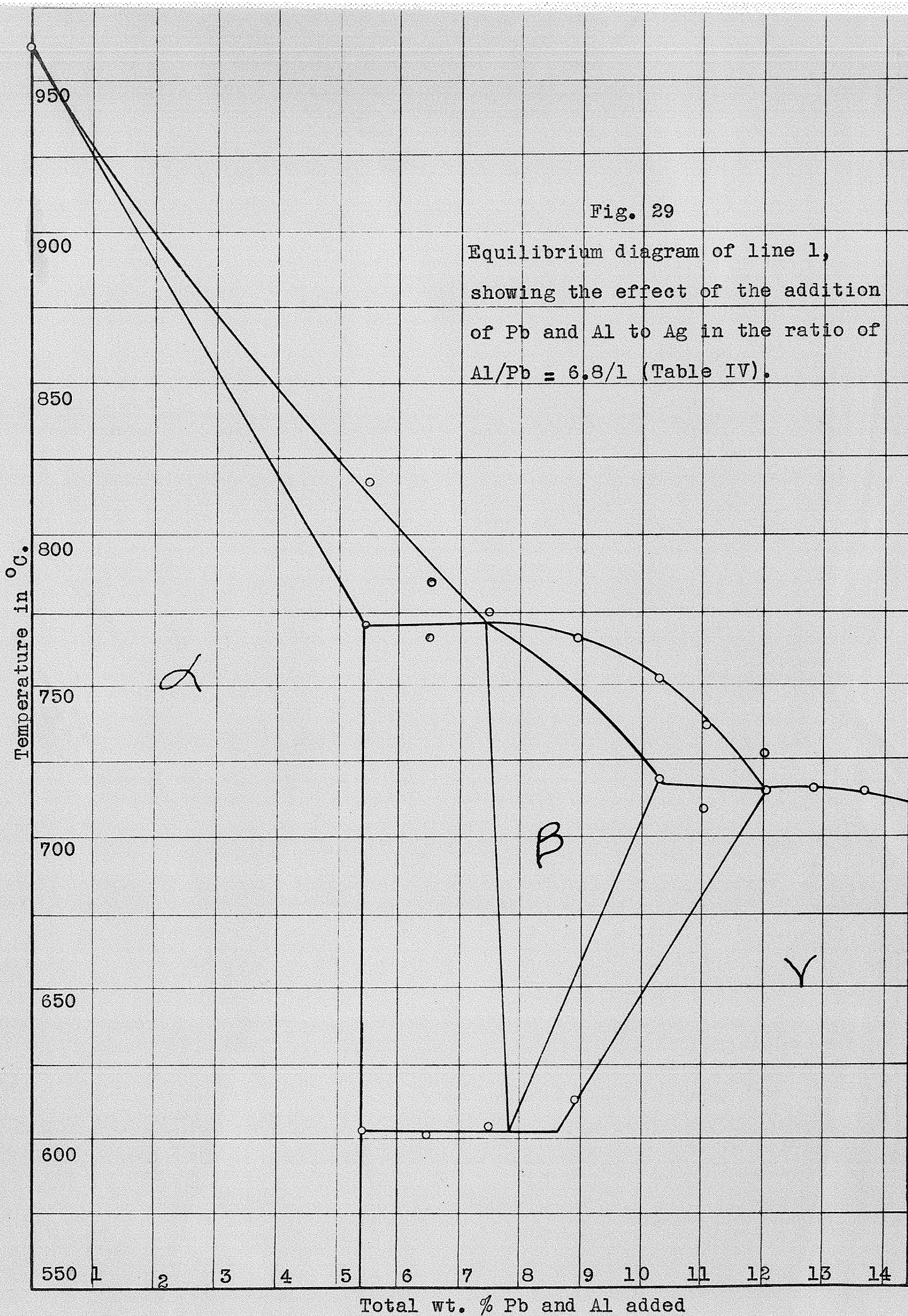


Fig. 29 shows the plane vertical section.

The limit of the  $\alpha$ -solubility = 4.90%Al and .70%Pb. The first peritectic occurs at a composition of Al = 6.60%, Pb = 1.00%, Ag = 92.40% and at a temperature of 769.0°.

The second peritectic occurs at a composition of 10.6%Al, 1.50%Pb and 87.9%Ag, at a temperature of 716.0°.

Width of the first peritectic gap = 1.70%Al and .30%Pb.

The maximum width of  $\beta$  = 2.40%Al and .40%Pb.

Width of the second peritectic gap = 1.60%Al and .30%Pb.

The eutectoid temperature remains constant at 601°.

The temperature of compound separation varies from 390-410°.

Table V corresponds to line 2 in the sectioning diagram.

Pb and Al were added to Ag in the ratio of Al/Pb = 4.5/1.

Table V(a)  
Analysis of the alloys.

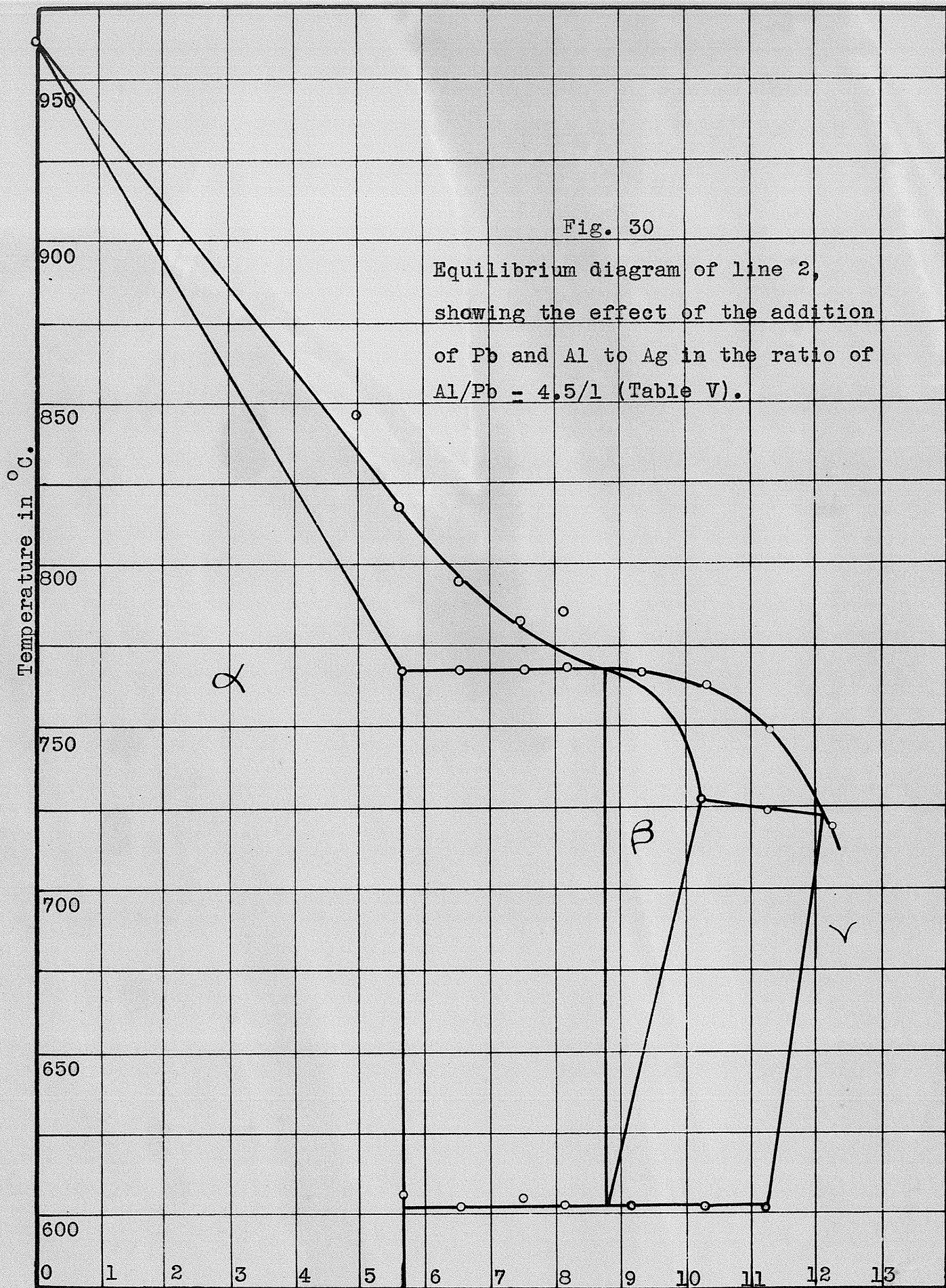
No.	wt. % Pb	wt. % Al	wt. % Ag
1.	1.00	3.90	95.10
2.	1.10	4.60	94.30
3.	1.30	5.20	93.50
4.	1.40	6.00	92.60
5.	1.60	6.60	91.80
6.	1.83	7.32	90.85
7.	1.90	8.40	89.70
8.	2.00	9.25	88.75
9.	2.30	9.85	87.85



Thermal effects noted in the examination of the above alloys.

Table V(b)

<u>Alloy No.</u>	<u>Temp. of Thermal Effect</u>	<u>Nature of Thermal Effect</u>
1.	844.0°C.	$\alpha$ -crystallisation
2.	817.6	$\alpha$ -crystallisation
	763.0	First Peritectic
	603.0	Eutectoid
3.	793.5	$\alpha$ -crystallisation
	766.7	First Peritectic
	598.0	Eutectoid
	401.9	Compound Separation
4.	780.0	$\alpha$ -crystallisation
	764.0	First Peritectic
	603.0	Eutectoid
	404.0	Compound Separation
5.	784.7	$\alpha$ -crystallisation
	767.7	First Peritectic
	601.3	Eutectoid
	395.4	Compound Separation
6.	760.5	$\beta$ -crystallisation
	598.3	Eutectoid
	389.0	Compound Separation
7.	760.5	$\beta$ -crystallisation
	725.0	Second Peritectic
	709.1	Liquidus
	599.2	Eutectoid
	406.2	Compound Separation



Total wt. % Pb and Al added.



Continuation Table V(b)

Alloy No.	Temp. of Thermal Effect	Nature of Thermal Effect
8.	747.7	$\beta$ -crystallisation
	720.8	Second Peritectic
	705.2	Liquidus
	598.0	Eutectoid
	389.0	Compound Separation
9.	717.1	$\gamma$ -crystallisation
	704.1	Liquidus

Fig. 30 shows the plane vertical section.

The limit of the  $\alpha$ -solubility = 4.60%Al and 1.10%Pb.

The first peritectic occurs at a composition of 7.20%Al, 1.60%Pb, 91.20%Ag, and at a temperature of 764.0°.

The second peritectic occurs at a composition of 10.23%Al, 2.27%Pb, and 87.50%Ag, at a temperature of 720.0°.

Width of the first peritectic gap = 2.60%Al and .50%Pb.

The maximum width of  $\beta$  = 1.20%Al and .30%Pb.

Width of the second peritectic gap = 1.83%Al and .37%Pb.

The eutectoid temperature remains constant at 601°.

The temperature of compound separation varies from 389° to 406°.

Table VI corresponds to line 3 in the sectioning diagram. Pb and Al were added to Ag in the ratio of Al/Pb = 2.93/1.

Table VI(a)  
Analysis of the Alloys.

No.	wt. % Pb	wt. % Al	wt. % Ag
1.	1.60	4.40	94.00
2.	1.80	5.20	93.00
3.	2.00	6.00	92.00
4.	2.30	6.70	91.00
5.	2.60	7.40	90.00
6.	2.80	8.20	89.00
7.	3.10	8.90	88.00
8.	3.30	9.70	87.00
9.	3.60	10.40	86.00

Table VI(b)

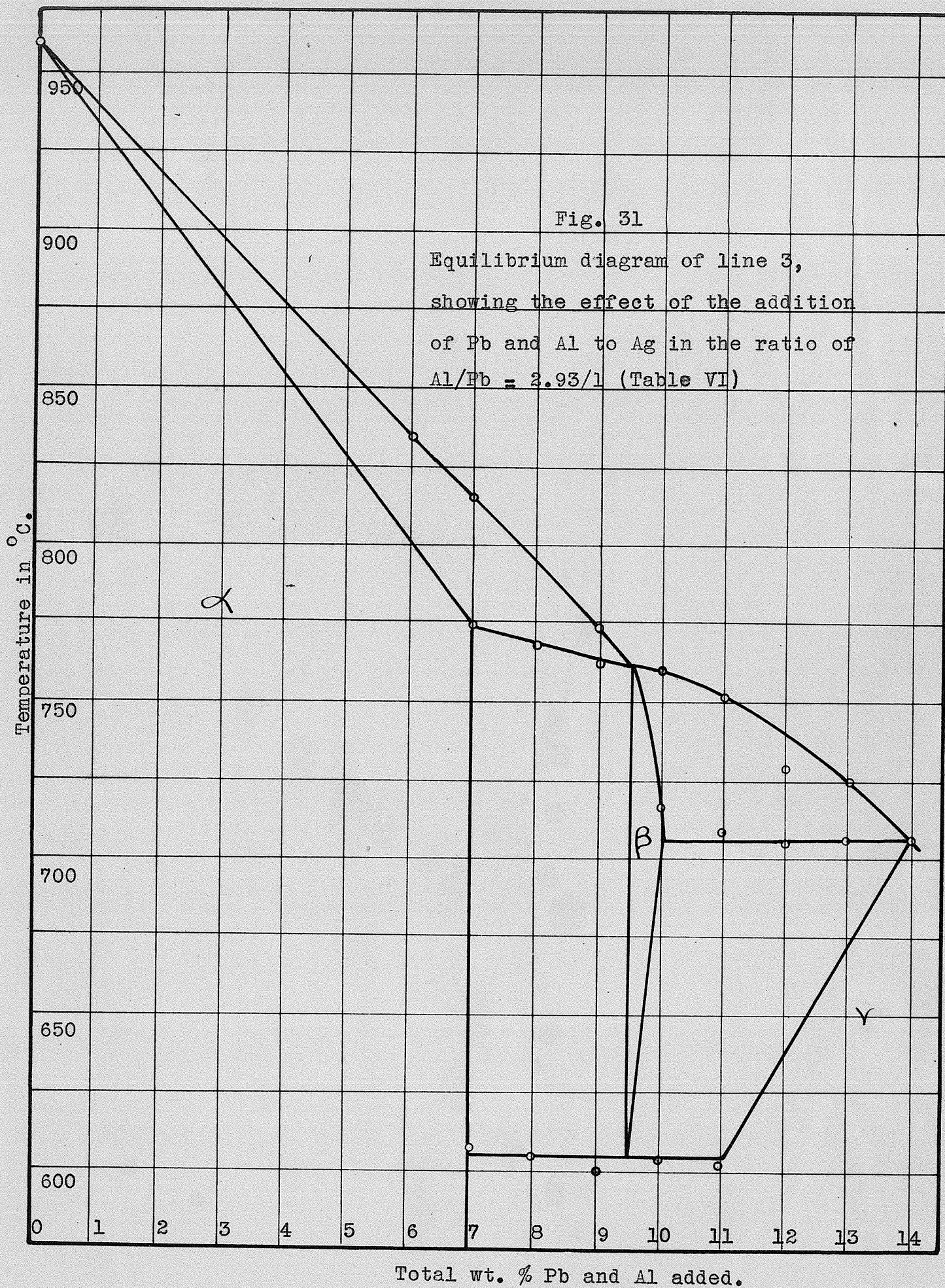
Thermal effects noted in the examination of the above alloys.

Alloy No.	Temp. of Thermal Effect	Nature of Thermal Effect
1.	834.5°C.	$\alpha$ -crystallisation
2.	815.2	$\alpha$ -crystallisation
	774.5	First Peritectic
	606.7	Eutectoid
	380.7	Compound Separation
3.	768.5	First Peritectic
	604.5	Eutectoid
	377.0	Compound Separation
4.	774.0	$\alpha$ -crystallisation
	761.0	First Peritectic
	599.0	Eutectoid
	397.0	Compound Separation



Fig. 31

Equilibrium diagram of line 3,  
showing the effect of the addition  
of Pb and Al to Ag in the ratio of  
 $Al/Pb = 2.93/1$  (Table VI)



Continuation of Table VI(b)

<u>Alloy No.</u>	<u>Temp. of Thermal Effect</u>	<u>Nature of Thermal Effect</u>
5.	760.0	$\beta$ -crystallisation
	717.0(very weak)	Second Peritectic
	603.0	Eutectoid
	393.0	Compound Separation
6.	751.5	$\beta$ -crystallisation
	709.5	Second Peritectic
	600.5(very weak)	Eutectoid
	392.5( " " )	Compound Separation
7.	729.0	$\beta$ -crystallisation
	706.0	Second Peritectic
8.	725.0	$\beta$ -crystallisation
	707.0	Second Peritectic
9.	708.0	Second Peritectic

Fig. 31 shows the plane vertical section.

The limit of the  $\alpha$ -solubility = 5.20%Al and 1.80%Pb.

The first peritectic occurs at a composition of 7.10%Al, 2.4%Pb and 90.50%Ag, at a temperature of 760.0°.

The second peritectic occurs at a composition of 10.40%Al, 3.60%Pb and 86.00%Ag, at a temperature of 708.0°.

Width of the first peritectic gap = 1.86% Al and .64%Pb.

The maximum width of  $\beta$  = 0.37%Al and 0.13%Pb.

Width of the second peritectic gap = 3.00%Al and 1.00%Pb.

The eutectoid temperature remains constant at 603°.

The temperature of compound separation varies from 377 to 397°



Table VII corresponds to line 4 in the sectioning diagram.  
Pb and Al were added to Ag in the ratio of Al/Pb = 1.34/1.

Table VII(a)  
Analysis of the alloys.

No.	wt. % Pb	wt. % Al	wt. % Ag
1.	4.70	6.30	89.00
2.	5.00	6.70	88.30
3.	5.35	7.23	87.42
4.	5.59	7.55	86.86

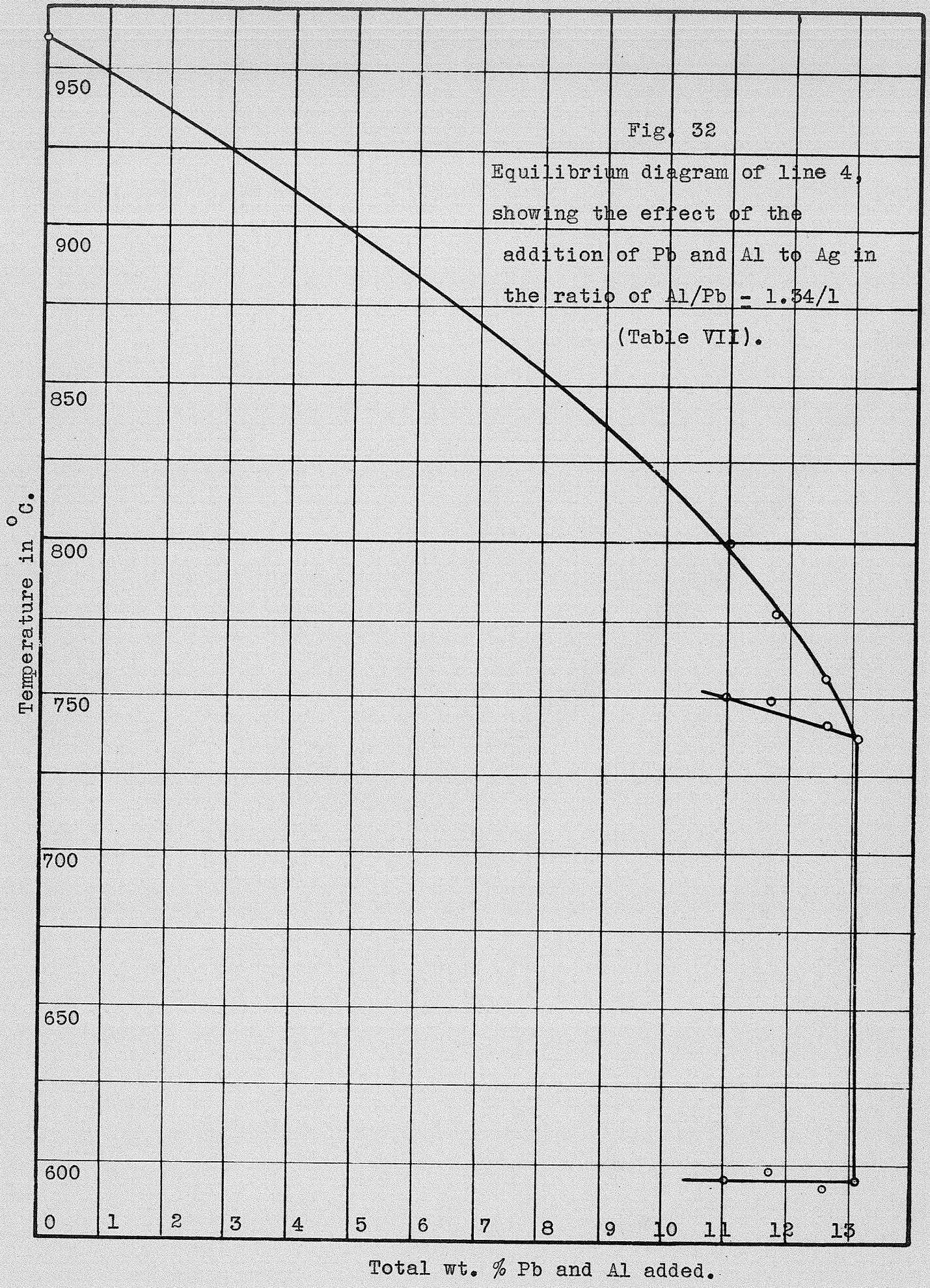
Table VII(b)

Thermal effects noted in the examination of the above alloys.

Alloy No.	Temp. of Thermal Effect	Nature of Thermal Effect
1.	799.5°C.	$\alpha$ -crystallisation
	750.5	First Peritectic
	710.3(very weak)	Liquidus
	595.3	Eutectoid
	383.0	Compound Separation
2.	777.7	$\alpha$ -crystallisation
	749.7	First Peritectic
	713.7(weak)	Liquidus
	598.3	Eutectoid
	384.3	Compound Separation
3.	757.8	$\alpha$ -crystallisation
	740.8	First Peritectic
	708.1(weak)	Liquidus
	591.5	Eutectoid
	380.0	Compound Separation

Fig. 32

Equilibrium diagram of line 4,  
showing the effect of the  
addition of Pb and Al to Ag in  
the ratio of Al/Pb = 1.34/1  
(Table VII).



Total wt. % Pb and Al added.

Continuation of Table VII(b)

<u>Alloy No.</u>	<u>Temp. of Thermal Effect</u>	<u>Nature of Thermal Effect</u>
4.	738.8	First Peritectic
	711.0(weak)	Liquidus
	594.2	Eutectoid
	381.5	Compound Separation

Fig. 32 shows the plane vertical section.

The first peritectic occurs at a composition of 7.55%Al, 5.59%Pb and 86.86%Ag, at a temperature of 738.8°.



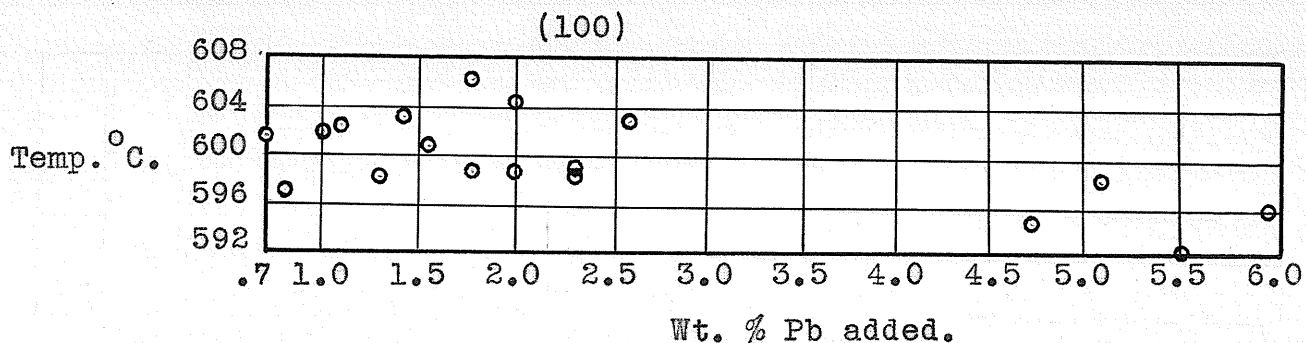
Discussion of Results.

The results shown in Table I and II show that only one ternary eutectic point exists, being almost identical with the binary Ag-Pb eutectic in temperature and composition. The phases in equilibrium with the liquid melt are Ag, Pb and presumably  $\gamma$ . The end member of the  $\gamma$  series of solid solutions is either the compound  $\text{AgAl}_2$ , as found by many previous workers, or the compound  $\text{AlAg}_2$ , as found by Tishtchenko and Lukash<sup>38</sup>.

The examination of certain singular alloys prepared by Wallace<sup>46</sup> showed good agreement, within the limits of experimental error with his results, except in the case of alloys No. 8 and 9, as shown in Table III. The difference in results found in these two alloys was due to a difference in the calibration curve of the absolute thermocouple, since potentiometric readings almost identical with his were obtained. Since our calibration curve was plotted with several points occurring directly in the area under consideration, and since later results obtained were found to bear out our results here, it must be assumed that the data obtained for these two alloys is more accurate, and accordingly they were placed in the diagram.

Thermal analysis does not show any solid solubility of Pb in the  $\alpha$ ,  $\beta$  and  $\gamma$  phases. The eutectoid reaction  $\beta \rightleftharpoons \alpha + \gamma$  would show a temperature change if solid solubility occurred in any of these phases. However as the following graph shows, the eutectoid temperature variation is due only to experimental error, the temperatures varying in different directions, regardless of the amount of Pb added.





The eutectoid temperature has been found by various workers to be "around 610°"<sup>22</sup>, 600°<sup>32</sup>, 615°<sup>36</sup>, 606°<sup>42</sup>. Our results show an average of 601°.

The temperature of compound separation also gives no clue to any solubility. It was found to vary between 385° and 405°, regardless of the amount of Pb added. This variation is also found in results given in the literature. Different investigators place this temperature at 400°<sup>32</sup>, 400°<sup>33</sup>, 420°<sup>36</sup>, and 456°<sup>42</sup>.

Investigation into the  $\delta$ -Untmischung proved fruitless since even with very slow cooling (1° per minute), the effect could not be detected thermally in the Ag-Al system. This is borne out by Hansen<sup>21</sup>, who determined the  $\delta$  region micrographically.

The solubility of Pb in the  $\alpha$ ,  $\beta$  and  $\gamma$  regions is being determined micrographically. Solubility of Pb in the  $\alpha$  phase is extremely improbable, however, since the  $\alpha$  phase will bear the Ag space lattice, and the Pb-Ag binary system shows that Pb and Ag are mutually insoluble in the solid state. Micrographic determination is not possible however for the  $\beta$  region, since according to Obinata and Hagiya<sup>36</sup>, Westgren and Bradley<sup>22</sup>, and Ageew and Shoyket<sup>32</sup>, the  $\beta \rightleftharpoons \alpha + \gamma$  reaction cannot be repressed by quenching. Thus X-ray analysis is necessary to prove the matter conclusively. The thermal analysis shows negative results.

Magnified Liquidus Diagram  
of the Ag-Al-Pb system.

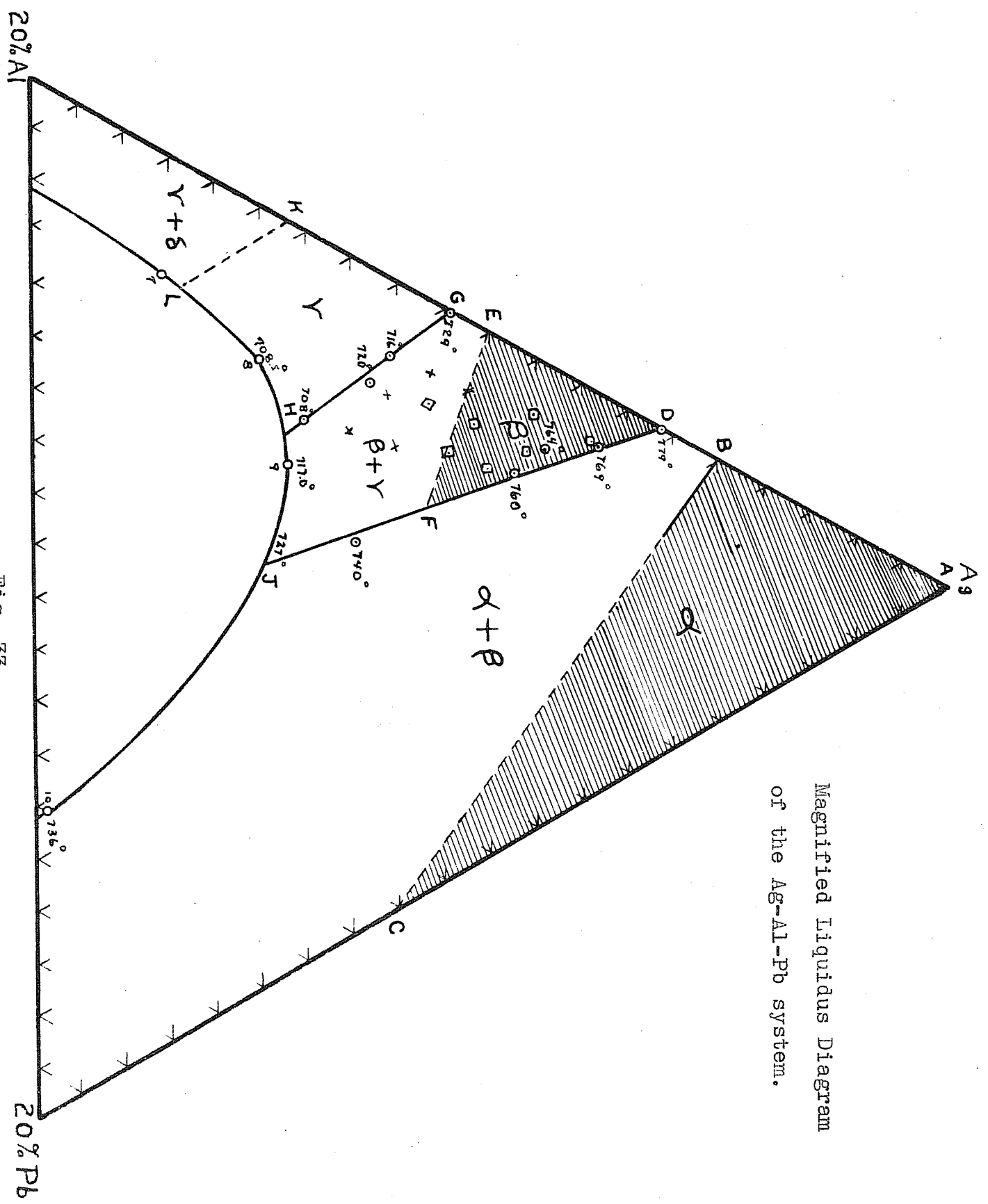


FIG. 33

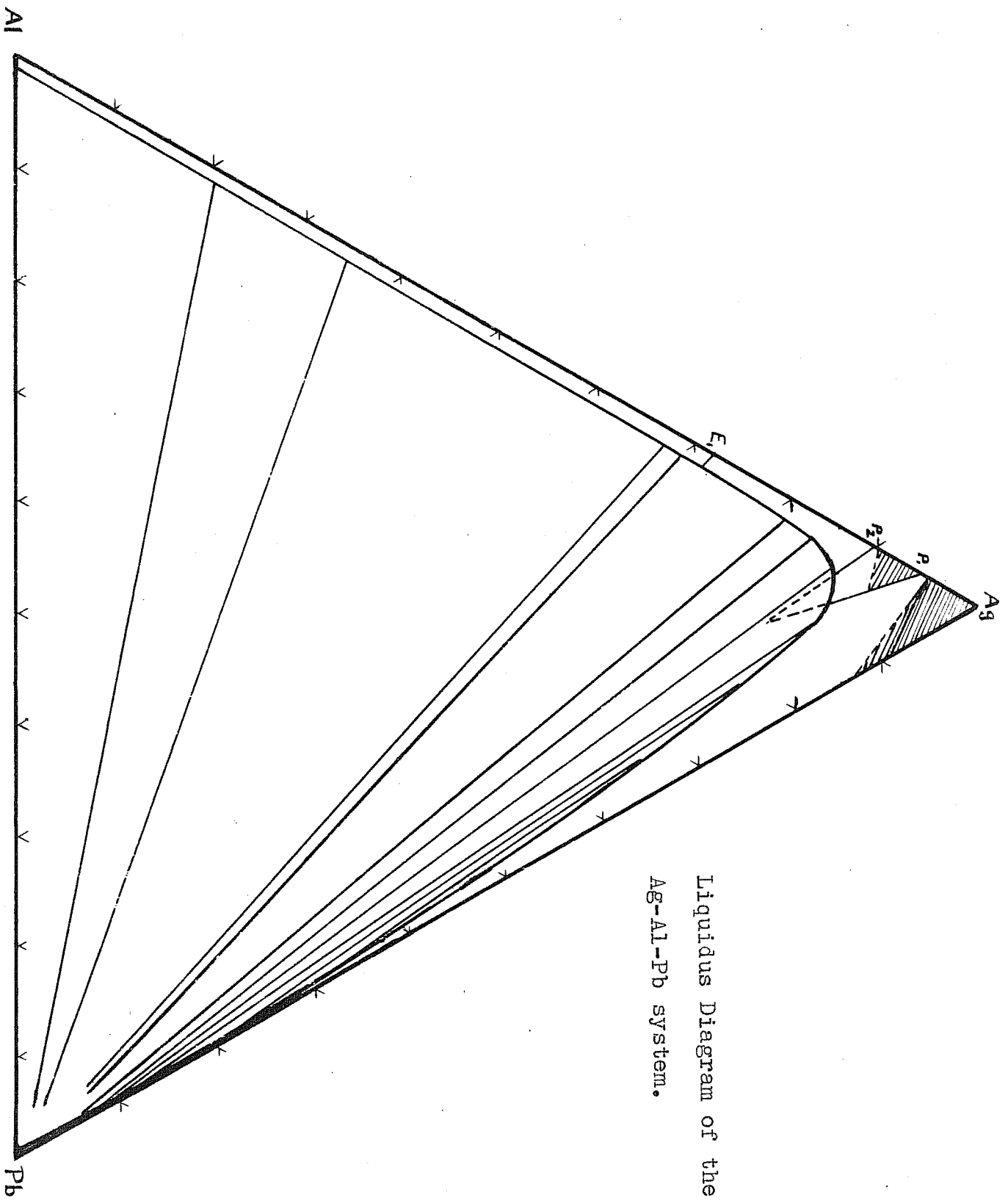
Fig. 33 is a magnified section, being a projection on the base of the right prism. The results of Figs. 29-32 are plotted on this section, and the liquidus diagram is thus shown, with appropriate temperatures.

In the area ABC primary crystallisation of a solid solution of the  $\alpha$  series would take place, corresponding to the composition of the melt. The Pb will remain in the residual liquid which will solidify at the ternary eutectic point.

In the region bounded by the lines BD, BC, DJ, and the miscibility curve, heterogeneity will occur. A solid solution of the  $\alpha$ -phase will be the primary crystallisation. With falling temperature at the transition point the  $\beta$  phase will form. The residual liquid will then solidify at the ternary eutectic. Part of the  $\alpha/\alpha+\beta$  boundary is drawn dotted since time did not permit its complete determination. This is being done by the thermal analysis of another sectioning line.

The region of occurrence of homogeneous  $\beta$  is bounded by the area DEF. Thus the  $\beta$  phase will be the primary crystallisation. The Pb will remain in the residual liquid, which will finally solidify at the ternary eutectic.

The area EGHJF will also be an area of heterogeneity. The primary crystallisation is  $\beta$  which will change to  $\gamma$  at the appropriate transition point. The residual liquid containing the Pb solidifies at the ternary eutectic. The  $\beta/\beta+\gamma$  boundary is shown dotted. The points shown in squares represent the alloys which show homogeneous  $\beta$  crystallisation. That is, no second peritectic occurs to show a transition to the  $\gamma$  phase. The alloys also show the eutectoid, and compound separation. The points



Liquidus Diagram of the  
Ag-Al-Pb system.

indicated by crosses represent the composition of the alloys which show heterogeneity, as evidenced by a transition to the  $\gamma$ -phase at the second peritectic, and thus do not show the eutectoid, or compound separation. As can be seen a slight hysteresis occurs in the case of one alloy. However it must be remembered that the diagram is greatly magnified and slight errors in analysis would show up greatly. Also, the solid separating is not of exactly the same composition as the melt, and this would introduce a small error in plotting.

The first peritectic line in the Ag-Al system on the addition of Pb intersects the partial miscibility curve at 7.90% Al, 7.60% Pb, 84.50% <sup>Al</sup>. The temperature drops from 779° to 727°.

The second peritectic line intersects the partial miscibility curve at 10.30% Al, 4.10% Pb and 85.60% Ag. The temperature drops from 729° to 708°.

If the partial miscibility curve had not intervened the two lines would have intersected at 11.00% Al, 15.50% Pb and 73.50%

Conclusions.

The ternary alloys of the system, silver, lead, and aluminum have been investigated and the liquidus diagram completed.

1. No ternary compounds were found to have formed.
2. No solubility of Pb in the  $\alpha$ ,  $\beta$  and  $\gamma$  phases was found.
3. The first peritectic line in the Ag-Al system, with the addition of Pb, intersects the partial miscibility curve at 7.90% Al, 7.60% Pb and 84.50% Ag. The temperature drops from 779.0° to 727.0°.
4. The second peritectic line intersects the partial miscibility curve at 10.30% Al, 4.10% Pb and 85.60% Ag. The temperature drops from 729.0° to 708.0°.
5. If the partial miscibility curve had not intervened, the two lines would have intersected at 11.00% Al, 15.50% Pb and 73.50%



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