

THE SYSTEM ALUMINUM-INDIUM-SILVER

by

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TO MY WIFE

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ABSTRACT

An investigation of the "miscibility gap" in the binary system Al-In has been made. The critical temperature and composition were estimated as 945°C and 68.8% In, 31.29 Al (by weight).

In the ternary system Al-In-Ag the liquid-liquid partial miscibility region has also been determined. The lowest temperature at which the two liquids can exist in equilibrium before a third phase appears was found to be approximately 590°C . The "ternary gap" extends to 30.5 % Ag, 34.7 % Al, 34.7 % In, at this temperature. Isotherms of the "ternary gap" have been constructed at 50°C intervals between 650°C and 900°C . A ternary critical point does not exist i.e. the binary critical temperature is lowered continuously on addition of silver.

Three vertical sections through the ternary system were made by means of thermal analysis. Four ternary peritectic points either of the first or second kind exist at approximately

- 1) 65% Ag, 32% In, 3% Al;
- 2) 45% Ag, 45% In, 10% Al;
- 3) 9% Ag, 90% In, 1% Al;
- 4) 4% Ag, 95% In, 1% Al.

The corresponding temperatures of the four-phase isothermal planes are: 588° , 506° , 241° , 148°C , respectively.

A ternary eutectic point exists at approximately

3% Ag, 96% In, 1% Al. The corresponding four-phase isothermal plane lies at 143°C.

A good approximation to the whole ternary liquidus was obtained.

A basal projection of the liquidus surface has been made.

The identity of some of the solid phases present in equilibrium with liquid has been deduced.

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INTRODUCTION

The investigation of the system aluminum-indium-silver, which had not been studied previously, was suggested to me by Dr. A.N. Campbell.

The system aluminum-indium has not hitherto been investigated completely. The upper limits of the miscibility gap are still unknown.

Before proceeding to the ternary system aluminum-indium-silver it was necessary to complete the binary system aluminum-indium. On the other two contiguous binary systems extensive investigations had been carried out in the past by a large number of workers. These systems are therefore considered to be completely known. A discussion of the binary systems is given under "Previous Relevant Investigations".

It was intended to investigate the ternary system as completely as possible, but it was clear from the beginning that the complete ternary system, involving photomicrography and x-ray investigation could not be studied completely in the time available, because of the rather complex nature of the system.

Efforts were directed mainly towards the determination of the liquidus, the "ternary troughs" and the ternary "gap".

CHAPTER I

CONSIDERATION OF METHODS AND TECHNIQUES

a. The Phase Rule

The phase rule (phase law) will be merely stated and the terms defined. The derivation of the phase law can be found in any standard text on phase theory or chemical thermodynamics (11, 70). In mathematical form this law is stated as follows: $P + F = C + 2$, provided the variables are limited to P, T, and Composition. It must be obeyed by every system at equilibrium. P, F, and C are the total number of phases, degrees of freedom and components respectively in a system at equilibrium.

A phase is a homogeneous part of the system, bounded by surfaces and separable in principle by mechanical means.

A degree of freedom is an intensive variable which may be changed independently at equilibrium without altering the number or kind of phases present and which must be specified in order to define the state of the system completely at equilibrium..

C, a component, is an independent composition variable. The total number of components is the smallest number of independent

composition variables necessary to define the composition of every phase in the system. In alloy systems, it is the number of metals present.

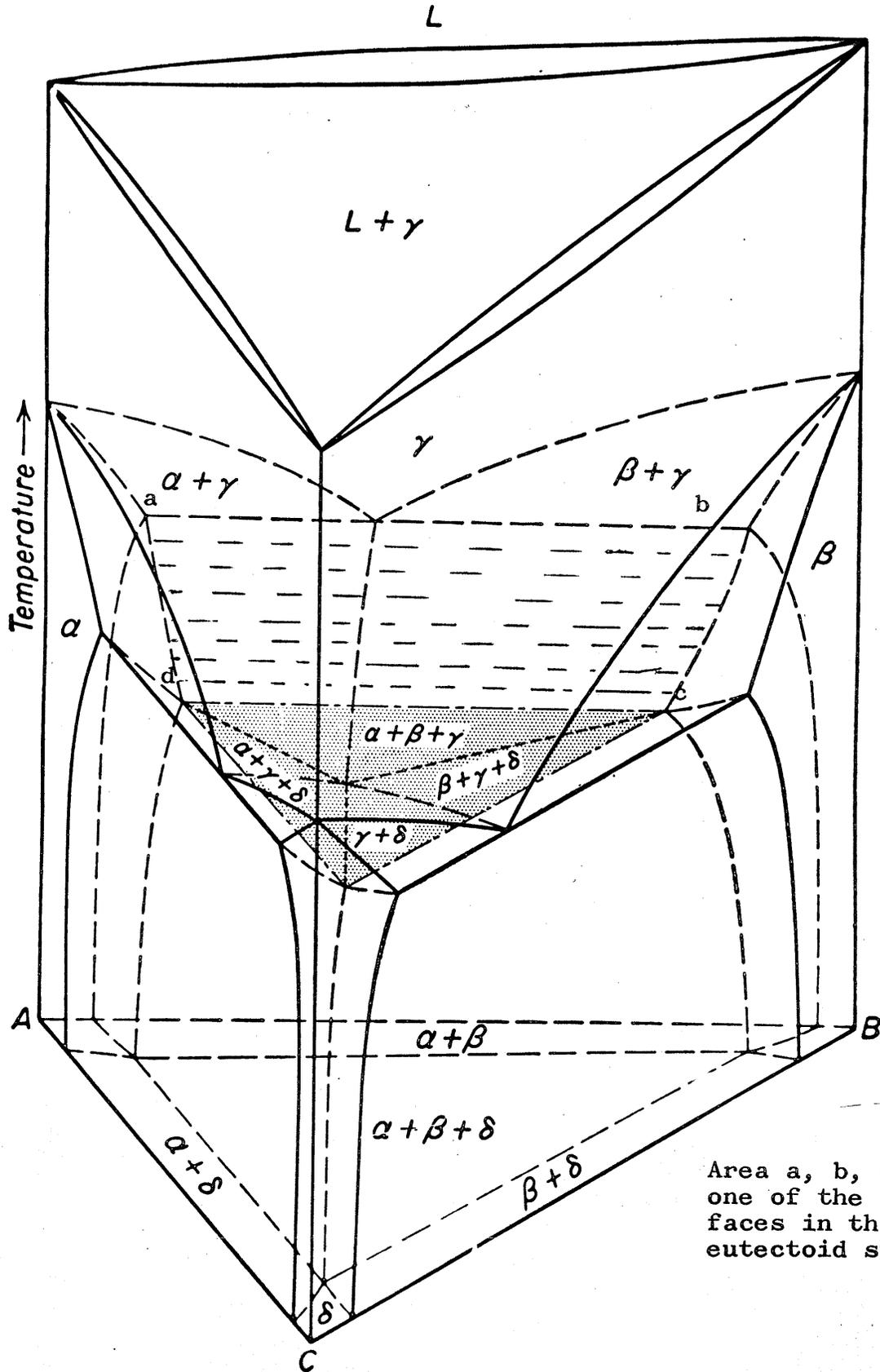
The phase rule is also usefully stated in terms of "rules of construction" of phase diagrams. In an isobaric binary system:

1. one-phase regions may touch each other only at single points, not along boundary lines.
2. adjacent one-phase regions must be separated from each other by two-phase regions which have phases that occur in the adjacent one-phase regions.
3. three two-phase regions must originate upon every three-phase isotherm.
4. two three-phase isotherms may be separated by two-phase regions if the two phases are common to both three-phase equilibria.

In an isobaric ternary system similar rules hold, but they may be summarized by the general statement: A region of the phase diagram representing equilibrium of a number of phases can be bounded only by regions which have one more or one less equilibrium phases than the number of phases in the region in question.

Since the boundaries between three-phase regions and two-phase regions are always "ruled" surfaces, a three-phase region shown in an isothermal section is always bounded by straight lines, Page 27.

The construction of equilibrium phase diagrams from experimental data must comply with the phase rule if the diagram



Area a, b, c, d, is one of the ruled surfaces in this simple eutectoid system.

FIGURE 27

is to be theoretically correct. The phase rule, in the form of "construction rules", may also serve as a convenient labour-saving device.

Terms commonly used in phase theory are explained in section "d" of this chapter.

b. Thermal Analysis

Thermal analysis is simple in principle. If a substance which undergoes no phase change is cooled, then the "cooling curve" i.e. temperature recorded as a function of time, will be a smooth exponential curve (normal cooling) as shown in Fig. 1. If a substance undergoes a phase change while it is cooled, such as crystallization from a melt, a delay in cooling sets in, which is due to thermal effects arising from different energy contents of the phases involved. The cooling curve for a pure metal with its cooling delay or "thermal arrest" is shown in Fig. 2. At the "thermal arrest" (freezing point) the temperature remains constant until freezing is complete whereupon the temperature falls again exponentially with time. In many instances the temperature falls below the equilibrium freezing temperature (under cooling). When the delayed crystallization finally sets in, it proceeds rapidly with evolution of heat which raises the temperature almost to the equilibrium freezing temperature. This temperature rise is called "recalescence"; Fig. 3. At the completion of freezing, normal cooling may be resumed gradually, rather than abruptly, showing a "rounding" of the curve, which may be due to impurities

and or improper experimental arrangement. Upon heating, slight overheating may occur, i.e. the thermal arrest will lie slightly above the equilibrium melting temperature. The equilibrium freezing temperature lies between the cooling and heating "arrests". This temperature range can be reduced to a fraction of a degree if the cooling and heating rates are very slow.

Bivariant transformation such as the freezing of solid-solution gives rise to a "non-isothermal arrest" rather than "a thermal arrest" as shown in Fig. 5. In practice, undercooling, recalescence and rounding of the curve when solidification is complete all take place. These effects modify the ideal curve to give the appearance of Fig. 6. The equilibrium liquidus temperature is usually taken to be the point of intersection of the extrapolated non-isothermal arrest with the exponential (normal) curve. This point of intersection is a closer approximation to the liquidus temperature than that given by the first recorded "break" in the cooling curve. Usually, the temperature at which normal cooling resumes (i.e. completion of solidification) is indistinct (rounding) due to coring. Heating curves of previously homogenized samples give a more distinct solidus temperature.

In two-component systems univariant transformations such as peritectics and eutectics produce an isothermal (horizontal) arrest, Fig. 7, curve E. In these transformations, under-cooling and recalescence are often pronounced. Cooling curves

of hypo- and hyper eutectic alloys (i.e. alloys to the left and right of the eutectic composition) are a combination of the solid-solution and eutectic type curves, Fig. 7, curve H. Isothermal arrests of the latter alloys are always shorter than those of the eutectic alloy itself, under the same conditions. Peritectic alloys often yield very short isothermal arrests due to gradual merging of the arrest into the normal curve. Of all the transformations the peritectic type tends to undercool most. Undercooling is also more pronounced in a eutectoid transformation than in a eutectic or monotectic transformation. Bivariant transformations in the solid (solvus) are rarely detectable thermally.

More complex cooling curves are obtained with ternary and higher order alloys. A typical ternary eutectic type cooling curve is shown in Fig. 8.

A series of cooling curves "taken across" a ternary system will give a good approximation to the complete liquidus surface and will show eutectic and peritectic troughs as well as congruently melting intermediate phases, monotectics and syntectics and most isothermal reactions occurring in the solid state.

To accentuate thermal arrests the "inverse rate curve" is preferable. It is obtained by plotting the time interval in which the temperature falls a stated number of degrees as a function of temperature. By controlling the heating or cooling rates the

curves may be made linear (Platonic cooling) and phase changes, i.e. deviations from the linear path may be more easily detected. One such device among several for controlling the rate of cooling is described by C.S. Smith (53). To eliminate external effects differential thermal analysis can be used to advantage. This is done by plotting the temperature of the specimen against the temperature difference between the specimen and a neutral body which does not undergo any transformations in the temperature range under investigation and which has approximately the same heat capacity. Two thermocouples, one for the specimen and one for the neutral body are required. Devices for recording such graphs automatically are available. An "inverse rate" graph is shown in Fig. 4. The peak indicates a transformation. If the derivative of the differential curve is plotted against temperature, transformation temperatures are again accentuated. This latter method is known as the "derived differential" method. A more detailed description of experimental techniques and a discussion of metallographic principles can be found in a text by George L. Kehl (38).

c. Location of Boundaries of Liquid Immiscibility

Liquid-liquid immiscibility boundaries are in general not detected by thermal analysis. If the components can be determined accurately by chemical analysis or other reliable means, then the location of two-liquid (or multiliquid) fields is simple. The system is equilibrated at each of a series of fixed temperatures and samples for analysis are withdrawn from each layer at each temperature.

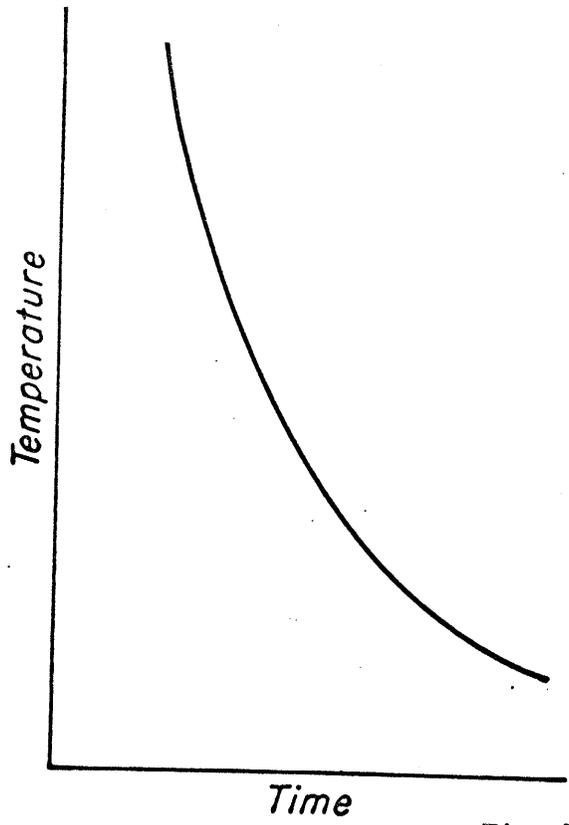


Fig. 1

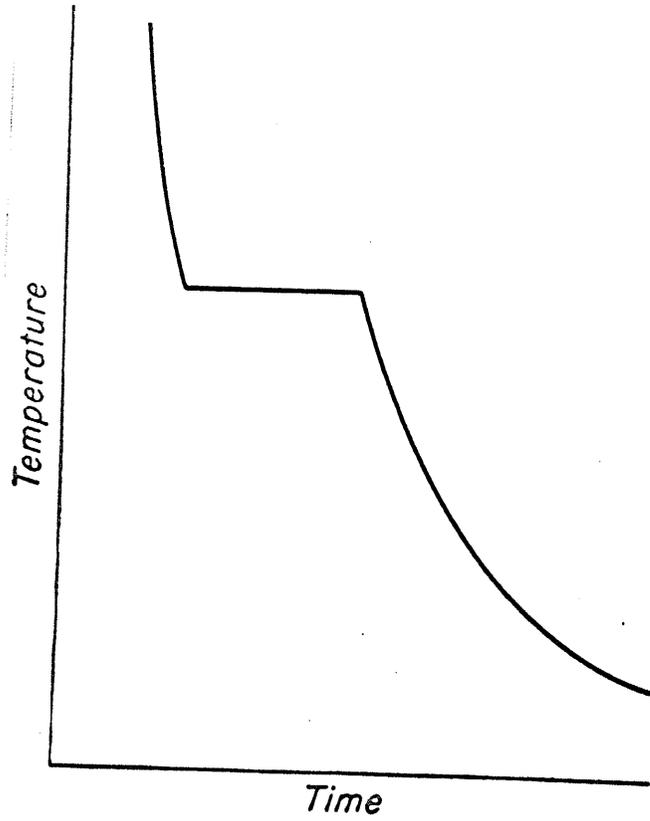


Fig. 2

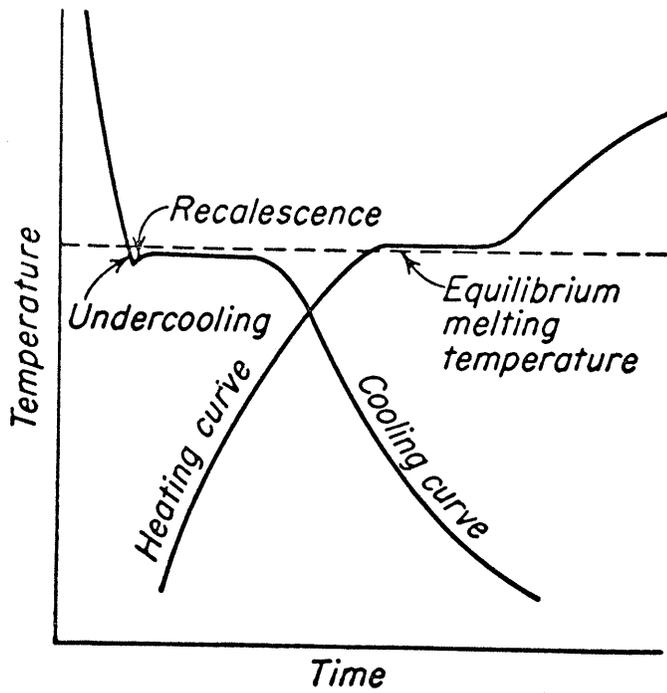


Fig. 3

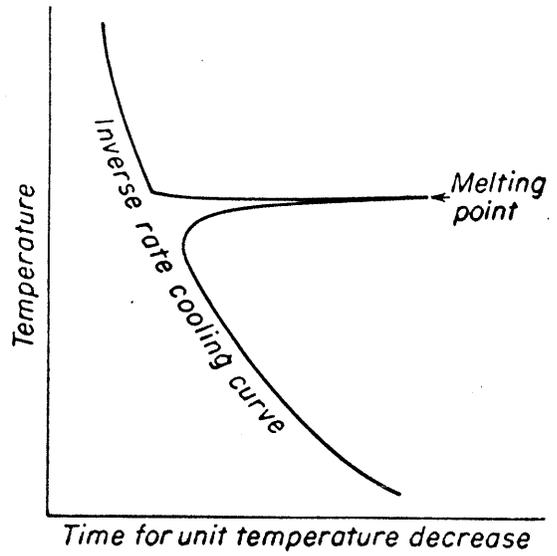


Fig. 4

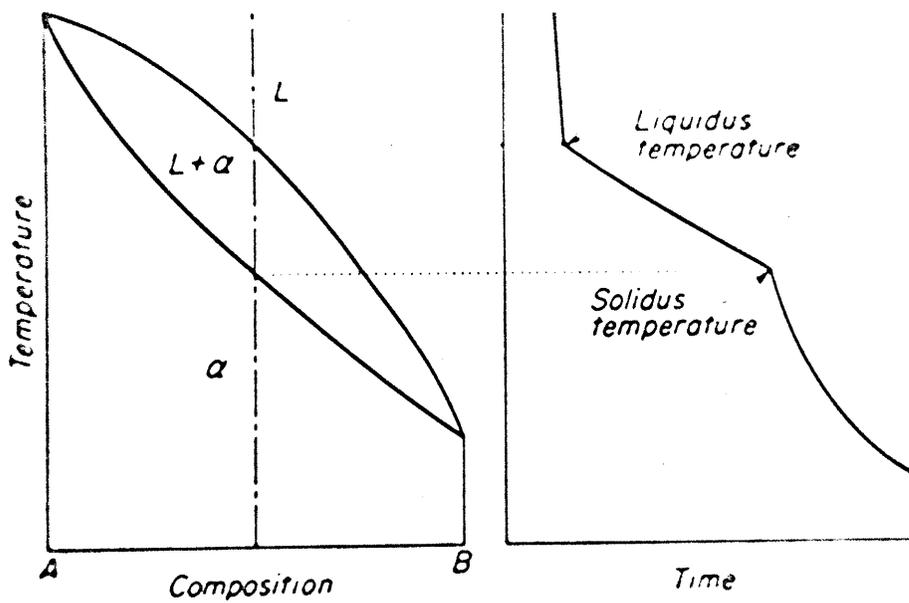


Fig. 5

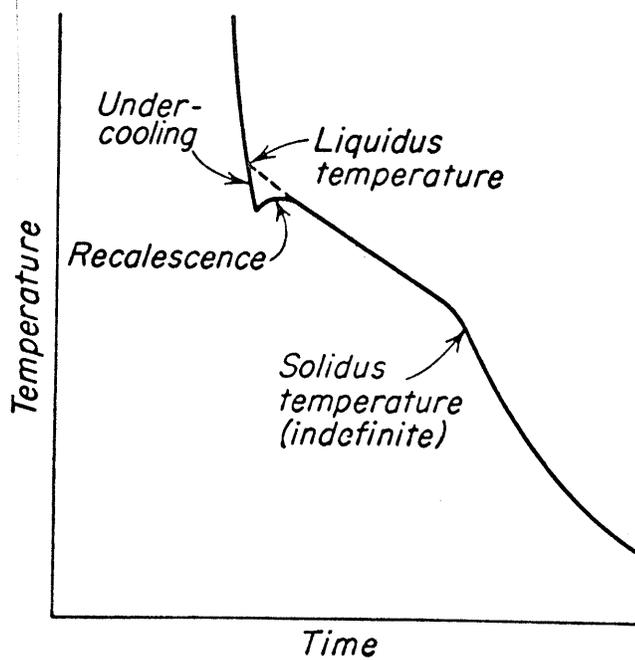


Fig. 6

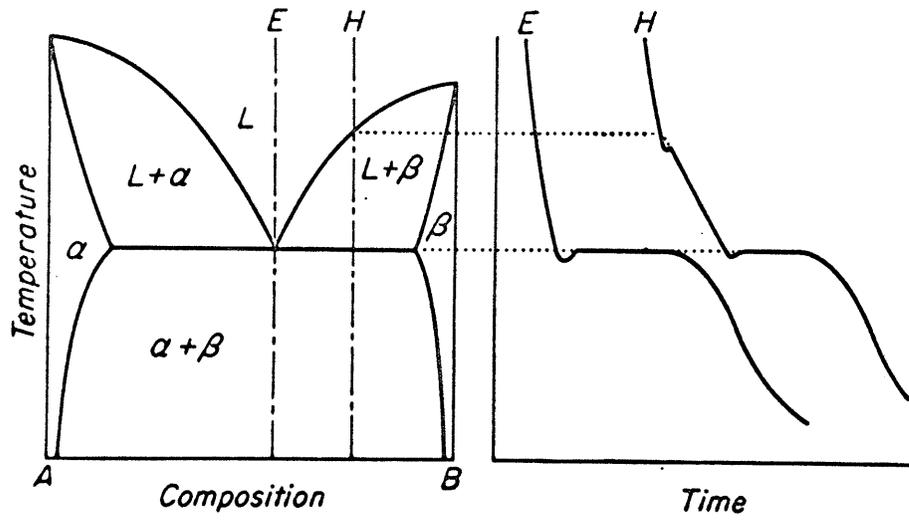


Figure 7

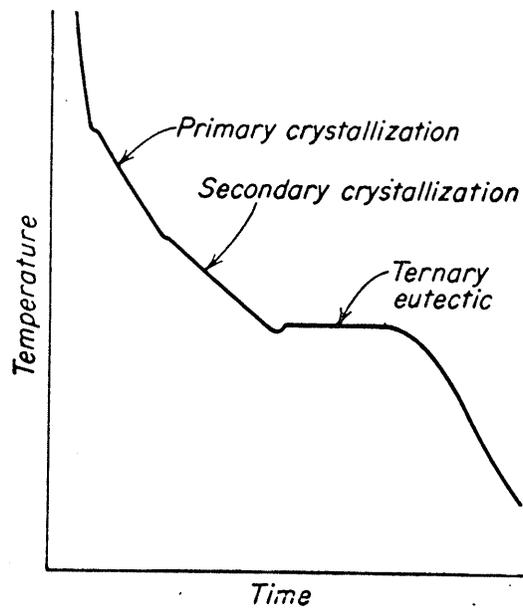


Figure 8

In alloy systems withdrawing of samples may be experimentally difficult and quenching from the desired temperature may be employed if quenching is sufficiently rapid so that the equilibrium is not shifted appreciably.

In two-component systems it is possible to determine the boundaries without resorting to chemical analysis. After equilibrium is established the sample is quenched and the individual layers are separated at the interface and weighed. If the overall composition of the alloy is accurately known, two such experiments carried out at the same temperature but at two different overall compositions could yield the composition of each layer at the particular temperature by applying the "lever principle" in each case, and solving the two equations for two unknowns viz. the composition of the two layers. This simple method is not applicable to three or more component systems.

d. Explanation of Terms

Eutectic: In a binary system a transformation of the type

$L \rightleftharpoons S_1 + S_2$ is a eutectic transformation. The corresponding

ternary transformation is $L \rightleftharpoons S_1 + S_2 + S_3$. These transforma-

tions necessarily occur at constant temperature. "L" represents a

liquid phase, S_1 , S_2 , S_3 , represent different solid phases. The

arrow pointing to the right represents loss of heat.

Peritectic: In a binary system a transformation of the type

$L + S_1 \rightleftharpoons S_2$ is a peritectic. Upon heating, decomposition of a

solid phase into a liquid and a new solid phase occurs i.e. the solid phase melts incongruently. If S_1 and S_2 are solid solutions rather than pure substances the term "meritectic" is sometimes used, but usually the term "peritectic" is applied to both cases. In the ternary system there are two corresponding transformations,

1) $L + S_1 + S_2 \rightleftharpoons S_3$ 2) $L + S_1 \rightleftharpoons S_2 + S_3$, the first is referred to as "ternary peritectic of the first kind" or simply "ternary peritectic", the second is referred to as "ternary peritectic of the second kind". (70). The latter transformation can be thought of as being intermediate between a eutectic and a peritectic.

Eutectoid and Peritectoid: In the binary system $S_3 \rightleftharpoons S_1 + S_2$ and $S_1 + S_3 \rightleftharpoons S_2$ represent the eutectoid and peritectoid transformations respectively. They are related to the binary eutectic or peritectic by replacing the liquid by a solid. The corresponding ternary transformations are $S_1 \rightleftharpoons S_2 + S_3 + S_4$ and $S_1 + S_2 + S_3 \rightleftharpoons S_4$ respectively. No special name has been given to the ternary transformation $S_1 + S_2 \rightleftharpoons S_3 + S_4$ although such a transformation may occur.

Monotectic: In a binary system $L_I \rightleftharpoons L_{II} + S_1$ represents a monotectic transformation. Upon cooling a liquid phase transforms into a solid and another liquid. The corresponding ternary transformation is $L_I \rightleftharpoons L_{II} + S_1 + S_2$. No special name has been given to this transformation.

Syntectic: $L_I + L_{II} \rightleftharpoons S_2$ represents a syntectic transformation in the binary system. An intermediate solid phase decomposes upon

heating into two immiscible liquids. The corresponding ternary transformation is $L_I + L_{II} \rightleftharpoons S_1 + S_2$. No special name has been given to this transformation.

Simple diagrams of some of the basic binary transformations are given in Fig. 26.

Ruled Surface: A surface generated by the motion of a tie-line (Fig. 27).

Coring: Deposition of successive layers of a solid phase which are not in equilibrium with one another. Equilibrium among solids can only be established by diffusion through solids, which is necessarily slow hence coring results with rapid cooling rates, and is a common phenomenon in the industrial preparation of alloys.

Lever Principle: (By analogy with a mechanical lever). In any system the amounts of the individual two phases which are in equilibrium are inversely proportional to the lengths of the tie-line from the fulcrum to the respective phases, where the fulcrum is on the tie-line at the point representing the overall composition of the two phases.

BASIC BINARY PHASE DIAGRAMS

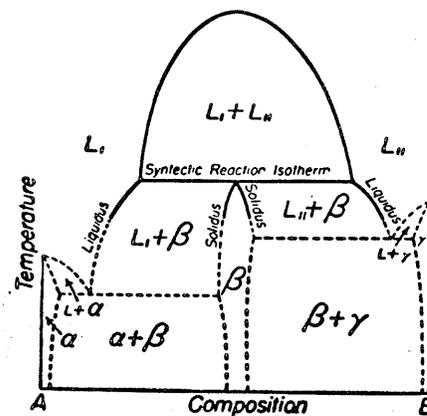
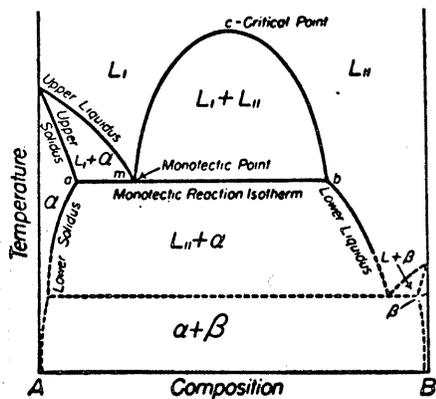
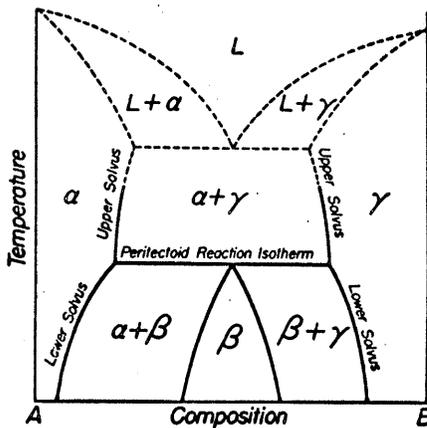
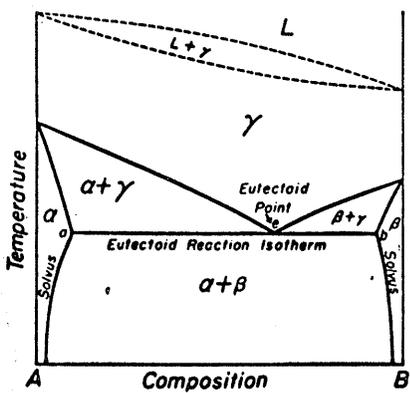
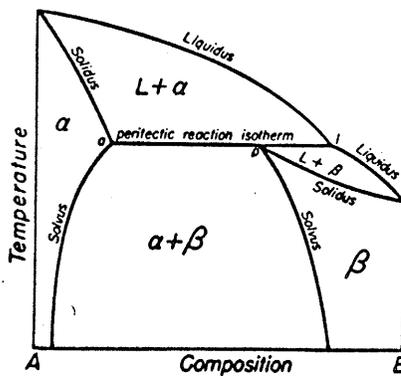
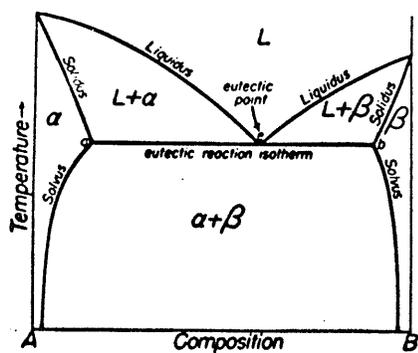


Fig. 26

CHAPTER II

PREVIOUS RELEVANT INVESTIGATIONS

a. The Pure Metals

1. Silver crystallizes with a face-centered cubic lattice of cell length 4.0772 \AA (1). The interatomic distance in the lattice is 2.882 \AA (1). The melting point of pure silver is 960.5°C (1). Silver is not attacked by oxygen, but liquid silver dissolves oxygen, about twenty times the volume of the metal at the melting point (16). All oxygen is rejected on solidification.

2. Indium crystallizes with a face-centered tetragonal lattice with cell dimensions $a = 4.583 \text{ \AA}$, $c = 4.936 \text{ \AA}$ (1). The interatomic distance is 3.24 \AA (1). The crystal structure is also described as "cubic close-packed with some distortion" (62). The melting point of indium is $156.4 \pm .1^{\circ}\text{C}$. Cold air has no action on indium, but, when hot, indium is oxidized by air to In_2O_3 . Nitrogen and hydrogen do not react with indium up to 900°C (17). No allotropic forms of indium have been observed.

3. Aluminum crystallizes with a cubic face-centered lattice of cell edge 4.0776 \AA (1). The melting point of aluminum is 659.7°C . In spite of the presence of oxide film, aluminum is attacked by oxygen or by air at 800°C to form Al_2O_3 (18). Aluminum absorbs hydrogen at high temperatures (e.g. 1.87 cc. at $900^{\circ}\text{C}/100 \text{ gm. Al}$). When heated it reacts with nitrogen to form AlN . Above 1000°C aluminum reacts with carbon to form Al_4C_3 (18).

b. The Binary Systems

1. The system indium-aluminum: This binary system was first investigated by S. Valentiner and I. Puzicha (60). Fig. 9 is a reproduction of their phase diagram. Their experimental methods were thermal analysis, photomicrography, x-ray powder diffraction and electrical resistance measurements. The last-named method did not yield much useful data. They found that the two elements are largely immiscible in the solid and liquid states. Their data show a monotectic and eutectic halt at 634°C and 156°C respectively. They determined the limits of the miscibility gap at 634°C as 13 and 98 per cent indium by weight respectively. The low-indium value they obtained by extrapolation of the liquidus curve. The high-indium value they obtained from the composition of the alloy which still showed a monotectic halt on successively increasing the indium concentration. Aside from these two points they did not determine the miscibility gap boundary any further.

Employing the same experimental techniques as S. Valentiner and I. Puzicha (60), except resistance measurements, E. Raub and M. Engel (48) obtained much the same quantitative results except for the miscibility gap boundary for which they found 17.3 and 90 "or more" per cent indium respectively at 634°C .

Using the technique of quenching followed by analysis of the top and bottom layer of the ingot, L. Buchanan (10) determined the indium-rich liquidus curve, Fig. 11. Thermal analysis was

(Valentiner and Puzicha)

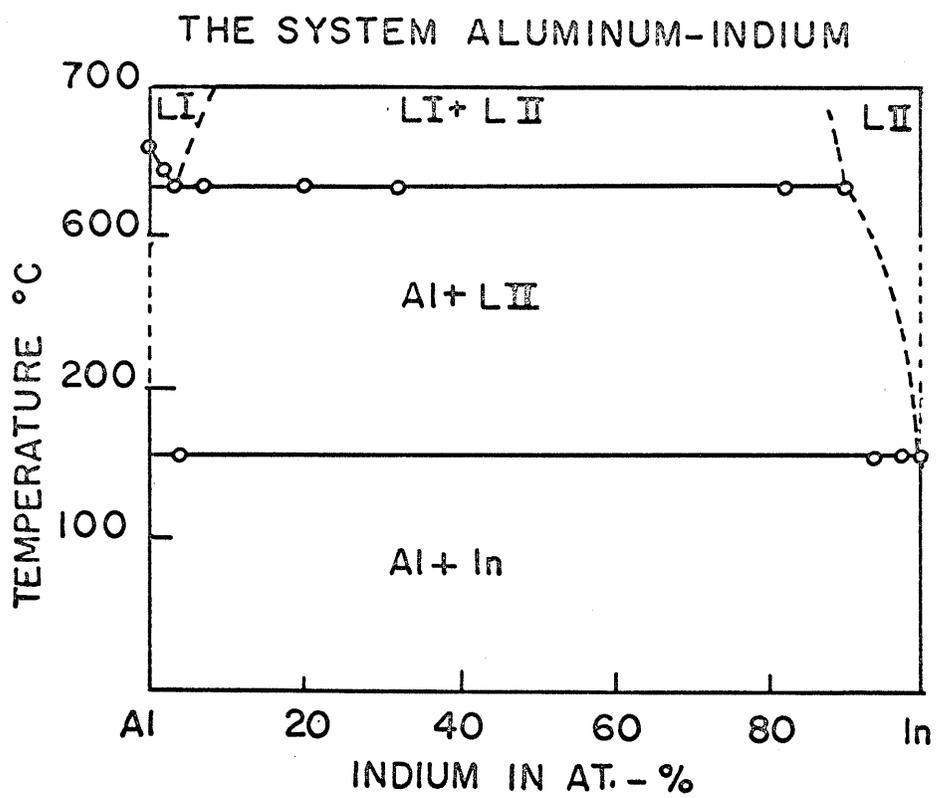


Fig. 9

(L. Buchanan)

SYSTEM ALUMINUM-INDIUM

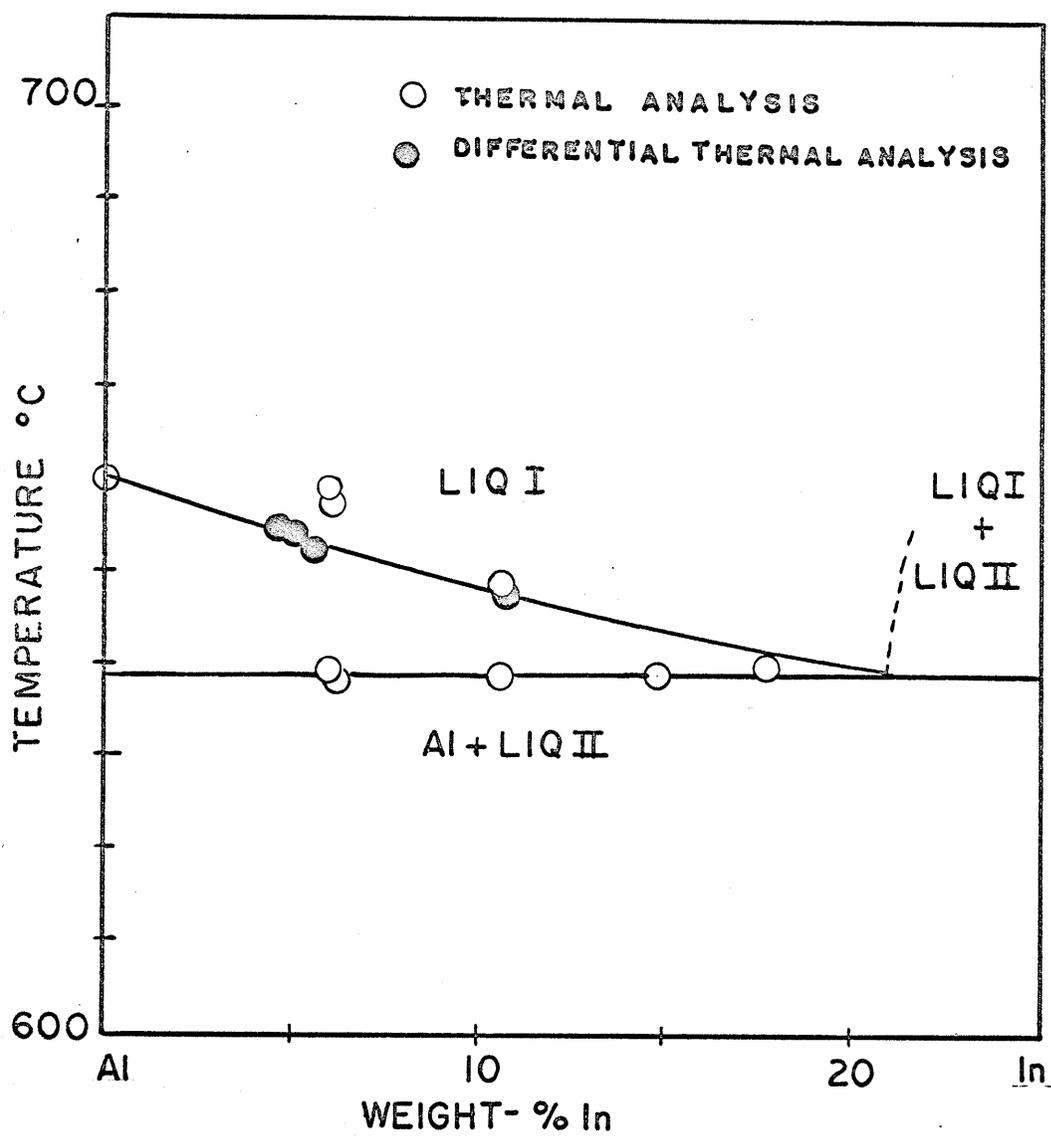


Fig. 10

(L. Buchanan)

THE SYSTEM ALUMINUM-INDIUM

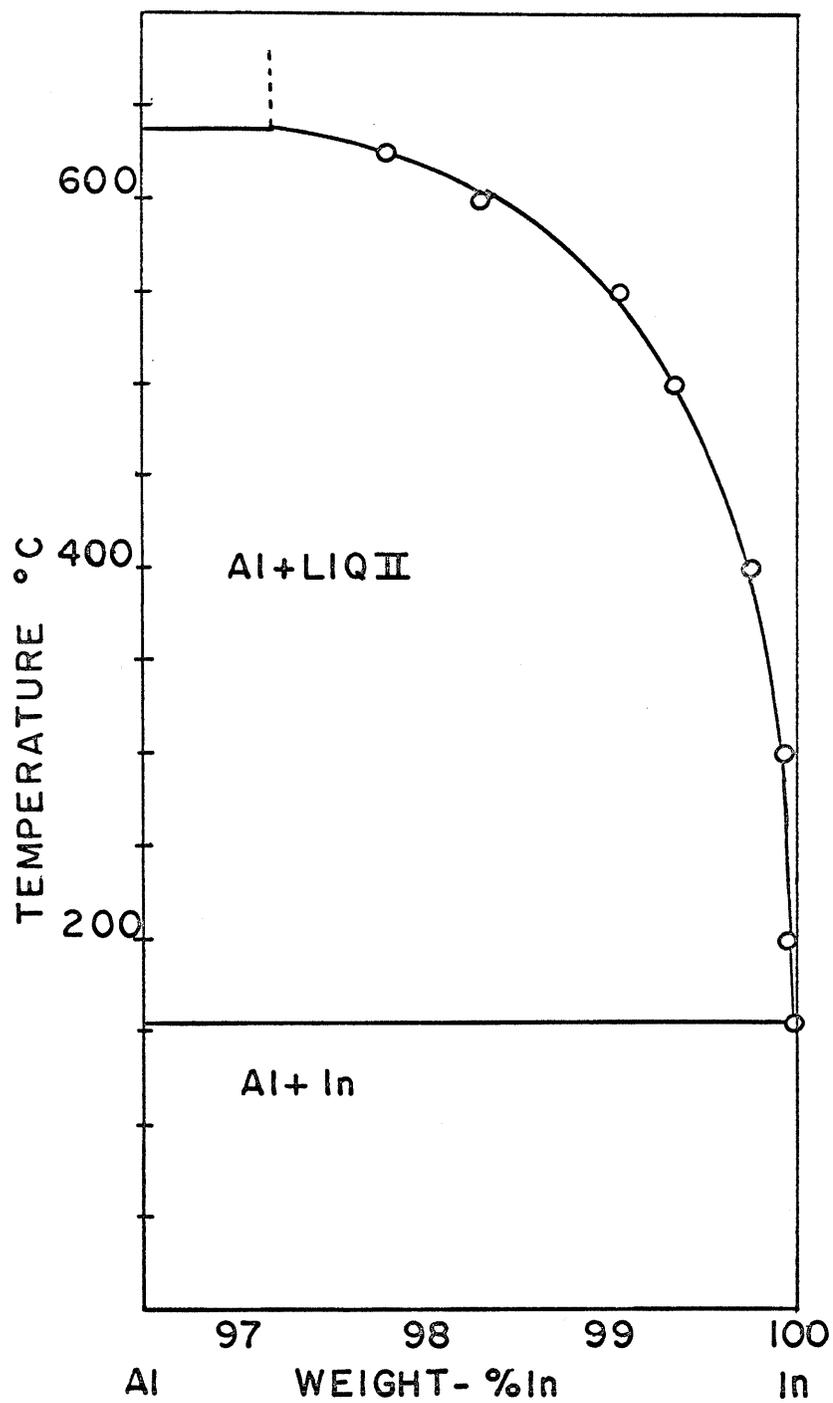


Fig. 11

apparently not satisfactory for this purpose. He also redetermined the low-indium liquidus curve which he found to lie at a higher temperature than previously reported, Fig. 10. Similarly, he reports 638.6°C as the monotectic temperature, i.e. 4.6°C higher than previously reported. The miscibility gap boundaries he found to be 20.5 and 97.2 per cent indium (by weight) respectively at 638.6°C . Because of experimental difficulties he considered these values to be uncertain. The eutectic composition he found "to contain less than 0.05 per cent aluminum". The eutectic temperature was not given. He obtained some values for the miscibility gap boundary between 640°C and 650°C which are given in Table I.

TABLE I

L. BUCHANAN'S DATA FOR THE SYSTEM Al-In

Temp $^{\circ}\text{C}$	In-Rich Layer		Al-Rich Layer	
	% Al	% In	% Al	% In
640	2.82	97.18	21.0	79.0
645	2.69	97.31	20.3	79.7
650	2.77	97.23	20.6	79.4

J.M. Kuzmak (41) attempted to close the miscibility gap, but he could carry his work only to a temperature of 800°C due to great experimental difficulties. His results are shown in Table II.

TABLE II

J.M. KUZMAK'S DATA FOR THE SYSTEM Al-In

Temp °C	In-Rich Layer		Al-Rich Layer	
	% In	% Al	% In	% Al
650	---	---	18.6	81.4
700	96.6	3.4	22.7	77.3
800	92.2	7.8	32.0	68.0

2. The System Silver-Indium: F. Weibke and H. Eggers

(61) investigated this system extensively by means of thermal analysis, x-ray powder diffraction, and photomicrography. The α -phase (same crystal structure as pure silver) extends to 19.4% indium (by weight) at room temperature, and 19.8% indium (by weight) at 693°C. They did not determine the crystal structure of the intermediate phases. They found a σ -phase lying within 26.8% and 33.1% indium (by weight) at room temperature. Neither Ag_3In (26.2% In) nor Ag_2In (34.7%) lie within this composition range i.e. in the homogeneous σ -region. Other workers (24, 29) place the silver-rich boundary of the σ -phase (or δ') at a somewhat different composition. All transformation temperatures are given in the diagram, Fig. 12 which is essentially that of F. Weibke and H. Eggers (61). (The eutectic lies at 97.0% In (wt.) at 141°C.)

Earlier investigations of V.M. Goldschmidt (24) showed that at a composition of 26.2% In (Ag_3In , i.e. δ') a homogeneous phase exists (σ or δ') having a hexagonal close-packed lattice structure with lattice constants $a = 2.95 \text{ \AA}$, $c = 4.76 \text{ \AA}$. or $c = 4.79 \text{ \AA}$

(61 Footnote).

L.L. Frevel and E. Ott (21) reported three homogeneous stable intermediate phases to exist at room temperature, two having a hexagonal lattice and the third a cubic face-centered lattice, which presumably correspond to σ , ϵ , and γ phases respectively.

According to Hume-Rothary and associates (34,) the δ -phase which exists between 660° and 693°C has a cubic body-centered crystal structure. No lattice parameters were reported. The liquidus and solidus as redetermined by these authors agree well with that of F. Weibke and H. Eggers (61). They differ in the position of the δ -boundary by approximately 1%.

V.E. Hellner (29,30) investigated the system with the aim of determining the structures and regions of the intermediate phases. He found that an alloy of a composition corresponding to Ag_3In (26.2% In) was homogeneous at 150°C and 600°C respectively with no appreciable difference in the crystal structure at these two temperatures. The transformation at 187°C detected thermally by F. Weibke and H. Eggers (61) he explains as an order-disorder transformation ($\gamma \rightarrow \gamma'$) which is not shown by x-ray diffraction due to the nearly equal scattering of x-rays by silver and indium atoms. This homogeneous phase below 187°C (γ') of composition Ag_3In (presumably with a very narrow composition range of existence) has a crystal structure of the type Mg_3Cd .

F. Weibke and H. Eggers (61) did not detect this phase. Furthermore, the σ -phase does not exist according to V.E. Hellner,

instead, it is to be replaced by a heterogeneous field $\gamma' + \epsilon'$.

At higher temperatures the γ -phase ranges in composition from Ag_3In to Ag_2In with a hexagonal close-packed structure with $a = 2.948$, $c = 4.794 \text{ \AA}$ in good agreement with V.M. Goldschmidt (24). The ϵ' -phase lies at a composition corresponding to Ag_2In (34.7% In) and is formed by transformation in the solid state from the γ -phase. Here too V.E. Hellner states that ϵ and ϵ' have the same crystal structure with a similar explanation for the transformation $\epsilon' \rightarrow \epsilon$ at 204°C as for $\gamma \rightarrow \gamma'$. He reports the structure of the ϵ -phase (and ϵ') to be of the type γ -brass with a lattice constant $a = 9.885 \text{ \AA}$. The η -phase exists at a composition corresponding to AgIn_2 with a lattice of the type CuAl_2 and lattice constants $a = 6.869$, $c = 5.604$, as reported by V.E. Hellner. (29)

3. The System Silver-Aluminum: H. Gautier (22) was the first to investigate the liquidus. He found a maximum in the liquidus curve at 11.11% aluminum (by weight) corresponding to Ag_2Al .

C.R.A. Wright (69) showed that the two metals are completely miscible in the liquid state.

The complete diagram was first established by G.T. Patrenko (46) by thermal analysis and photomicrography. He believed that distinct compounds Ag_2Al (11.11% Al) and Ag_3Al (7.69% Al) existed, but did not obtain a maximum in the liquidus curve as found by H. Gautier (22).

A. Westgreen and A.J. Bradley (63) employing x-ray diffraction, found a homogeneous phase corresponding in composition

THE SYSTEM SILVER-INDIUM

(Weibke & Eggers)

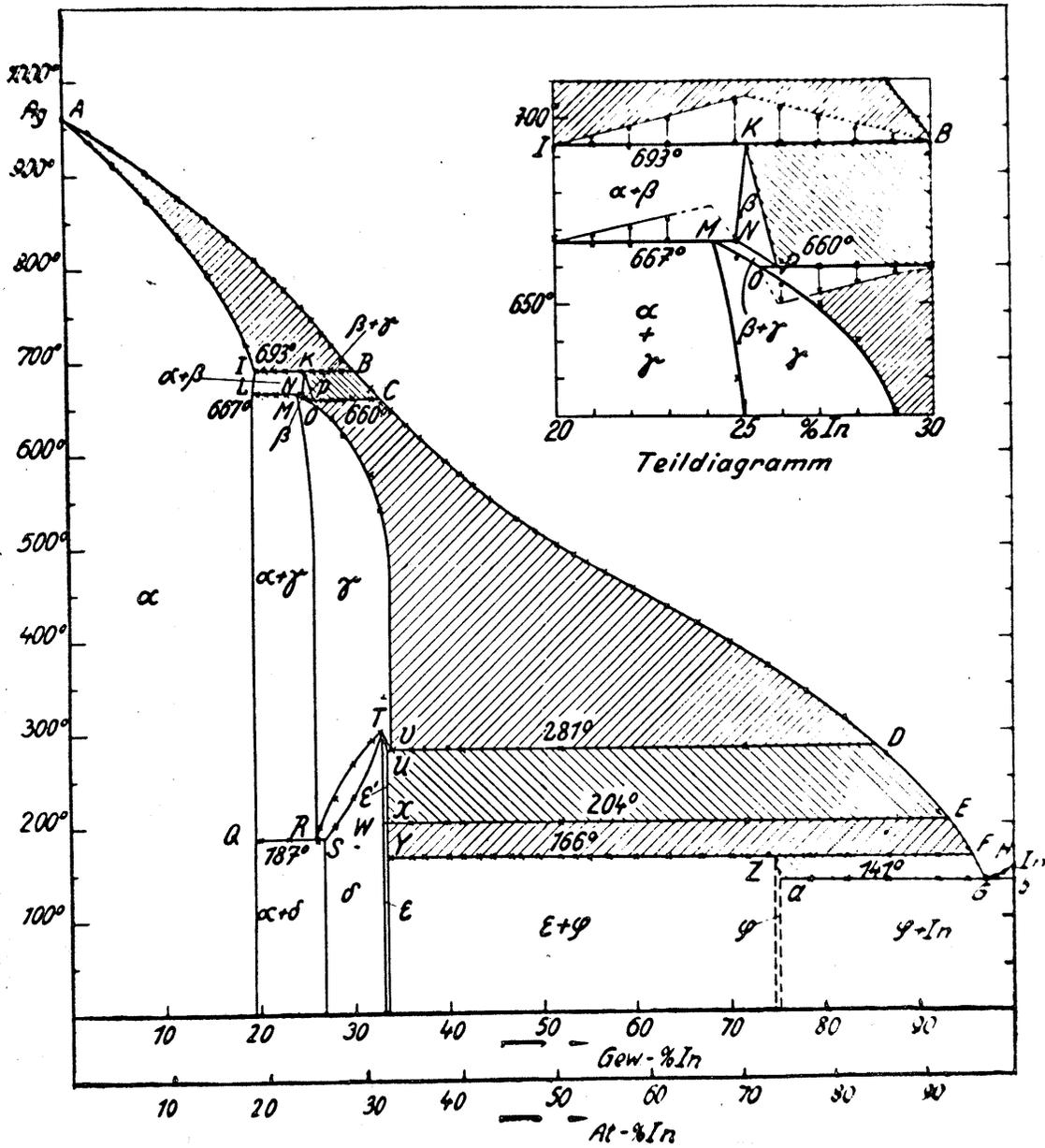


Fig. 12

to Ag_3Al (β'), existing only within a very narrow composition range, and having a structure of the β -manganese type with twenty atoms per unit cell. In addition they found a second intermediate phase (δ), having a hexagonal close-packed crystal structure and extending from 8.5% aluminum to 14.5% Al (by weight) presumably at a temperature of maximum field-width. The β' and δ phases are later designated by W. Hume-Rothery and associates (33) as μ and ξ respectively.

According to A. Westgreen and A.J. Bradley (63) distinct compounds Ag_2Al and Ag_3Al_2 do not exist; the latter compound was reported by W. Broniewski (8) on the basis of resistance and temperature-coefficient of resistance measurements.

Although nearly all investigators seemed to agree that a high temperature β -phase existed, there was disagreement regarding the transformation of the β -phase. According to G.J. Petranko (46) and W. Westgreen and A.J. Bradley (66) β transforms into β' at approximately 610°C . The findings of H. Hoffman and K.E. Volk (32) indicated that the high-temperature β -phase had a cubic body-centered crystal lattice above 605°C , transforming into a hexagonal close-packed phase at some temperature between 605°C and 570°C and not into β' . These findings are in accord with more recent investigations. N. Ageew and I. Shoyket (2,3,4) found the β -phase to break up into a mixture of two phases ($d + \delta$) at 610°C , and at slightly below 400°C the two phases supposedly recombine to form a single phase (β'). F.E. Tischenko (56,57) found that β -phase (which he calls Ag_3Al) transforms into β' at 606°C . He also

reported the compound Ag_3Al_2 having a melting point of 752°C (61,62) and being stable only above 711°C . Below this temperature it supposedly decomposes into solid solution of aluminum in Ag_2Al . According to N. Hansen (26), his conclusions seem to be erroneous as regards the compound Ag_3Al_2 .

The partial phase-diagrams of E. Crepaz (12,13), N. Ageew and D. Shoyket (2,3,4), S. Ishida and H. Tajiri and M. Karasawa (36) and I. Obinata and M. Hagiya (45) given in Fig. 14 reflect the controversy of that time over this binary system. T.P. Hoar and R.K. Rowntree clarified some of the controversy (31).

Two Peritectic reactions occur in this system, which have been variously determined by different workers: for $\alpha + L \rightleftharpoons \beta$ 770°C (63); 779°C (31); 770°C (46); 779.8°C (33); 771°C (57,58); for $\beta \rightleftharpoons L + \delta$ (at 10.0 - 10.8% Al wt.), $718 - 723^\circ\text{C}$ (63); 729°C (31); 722°C (57,58); 718°C (46); 726.9°C (33). According to E. Crepaz (13) a third peritectic reaction takes place at 698°C due to decomposition of Ag_3Al_2 . Similarly, the eutectic temperature and composition were variously determined as 567°C (46); 558°C (27); 568°C (13); 566°C (49); at 30% Al (27,46); 38.0% Al (28); 35% Al (12); 25.5% Al (13).

The α -solid solution boundary was first determined by G.J. Petrenko (46) and redetermined by A. Westgreen and A.J. Bradley (63), W. Bromiński (9), B. Beckmann (6), M. Hansen and G. Sachas (27) and W. Hume-Rothery, G.W. Mabbott and K.M.C. Evans (34), with results

which agreed fairly well. By means of density and lattice parameter measurements, A. Westgreen, A.J. Bradley (63), C.S. Barrett (5); E. Jette-F. Foote (37) and S. Kukubo (40) showed that the α -solid solution is of the substitutional type. R.T. Phelps and W.P. Davey (47) disagreed with this conclusion.

The σ -phase boundary was determined by N. Hansen (27,28). Apparently no such σ -phase was found previously by G.J. Petrenko (46). W. Bromiewski (8,9) did find such a terminal phase. W. Kroll (39) and M. Tazaki (55) later confirmed M. Hansen's (27,28) work.

G.V. Raynor and D.W. Wakeman (49) later redetermined the solid-phase boundaries. In contrast to reports of previous workers they found that the σ -boundary is not smooth, but exhibits a marked change in direction in the region of 49.4% Ag by weight at a temperature of 526°C. The maximum solid solubility is 55.6% Ag by weight at the eutectic temperature of 566°C.

W. Hume-Rothary, G.V. Raynor, P.W. Reynolds and H.K. Packer (33) confirmed the existence of a high-temperature β -phase, established the boundaries and redetermined the crystal structure, viz. cubic body-centered, and found the transformation temperature $\beta \rightarrow \gamma$ (5) to be 603°C. They confirmed the structure of γ (5) to be hexagonal close-packed. They also confirmed the structure of β' (μ) to be of the β -manganese type, and established that it exists at 7.7% Al (by weight or 25% Al atomic %) within a narrow range of composition.

The binary phase diagram as given in Fig. 13 embodies the results of many workers. The aluminum-rich side is mainly due to M. Hansen (27,28) while the silver-rich side in its finer details is due to W. Hume-Rothary and associates (33).

The ternary system Ag-In-Al has not been investigated hitherto.

THE SYSTEM SILVER-ALUMINUM

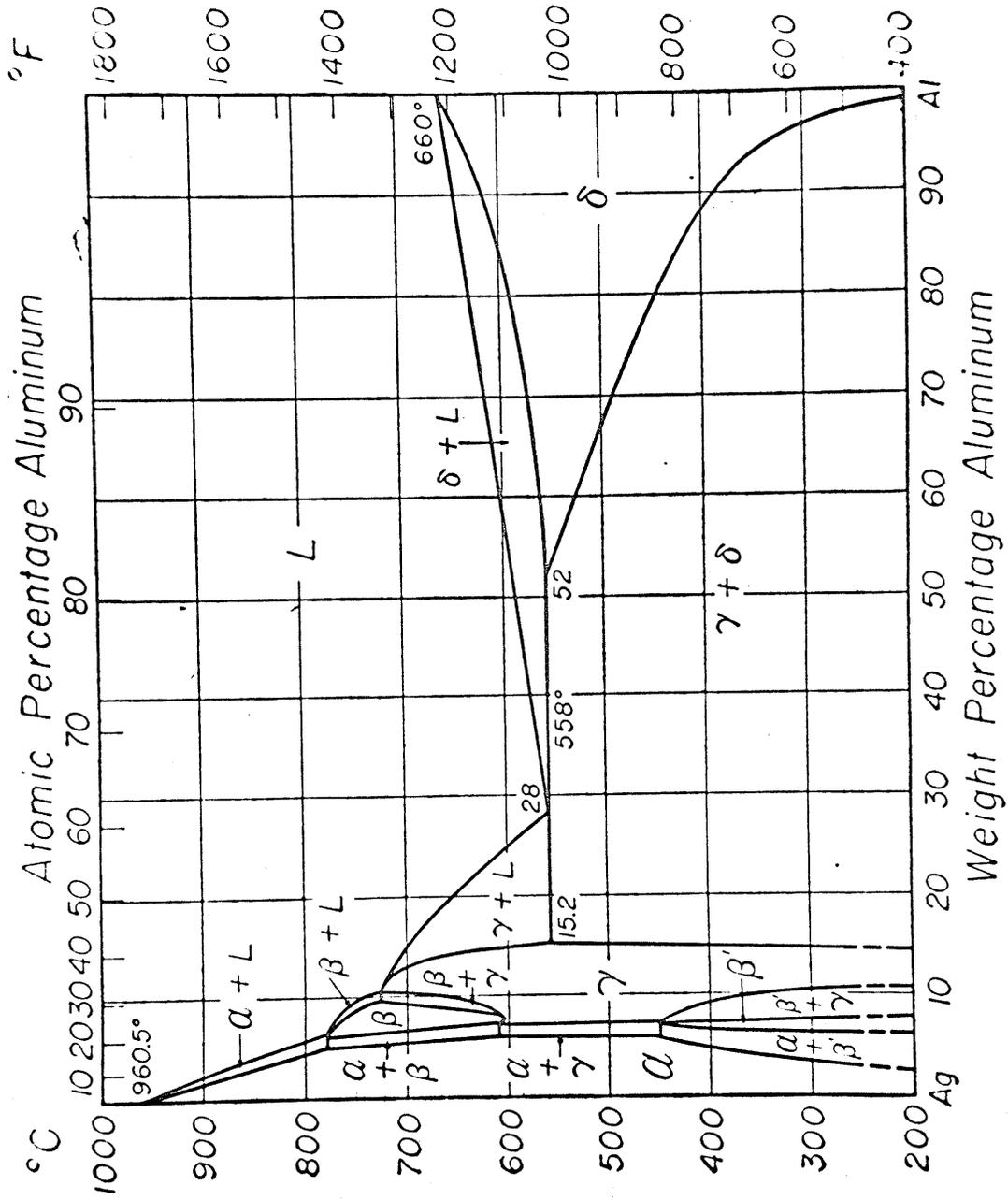


Fig. 13

13

THE SYSTEM SILVER-ALUMINUM

(Various Workers)

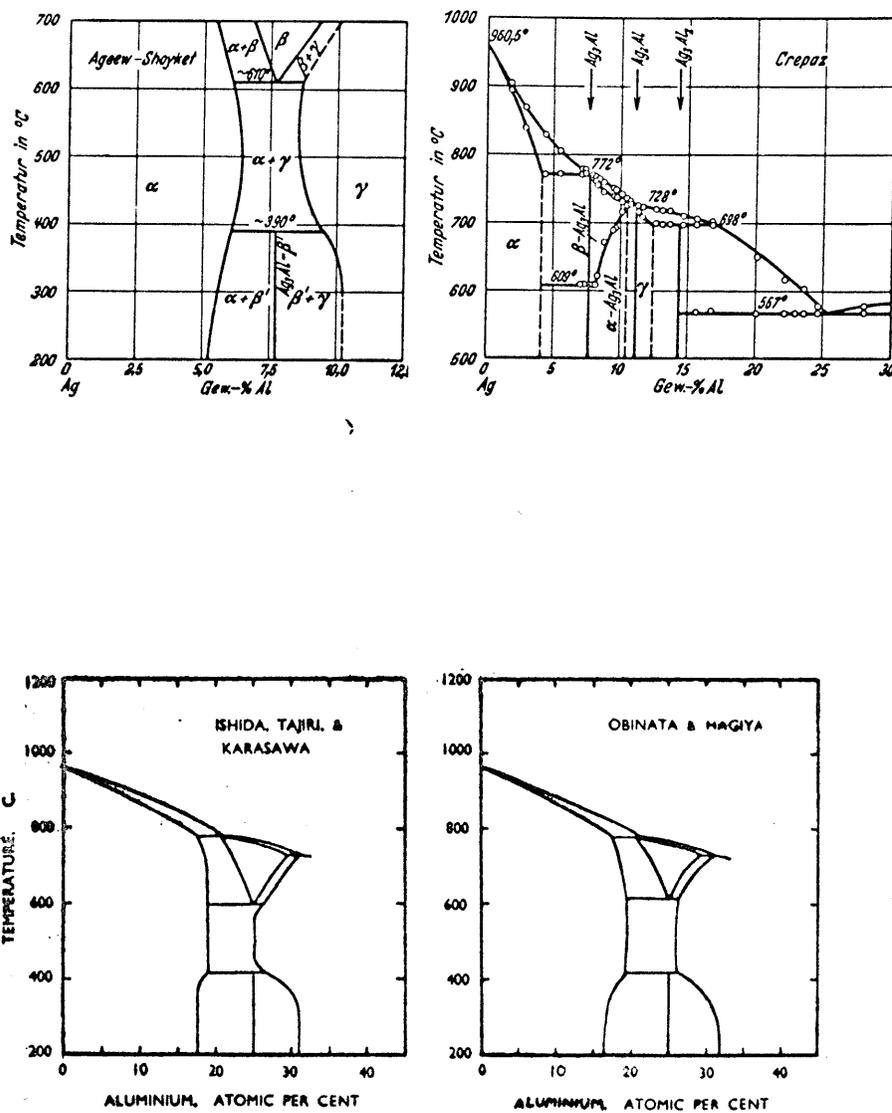


Fig. 14

14.)

CHAPTER III

EXPERIMENTAL TECHNIQUES

a. Purity of Metals

1. Silver (Johnson Matthey, Ltd.) highest purity silver: 99.995% Ag.
2. Indium (Consolidated Mining and Smelting Company of Canada, Ltd.) standard grade indium, 99.99% In. or better.
3. Aluminum (Department of Mines and Technical Surveys, Mines Branch, Ottawa) Al, 99.994%; Fe, 0.0019%; Si, 0.0018%; Cu, 0.0018%.

b. Preliminary

In the binary system aluminum-indium a miscibility gap in the liquid state exists above 638.6°C (10,41). Indications were that the gap might close between 900°C to 950°C . Several isothermal sections through the ternary system between 600°C and 900°C would show the extent of the gap in the ternary diagram. To determine the miscibility gap boundary in the individual isothermal sections the composition of the two liquid phases had to be determined for different overall compositions at the desired temperature. To this end the alloys could be either quenched from the temperature in question or molten alloy samples from the two liquid layers could be withdrawn. For reasons to be discussed later, the latter method was followed.

The determination of the ternary miscibility gap presented experimental difficulties which were due, first to a lack of an accurate method of chemical analysis for indium in the presence of aluminum or vice versa, and secondly to the relatively high temperatures at which samples had to be withdrawn for analysis.

The first difficulty was circumvented by taking advantage of the relatively large difference in densities of the pure metals and using density determinations of the alloy together with chemical analysis for silver to attain the composition of the two layers. The difficulties arising in connection with the withdrawing of molten alloy samples were eliminated by developing a suitable pipette which is shown in Fig. 16. A more detailed description is given elsewhere.

The ternary troughs can be established by trial and error, i.e. by guessing the course of a trough, making up alloys of such compositions as were thought to fall on the trough, analyzing them thermally and proceeding in this way along the entire length of the trough. In the present case, however, several vertical sections which cut the ternary troughs at a constant concentration ratio of two components served to establish the course of the troughs in the ternary system. In this way the investigation was carried out systematically and more information^{was} gained than from the trial and error method.

These vertical sections were constructed from thermal analysis data.

C. Thermal Analysis Apparatus

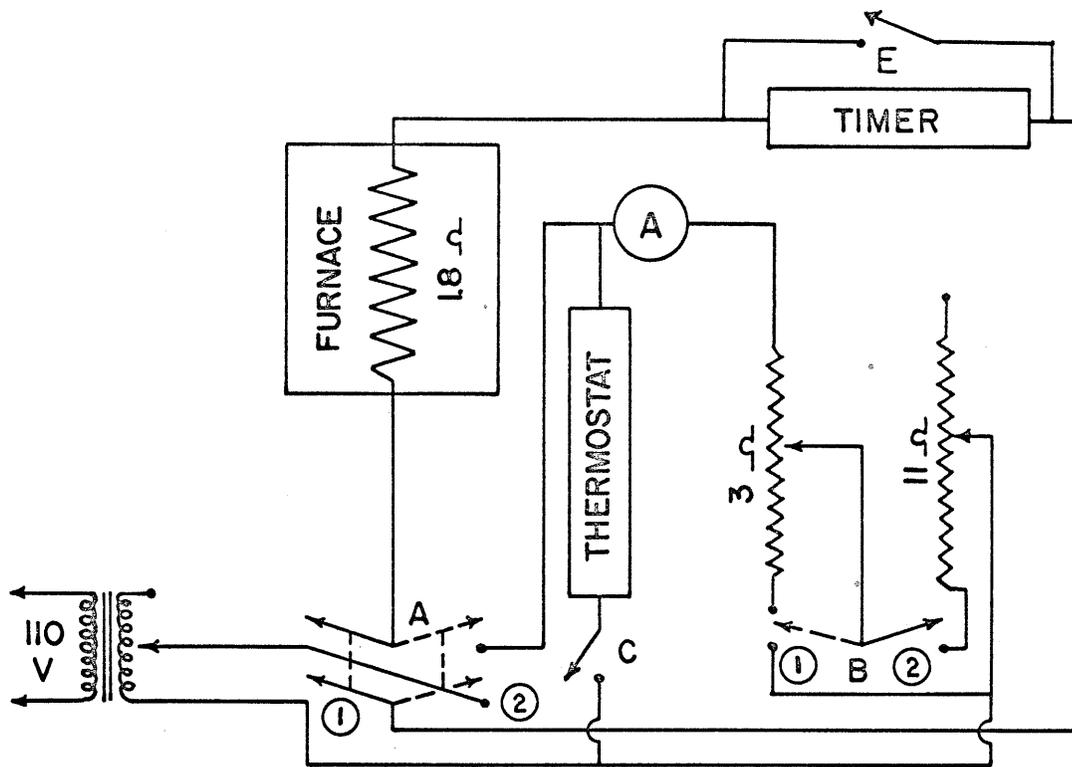
For thermal analysis a "Hoskins" resistance-type furnace (1.8 Ω) was used. It consisted essentially of a vertical cylinder fifteen inches high, 1 3/4 inches internal diameter, closed at the bottom and packed inside with quartz wool to a height of five inches from the bottom. The whole cylinder upon which the heating element was wound was thermally insulated.

Current was drawn from a "Surges" variable transformer with ten and thirty amperes at forty and twenty-five volts respectively, minimum and maximum output. Fig. 15 is a schematic diagram of the simple electric circuit of this apparatus. The following description refers to the circuit with switch "C" open.

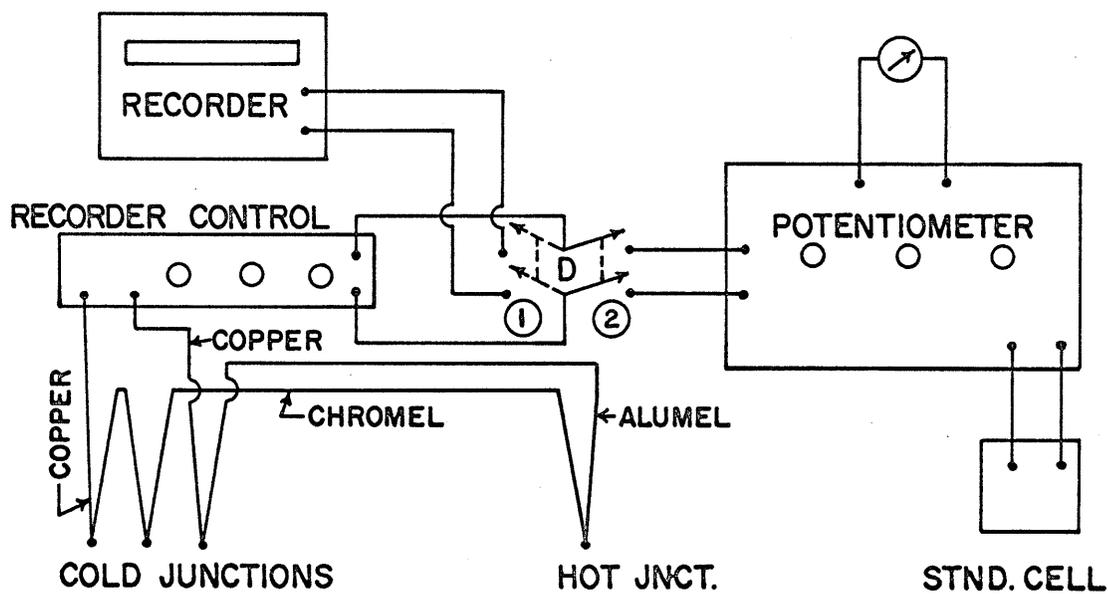
Switch "A" when in position 1, permits the rapid preheating of the furnace to a desired temperature by connecting the furnace directly to the variable transformer. Cooling or heating can be initiated at a pre-set time by opening switch "E". With switch "A" in position 2, either one or both water-cooled variable resistors (3 Ω , 11 Ω) can be introduced into the circuit depending on the position of switch "B". With switch "A" in the latter position, the current through the heating element can be varied from approximately one to thirty amperes, corresponding to a variation in temperature inside the furnace from approximately fifty to over a thousand degrees centigrade.

For purposes of estimating approximately the furnace-temperature from ampere-meter readings, a graph of current versus furnace temperature was made. A chromel-alumel thermocouple was used for temperature measurements. The cold junction was thermostated at $25^{\circ} \pm .1^{\circ}\text{C}$. At the hot junction the thermocouple wires were insulated with small ceramic beads and a thin "alundum" tube slipped over one wire as seen in Fig. 16. The schematic diagram of the thermocouple circuit is given in Fig. 15.

The potential across the thermocouple leads was measured with a "Minneapolis Honeywell Brown Recorder Potentiometer" model 153 X10V-40F1. The recorder had a potential range of zero to ten millivolts which corresponded to a temperature range of approximately 250°C . A "Cahn Recorder Control" was inserted into the thermocouple circuit and adjusted so that 1000°C corresponded approximately to nine millivolts on the recorder. The calibration was made in terms of millivolts of the recorder against the known freezing points of the following pure metals: silver, aluminum, antimony, zinc, cadmium, bismuth, tin, indium. The above metals were either of highest purity, i.e. 99.99% + or standard reagent grade. At the same time the potential across the recorder leads was measured with a "Tinsley Potentiometer" type 3387B against a standard cell. The null-point detector was a "Leeds Northrup" galvanometer, sensitivity $.0004\mu\text{A}/\text{mm}$. Such measurements with the potentiometer were performed later periodically as a check on the recorder measurements.



THERMAL ANALYSIS APPARATUS



THERMOCOUPLE CIRCUIT

Fig. 15

Free cooling was employed i.e. the temperature vs time curve was of exponential form. To obtain a slow enough initial rate of cooling from high temperature, cooling was done in two stages, viz. from high temperature to approximately 400°C and then to room temperature. This was achieved by lowering the current first to the desired value (as read off the "amperes vs. temperature" graph) then when this temperature (400°C) was nearly reached the current was shut off and the furnace allowed to reach room temperature. The average rate of cooling was 1.5°C per minute. Inflection points which were difficult to discern from cooling curves were re-investigated by heating curves.

The potential could be read off the recorder-graph to within $\pm .01$ millivolts which corresponded to $\pm 1.0^{\circ}\text{C}$. The error in temperature due to reading off temperatures from the calibration graph was $\pm .5^{\circ}\text{C}$. The temperatures given in the "thermal analysis data" are considered to be accurate to within $\pm 2.0^{\circ}\text{C}$.

To prevent reaction of the molten alloy with atmospheric constituents, alloys were melted and cooled under argon atmosphere in a "vicor" cell shown in Fig. 16. The cell could be evacuated, filled with argon and connected to a mercury valve to allow for expansion of the gas during heating.

The leads of one thermocouple were sealed into a ground glass stopper which fitted into the top of the cell. The second

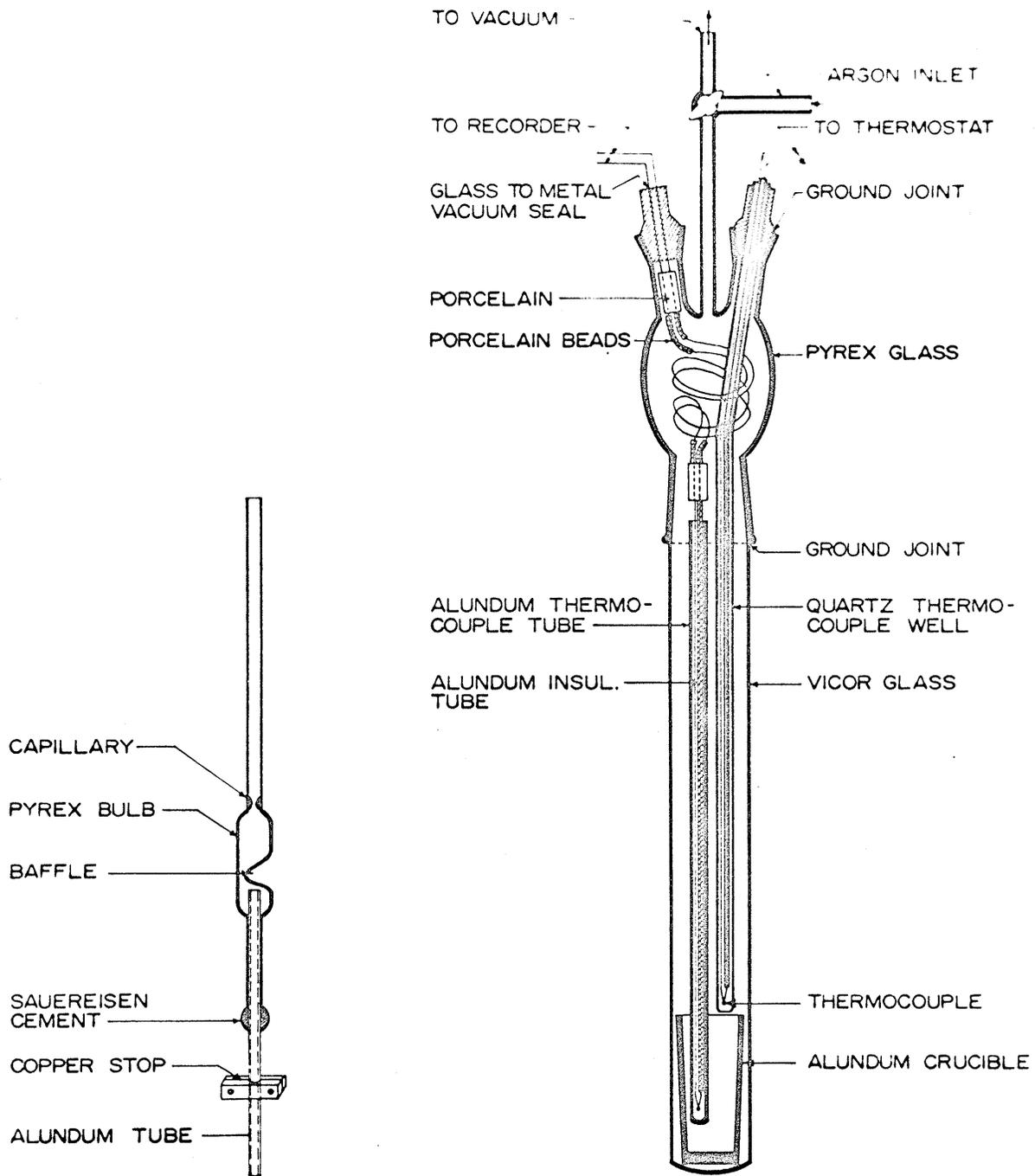
thermocouple was introduced into a thermocouple well formed by sealing the quartz glass thermocouple shield to a ground glass joint which fitted also into another socket in the cell top.

d. Isothermal Apparatus

The schematic circuit diagram of Fig. 15 with switch "A" in position 2 and switch "C" closed refers to this apparatus. Switch "C" introduces a "Wheelco" thermostat into the circuit. The thermostat was sensitive to 1°C temperature fluctuations.

Two chromel-alumel thermocouples were used simultaneously. One, alundum-shielded, placed in the melt and connected to the "Brown" recorder (described under "Thermalanalysis") served as a temperature indicator. The second thermocouple, quartz-glass shielded, placed just above the alloy was connected to the thermostat and served as a temperature control. This arrangement minimized temperature fluctuations. A thermocouple which is not immersed in the alloy can follow temperature fluctuations of the heating element with much less lag in time than one which is placed in the alloy. The thermostat was calibrated in terms of the thermocouple placed in the alloy, using the same standards as previously described. The thermocouple circuit is shown in Fig. 15 . The control-thermocouple which activates the thermostat is not shown in the circuit diagram, but is shown in Fig. 16 .

An example will illustrate the operation of this apparatus.



ALLOY PIPETTE

ISOTHERMAL AND THERMAL ANALYSIS CELL

Fig. 16

Suppose 700° was the desired temperature to be kept constant. Firstly, with switch "A" in position 1, the current through the heating element was adjusted with the variable transformer to give approximately 720° C. The value of this current was read off the "temperature vs. current" graph. Secondly, with switch "A" in position 2, the current was adjusted to give approximately 690° C. With switch "A" in the latter position, and switch "C" closed the thermostat was set at 700° C to maintain this temperature constant.

With this arrangement current was flowing through the heating element at all times, and only an additional small current was drawn when the thermostat closed. If the desired temperature was "bracketed" closely enough the temperature could be maintained constant within $\pm 1.0^{\circ}$ C over the entire temperature range of 900° C.

e. Preparation of Alloys

Three milliliters capacity zircon-ceramic crucibles were used for melting alloys for density determinations. The components were weighed out to $\pm .0002$ gms to give the desired composition with a total volume of alloy of two milliliters.

Alloys were prepared for density determinations at 10% composition intervals in each component throughout the ternary system. The alloys were melted in an "Ajax" induction furnace under argon atmosphere.

For thermal and isothermal analysis larger samples of alloy were used; approximately forty grams to begin with. These alloys were melted in twenty-five ml capacity "high purity" alundum crucibles. For thermal analysis successive alloys were obtained from the original alloy by adding increments of one component along a line of constant ratio of concentration of the other two components.

An "Ajax" induction furnace was used for melting the alloys. The furnace had the dual advantage of rapidly attaining high temperature and of stirring the molten metal by induced currents. To ensure homogeneous composition the alloys were held at approximately 1000°C for ten minutes in the induction furnace. The density-alloys were then cooled to room temperature. The thermal analysis and isothermal analysis alloys were transferred to the preheated resistance furnace.

To prevent reaction with atmospheric constituents all alloys were melted in a "vicor" cell (Fig. 16) which fitted into the induction furnace as well as into the resistance furnace. Prior to melting the cell was evacuated and filled with argon. The arrangement was such that the cell with the molten alloy and the thermocouples properly inserted could be transferred from the induction furnace to the resistance furnace in a matter of seconds without having to open the cell and remove the alloy.



f. Sampling

For isothermal analysis the alloys were equilibrated at the desired temperature for fourteen hours. The cell top could be removed for sampling without having to remove the thermocouple which was in the alloy. Samples of alloy were withdrawn from the top and bottom layers at the desired temperature with the pipette shown in Fig. 16. The depth to which the lower end of the pipette tube was to be introduced into the molten alloy could be controlled

by means of a clamp which was attached to the pipette tube and which served as a stop (Fig. 16). The part of the pipette which was introduced into the alloy, a thin alundum tube, was cemented into the pyrex glass pipette bulb.

Before samples were withdrawn argon was flushed through the pipette and the rate of flow was then reduced sufficiently so as not to stir up the alloy when the pipette was introduced into the molten alloy. The slight pressure in the pipette prevented the top layer from entering the pipette if the bottom layer was to be sampled. Molten alloy was sucked into the pipette by connecting it to a vacuum line for a very short time by means of a three-way stopcock, and then switching back again quickly to the argon line. Two to three milliliters of sample were withdrawn. Immediately after a sample was withdrawn, the pipette was removed from the cell and quickly immersed in cold water. The time required for withdrawing the sample and quenching was usually less than thirty seconds. The cracked glass was carefully removed from the alloy which was then chopped up into small pieces on a shear for density determinations and chemical analysis.

g. Density Determination

Densities were determined with a 25 ml pycnometer in the usual manner. "Practical" redistilled n-butyl ether was used as a density medium. Distilled water could not be used because some alloys

reacted with it. All densities given in table I were determined at $(25.00 \pm 0.02)^{\circ}\text{C}$. The time allowed to reach equilibrium was thirty minutes.

The volume of the pycnometer was established from the known density of water at 25°C (25). The density of n-butyl ether at the same temperature was then determined. The density of the alloy was then calculated from the following formula after the necessary weighings were performed.

$$D_M = \frac{W_M D_E}{W_E - W_{(E' + M)} + W_M}$$

Where D_M = density of alloy in gm/cc at 25°C
 D_E = density of ether in gm/cc at 25°C
 W_E = weight of pycnometer plus weight of ether
 $W_{(E' + M)}$ = weight of pycnometer plus ether plus alloy
 W_M = weight of alloy

Each density given in Table III is the average of at least two separate density determinations performed on the same alloy. The error in the density is considered to be ± 0.002 gm/cc. A single-pan balance was used, and no correction for variation in atmospheric pressure was made. In Fig. 17 density vs. concentration of silver in the alloy was plotted at constant concentrations of indium. From these graphs the composition of ternary alloys was

was determined after the density and the silver concentration were ascertained. In practice the densities were plotted on a large-enough scale so that the error in reading the graph was not larger than the experimental errors. A more detailed description is given on page 49.

h. Chemical Analysis

Because of the chemical similarity of indium and aluminum, the determination of one element in the presence of the other by chemical means is difficult.

It was attempted at first to determine indium in the alloy by flame photometry. The two strong lines of indium at 4102 Å and 4511 Å were utilized for this purpose (14). Indium can apparently be determined successfully by flame photometry with an oxygen-acetylene flame (51,52), and with an oxygen-hydrogen flame (23,43). The instrument used in the present work was a "Perkin-Elmer" model 146 flame photometer, which was not easily adaptable for use with oxygen-acetylene or oxygen-hydrogen. These trial analyses were carried out with an air-acetylene flame.

The alloys were dissolved in concentrated nitric acid; the final solutions were approximately 1 M or less in nitric acid. Standard solutions were prepared from standard grade indium metal.

The analysis for indium by this method was always low, from one to three per cent at both wave lengths, with no consistency

in low results. To ascertain if the low results were due to loss of solution in the preliminary preparations, analysis for silver (AgCl) was carried out subsequent to flame photometry in each case. The results for silver gave within experimental error (7.5 parts per thousand), the synthetic composition. Aluminum could not be analyzed for at all by this method, presumably because of the low emission intensity of aluminum from aqueous solutions (15).

The low precision obtained with this particular apparatus made it impossible to analyze for indium to the desired accuracy and the method was abandoned.

According to M. Flaschka and F. Sadek (20) V. Suk and M. Malat (54) indium and aluminum can be determined in the presence of each other by E.D.T.A. titration. The procedure adopted was that of C.L. Wilson and D.W. Wilson (65) which is essentially that of M. Flaschka and F. Sadek (20).

A calculated excess of standard E.D.T.A. was added to the aqueous sample, containing indium, aluminum and silver. The pH was adjusted to 2.5 with ammonia and the excess E.D.T.A. was back-titrated with standard bismuth nitrate solution, using pyrocatechol violet as indicator. Before the end point was reached the pH was checked and re-adjusted if necessary. At this low pH value only, indium forms a sufficiently strong complex with E.D.T.A. If the pH is lowered to 4.5 after indium has been titrated, aluminum can be determined in the same sample in the same manner.

In practice a very indistinct end point was obtained.

Titration very slowly and heating the solution to 60°C did not improve the end point. H. Flaschka and F. Sadek (20) state that the back titration with bismuth in the presence of aluminum is characterized by a very poor end point and only if the amount of aluminum present is small is it possible to determine indium in the presence of aluminum. The direct titration of indium with E.D.T.A. is usually considered impractical because of the slow rate of indium-E.D.T.A. complex formation.

The precision of results attained due to the poor end point was such that the method had to be abandoned.

The method of precipitating aluminum and indium by the 8-hydroxy quinoline, weighing them as a mixture of $\text{Al}(\text{C}_9\text{H}_7\text{NO})_3$ and $\text{In}(\text{C}_9\text{H}_7\text{NO})_3$ then igniting to the oxides and weighing as such was thought to be worthwhile investigating.

The determination of aluminum by 8-hydroxy quinoline is well known (64), (42). The pH range for quantitative precipitation is 4.2 to 9.8 (19). Similarly, indium is precipitated with the same reagent (50) though the procedure differs somewhat from that for the aluminum precipitation and the pH range for complete precipitation is apparently not established. The procedure adopted was that for the determination of indium given by S.J. Lyle (66).

When standard solutions of indium plus aluminum were analyzed in this way the results obtained from the quinolate precipitation were always somewhat low. When the mixture of quinolates was ignited to the oxide according to standard procedure (42)

the precipitate melted in each case before it was oxidized. Slow heating and introducing a stream of oxygen into the furnace did not eliminate this difficulty. Since the precipitates were contained in porous-bottom porcelain crucibles the melting of the precipitate and the consequent loss of precipitate through the bottom of the crucible could not be tolerated. This method of analysis was not pursued any further.

A separation of indium from aluminum was attempted. After silver was removed as AgBr, indium was extracted with ethyl ether from 4 M aqueous HBr (35,44). It was found that when the ratio of aluminum to indium was approximately 50:50 percent or higher, some aluminum was extracted with the indium in one extraction. This was deduced from the fact that the determination of aluminum in the aqueous layer (quinolate) were low and the indium determination in the organic layer (quinolate) was high. Two or more extractions increased the extent of co-extraction.

Since the alloys to be analyzed would contain more aluminum than indium in many instances, this method of analysis was also abandoned.

One of the earliest methods of determining indium was tried, viz. titration with ferrocyanide. The method followed was that given by (68) which is essentially the same as that of R. Belcher and associates (7). 3:3' dimethylnaphthidine was used as visual indicator.

Indium could not be determined satisfactorily in the presence of aluminum by this method because of a very indistinct end point, hence this method was abandoned after some trials. When pure indium solutions were titrated, the end point was sharp.

Finally, a combination of physical and chemical methods was found to be satisfactory for the determination of composition.

Densities of alloys varying in composition by ten per cent in each component throughout the ternary system were determined and plotted versus the percentage of silver at ten per cent intervals of indium as shown in Fig. 17. Silver was determined satisfactorily in the presence of indium and aluminum by Volhard's method (67) which is well known and will not be described in detail here.

To determine the composition of an alloy its density and silver content were determined; this fixed a point between two lines of constant-indium composition in Fig. 17. To obtain the composition of indium, the distance between the two constant indium composition lines was divided into ten equal parts along the vertical given by the percentage of silver. The percentage of indium could be read off to ± 0.5 to ± 0.3 per cent depending on the distance the two constant-indium lines were apart. The knowledge of the percentages of indium and silver determined the composition of the alloy.

CHAPTER IV

EXPERIMENTAL RESULTS

The results are given in tabulated and graphical form.

TABLE III

a.) COMPOSITION - DENSITY

Alloy Number	Alloy Composition as Weight %			gm/cc
	In	Ag	Al	Density
Al	0	0	100.00	2.697
1 D	0	10.00	89.99	2.885
2 D	0	20.00	79.99	3.125
3 D	0	30.03	69.97	3.477
4 D	0	39.99	60.00	3.860
5 D	0	50.00	49.99	4.268
6 D	0	60.00	39.99	4.891
7 D	0	69.99	30.00	5.666
8 D	0	79.97	20.02	6.704
9 D	0	89.98	10.01	8.352
Ag	0	100.00		10.648
19 D	10.00	0	90.00	2.884
10 D	9.98	10.02	88.00	3.177
11 D	9.97	20.45	69.58	3.499

Continued

TABLE III - Continued

Alloy Number	Alloy Composition as Weight %			gm/cc
	In	Ag	Al	Density
12 D	9.99	30.00	60.00	3.814
13 D	9.99	40.00	50.00	4.232
14 D	10.00	50.00	40.00	4.825
15 D	10.00	60.00	30.00	5.570
16 D	9.99	69.99	20.00	6.593
17 D	10.00	80.00	70.00	8.130
18 D	9.63	90.36	0	10.334
20 D	20.00	0	79.99	3.180
21 D	20.00	10.00	70.00	3.430
22 D	20.00	20.00	60.00	3.782
23 D	19.99	30.00	50.00	4.192
24 D	20.00	40.00	39.99	4.624
25 D	22.01	44.96	33.03	5.452
26 D	20.00	59.98	20.00	6.460
27 D	20.00	70.00	10.00	7.802
28 D	20.00	79.99	0	10.126
29 D	29.99	0	70.00	3.332
30 D	30.00	9.99	60.00	3.688
31 D	30.00	20.00	49.99	4.125
32 D	30.00	30.00	40.00	4.732
33 D	30.00	39.99	29.99	5.482

Continued

TABLE III - Continued

Alloy Number	Alloy Composition as Weight %			gm/cc
	In	Ag	Al	Density
34 D	30.00	50.00	19.99	6.371
35 D	30.00	60.00	10.00	7.528
36 D	29.99	70.00	0	9.916
37 D	40.00	0	60.00	3.612
38 D	40.00	9.99	49.99	3.943
39 D	40.00	20.00	40.00	4.614
40 D	40.00	30.01	29.97	5.303
41 D	39.99	40.00	20.00	6.075
42 D	40.00	49.99	10.00	7.283
43 D	40.00	59.99	0	9.521
44 D	50.00	0	50.00	3.944
45 D	50.00	10.01	39.99	4.344
46 D	50.00	19.99	30.00	5.000
47 D	50.00	30.00	20.00	5.886
48 D	49.99	40.00	10.00	7.075
49 D	49.99	49.99	0	9.116
50 D	60.00	0	40.00	4.343
51 D	59.99	10.00		4.825
52 D	60.00	20.00	20.00	5.743
53 D	60.00	29.99	10.00	6.796
54 D	59.99	40.00	0	8.568
55 D	70.00	0	29.99	4.833
56 D	70.00	10.00	19.99	5.570

Continued

TABLE III - Continued

Alloy Number	Alloy Composition as Weight %			gm/cc
	In	Ag	Al	Density
57 D	69.99	20.00	10.00	6.755
58 D	69.99	30.00	0	8.213
59 D	80.00	0	20.00	5.446
60 D	79.98	10.01	10.00	6.550
61 D	79.99	20.00	0	7.855
62 D	90.00	0	10.00	6.238
63 D	90.00	10.00	0	7.521

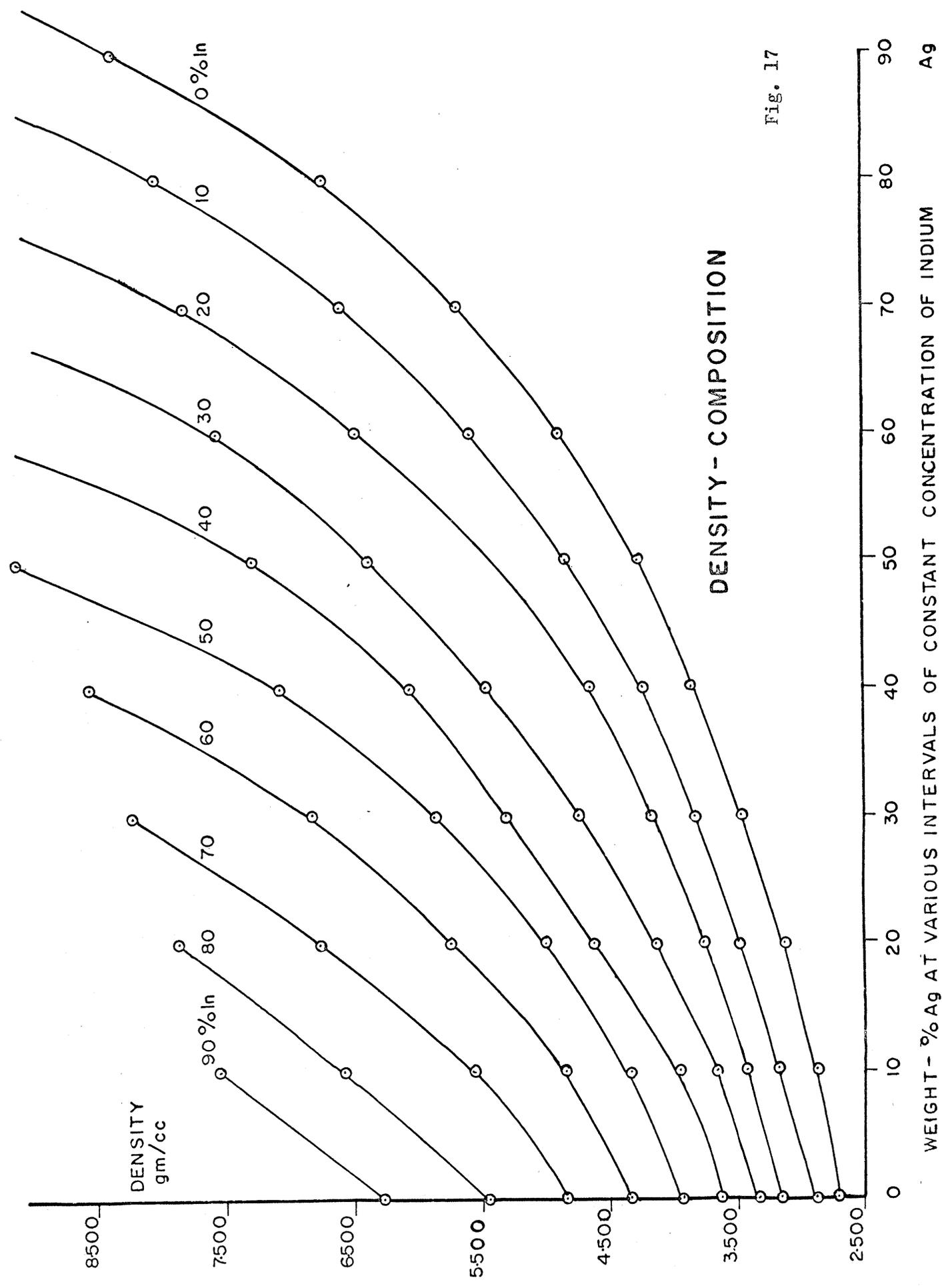


Fig. 17

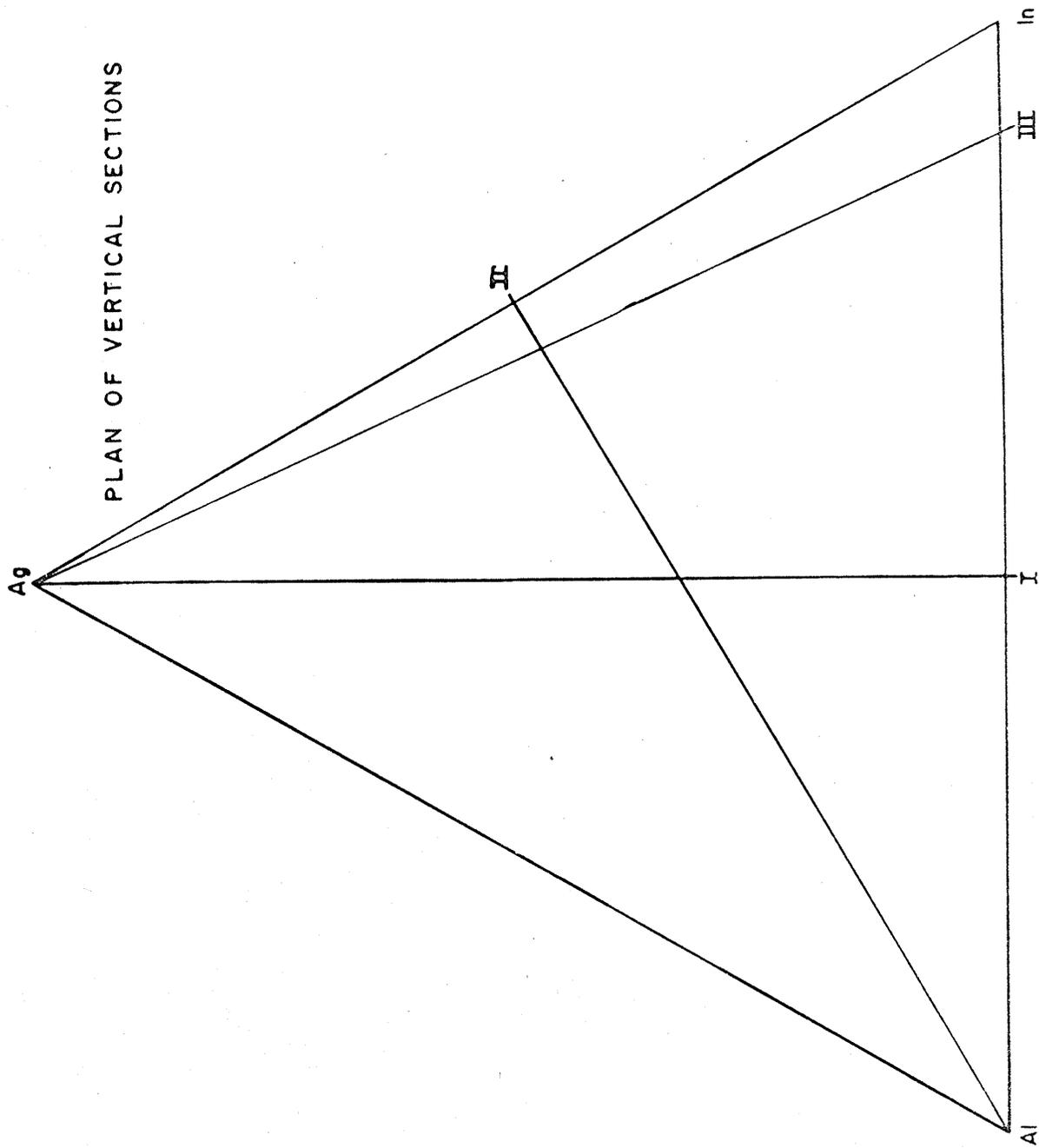


Fig. 18

TABLE IV

b.) THERMAL ANALYSIS DATA, VERTICAL SECTION I

	Composition in Weight - %			Temp. °C Liquidus	Temp. °C Inflections	Temp. °C Halts
	In	Ag	Al			
1	1.00	98.00	1.00	921.0	884.0	
2	1.96	96.08	1.97	887.0	822.0	
3	3.00	94.00	3.00	849.0	779.0	
4	4.00	92.00	4.00	814.0	760.0	
5	4.50	91.00	4.50	796.0	762.0	
6	5.00	90.00	5.00	774.0	761.0	590.0
7	5.50	89.00	5.50	757.0		588.0
8	7.00	88.00	6.00	748.0		588.0
9	6.50	87.00	6.50	742.0	737.0 613.0 597.0	
10	7.00	86.00	7.00	732.0	722.0 699.0 635.0	
11	7.50	85.00	7.50	724.0	713.0 678.0 663.0	
12	8.00	84.00	8.00	712.0	682.0	
13	8.50	83.00	8.50	697.0	690.0 375.0	
14	9.00	82.00	9.00	688.0		
15	9.50	81.00	9.50	683.0		
16	10.00	80.00	10.00	678.0		

Continued

TABLE IV - Continued

	Composition in Weight - %			Temp. °C Liquidus	Temp. °C Inflections	Temp. °C Halts
	In	Ag	Al			
17	11.01	77.99	11.00	663.0		
18	12.00	76.00	12.00	652.0		143.0
19	13.27	73.46	13.27	631.0	507.0	144.0
20	15.01	69.99	15.00	601.0	512.0	143.0 148.0
21	16.91	66.19	16.90	573.0	518.0	143.0 148.0
22	18.76	62.49	18.75	546.0	522.0 483.0 458.0	143.0 147.0
23	20.01	59.99	20.00	528.0	524.0	143.0 148.0
24	23.00	54.02	22.98	542.0	518.0	143.0 148.0
25	26.26	47.50	26.25	559.0	512.0	143.0 147.0
26	28.64	42.72	28.64	570.0	510.0 165.0	143.0 147.0
27	31.03	37.94	31.03	581.0	506.0 188.0 165.0	143.0 148.0
28	33.27	33.37	33.36	588.0	507.0	143.0 148.0
29	35.01	29.99	35.00		591.0 506.0	144.0 149.0
30	37.51	24.99	37.50		600.0 503.0	141.0 148.0
31	39.52	20.97	39.51		606.0 494.0	143.0
32	41.11	17.79	41.10		611.0	143.0

Continued

TABLE IV - Continued

	Composition in Weight - %			Temp. °C Liquidus	Temp. °C Inflections	Temp. °C Halts
	In	Ag	Al			
33	44.41	11.20	44.40		621.0	143.0
34	47.31	5.40	47.30		629.0	143.0
35	48.51	3.00	48.50		635.0	143.0
36	50.01	49.99			644.0	154.0

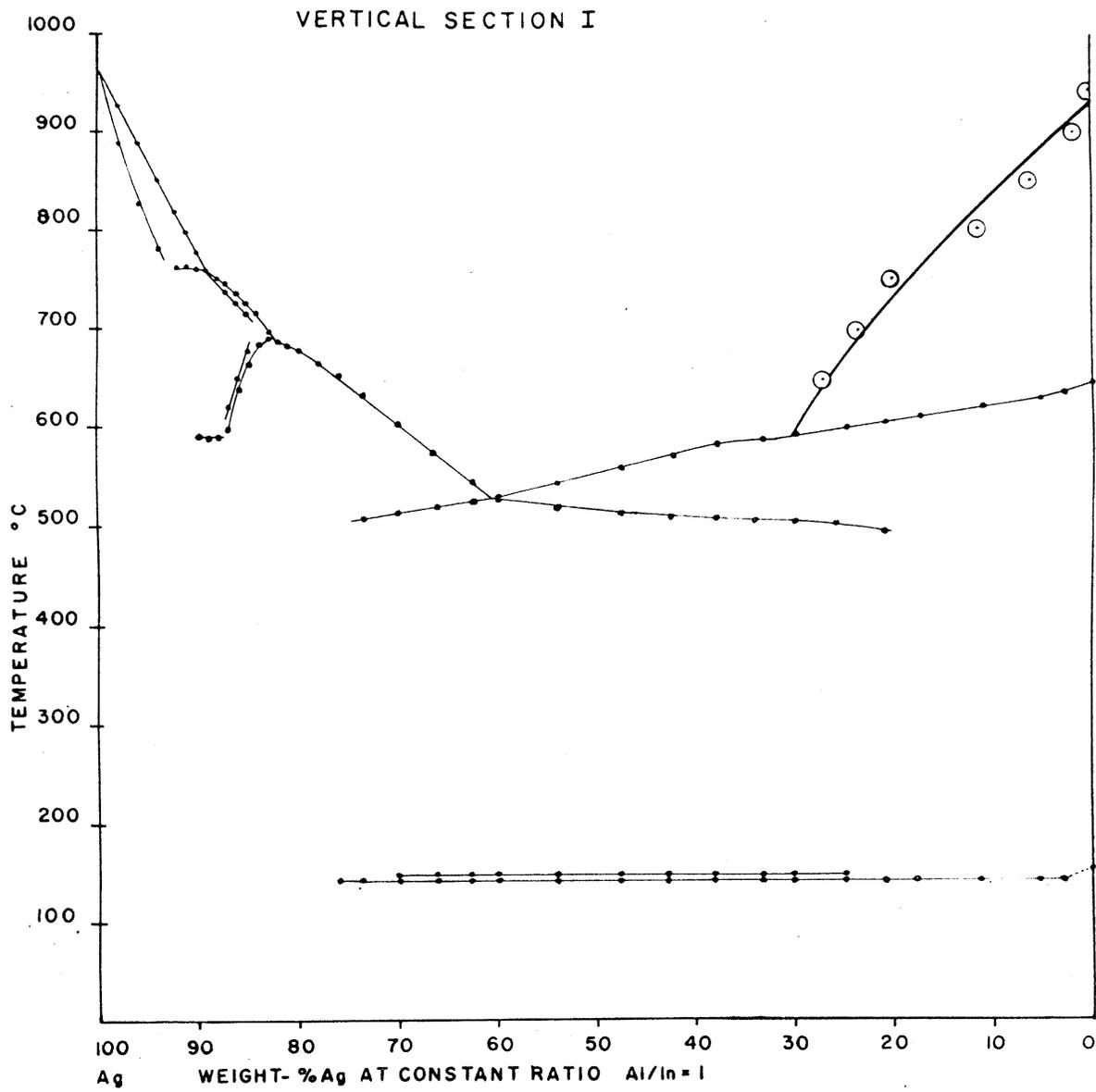


Fig. 19

TABLE V
THERMAL ANALYSIS DATA, VERTICAL SECTION II

	Composition in Weight %			Temp. °C Liquidus	Temp. °C Inflections	Temp. °C Halts
	In %	Ag %	Al %			
37	50.00	50.00		525.0		207.0 166.0 143.0
38	49.75	49.75	.50	482.0	232.0 152.0 164.0	143.0
39	49.49	49.49	1.01	483.0	178.0 159.0	143.0
40	49.00	49.00	2.00	509.0	403.0 398.0 330.0 323.0	239.0 147.0 143.0
41	48.75	48.75	2.50	521.0		239.0 147.0 144.0
42	48.50	48.50	3.00	528.0		241.0 --- 143.0
43	48.01	48.01	3.98	173.0		--- --- 141.0
44	47.50	47.50	5.00	537.0	482.0 192.0 150.0	241.0 143.0
45	47.00	47.00	6.00	533.0		143.0
46	46.50	46.50	7.00	528.0	154.0 192.0	243.0 141.0
47	46.00	46.00	8.00	524.0	500.0 447.0	148.0 143.0

Continued

TABLE V - Continued

	Composition in Weight %			Temp. °C Liquidus	Temp. °C Inflections	Temp. °C Halts
	In %	Ag%	Al %			
48	45.81	45.81	8.38	520.0	503.0 447.0	147.0 143.0
49	45.46	45.46	9.09	516.0		505.0 148.0 143.0
50	45.00	45.00	10.00	510.0	442.0	506.0 148.0 143.0
51	44.50	44.50	11.00	524.0	334.0	506.0 149.0 143.0
52	44.00	44.00	12.00	536.0	273.0	506.0 148.0 143.0
53	43.50	43.50	13.00	532.0	199.0	506.0 148.0 143.0
54	43.25	43.25	13.50	532.0	179.0	507.0 148.0 143.0
55	43.00	43.00	14.00	541.0	172.0	507.0 148.0 143.0
56	42.50	42.50	15.00	546.0	348.0 177.0	506.0 148.0 143.0
57	42.25	42.25	15.50	547.0	435.0	510.0 148.0 143.0
58	41.98	41.98	16.04	554.0		510.0 148.0 143.0

Continued

TABLE V - Continued

	Composition in Weight %			Temp. °C Liquidus	Temp. °C Inflections	Temp. °C Halts
	In	Ag	Al			
59	41.50	41.50	17.00	561.0		508.0 148.0 143.0
60	41.00	41.00	18.00	563.0		508.0 148.0 143.0
61	40.50	40.50	19.00	567.0		508.0 148.0 143.0
62	40.00	40.00	20.00	569.0		507.0 148.0 143.0
63	39.00	39.00	22.00	571.0		507.0 148.0 143.0
64	37.50	37.50	25.00	576.0		506.0 149.0 143.0
65	33.27	33.37	33.36	587.0		506.0 149.0 144.0
66	32.50	32.50	35.00	588.0		507.0 148.0 143.0
67	28.60	28.60	42.80	599.0		505.0 --- ---
68	23.00	23.00	54.00	609.0	457.0	--- --- ---
69	16.80	16.80	66.40	623.0		143.0
	---	---	100.00	659.7	---	

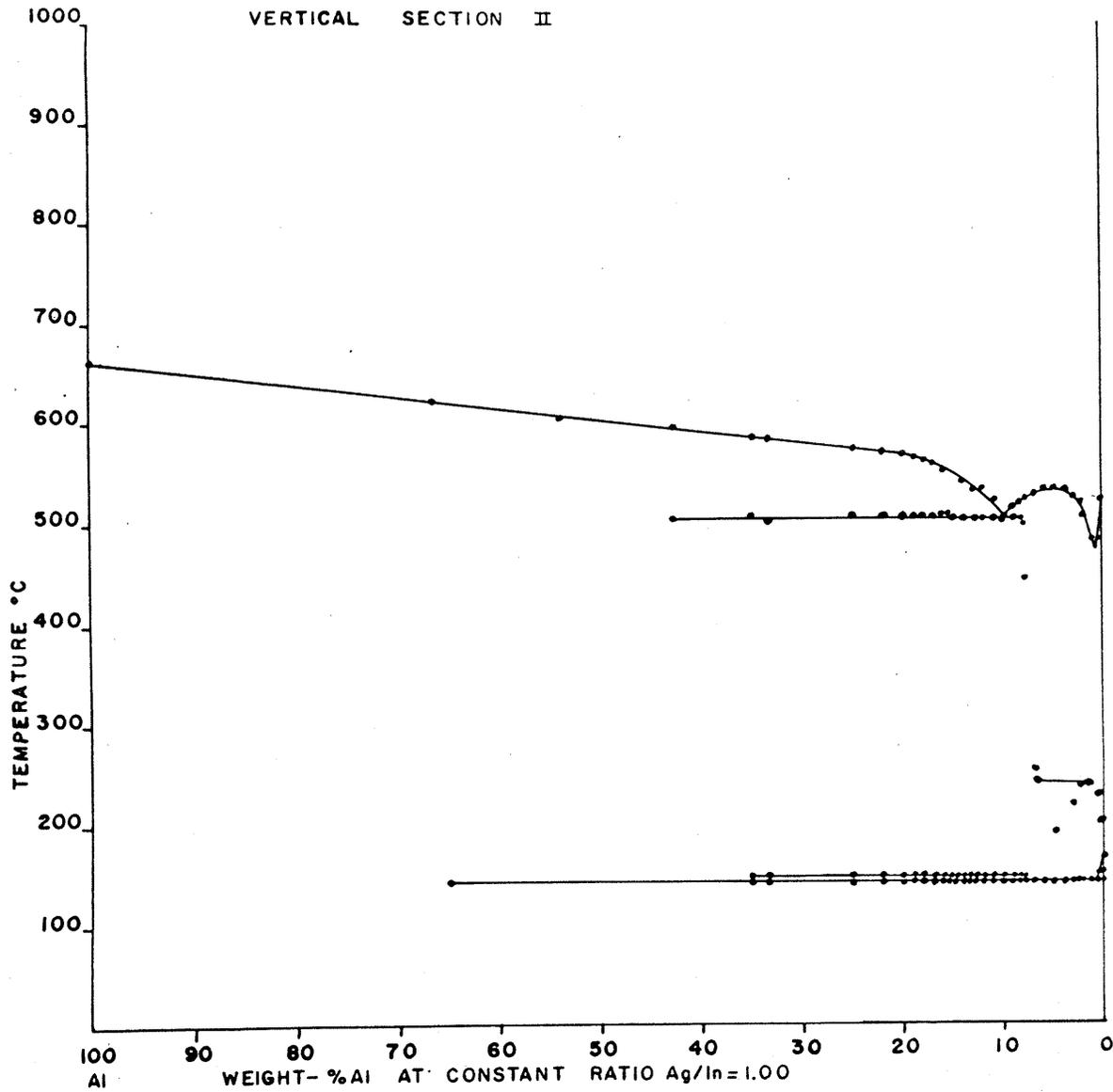


Fig. 20

TABLE VI
THERMAL ANALYSIS DATA, VERTICAL SECTION III

	Composition in Weight %			Temp. °C Liquidus	Temp. °C Inflections	Temp. °C Halts
	In %	Ag %	Al%			
70	89.11	.90	9.99	639.0		148.0 143.0
71	87.22	3.00	9.78	634.0		143.0 143.0
72	85.43	5.00	9.57	631.0		--- 143.0
73	83.63	7.00	9.37	628		--- 143.0
74	81.83	9.00	9.17	622.0		--- 143.0
75	80.03	11.00	8.97	614.0		148.0 143.0
76	78.23	13.00	8.77	609.0		--- ---
77	76.43	15.00	8.57	605.0		148.0 143.0
78	74.63	17.00	8.37	601.0		--- 143.0
79	72.84	19.00	8.16	595.0		148.0 143.0
80	71.04	21.00	7.96	589.0	458.0	150.0 143.0
81	69.24	23.00	7.76	581.0	473.0	--- ---
82	67.44	25.00	7.56	572.0	483.0	149.0 143.0
83	65.64	27.00	7.36	560.0	490.0	--- 143.0

Continued

TABLE VI - Continued

	Composition in Weight %			Temp. °C Liquidus	Temp. °C Inflections	Temp. °C Halts
	In %	Ag %	Al %			
84	63.84	29.00	7.16	549.0	495.0	--- 143.0
85	62.05	31.00	6.95	539.0	499.0	--- ---
86	60.25	33.00	6.75	531.0	504.0	--- ---
87	58.45	35.00	6.55	524.0	502.0	148.0 143.0
88	56.62	37.04	6.35	512.0	501.0	--- 143.0
89	54.85	39.00	6.15	520.0	490.0	143.0
90	53.05	41.00	5.95	527.0	368.0	143.0
91	51.25	43.00	5.74	531.0		143.0
92	49.46	45.00	5.54	533.0		143.0
93	47.66	47.00	5.34	541.0		143.0
94	45.86	49.00	5.14	548.0		143.0
95	44.06	51.00	4.94	552.0		143.0
96	42.26	53.00	4.74	556.0	222.0	143.0
97	40.46	55.01	4.53	562.0	227.0	144.0
98	38.67	57.00	4.33	568.0		240.0 145.0 ? 143.0
99	36.87	59.00	4.13	573.0		242.0 145.0
100	35.07	61.00	3.93	576.0		241.0 143.0

Continued

TABLE VI - Continued

	Composition in Weight %			Temp. °C Liquidus	Temp. °C Inflections	Temp. °C Halts
	In	Ag	Al			
101	33.27	63.00	3.73	584.0		241.0 143.0
102	31.47	65.01	3.53	597.0		240.0 143.0
103	29.67	67.00	3.33	611.0		240.0 143.0
104	27.87	69.00	3.12	630.0	235.0	---
105	76.08	71.00	2.92	662.0	625.0	---

TABLE VII

POINTS ON "TROUGHs" IN TERNARY SYSTEM

Temp. °C	Composition in Weight - %			Vertical Section
	% In	% Ag	% Al	
760.0	5.4	89.3	5.3	I
692.0	8.6	82.7	8.7	I
527.0	19.7	60.5	19.8	I
590.0	34.7	30.5	34.8	I
468.0	49.7	49.7	0.6	II
510.0	45.0	45.0	10.0	II
610.0	79.4	11.7	8.9	III
513.0	56.7	37.0	6.3	III
577.0	34.0	62.2	3.8	III
620.0	28.3	68.5	3.2	III

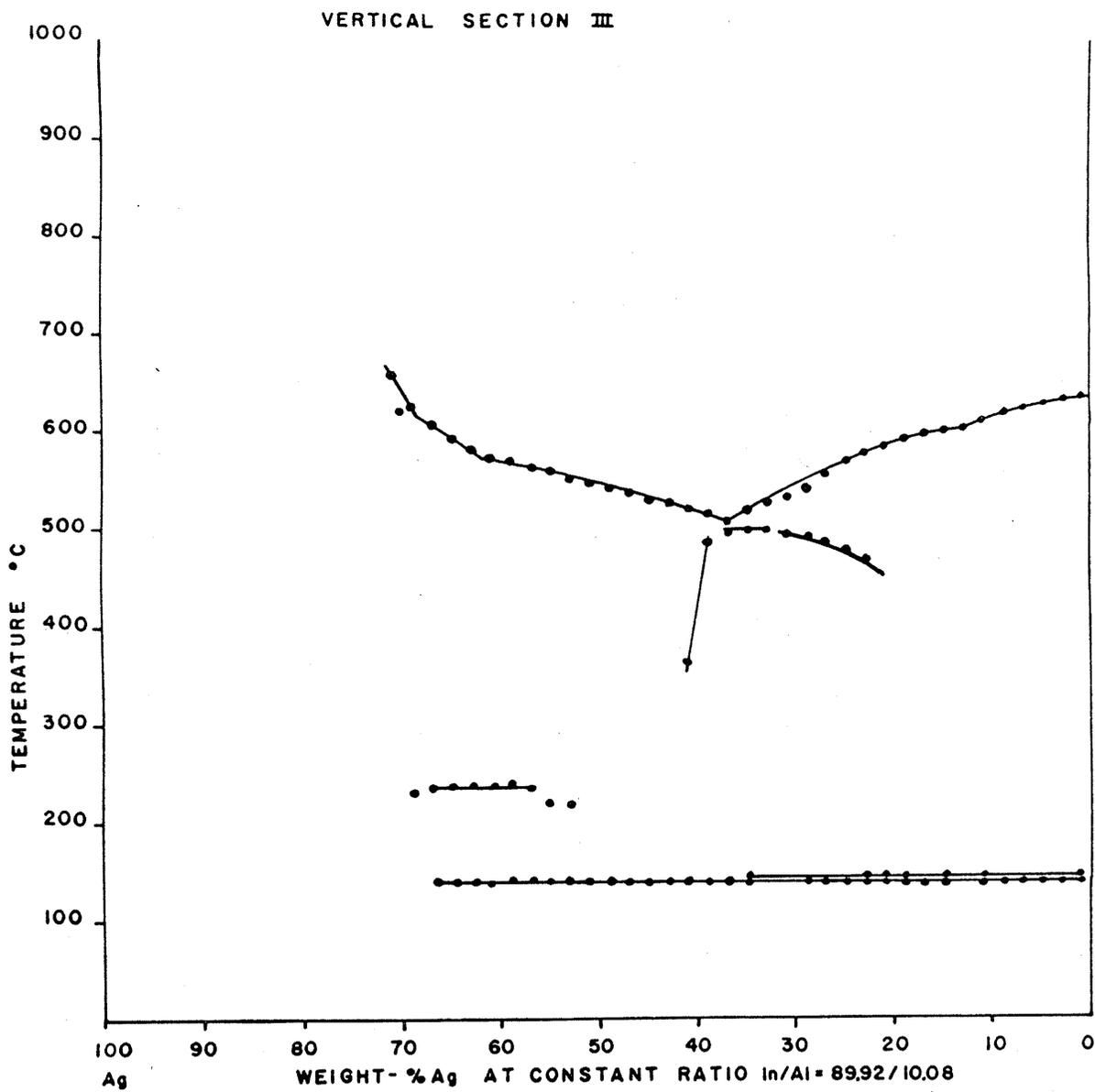


Fig. 21

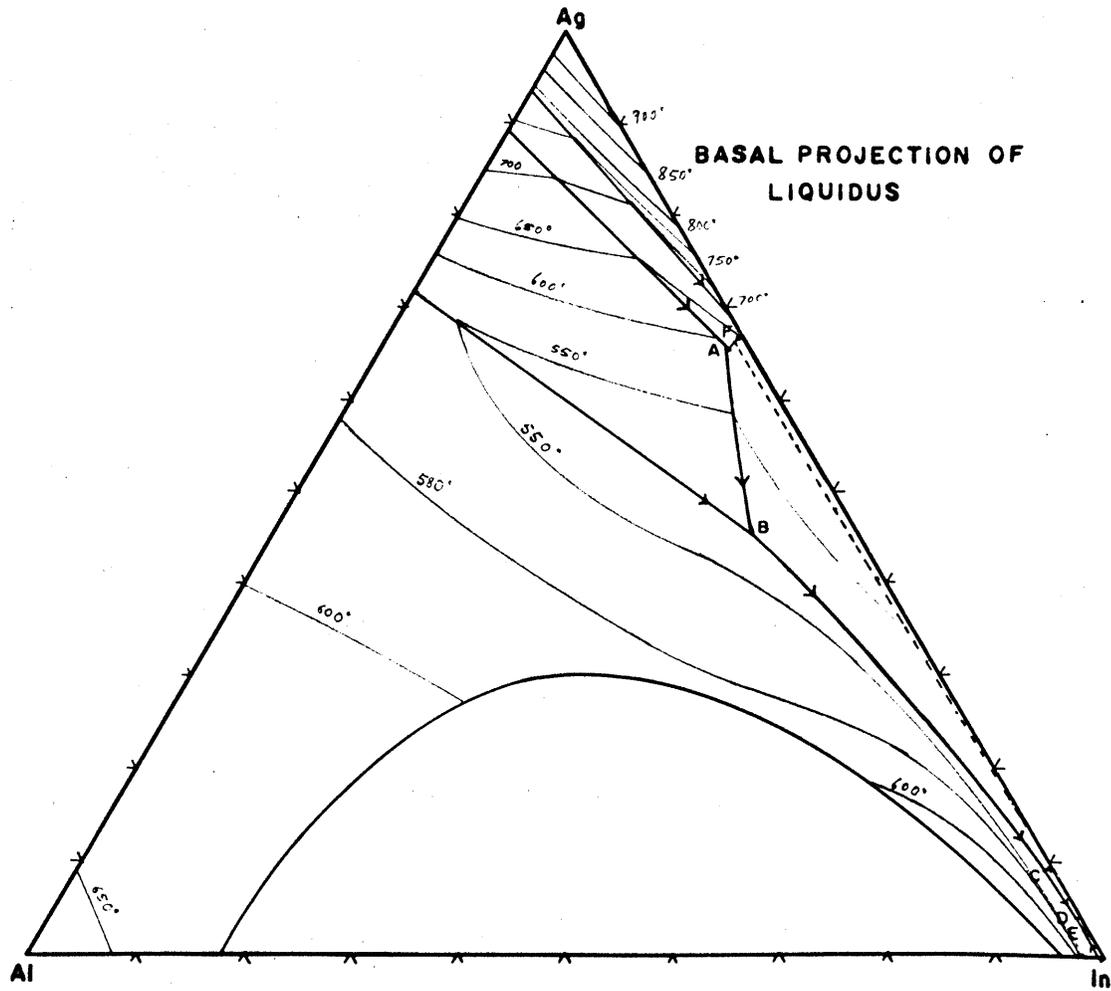


Fig. 22

TABLE VIII

c.)

TERNARY "GAP" ISOTHERMS

Temp. °C	Composition in Weight Percent					
	Al - Rich Layer			In - Rich Layer		
	% In	% Ag	% Al	% In	% Ag	% Al
650	19.1	---	80.9	96.5	---	3.5
"	18.2	8.0	73.8	91.4	4.1	4.5
"	---	---	---	86.8	7.4	5.8
"	21.6	20.7	57.7	80.1	12.1	7.8
"	39.0	27.2	33.8	58.7	23.6	17.7
700	22.1	---	77.9	96.8	---	3.2
"	23.6	13.0	63.4	85.2	7.5	7.3
"	-----	---	---	90.0	3.9	6.1
"	28.1	21.2	50.7	80.0	11.9	8.1
"	36.0	24.1	39.9	55.9	23.0	21.1
750	26.9	---	73.1	93.9	---	6.1
"	32.5	11.5	56.0	88.7	3.8	7.5
"	---	---	---	82.9	7.6	9.5
"	40.9	20.0	39.1	74.2	13.2	12.6
"	51.2	22.5	26.3	56.9	21.0	22.1
800	33.6	---	66.4	91.5	---	8.4
"	37.2	6.1	56.7	81.0	4.7	14.3
"	43.8	11.8	44.4	78.8	7.8	13.4
"	46.4	12.5	41.4	75.0	10.0	15.0
"	56.0	16.9	27.1	59.7	15.0	25.3
850	40.0	---	60.0	90.8	---	9.2
"	46.4	5.2	48.4	84.4	3.9	11.7
"	56.3	10.5	33.2	72.3	8.8	18.9
900	48.2	---	51.8	87.2	---	12.8
"	59.1	4.9	36.0	62.2	5.6	32.2

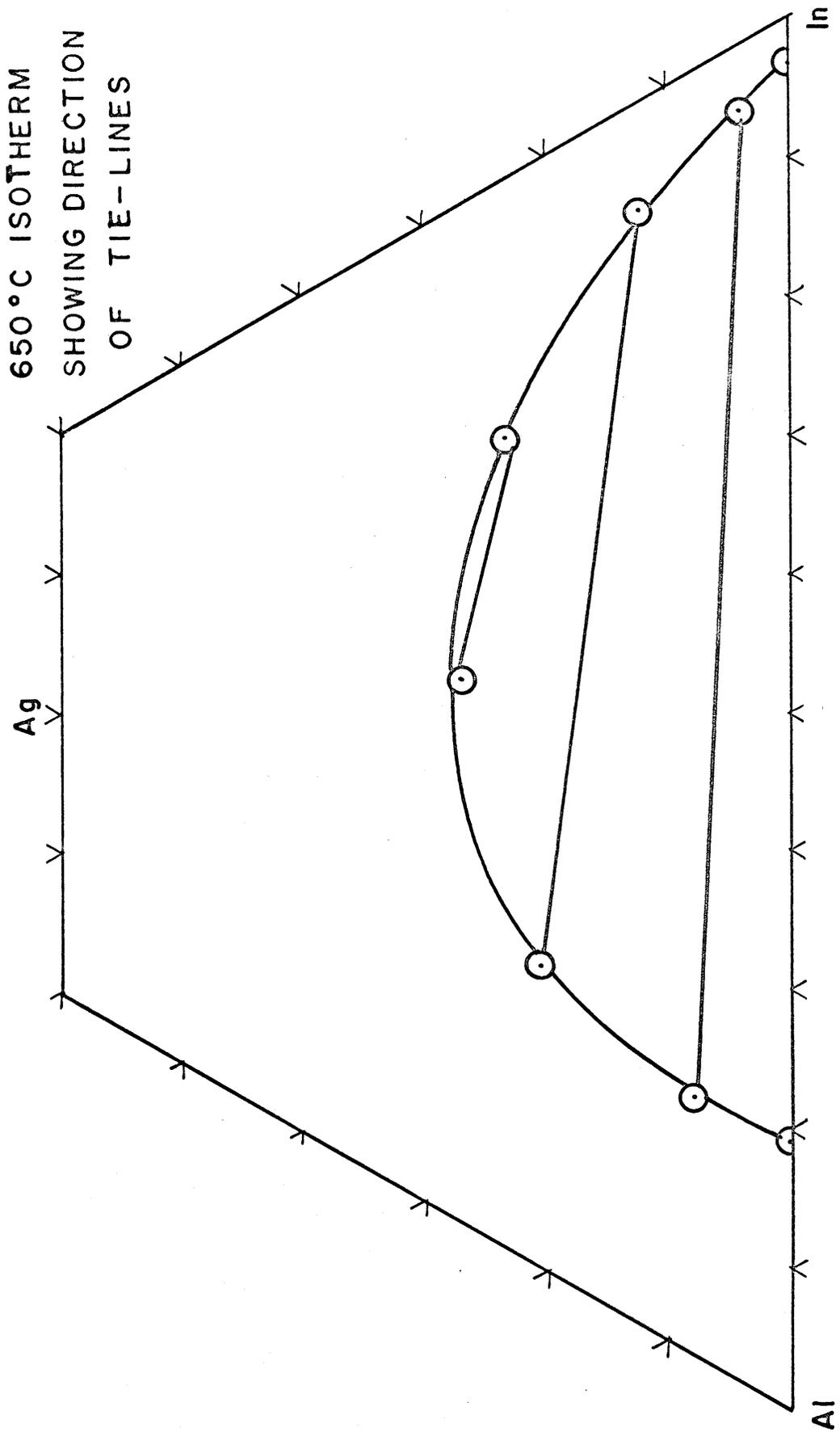


Fig. 23

650, 700, 750, 800, 850, 900 °C

ISOTHERMS THROUGH
LIQUID-LIQUID

IMMISCIBILITY SPACE

Ag

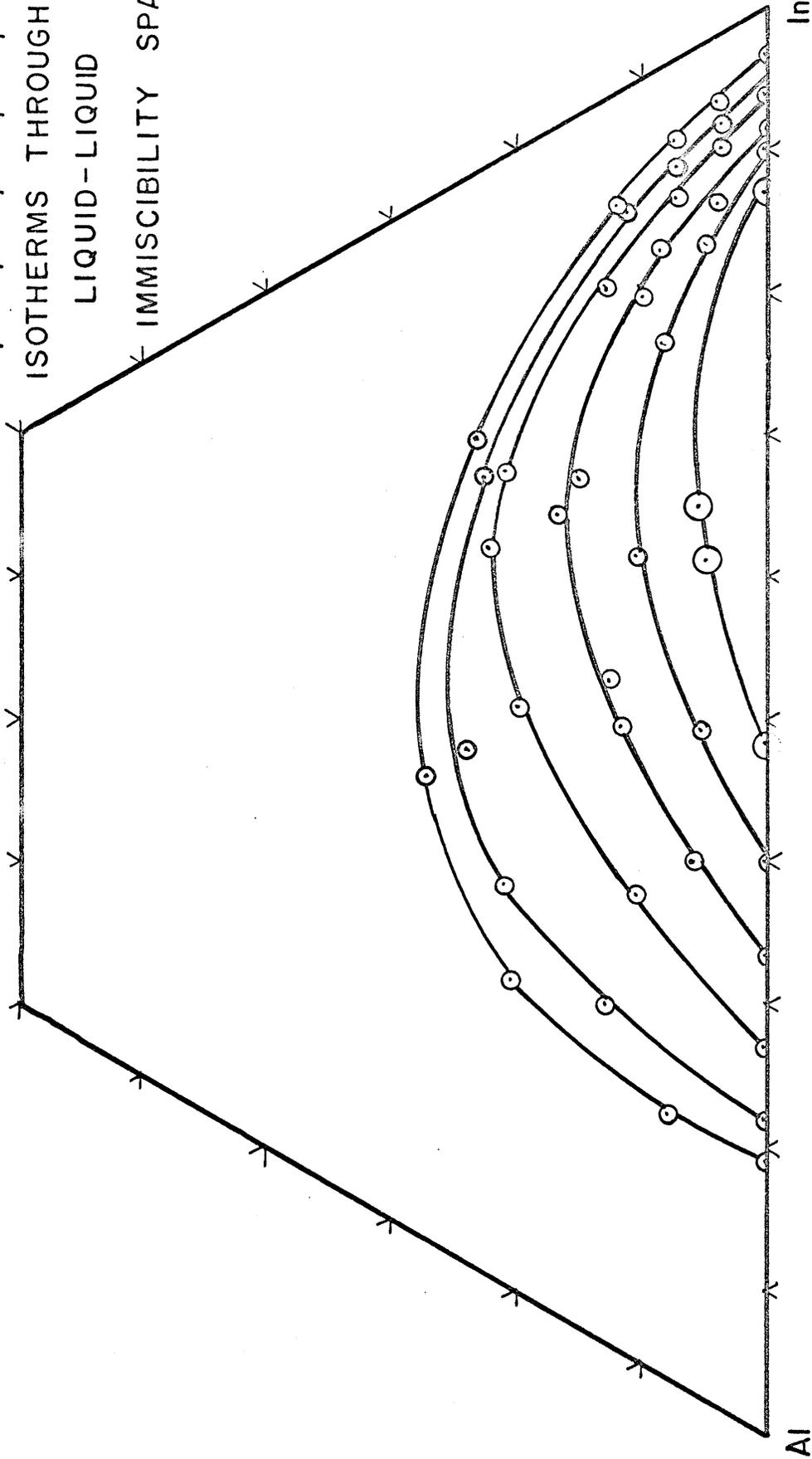


Fig. 24

TABLE IX

d.)

BINARY "MISCIBILITY GAP" DATA

Temp. °C	Al - Rich Layer		In - Rich Layer	
	% I (wt.)	% Al (wt.)	% In (wt.)	% Al (wt.)
650	19.1	80.9	96.5	3.5
700	22.1	77.9	96.8	3.2
750	26.9	73.1	93.9	6.1
800	33.6	66.4	91.6	8.4
850	40.0	60.0	90.8	9.2
900	48.2	51.8	87.2	12.8

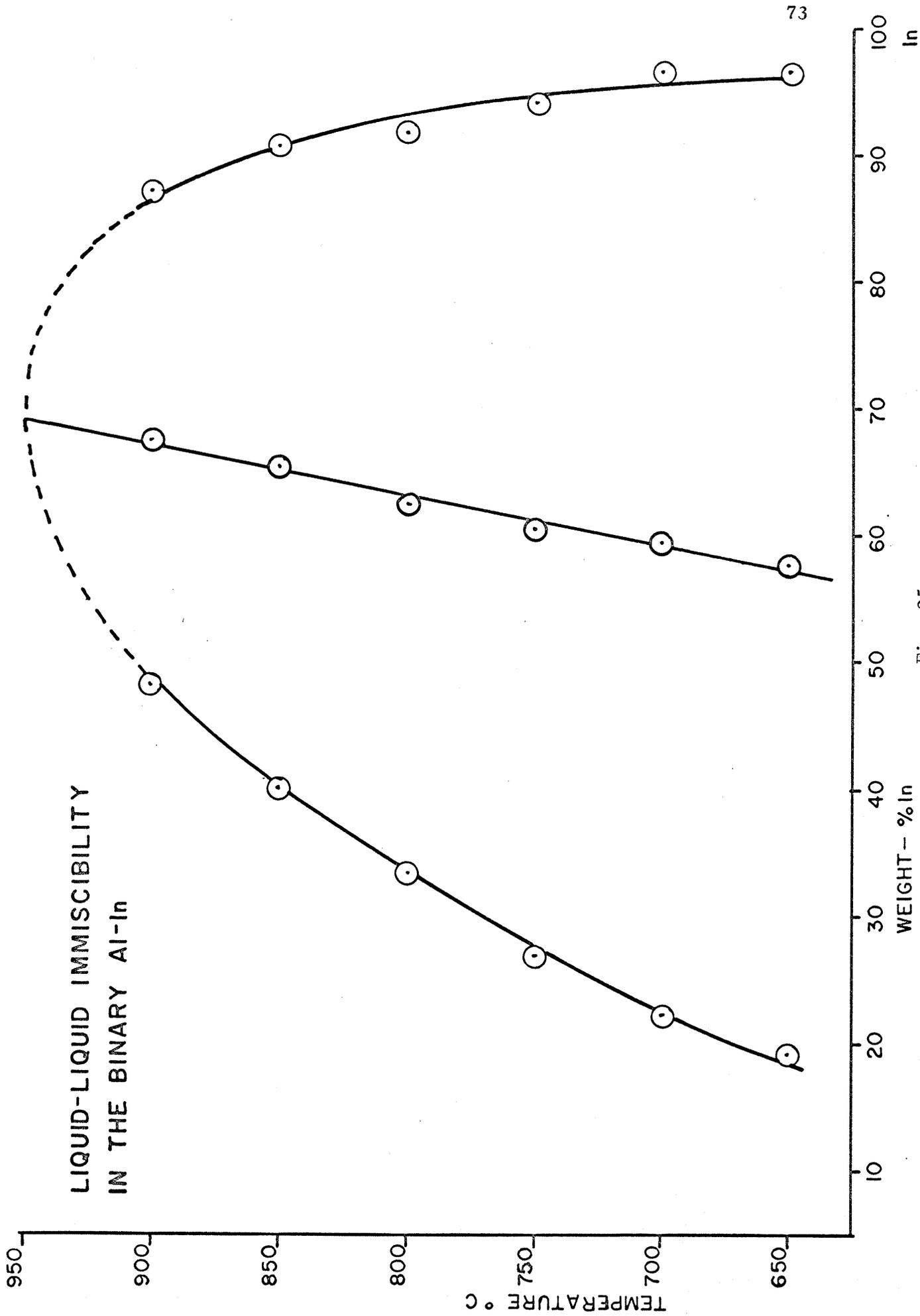


Fig. 25

CHAPTER V
DISCUSSION OF RESULTS

a.) Thermal Analysis

The contiguous binary systems have been discussed extensively under "Previous Relevant Investigations". The discussion at this point will pertain to the extension of the binary transformations into the ternary system as they were determined during the present investigation.

The peritectic reactions which occur at 779.8°C (33) and 693°C (34) in the systems Ag-Al and Ag-In respectively are joined in the ternary system by a "trough" which is nearly a straight line in the basal projection of Fig. 22. (The direction of lower temperature is indicated by arrows). A three-field space therefore joins these two binary peritectics. It follows that the two solid phases in equilibrium with liquid must be silver-rich terminal solid solutions and the β -phase which is designated as such in both binary systems.

The next two peritectic reactions which occur at 726.9° (33) and 660°C (34) in the binary systems Ag-Al (Fig. 13) and Ag-In (Fig. 12) respectively are joined at point "A". A third trough leaves point "A" at lower temperature, therefore, four-phase equilibrium must occur at "A", which must involve three solid phases of which two must be the γ -phase and β -phase of the system Ag-Al (Fig. 13). The third

solid phase cannot be predicted with certainty because the existence of point "F" is not certain. It is, of course, understood that phases which occur in the binary systems and which are said to occur in the ternary system are essentially the same in structure but not necessarily in composition.

The binary eutectic at 558°C (27) which occurs in the system Ag-Al (Fig.13) is joined in the ternary system at point "B" by another trough which emanates from point "A". At lower temperature a third trough emanates from point "B" and four-phase equilibrium must again exist at point "B", of which three phases are solids. Two of these solid phases must be the δ -phase and σ -phase which occur in the binary system Ag-Al (Fig. 13). Furthermore, since δ occurs at points "A" and "B" one of the solid equilibrium-phases at "B" must then be the δ -phase. Since the β -phase exists only at high temperature in the two binary systems Ag-In and Ag-Al it is very probable that the β -phase disappears at the temperature of "A". Consequently, the second solid equilibrium phase along the trough AB must be the "unknown" phase together with δ -phase and not β and γ .

The 207°C peritectic of the system Ag-In (Fig. 12) extends only a short distance into the ternary system i.e. to point "C" (Fig.22), where four-phase equilibrium exists. Two of the solid equilibrium phases at "C" must be the ξ' and δ which occur in the binary system Ag-In (Fig. 12). This latter δ -phase is not the same as that which occurs in the Ag-Al system and which is designated by the same symbol. The nomenclature followed here is simply that which

occurs in the binary systems. The σ -phase of the binary system Ag-Al (Fig. 13) must, of course, take part in two three-phase equilibria; hence it must be one of the equilibrium-phases, at the four-phase equilibrium plane at "C". As in the previous case, the 166^oC peritectic of the system Ag-In (Fig. 12) extends only a short distance into the ternary system i.e. to the point "D". The two solid equilibrium phases in the three-phase space along this short trough are ξ and ξ' which follows from the binary system Ag-In (Fig. 12). At the four phase equilibrium plane "D" a third solid phase exists whose identity cannot be deduced without establishing the solid phase boundaries.

Since all liquid disappears at the temperature of point E, this point is a ternary eutectic point. Two of the three solid phases present at equilibrium at E are of necessity the phase \mathcal{J} which occurs in system Ag-In and the indium-rich terminal solid solution (nearly pure indium). Below the temperature of E (143^oC) one large three-phase space exists (all solids) involving the same three solids as exist immediately above this temperature.

From Fig. 22 it is evident that four different four-phase equilibria exist viz. A, B, C, and D, which are ternary peritectics either of the first or second kind, and a fifth four-phase equilibrium exists at E which is of the ternary eutectic type.

The probable course of the ternary "trough" which originates at the 281°C binary peritectic in the system Ag-In is indicated by a dashed line in Fig. 22. This hypothetical trough terminates at point "F", where a sixth isothermal plane (four-phase equilibrium) must exist, which was, however, not encountered, presumably because of its small extent. In the construction of "Vertical Section II" (Fig. 20) the inflections in the temperature curve due to primary crystallization in the region of 0 % to 2 % Al were very weak making it difficult to plot the liquidus with certainty in this region. Furthermore, an alloy of composition 50.00% Ag and 50.00% In gave no indication of a peritectic at 281°C by thermal analysis. For the above reasons the existence of this "trough" is uncertain. The same alloy gave a distinct temperature "halt" at 143°C which is presumably the eutectic halt found by Weibke and Eggers (61) at 141°C . In their diagram this temperature horizontal reaches only to approximately 25% Al (by wt.) whereas in the present case this temperature horizontal reaches to at least 50% Al (if it is the same temperature horizontal). The other two peritectics found by Weibke and Eggers (61) at 204°C and 166°C were encountered at 207°C and 166°C respectively in the present investigation. It would be necessary to reinvestigate the binary system Ag-In in the region of 20% Al to 60% Al before any definite statements can be made regarding the correctness of the presently available diagram of this system (Fig. 12).

Most of the three-phase boundaries involving one liquid and two solids were detected by thermal analysis; they are shown in the vertical sections as lines radiating from the troughs. The three-phase region involving two liquids and one solid, which must lie below the "ternary gap", was not detected systematically by thermal analysis.

The positions of the ternary points labelled A, B, C, D and E in Fig. 22 were determined by extrapolating the ternary "trough" to the temperature of the respective isothermal planes. The above points have the following approximate compositive coordinates: A, 65% Ag, 32% In, 3% Al; B, 45% Ag, 45% In, 10% Al; C, 9% Ag, 90 % In, 1% Al; D, 4% Ag, 95% In, 1 % Al; E, 3% Ag, 96% In, 1 % Al. The four-phase isothermal planes lie at the following temperatures: 588^oC (A), 506^oC (B), 241^oC (c), 148^oC (D), 143^oC (E). The extent of these isothermal planes can be judged from the length of the horizontal lines in the respective vertical sections. The 143^oC plane is the largest, reaching nearly to the Ag-In and Al-In binary systems, and approximately to the 15% In line along the Ag-Al binary system. Below the 143^oC isothermal plane there exists a correspondingly large three-phase space, all three phases being solids. Since the isothermal planes are in general not triangular in shape (apart from the eutectic plane) more vertical sections which cut these planes are needed to determine their extent with certainty.

An attempt was made to construct a vertical section at 1% Al parallel to the binary system Ag-In, but inflections in the temperature curve due to primary crystallization were very weak in the indium-rich region. Such a section would cut the troughs in this region, giving more accurate information regarding the course of these troughs. A more sensitive apparatus, would have to be used for such a task. The small heat effect accompanying primary crystallization is undoubtedly due to the steep fall of the liquidus in the indium-rich region.

Though a large body of data has been gathered (over 100 analysis) and interpreted, giving information about the liquidus, the type of equilibria present, and the identity of some of the solids without resort to x-ray work, the construction of a complete three-dimensional picture of the ternary system would involve more labour. To determine the ternary system completely, photomicrography and x-ray powder - diffraction techniques would have to be used. Since some transformations occur completely in the solid state in this system as can be seen from the contiguous binary systems, the determination of the liquidus and the troughs can say nothing about these transformations.

b.) The Binary "Miscibility Gap"

In the binary system aluminum-indium the approximate critical temperature of 945°C was obtained by extrapolating the two gap-boundary curves as shown in Fig. 25 The critical composition of 68.8% In,

31.2% Al was obtained by extrapolating the line of rectilinear diameters to the gap boundary (Fig. 25). Accordingly, the system should be homogenous above 945°C and the densities of the top and bottom of an alloy of a composition falling within the gap should be equal at that temperature. This was found to be the case with an alloy of overall composition of 70% In and 30% Al at 950°C.

c.) The Ternary "Miscibility Gap"

Isotherms through the ternary liquid-liquid immiscibility space (ternary gap) at 650°, 700°, 750°, 800°, 850°, and 900°C are shown as a polythermal projection in Fig. 24. A ternary critical temperature does not exist in this system as can be seen from Fig. 19, i.e. the addition of silver to the binary system Al-In lowers the binary critical temperature. The lowest temperature at which only the two liquids can co-exist at equilibrium in the ternary system is approximately 590°C. This value is the point of intersection of the liquidus and the liquid-liquid surface in Fig. 19. The critical composition in the 650°C isotherm (Fig. 23) is approximately 26% Ag, 47% In, 27% Al. At the same temperature the gap extends into the ternary system to approximately 27% Ag, and at 590°C to approximately 30% Ag. The boundaries of the three-phase region ($L_1 + L_2 + S$) which must lie below the ternary "miscibility gap" were not detected by thermal analysis.

d.) Summary

The binary miscibility gap in the system Al-In has been "closed". The ternary "miscibility gap" in the system Ag-In-Al has been determined. The liquidus has been largely determined. Five four-phase isothermal planes have been found, and a sixth postulated. The course of the ternary "troughs" has been determined, with less certainty, however, in the indium-rich region than in the remaining region of the system.

The identity of some of the solid phases in the ternary system has been deduced.

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