

THE SYSTEM INDIUM-ALUMINUM-TIN

by

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To Dr. A. N. Campbell
in appreciation of his
helpful guidance and
infinite patience.

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INTRODUCTION

INTRODUCTION

This research problem was commenced in the fall of 1948 by Mr. L. B. Buchanan at the University of Manitoba, at the suggestion of the Consolidated Mining and Smelting Co., Ltd. of Trail, B. C. They were investigating uses for the comparatively rare metal indium, which is now being produced in commercial quantities, and desired information concerning the alloy systems of indium and other metals, which might prove valuable.

The company was especially interested in the binary system In-Al which Valentiner was investigating in Germany. Buchanan checked the lower limits of the binary miscibility gap and commenced investigations of the gap at higher temperatures with a view to determining the upper critical solution composition and temperature. He then proceeded to investigate the ternary system In-Al-Sn, determining the ternary eutectic and starting a determination of the extent of intrusion of the binary miscibility gap into the ternary system.

The research was continued in 1949 by Mr. J. M. Kuzmak, who extended the knowledge of the binary miscibility gap and also determined a ternary binodal curve at 700° C.

The work was recommenced last fall with a view to closing the binary gap and determining several isothermal sections of the three dimensional ternary solid model. If time would permit, an X-ray investigation of the solid solutions at lower temperatures would be undertaken.

METHODS AND TECHNIQUES

METHODS AND TECHNIQUES

In an investigation such as the one described here, the aim of the research worker is the construction of a phase diagram for the particular system under consideration. This phase, or equilibrium, diagram indicates the various phases in equilibrium for any combination of the variables such as temperature and composition of the mix. For any system such as the one under consideration, the pressure is not a variable, since the system is open to the constant pressure of the atmosphere.

The four principal methods of determining phase diagrams are thermal analysis, isothermal analysis, microscopic analysis, and X-ray diffraction, and in general, the four are used in conjunction. Microscopic analysis was not used in this investigation, but a brief discussion of the other three methods will be given.

Isothermal Analysis

Not many workers have used this procedure for the investigation of alloy systems, although it has been very popular for the study of salts and water systems. The sample of metals is kept at the desired temperature by some means for a sufficient period to ensure the attainment of equilibrium. When equilibrium has been attained, the samples for analysis may be obtained, as in this investigation, by one of two methods. In the first method the whole sample is quenched by

plunging into a cold bath such as a salt-ice-water mixture. Then samples are removed from the solid alloy as required for analysis. In the second method samples are removed by direct pipetting from the melt, the molten alloy solidifying in the pipette, which must then be broken for recovery of the sample. This method is especially valuable if the melt consists of two liquid layers. However, in the recovery of the lower layer, a slight error is introduced when a small amount of the upper layer enters the pipette as it is passed through.

Isothermal analysis is mainly used in determining the composition of two congruent liquid layers or of a liquid in contact with a solid phase. The different phases, however, must not contaminate each other if suitable samples are to be withdrawn for analysis.

A variation of this method has been introduced by Alexejeff (1). A series of samples varying only slightly in composition are equilibrated at the same temperature and quenched. If the composition range includes a transition from two liquid layers to one, or from a solid in equilibrium with liquid to homogenous liquid, an examination of the quenched samples should show within small limits of concentration where this change occurs. Thus, by varying the temperature and repeating the procedure, a liquidus or miscibility gap may be determined. The disadvantage, of course, is the large amount of effort required to obtain a single point.

Now, in the quenching process the objective is to obtain the sample in a solid condition identical with the

condition of the liquid, or partially liquid, sample at the equilibration temperature. Thus the whole aim of the process is the elimination of any changes which would tend to occur in the sample on cooling. These might include the separation into two liquid layers, or the separation of one or more solid phases. It is obvious that the more rapid the quenching process, the more successful it will be in its aim. Certain processes occurring, such as the separation of a solid phase, may, however, be so rapid that they will render the process unreliable. It is, therefore, up to the experimenter to convince himself that the solid sample obtained by quenching is a true replica of the sample at the equilibration temperature. It should be noted that it is only the composition of the alloy which remains constant in a perfect quench, the structure of the quenched solid obviously not being the same as that of the liquid.

Thermal Analysis

The use of thermal analysis in the preparation of equilibrium diagrams involves the determination and study of cooling curves, i.e., temperatures vs. time plots. Whenever a phase reaction occurs in a system at equilibrium, it is accompanied by a heat effect. These heat effects produce breaks in the cooling curve in such a manner that the temperature of occurrence of the phase reaction may be estimated. Thus points on a liquidus curve may be determined by observing the temperature of the break corresponding to the separation

of the solid phase for different compositions. At an invariant point such as a eutectic, the cooling curve should, of necessity, exhibit a horizontal portion.

If a sample were allowed to cool without interference and without phase reactions, the cooling curve would be exponential as required by Newton's Law of Cooling. It can be seen that a small break in a cooling curve would be more easily discernible if the cooling were linear instead of exponential. Accordingly, Plato (2) introduced this innovation of linear cooling, which is maintained by regularly and progressively reducing the temperature of the furnace surroundings.

The ease with which phase reactions can be observed as breaks on a cooling curve depends, of course, on the magnitude of the accompanying heat effect, and also on the rate of cooling employed. The smaller the heat effect, the slower must the cooling rate be. Certain reactions, such as the separation of a homogeneous liquid into two liquid layers, may or may not involve a sufficiently large heat effect to show as a cooling curve break. This point will be mentioned later.

X-ray Analysis (3)

The atoms in a crystal are arranged in a regular pattern and act towards X-rays as a three dimensional diffraction grating, in much the same way as an optical grating acts towards light rays. An X-ray diffraction picture of a substance consists of a photograph of the rays as a thin beam is diffracted

through the substance. From a study of the picture several facts concerning the material photographed may be determined. It may be classified as crystalline or amorphous, its identity may be established, the crystal lattice perfection can be determined, single crystals can be distinguished from polycrystalline substances and the grain size estimated. Together with other information such as density, the worker can determine space lattices, space groups, and positions of atoms in the unit cell, together with the dimensions of the unit cell to a high degree of precision.

The law governing the diffraction of X-rays through a substance was enunciated by Bragg: $n\lambda = 2d \sin \theta$, where n is the order of the diffraction, λ is the wave length of the characteristic X-radiation used, d is the lattice spacing of the particular set of planes under consideration, and θ is the glancing angle.

A simple Debye camera may be used for the investigation, but back reflection cameras, which use large-angle diffracted rays only, give better precision for the determination of lattice spacings, etc. The size and shape of the unit cell of a crystal govern the "positions" of the diffracted rays, while the atomic arrangement within the unit cell controls the "intensities" of the rays. The accuracy of lattice dimension measurements with the Debye-Scherrer-Hull camera used in this investigation is from 0.1 to 0.02%, and using back reflection cameras from 0.02 to 0.003%.

A determination of the phases present in a sample may be done by a comparison of the pattern obtained from the sample with the patterns of identified material. The patterns may be compared side by side, or by superposition. For identification to be certain, every line must be accounted for. The importance of this X-ray method lies in the fact that only small quantities of material are required and that different compounds of the same elements are distinguishable, since they possess different crystal structures. This method is widely used for the identification of alloy phases, but is not generally applicable when a phase constitutes less than 1-5% of the weight of the alloy. The pattern for more than one phase consists of superimposed spectra with relative intensities depending on relative amounts of the two phases.

When two metals enter into solid solution, the dimensions of the unit cell are altered gradually, and if, for example, the series of solid solutions is complete, there will be a gradual change in cell dimensions from those of one component to those of the other. This will show on the X-ray photograph by a gradual displacement of the spectral lines. Vegard's approximate law states that the effect is proportional to the atomic per cent of the dissolved component. Samples for study are best prepared by annealing the solid solution and then quenching sufficiently rapidly to preserve the structure. Quenching stresses are best avoided by working with thin wires, foils, or fine powders.

PREVIOUS INVESTIGATIONS

PREVIOUS INVESTIGATIONS

The pertinent data for the pure metals, In, Al, and Sn, are to be found in the thesis of L. B. Buchanan. The considerable amount of research done on the binary systems, Al-In, Al-Sn, and In-Sn, will be outlined below.

The System Al-In

The first published research on this system was included in a paper by Raub and Engel (4), who state that the lower limits of the liquid miscibility gap are 17.3% In to nearly pure indium. In their investigation thermal analysis along with X-ray and microscopic techniques was used. The results which they obtained are given in the accompanying equilibrium diagram. The lower limit of the miscibility gap is placed at 634°.

As far as Raub and Engel could determine, Al has no effect on the melting point of In, so that the eutectic temperature is very close to the melting point of pure In, for which the values in the literature are in the range 155.5-156.4°.

It was also found, through a microscopic and X-ray investigation, that the solubility of indium in solid aluminum was extremely small.

A short time later, Valentiner (5) published some results which he obtained by thermal analysis, supplemented by X-ray analysis and electrical resistance measurements. His phase diagram (Figure 2) indicates that the miscibility gap extends from 13 to 98 weight per cent indium, which value for

THE SYSTEM AL-IN
(RAUB AND ENGEL)

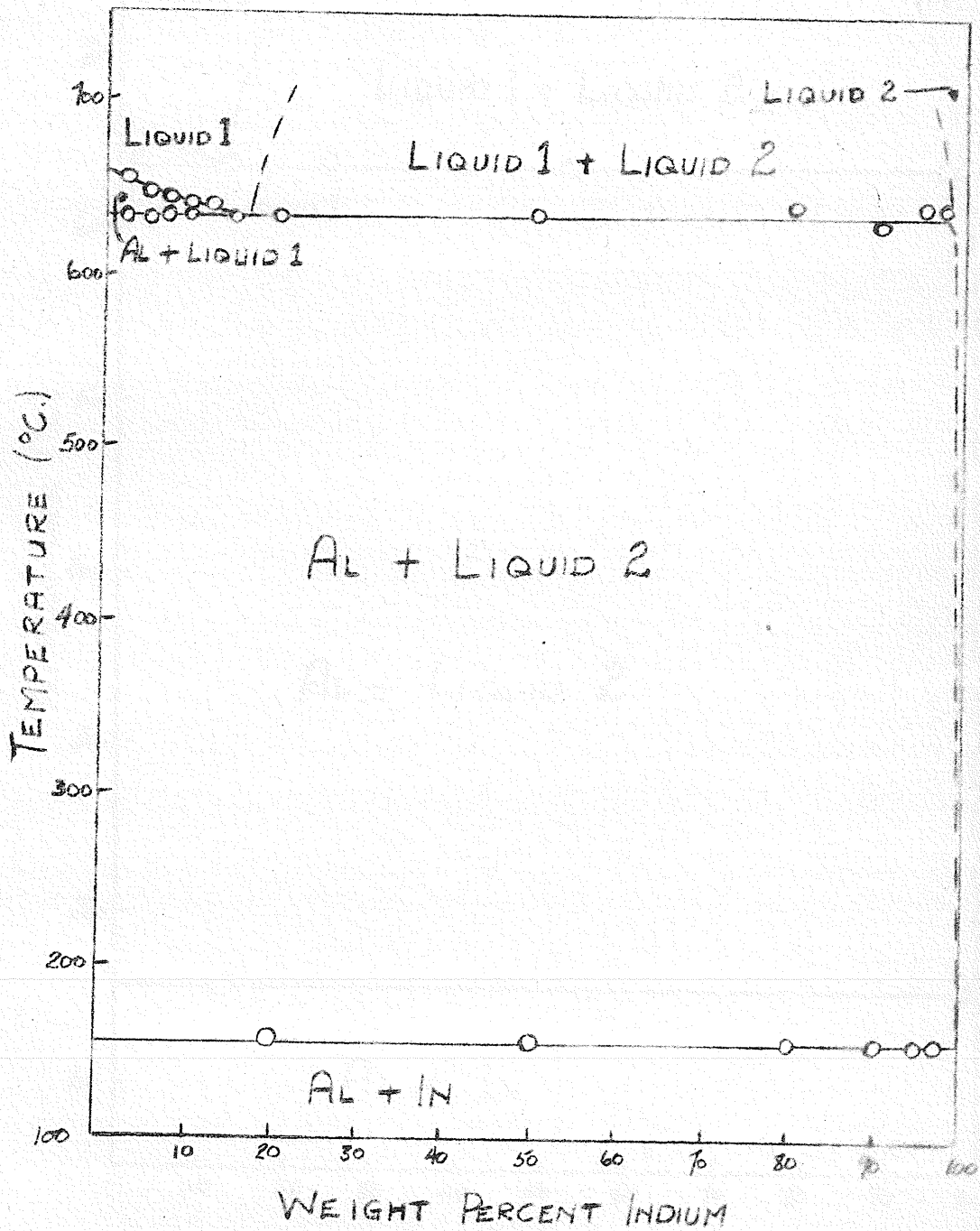


FIG. 1

the low indium end is appreciably different from that given by Raub and Engel. The invariant temperature is given as 634° and the eutectic as very close to 156° . The limits of the gap were obtained by the extrapolation of thermal analysis points on the high aluminum end, and on the low aluminum end Valentiner gave the limit as the last alloy that showed a gap halt. He stated that the solubility of the two metals in each other in the solid state can only be small.

In a paper by Klemm, Klemm and associates (6), an upper limit for the solubility of indium in solid aluminum is given as 0.05 atomic % by a microscopic investigation. It is also stated that there is at most 6 atomic % Al in the In-rich layer at the lower limit of the miscibility gap, while the Al-rich layer is shown to contain 94 atomic % Al. The temperature of the lower limit of the miscibility gap is given as 640° , while the eutectic is shown at about 155° .

From some unpublished work by Davies and Rowe, Davies (7) reports the construction of a diagram for the Al-In system (Figure 3). He states, "Indium apparently has a slight solubility in Al. The α phase at 250° contains enough indium to produce a barely discernible shift in the X-ray diffraction pattern from that of high purity aluminum."

From his work published in 1950 (8), Buchanan reports (Figure 4) the limits of the gap in this system to be 14.0% and 97.2% indium, respectively. However, by isothermal analysis of the binary miscibility gap, Buchanan obtained the value 20.6% In in the Al-rich layer, which is significantly different

from the value 14.0% obtained by thermal analysis. Perhaps the value 20.6% is the better, since Kuzmak (9) has shown that an extrapolation of the differential thermal analysis points of Buchanan gives a value of 20.5% In. The value of 97.2% In was obtained by extrapolation to the gap halt temperature of 638.6°.

In the ternary system In-Al-Sn, Buchanan reported a eutectic temperature of 117.1° and a eutectic composition of 0.14% aluminum, 51.03% indium, and 48.83% tin.

The System Al-Sn

In 1890 Heycock and Neville (10) showed that addition of aluminum up to 0.48% regularly lowered the freezing point of tin. According to their observations, the eutectic should be at 228.8° and 0.48% aluminum.

Gautier (11) published the first complete freezing point curve. His curve exhibits a maximum at 81% tin indicating a compound of the composition AlSn, and a minimum at 78% tin.

Campbell and Matthews (12) obtained analogous results, with a maximum at 83% and a minimum at 78%, with the eutectic at 99.52% tin and 229°. An odd point is that, to the authors, the eutectic "mixture" appeared microscopically to be a single solid solution of Al in Sn.

The latest and most significant work done on the system began with that of Gwyer (13) in which the eutectic halt times were accurately determined. As shown in Figure 5,

THE SYSTEM IN - AL (DAVIES)

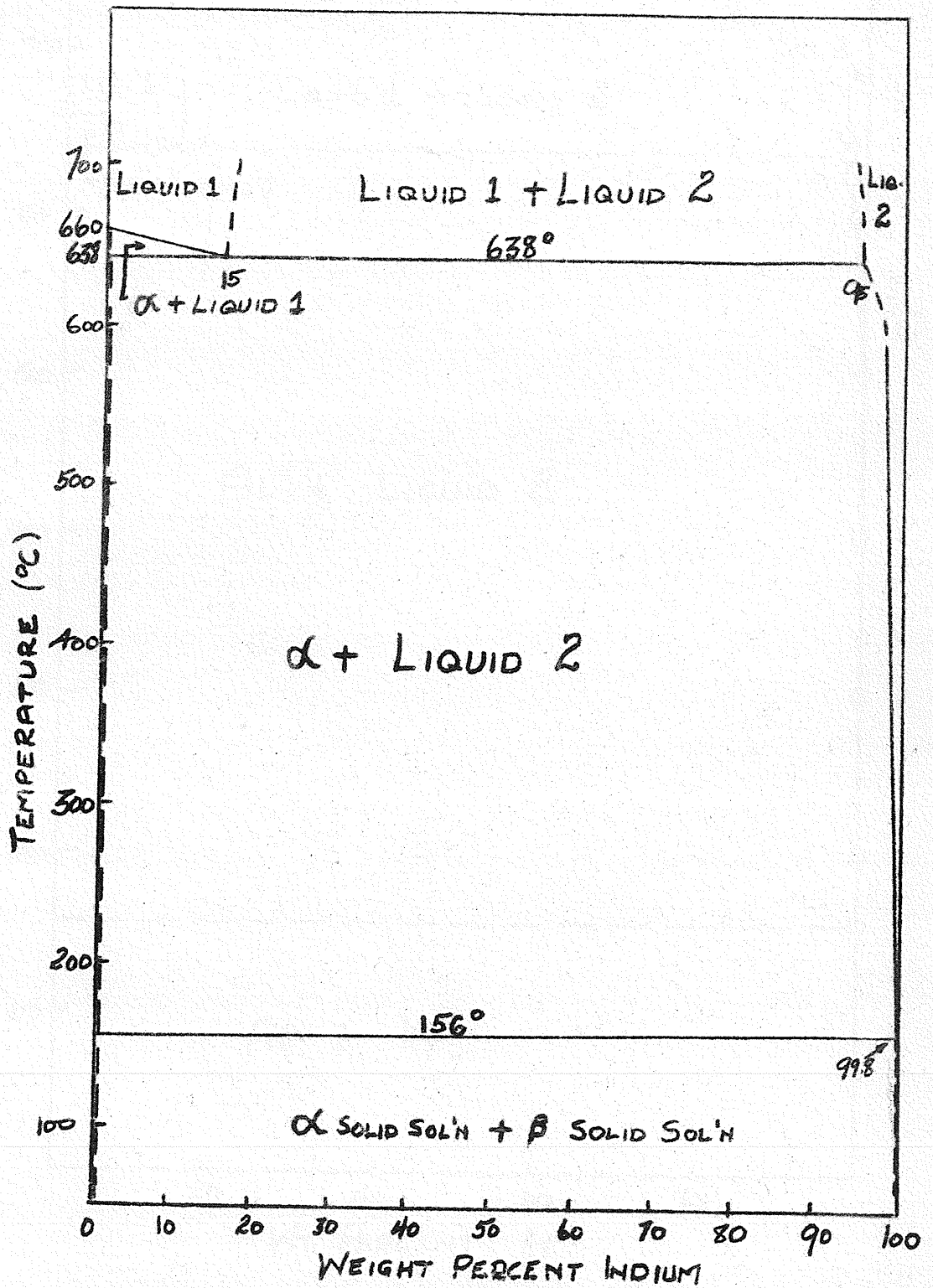


FIG. 3

THE SYSTEM IN - AL (BUCHANAN)

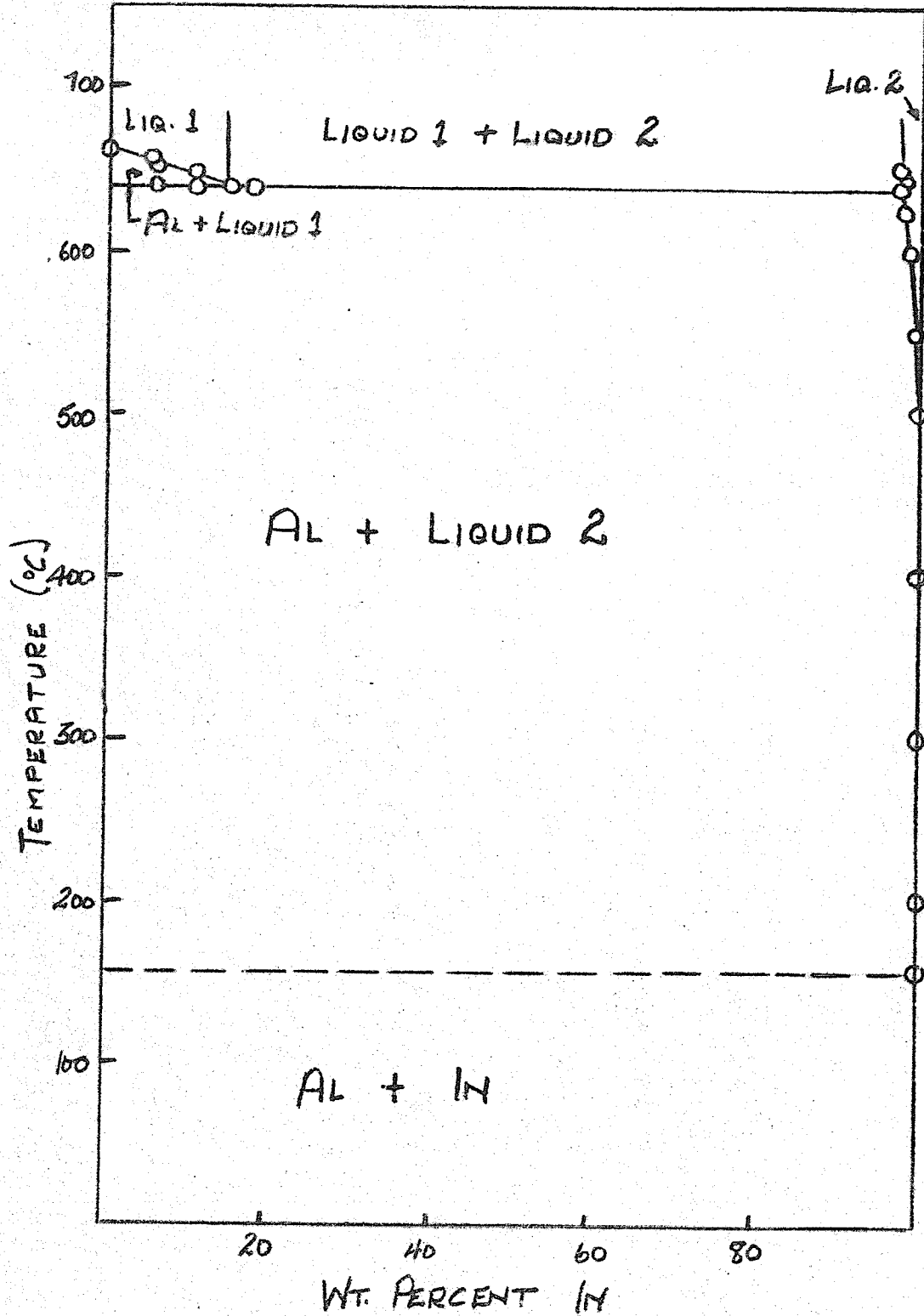


FIG. 4

THE SYSTEM AL-SN

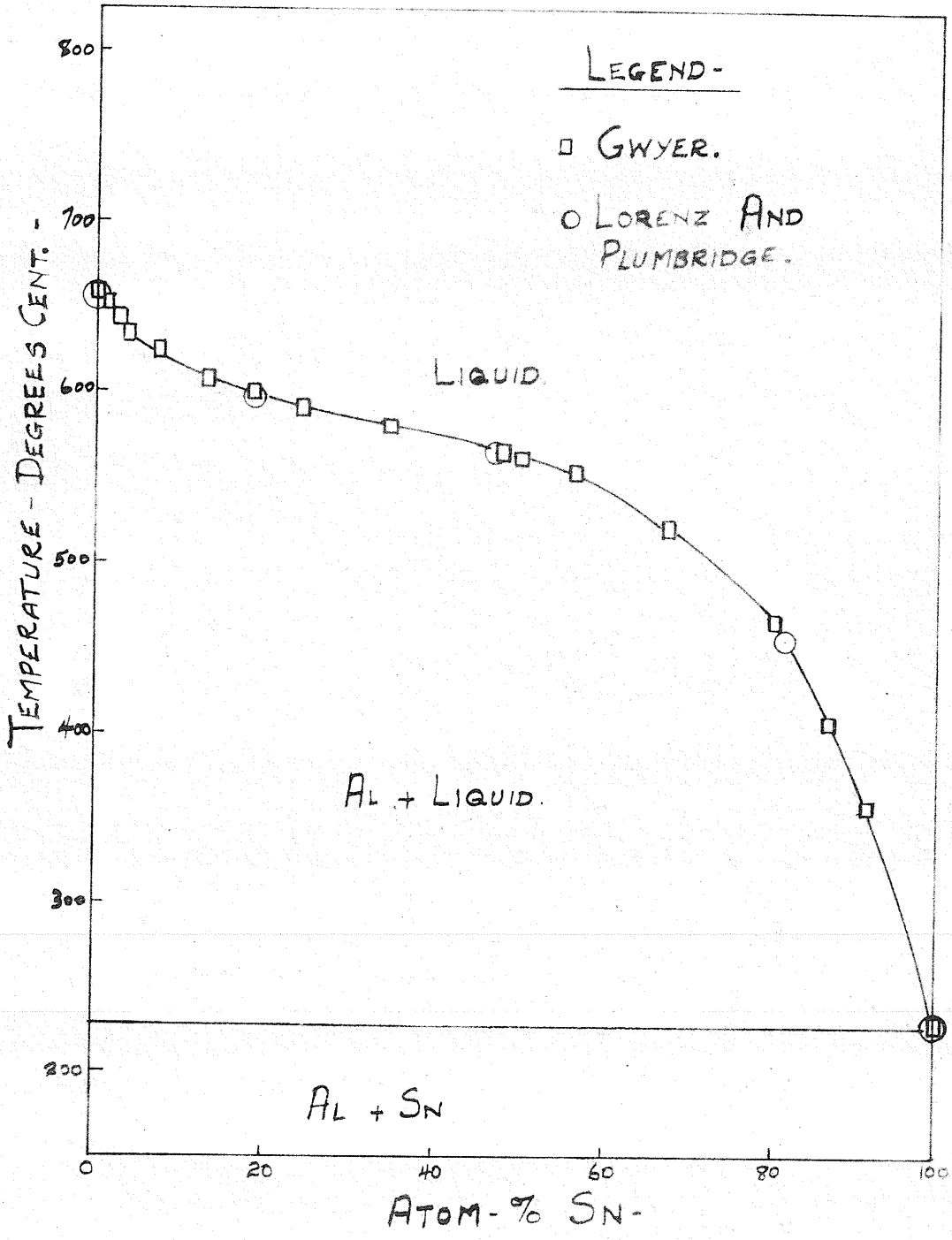


FIG. 5

THE SYSTEM IN-SN

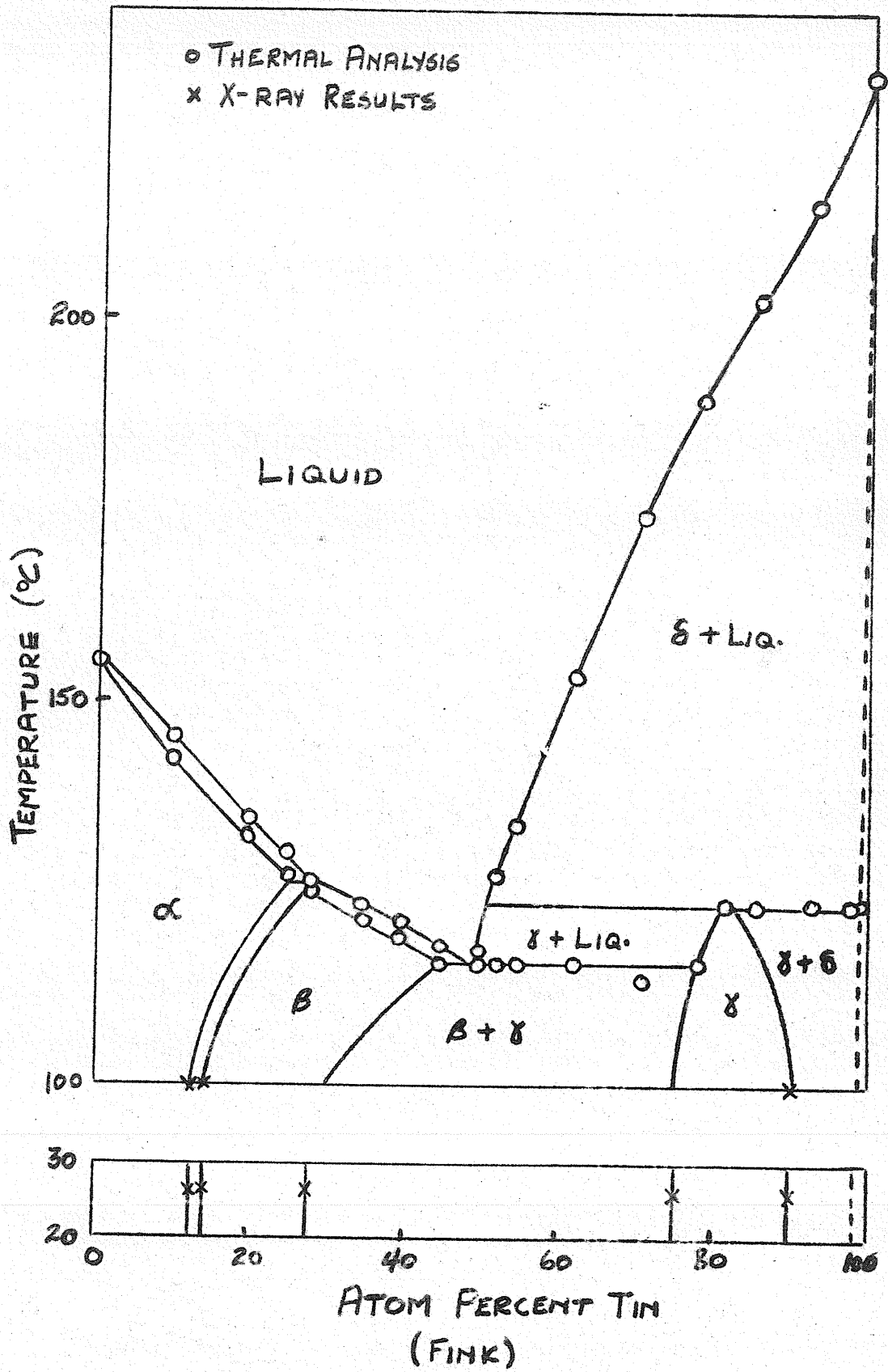


FIG. 6

he indicates that the freezing point curve is smooth and falls continuously from the melting point of pure aluminum to the eutectic. Gwyer also showed the nonexistence of the compound $AlSn$.

The research of Lorenz and Plumbridge has also been shown on Figure 5. Their investigations agreed well with those of Gwyer, as can be seen. Moreover, these authors showed microscopically that with all alloys over the range 0-98% tin, aluminum crystals separated first leading to a tin-rich eutectic.

The System In-Sn

In 1890 Heycock and Neville (15) published the first research on this system to the effect that indium dissolves readily in molten tin, at least up to one per cent.

It was not until 1939 that Fink and co-workers (16) used thermal analysis to determine the liquidus and some portions of the solidus. The eutectic was located at 116° and 48.5 atomic % tin, and a peritectic at 126° , and about 28 atomic % tin. It was shown that indium is only slightly soluble in tin (about 1.5% In), and that tin has a considerable solubility in indium (about 10% Sn). In a later paper (24) published by the same workers, a complete equilibrium diagram is given, showing a series of four solid solutions. The authors used density measurements and X-ray techniques in this investigation. The alpha solid solution of tin in indium has a solubility limit of approximately 13 atomic % tin. The

beta phase has a body-centered tetragonal structure and extends over the range 14 to 28 atomic % tin. The gamma phase is assumed to have a simple hexagonal structure and at room temperature is stable in the range 75 to 90 atomic % tin. For the delta phase the solid solubility determined in this investigation is approximately 3.3% In at room temperature and less than 1.3% at the peritectic temperature. The figures quoted have been shown in the accompanying Figure 6.

A short time after the publication of the above authors' first paper, Valentiner (17) in Germany published his work on the system. He used thermal analysis to obtain practically the same results as above. However, he found no peritectic, and his eutectic halt horizontal extended beyond the limits set by Fink. No solidus points were given until another paper (18), when using electrical resistance and X-ray measurements, the same author found the two compounds that were indicated by Fink as beta and gamma solid solutions.

Perhaps the most precise study was made by Rhines and co-workers (19) in 1947. Using precise thermal and metallographic methods, they found the limits for the four solid solution phases to be as follows: for 20° alpha-0 to 3 weight per cent tin, beta-14 to 27 weight per cent tin, gamma-75 to 88 weight per cent tin, delta-94 to 100 weight per cent tin. According to their phase diagram, the beta phase undergoes peritectic decomposition at 126°, and it is suggested that the gamma phase undergoes peritectoid decomposition about 80°, which is in opposition to the views held by Fink et al.;

compare Figures 6 and 7. Small disturbances in the liquidus curve were found at 17, 34 and 86% tin, but the only peritectic reaction found to occur was at the 34% inflection.

Thus except for one or two differences, the findings of Fink, Valentiner and Rhines are essentially in agreement.

CONSIDERATION OF THE PROBLEM

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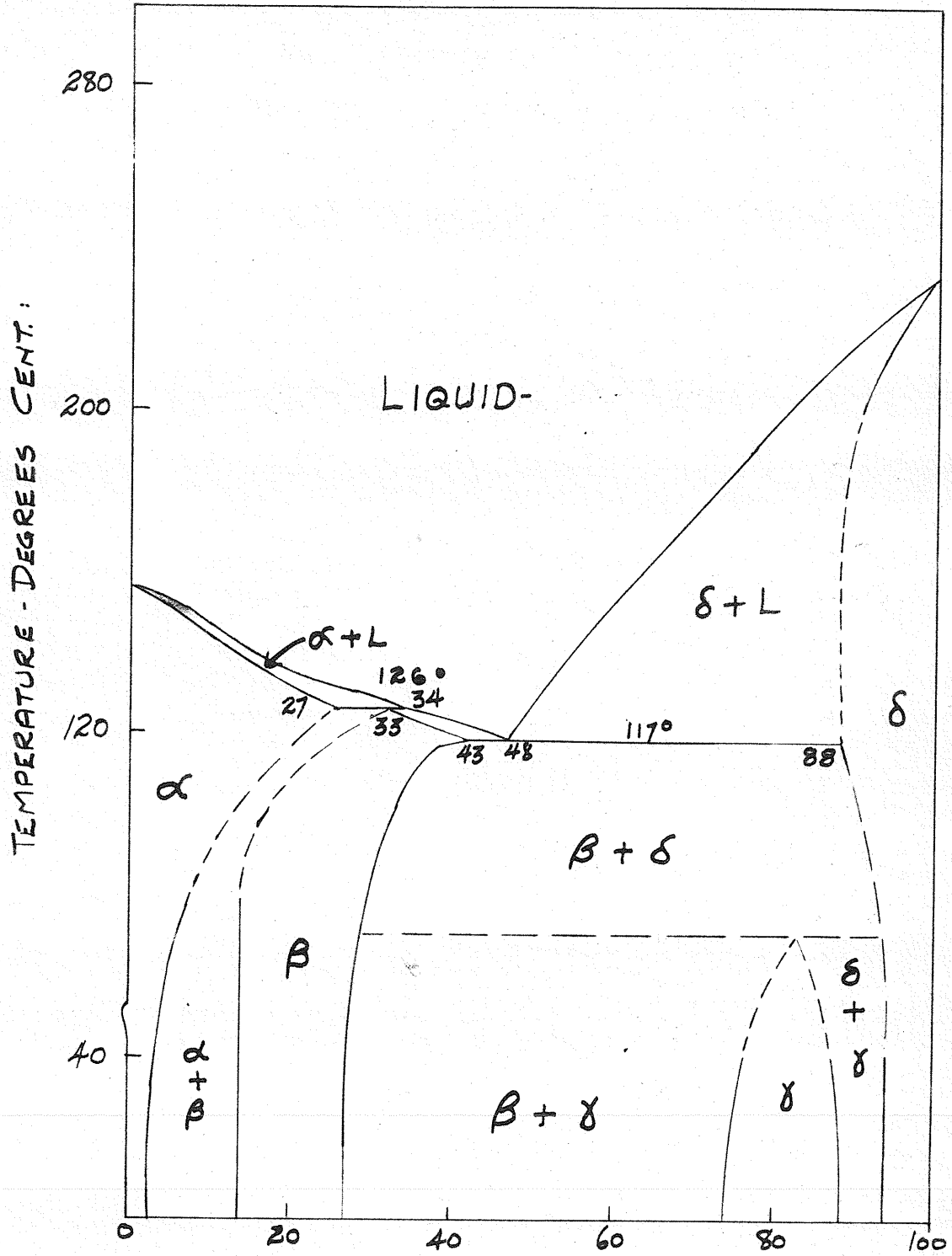
The lower limits of the binary miscibility gap in the system Al-In have been sufficiently well defined, as given in the previous discussion. Also Buchanan has determined the high and low In liquidi in the same system.

(1) It remains, therefore, to determine the limits of the binary miscibility gap at higher temperatures and, if possible, to determine the upper critical solution temperature and composition.

(2) The work of Kuzmak (9) on the investigation of the ternary isotherms should be continued with a view to completing the equilibrium diagram for the ternary system.

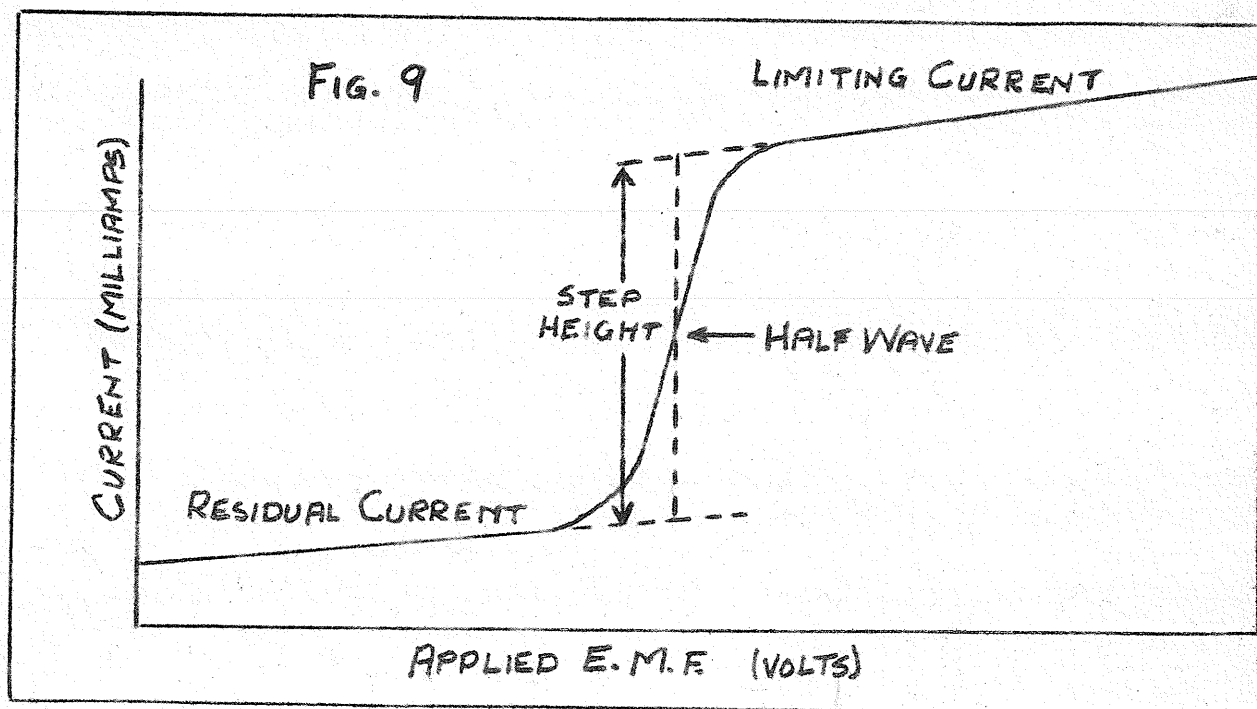
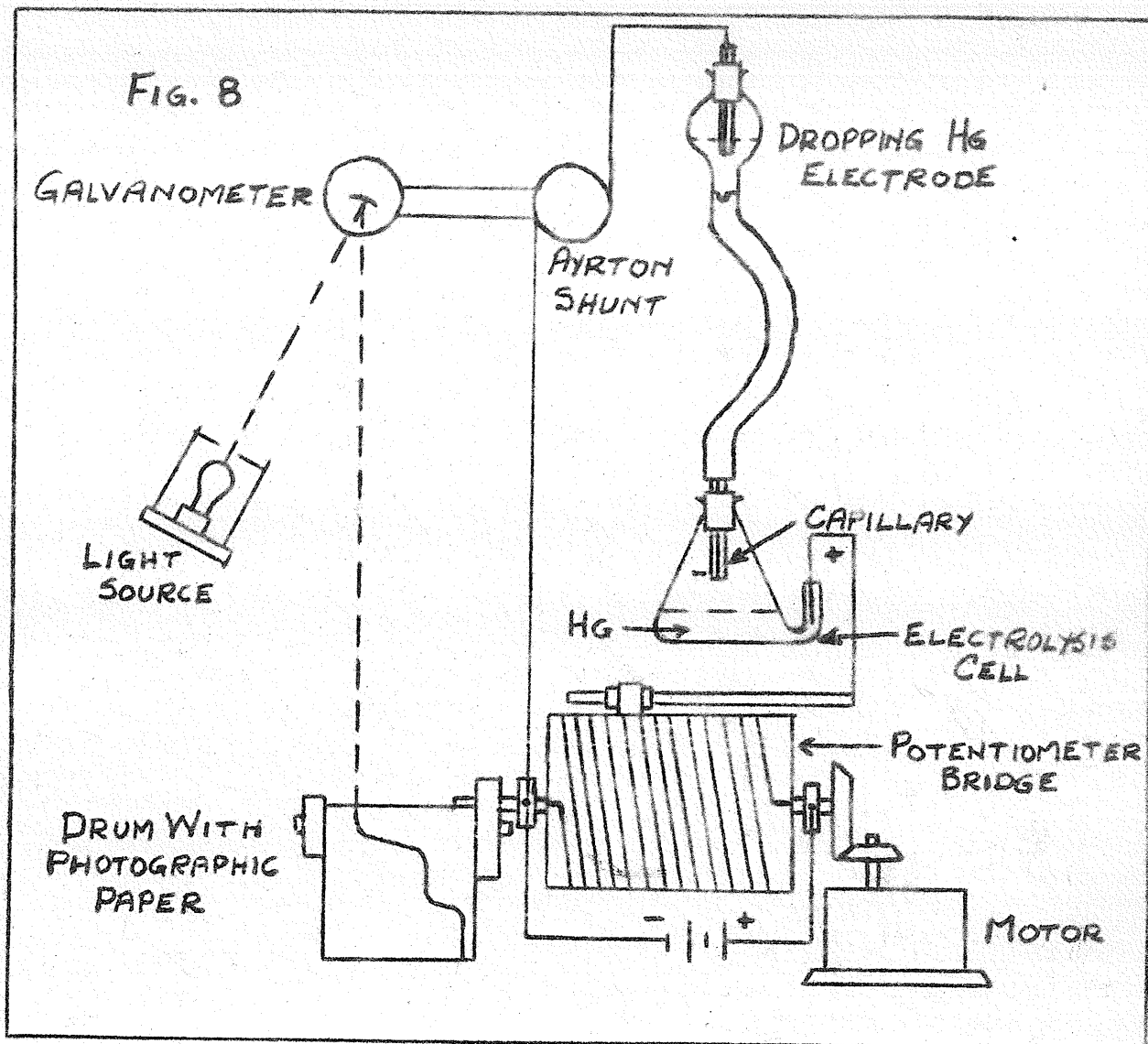
(3) Also an investigation of the ternary system at lower temperatures using either the microscope or X-ray technique, or both, would reveal the nature of the solid phases present.

THE SYSTEM - IN - SN:



(RHINES ET AL.)

FIG. 7



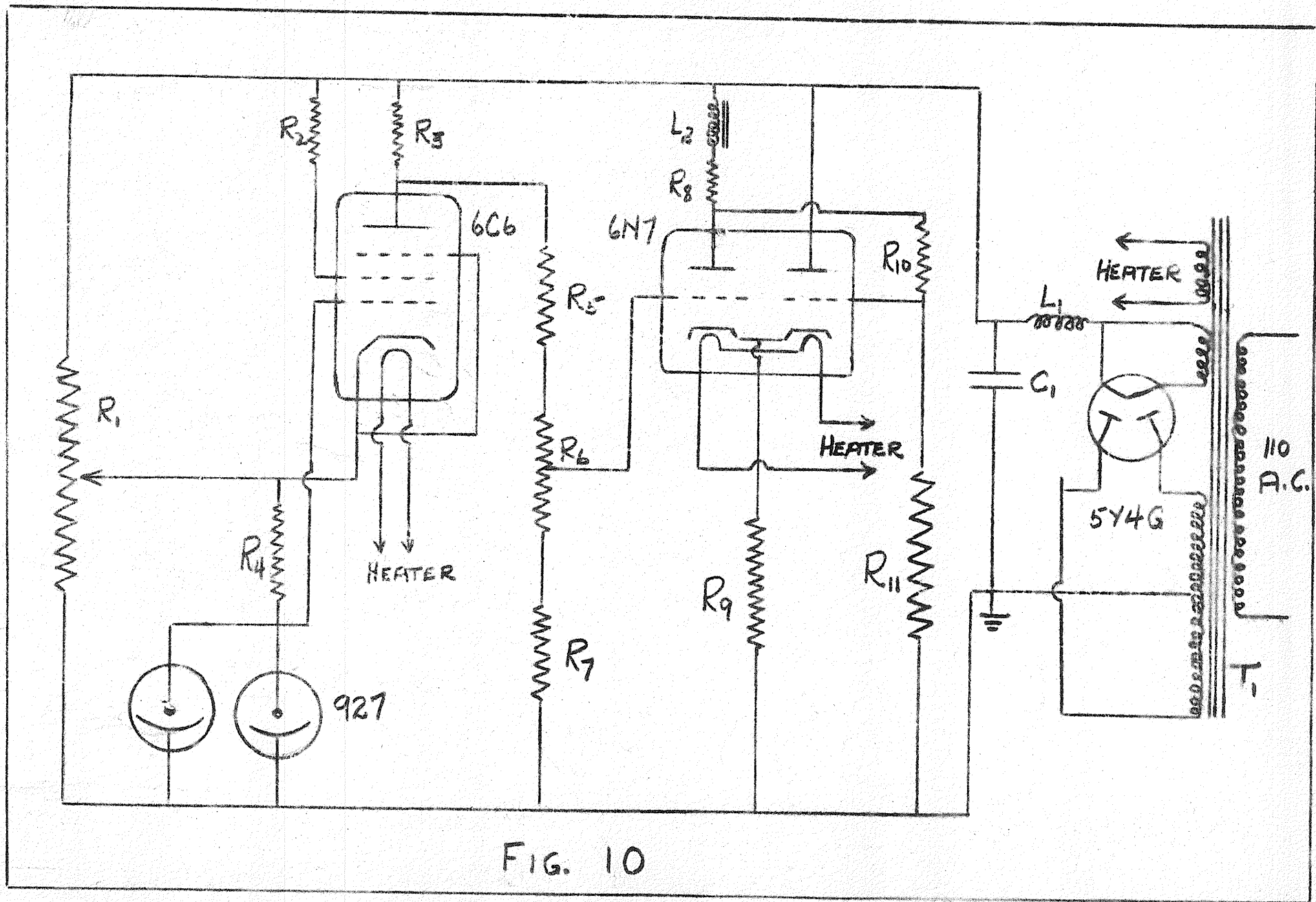


FIG. 10

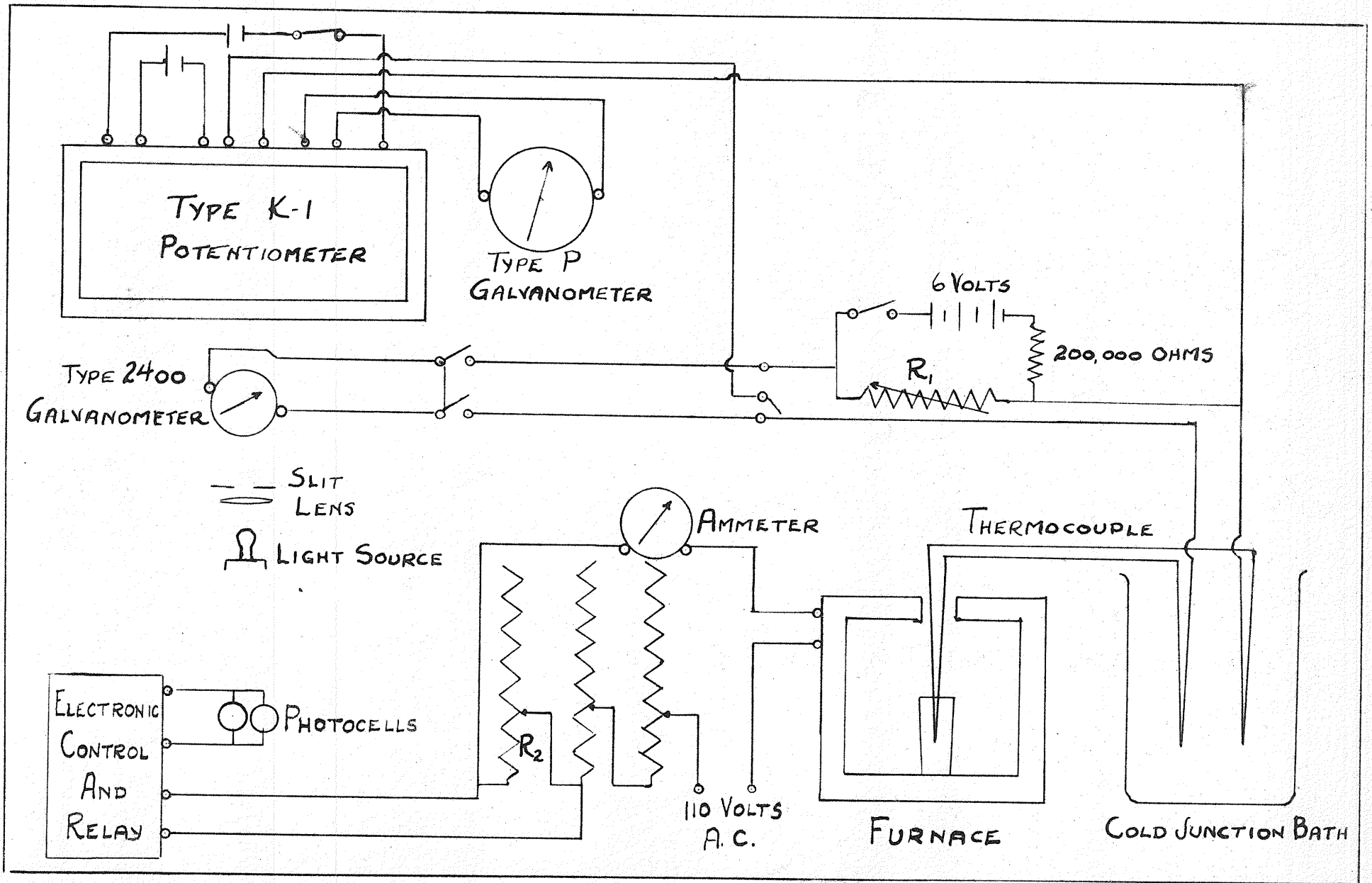


FIG. 11

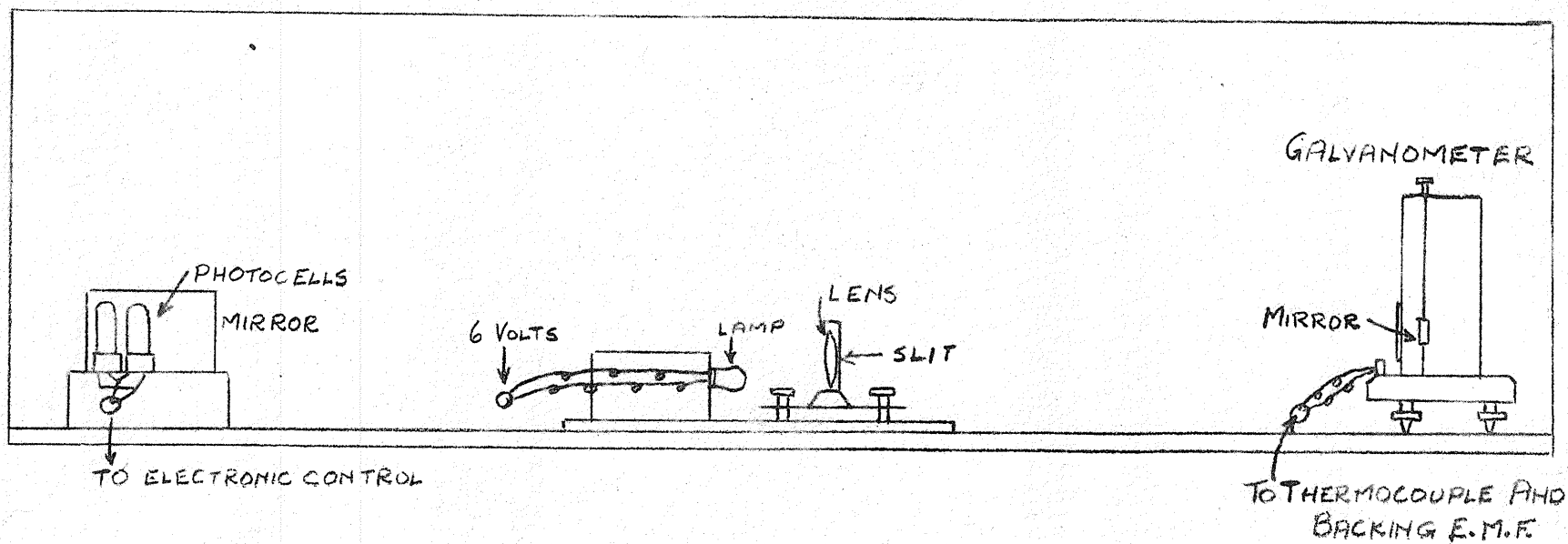


FIG. 12

EXPERIMENTAL PROCEDURE

EXPERIMENTAL PROCEDURE

Purity of the Component Metals

The aluminum, indium, and tin used in the investigation were analyzed as follows by the companies supplying them:

Aluminum (from the Aluminum Company of America)

Copper	0.0042%
Iron	0.0010%
Silicon	0.0014%
Magnesium	0.0009%
Sodium	0.0001%

Indium (from the Consolidated Mining and Smelting Co., Ltd.; marked Tadanac 99.95+Indium)

Lead	0.005%
Cadmium	0.001%
Iron	0.001%
Copper	0.001%
Tin	0.004%
Thallium	0.0005%

Tin (from Batch #73 of Vulcan "Commercial" Tin)

Iron	0.0020%
Antimony	0.0023%
Lead	trace
Copper	trace
Tin	99.9957% (by difference)

Methods of Chemical Analysis

Due to the pronounced oxidation of samples at higher temperatures (in spite of the reducing atmosphere to be mentioned later), the composition of an alloy could not be determined accurately from the weights of the metals used in the preparation of the sample. In other words, complete analysis of every alloy was necessary.

The estimation of the amount of aluminum in a sample involved the determination of the density of the alloy sample. It is obvious that for a binary alloy, if the density of the alloy be known, along with the density of the two component metals, it is a relatively simple matter to determine the percentage composition of the sample. Also, for dealing with ternary alloys, the percentage composition of two components may be determined, provided that of the third be known along with, as before, the densities of the three pure metals and the alloy. Thus for ternary alloys, the percentage of the indium, or tin, depending on which could be determined more accurately, was necessary for the estimation of the aluminum content of the sample.

The 5-ml. density bottle used in determining the volume of the alloy was calibrated using boiled distilled water whose density was accurately known. Then, a pipetted sample of the alloy, after being weighed, was placed in the bottle in small sections and the bottle filled with kerosene, whose density had been determined using the calibrated volume of the density bottle. The bottle was tapped sufficiently

with a rubber mallet to ensure the removal of any occluded air. Then, by weighing the bottle and contents of alloy and kerosene and knowing the weight of the bottle filled with kerosene alone, the volume of the alloy could be simply found. For every weighing the bottle and contents were brought to the temperature of a thermostatted bath at 29.5°. The densities used in this analysis were as follows: kerosene, 0.7946 g./ml.; indium, 7.284 g./ml.; tin, 7.275 g./ml.; aluminum, 2.703 g./ml. (9).

The equation used for the calculation of the amount of aluminum in a ternary sample is as follows:

$$\text{Wt. Al} = \frac{\left\{ \left(\text{Vol. alloy} - \frac{\text{Wt. In}}{d_{\text{In}}} \right) d_{\text{Sn}} - \text{Wt. alloy} + \text{Wt. In} \right\} d_{\text{Al}}}{d_{\text{Sn}} - d_{\text{Al}}}$$

where Wt. Al means the weight of Al in the sample, and d_{Al} means the density of pure Al, with the other symbolism analogous.

The indium percentage of a sample was determined using a Sargent-Heyrovsky polarograph. This method was invented by Heyrovsky (20) and is discussed by Kolthoff and Lingane (21).

In this method the analyses are obtained by the interpretation of curves showing the current vs. voltage plot for the electrolysis of appropriate solutions containing the ions for which an analysis is required. These ions may require either oxidation or reduction, since the polarograph is

equipped to give observations for both cases. The cell for electrolysis, as shown in Figure 8, consists of a small flask which contains the solution to be electrolyzed and a stationary mercury pool which acts as one electrode. The other "dropping" electrode is formed by droplets of mercury issuing from a fine capillary held in a cork in the mouth of the flask. With this set-up, exactly reproducible results are obtainable, since the current through the solution depends only on the nature of the solution and the voltage across it.

The resistance of the solution to be analyzed is made negligible by adding chlorides, such as potassium chloride which was used in this investigation, which have a high decomposition potential. With a chloride present, the relatively large mercury pool remains depolarized, and the cell resistance depends almost completely on the processes which occur at the interface of the drops from the mercury electrode and the solution. Oxygen dissolved in the solution will be reduced at the electrode and lead to irregular results, so that it is necessary to remove the oxygen prior to electrolysis by passing through the solution a stream of hydrogen for from five to ten minutes.

The recording apparatus is given in the diagram. As shown, the dropping electrode is connected to the negative pole of the E.M.F. from the potentiometer, in which case positive ions are reduced at this electrode. A motor moves the bridge and thus changes the E.M.F. automatically and simultaneously rotates a drum on which is wound a piece of

photographic paper. A light from the mirror on the galvanometer which measures the electrolysis current falls on the photographic paper and thus a current-voltage curve is traced on the paper, which is made visible by developing. An Ayrton shunt permits adjustment of the galvanometer sensitivity.

The type of curve obtained is represented schematically in Figure 9. Here the decomposition of a single ion in solution is represented. At first a small residual current flows, but when the E.M.F. across the cell reaches the decomposition potential of the ion in solution, this ion starts being discharged at the mercury droplets. The current increases as these ions contribute their share to the current-carrying capacity of the solution. As more and more of these ions are discharged, their concentration in the vicinity of the electrode is diminished finally to zero. This decrease is compensated by the migration of ions from the body of the solution, and since the concentration of ions in the body of the solution remains practically constant and that at the electrode remains essentially zero, the rate of diffusion of ions from the solution to the electrode will become constant. This requires that the current due to these ions being deposited becomes constant also, i.e., approach a limiting value as the E.M.F. increases. This limiting value obviously depends on the rate of diffusion of ions in the solution and, therefore, on the concentration of the ions. What is actually determined in a polarographic analysis, as carried out in

this research, is the increase in the current as the ion is being deposited. This step-height is proportional to the concentration in solution of the ion in question, and hence if a step-height be determined using a solution of known concentration, a comparison of this step-height with that obtained by electrolysis of the same ion in a solution of different concentration gives the unknown concentration by a direct ratio. This method of analysis may be applied to a great assortment of ions and hence is a valuable tool in the analytical field. It is a fact that the voltage of the mid-point on one of these step-height curves is constant for and characteristic of a given ion. Thus any ambiguity as to the nature of the ion responsible for a given current increase is easily resolved.

On an actual curve determined photographically or otherwise, there are disturbances due to the periodic variation in size of the mercury drops. This is due to the dependence of the current on the electrode size.

The solutions prepared for analysis must be 0.01 to 0.0001 M in the unknown ion, and therefore, very small samples may be analyzed. The greatest error in the determination is involved in measuring the step-height using a ruler and pencil. More than one estimation may be made using the same solution so that repetition and subsequent averaging will tend to reduce errors due to this cause. In fact, more than one ion may be analyzed for using the same solution.

A short summary of the experimental procedure used in the estimation of indium is now given:

An alloy sample of the order of one gram was dissolved in dilute hydrochloric acid and then diluted to 500 ml. in a volumetric flask. An appropriate aliquot to ensure the proper concentration in the final solution was taken, and together with 25 ml. each of concentrated hydrochloric acid and 1.0 N potassium chloride was diluted to 250 ml. Ten ml. of this solution was then saturated with hydrogen and electrolyzed, the polarogram developed, and compared with the one obtained using a solution of known indium concentration.

The tin content of a sample was determined by the ordinary gravimetric method. About one gram of the alloy was dissolved in 1-1 nitric acid and the solution evaporated on the steam bath to 10 ml. This was then diluted to 50 ml., digested at 80 to 90° and filtered hot. The precipitate was washed ten times with hot 1-20 nitric acid and then ignited to stannic oxide in a porcelain crucible.

Thus, in summary, when a sample for analysis was withdrawn, its density was first determined; then portions were taken, one for the polarographic indium analysis, and another for the gravimetric tin determination. Whichever of these two latter values was deemed to be the more accurate was then used, along with the density of the sample, to estimate the aluminum content. The three values, the aluminum one being dependent on one of the other two, should then add to give a total of 100% as a check. This was always obtained within the limits of experimental error.

Isothermal Analysis

Apparatus. As the title suggests, the main problem here was the maintenance of a constant temperature for the equilibration of alloy samples. The furnace was regulated using a thermocouple connected to a galvanometer. In short, a light shining on the galvanometer mirror is reflected onto a photocell connected to an electronic control which in turn operates a relay which regulates the amount of current delivered to the furnace heating circuit. Mr. K. I. Koulston, Assistant Professor of Physics, designed the electronic control used here.

The electronic control is pictured schematically in Figure 10. The component parts are given as follows:

R ₁ 10K ohms	R ₅ 200K ohms	R ₉ 7.5K ohms
R ₂ 200K ohms	R ₆ 250K ohms	R ₁₀ ... 200K ohms
R ₃ 200K ohms	R ₇ 200K ohms	R ₁₁ ... 100K ohms
R ₄ 30M ohms	R ₈ 5K ohms	
T ₁ Hammond Type 275 Transformer		
C ₁ 24 microfarads		
L ₁ 30 henries		
L ₂ Aminco supersensitive Hg relay (600 ohms)		
6C6 ... A triple grid amplifier tube used to amplify an impulse from the photocells		
6N7 ... A duo triode type tube used to operate the relay		
5Y4G .. A full wave rectifier duo diode type tube		
Two 927 photocells		

The circuit operates as follows: light from the galvanometer mirror falls on the photocells, which are in parallel, and lowers the potential where the resistor R_4 is connected to the photocells. The number one grid of the 6C6 tube is accordingly lowered and the potential of the anode raised. This raises the potential at the sliding contact of the resistor R_6 , which in turn raises the potential of the left-hand grid of the 6N7 tube. As the grid potential rises, the anode potential drops until the relay L_2 releases. When no light falls on the photocells, the opposite action occurs, and the relay is activated. The only adjustment required is that of R_1 , and this was simplified this year by the substitution of a Dejur potentiometer for the cruder adjustment previously in use. Rectification and the proper voltage supply were supplied by the portion of the circuit including the 5Y4G tube, the transformer T_1 , the inductance L_1 , and the capacitance C_1 . The control was mounted on a metal chassis with the leads to the photocells of grounded metal-sheathed cable.

The entire circuit for isothermal control, including the electronic control, is shown in Figure 11 and operates as follows: the thermocouple used in the experiments was calibrated using the melting points of several common metals, so that a temperature-E.M.F. curve was available. Thus when a certain temperature was required in the furnace, the E.M.F. corresponding to this temperature could be easily determined from the calibration curve. The cold junction of the

thermocouple was kept at the fixed temperature 29.5° . The E.M.F. corresponding to the temperature required was then placed across R_1 , which is variable and in series with six volts and 200,000 ohms. The correct setting of R_1 was obtained by balancing against the potentiometer. By setting the switches properly, R_1 can be opposed to any E.M.F. from the thermocouple with the Type 2400 galvanometer in series in the same circuit. Thus if the furnace is allowed to heat, the E.M.F. of the thermocouple will gradually reach a value equal and opposite to that across R_1 . The furnace will then be at the required temperature, and no current will flow in the circuit containing the thermocouple, R_1 , and the Type 2400 galvanometer in series, i.e., the galvanometer is at its null point. The position of the galvanometer has been so adjusted beforehand that when no current flows through it, the light reflected from its mirror as shown in the diagram will just fall on the first photocell and release the relay. This release inserts an added resistance R_2 into the furnace heating circuit, causing the heating current to fall, the furnace temperature to gradually drop, and the thermocouple E.M.F. to decrease also. This means that the constant backing E.M.F. across R_1 is now larger than that supplied by the thermocouple, and a current will flow through the galvanometer. Its mirror will swing slightly causing the light to fall off the photocells, in which case the relay is activated. The resistance R_2 is removed then from the furnace heating circuit and the furnace heats once more to a point such that

the light from the galvanometer just refalls on the photocells. This process must be repeated for as long as the constant temperature, as determined by the setting of R_1 , is required. The second photocell in the diagram is simply a safety measure in case the light from the galvanometer mirror should get past the first photocell. A mirror was also installed so that if by chance the light should get past both photocells, it would be reflected back on either one or the other. However, if the light should jump both photocells and mirror, it can be seen that R_2 would always be removed from the furnace heating circuit, and the furnace would overheat. The only remedy is to reset the furnace and hope that the same trouble does not occur again. A set-up in which the light beam could swing past either cell and still return had been designed by Lutz and Wood (22), but due to the complexity of the circuit, it was difficult to adjust or repair it.

It can be seen from the diagram that the temperature of the furnace can be observed at any time by reading the E.M.F. of the thermocouple using the K-1 potentiometer.

The photocells, light source and galvanometer were mounted in a box six feet long, six inches wide, and a foot high, as shown in Figure 12. The inside of the box was painted black to reduce internal reflection of light. The Leeds and Northrup Type 2400 Galvanometer had a sensitivity of 0.003 microamps per mm. at one meter. The light source was a Westinghouse Mazda #2330 automobile headlight bulb operating from a transformer on 6 volts A.C. The light was

transmitted through a lens which focussed the light beam through a slit onto the galvanometer mirror. The lens position could be varied until the light was at its focal point. The light beam was reflected from the galvanometer mirror over the light bulb and lens onto the photocells, which were at the opposite end of the box to the galvanometer. All parts were screwed down so that once adjustments were made, the whole apparatus could be made rigid. Thus readjustments were few.

At 700° the temperature could be controlled to within 1° and at 900° within 2° . The variation in the voltage of the power source was the determining factor in the accuracy of the temperature control.

The furnace used in this investigation was constructed in the following manner. Two pieces of rubber tubing, joined at both ends, were wound about a four inch diameter cylindrical cardboard box, so that there was a space of one inch between each turn, the total vertical height of the turns being four inches. The two joined ends were at top and bottom. Concentric with the cardboard box was placed a galvanized sheet iron cylinder seven inches in diameter. Into the space between box and cylinder was poured to a depth of five inches a fifty-fifty mixture of "insolute" cement and sand with water. This was set by drying in a furnace for two days during which time the temperature of the furnace was raised progressively from 50° to 150° . When the cement had hardened, the interior cardboard box was removed and the

rubber tubing withdrawn so as to leave grooves to support two nichrome heating elements of 1700 watts each. These elements were wound in parallel and connected to two copper terminals five-sixteenths of an inch in diameter which protruded through two holes drilled in the side of the furnace block so as to provide outside connections for the 110 volt input.

This furnace block, complete with heating elements and terminals, was placed in the center of the base of a sheet iron cylinder seventeen inches in diameter and nine inches in height, and rested on a circular mortar stand about two inches in height. The space between the furnace block and iron cylinder was filled with asbestos powder, and the terminals reached through it and through holes in the galvanized iron cylinder. A lid having holes for the thermocouple, sampling tubes and reducing atmosphere inlet tube was made of one half inch transite. The thermocouple used was of chromel-P-Alumel, the hot junction protruding into the furnace and the cold junction being in the constant temperature bath at 29.5° . The leads from the cold junction were of copper wire.

The E.M.F. measuring set-up consisted of a Leeds and Northrup Type K-1 potentiometer coupled with a Leeds and Northrup Type P wall galvanometer of sensitivity 0.0015 microamps per mm.

The cold junction bath which contained the cold junction ends in sealed Pyrex tubes was thermostatted using

a mercury regulator in series with a relay which operated a forty watt light bulb as a heater.

Two practically identical calibration curves for the thermocouple used were prepared by Buchanan (8) and Kuzmak (9) and were checked using the freezing points of pure Al-659.9, Zn-419.4, and Pb-327.4°. These points checked almost perfectly with those obtained a year previously by Kuzmak and were, therefore, assumed sufficient for calibration purposes. Since the thermocouple cold junction was maintained at 29.5° and not 0°, the value 29.5° was subtracted from the calibration metals' freezing points, so that a temperature reading for a given E.M.F. on the calibration curve indicated the temperature difference of the two junctions.

In order to prevent oxidation of alloy samples which had to be equilibrated for three days at temperatures in excess of 800°, a reducing atmosphere of hydrogen and nitrogen was passed over the melt. This atmosphere was obtained by cracking ammonia over heated steel wool in the specially designed apparatus built by Skinner (23). The cracked ammonia was passed through dilute sulfuric acid to remove any undecomposed ammonia, dried over calcium chloride, passed through a flow-meter, and then admitted to the sample container. A current of 8 amperes was passed through the nichrome heating element in the body of the ammonia cracker, giving a temperature of about 650°.

Procedure. During the Manitoba spring floods of 1950, the room in which the preliminary researches of Buchanan and Kuzmak had been done was completely flooded so that the apparatus had to be totally dismantled. The more important equipment, such as the electronic control, potentiometers, galvanometers and polarograph was saved, but more bulky apparatus such as the ammonia cracker, could not be removed in time. Therefore, the first task of the author was a complete rebuilding of the apparatus. The set-up for the maintenance of constant temperature was rewired, and a new box for the photocell arrangement was built. The ammonia cracker was overhauled, and the polarograph readjusted and dried thoroughly with a heat lamp. This phase of the work took a period of some two months before the furnace could be maintained at a constant temperature for the required equilibration times.

Kuzmak has shown that it is not practicable to use Pyrex containers for the alloy samples, since the aluminum reduced silicon from the glass, thus giving a four component system. The introduction of the silicon led to pronounced immiscibility of the metals, in the liquid phase at least.

Alundum (aluminum oxide) crucibles were then tried because of their inertness. The size suitable for this isothermal work was three and three-eighths high and had an upper outside diameter of one and three-eighths inches.

A suitable volume (about 20 ml.) of alloy sample of the required composition was melted and thoroughly mixed in the crucible set in an induction furnace which was operated

on 220 volts with a continuous input of three kilowatts giving 35 amperes. This furnace was of the Ajax high frequency converter type. The sample was allowed to cool and was placed in a container consisting of two iron caps on a three and one-half inch nipple. The upper cap was drilled to provide entry for a steel tube carrying the reducing atmosphere, and a smaller hole was drilled through which to pass the sampling tube (mentioned later).

The iron "bomb" was then placed in the furnace along with the thermocouple hot junction for the required equilibration time, three days being sufficient in most cases.

The most successful method of sampling was as follows: an alundum tube of outer diameter one-eighth inch and inner diameter one-sixteenth inch was passed into the molten sample and suction applied to the outer open end. The molten sample solidified in the tube, and the tube was broken for removal of the sample. This procedure was suitable for temperatures up to and including 850°, but at 900° the relatively low melting indium would not solidify in the tube and ran out as the tube was being withdrawn from the melt. It was assumed that the higher melting aluminum solidified first on the walls of the tube, the indium concentration increasing towards the center of the tube. In order to avoid any errors due to such concentration gradients in the sample, the whole sample withdrawn was analyzed, since the composition of the whole sample removed must necessarily be that of the portion of the melt into which the tube was thrust, regardless of any gradients.

At 900° and above, a quenching process was tried. Alundum tubes one and one-quarter inches long, one-quarter inch outside diameter and one-eighth inch inside diameter were filled with a sample of the desired composition. The alundum container was wrapped with copper foil until it fitted snugly into a copper tube which was pinched shut at both ends and inserted into the furnace at the desired temperature. After two days the sample was withdrawn from the furnace and thrust into ice water. The copper tubing was torn away and the crucible broken to yield a sample for analysis.

At temperatures below about 600° the possibility of the appearance of a solid aluminum phase becomes more acute. Therefore, in working in those regions of the ternary system where solid aluminum is present, special methods must be used in procuring a sample for analysis; since the low density of aluminum will cause it to be the uppermost phase when present as a solid, it was decided to attempt to drill through the aluminum crust in order to sample the liquid layers underneath by the alundum tube method. In case of difficulties using this method, quenching could always be resorted to.

Thermal Analysis

Apparatus. Thermal analysis was used in an effort to determine the upper critical solution temperature of the miscibility gap in the In-Al system.

The Hoskins electric furnace used in conjunction with a Surges transformer drew thirty amperes at a maximum

of fifty volts. The furnace oven consisted of a two-inch horizontal cylinder open at both ends and having a length of fifteen inches. For our purposes the furnace was placed on its side so that the oven cylinder was vertical, with the bottom five inches being packed with asbestos powder. One of the larger crucibles mentioned previously would then fit nicely. A cover was made of one-half inch transite and holes drilled for entrance of the thermocouple hot junction and the tube carrying the reducing atmosphere.

The furnace was connected in series with an ammeter of twenty-five ampere capacity, a variable rheostat of 10.1 maximum ohms, a knife switch, and the transformer. The temperature of the furnace was determined by measuring the E.M.F. of the thermocouple, using the necessary equipment from the set-up for isothermal analysis. The furnace temperature was adjusted by varying the current using the variable rheostat.

Procedure. The first part of the work involved obtaining a linear temperature vs. time curve for the furnace over a suitable range assumed to include the upper critical solution temperature. Any phase change registers as a break more clearly on a linear cooling curve than on an exponential one.

The temperature of the furnace was determined for a series of constant current values. Then the thermocouple was placed in the furnace, the end of the thermocouple casing being inserted into a copper tube of the same specific heat as the alloy sample to be used in the investigation. Copper was used, since it exhibits no phase changes over the temperature range for which linear cooling is required. A stream of the hydrogen and nitrogen mixture was passed into the furnace so as to duplicate the conditions to come with the alloy sample. The furnace was brought to equilibrium at about 1050° . Then an exponential cooling curve was obtained by shutting off the current. With the aid of this curve and by trial and error, a series of runs in which the current was cut down progressively using the variable rheostat finally culminated in one run which was linear in the range 1050° to 750° within the limits of the potentiometer used to measure the thermocouple E.M.F. A record of the currents used at the various times during the linear run was recorded for use with an actual melt. The cooling rate employed was about 2° per minute.

An indium-aluminum mixture of approximately 61 weight per cent indium (which earlier work had shown should be very close to the upper critical solution composition) was prepared and melted into the crucible in the induction furnace. This was then placed in the furnace and the thermocouple with cover inserted into the alloy when molten. The furnace was

maintained at a temperature of 1050° for some two hours to establish equilibrium. The reducing atmosphere was introduced via a sillimanite tube through the hole in the lid. The sample was then cooled according to the procedure as determined from the linear "dummy" run, i.e., by introducing resistance into the furnace heating circuit. Readings of the thermocouple E.M.F. were made every two minutes, and in this manner a temperature vs. time-"cooling"-curve was obtained for the alloy sample.

X-Ray Analysis

Apparatus. According to Fink (16) and Rhines (19) there are four series of solid solutions in the system In-Sn. In an attempt to determine the extent of solution of aluminum in these solid solutions, a brief X-ray investigation was undertaken.

The North American Philips Co., Inc., X-ray apparatus used drew twenty-five milliamperes. Three pictures could be taken simultaneously, simple Debye cameras being used.

Procedure. The samples for analysis were prepared according to the procedure of Fink et al. (24). Accurately weighed samples of the metals were sealed in evacuated Pyrex test tubes and heated until molten. The liquid was well shaken to ensure complete mixing. The solid ingot was then annealed for several days at 110° . The test tube was then broken, the ingot removed and cut into small pieces. Some of these small pieces were then rolled into foil of approximately 0.002 inch

thickness using a rolling machine of the Manitoba Dental Clinic. Foil was necessary, since powder was not obtainable from the alloys due to their extreme softness. The composition of the alloys could be taken from the weighed amounts of the metals, since the loss in weight due to melting was negligible.

The foil was annealed for several days also at 110°. Small rectangles of the foil were rolled into cylinders and placed in position in the X-ray cameras.

Pictures were taken of pure aluminum and of a representative binary solid solution of each series; thus, α series, pure indium; β series, 23% Sn, 77% In; γ series, 83% Sn, 17% In; δ series, pure tin. The values for these compositions were obtained from Fink (24).

Then five per cent aluminum was added to each of the binary samples and the pictures repeated, so that a total of nine different pictures were developed. A comparison of the four "ternary" pictures with the four "binary" pictures should indicate whether aluminum enters into the indium-tin solid solution or remains almost completely as an extra phase.

EXPERIMENTAL RESULTS

EXPERIMENTAL RESULTS

Table I

Composition Boundaries of the Aluminum-Indium Miscibility Gap

Temperature of Furnace °C	Sample Number	Al-Rich Layer		In-Rich Layer	
		% Al	% In	% Al	% In
675	1	79.4	20.6		
	2	81.2	18.8		
	3			4.6	95.4
	4			4.4	95.6
	5			4.1	95.9
	6	81.2	18.8		
	7	78.7	21.3		
750	1			7.5	92.5
	2	73.0	27.0		
	3			7.3	92.7
	4	74.3	25.7		
	5	74.1	25.9		
	6			8.3	91.7
800	1	70.7	29.3		
	2			9.7	90.3
850	1	57.3	42.7		
	2	60.9	39.1		
	3			20.8	79.2
	5			19.6	80.4
	6	62.8	37.2		
	7			18.7	81.3
	8	62.7	37.3		
	9	54.5	45.5		

Table II
 Summary of Composition Boundaries
 of Aluminum-Indium Miscibility Gap

Temperature °C	Al-Rich Layer % In	In-Rich Layer % In
675	19.9	95.6
750	25.3	92.3
800	29.3	90.3
850	41.1	80.3

Table III
 Isothermal Analysis of In-Al Miscibility Gap
 at Higher Temperatures

Temperature of Furnace °C	Portions Analyzed from Sample		
	Top	Middle % Indium	Bottom
926	65.6	69.7	70.4
900	64.8	63.1	65.4
850	18.5		96.0

Thermal Analysis of In-Al Miscibility Gap

Five dummy runs were made in an effort to obtain a standard linear cooling curve for use with the actual sample. The final run was sufficiently linear for the purpose of investigation, and a three-hour run was then made using a 61 weight per cent indium sample. The results have been plotted and are shown in Figure 13.

E.M.F. OF THERMOCOUPLE (MILLIVOLTS)

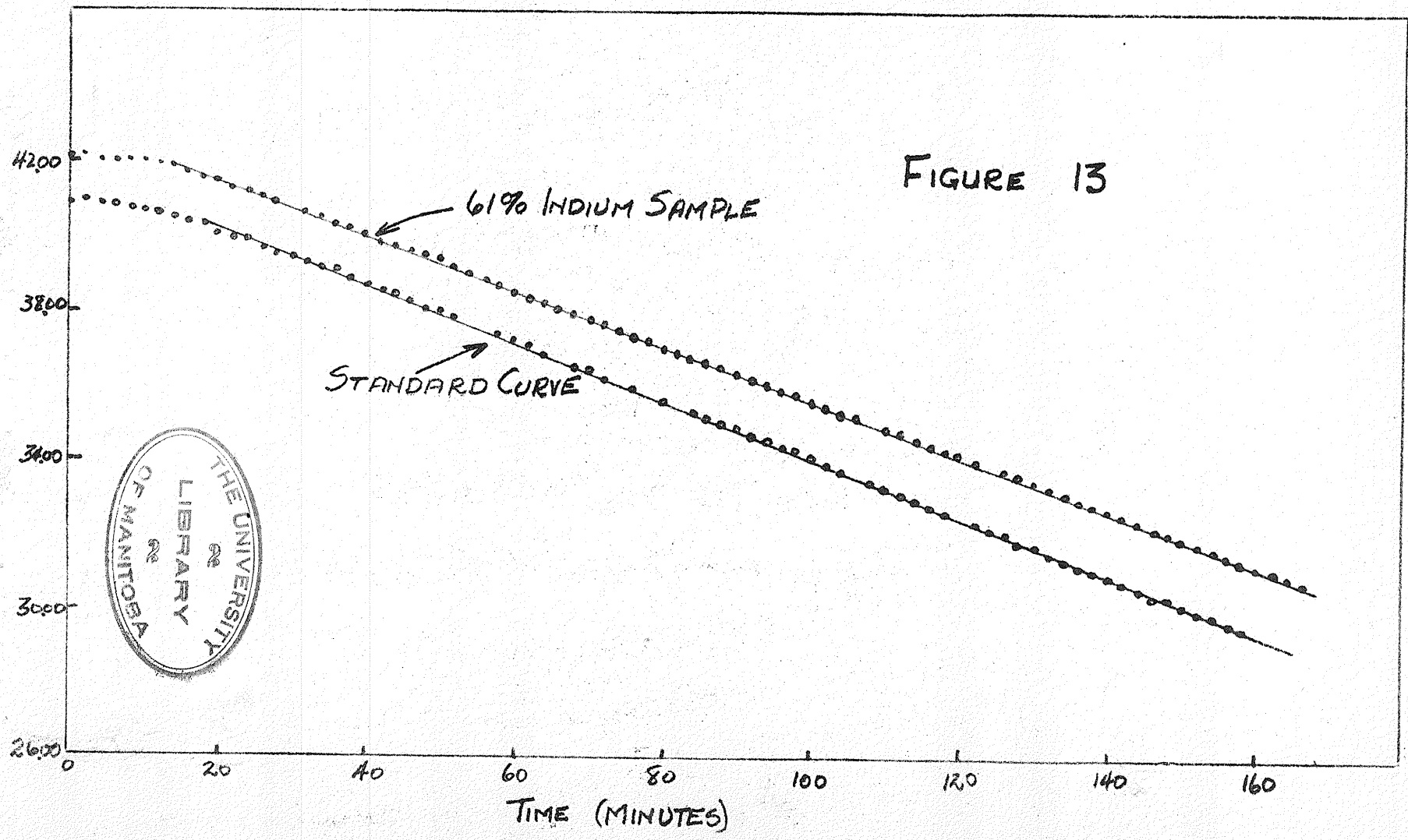


FIGURE 13

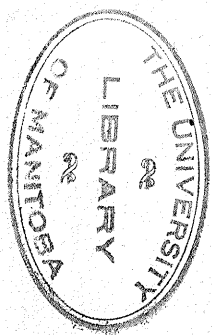


Table IV
 Composition Boundaries of Ternary
 Miscibility Gap at 750° C
 (Equilibration Time - Three Days)

Sample Number	Al-Rich Layer			In-Rich Layer		
	% Al	% In	% Sn	% Al	% In	% Sn
1	74.7	25.3	0.0	7.7	92.3	0.0
2	62.6	25.6	11.8	10.9	76.2	12.9
3	49.6	34.5	15.9	16.1	64.5	19.4
4	43.4	33.6	23.0	26.9	44.8	28.3

Table V
 Composition Boundaries of Ternary
 Miscibility Gap at 650°
 (Equilibration Time - Three Days)

Sample Number	Al-Rich Layer			In-Rich Layer		
	% Al	% In	% Sn	% Al	% In	% Sn
1	81.4	18.6	0.0	3.0	97.0	0.0
2	74.9	18.5	6.6	6.1	81.4	12.5
3	66.5	18.9	14.6	7.2	67.6	25.2
4	59.9	18.1	22.0	9.4	56.4	34.2
5	53.9	17.9	28.2	15.3	43.9	40.8
6	42.5	20.4	37.1	17.9	35.7	46.4

Table VI
 Composition Boundaries of Ternary
 Miscibility Gap at 700° C
 (Equilibration Time - Three Days)

Sample Number	Al-Rich Layer			In-Rich Layer		
	% Al	% In	% Sn	% Al	% In	% Sn
1	55.3	20.5	24.2	18.9	48.1	33.0
2	40.3	29.6	30.1	22.2	38.5	39.3

Table VII
 Isothermal Investigation of Ternary System at 450° C
 (Equilibration Times - Three Days)

Portions Analyzed from Sample

Sample Number	Top			Middle			Bottom		
	% Al	% In	% Sn	% Al	% In	% Sn	% Al	% In	% Sn
1	78.8	14.7	6.5	64.9	25.8	9.3	11.8	81.6	16.6
2	58.3	14.0	27.7				12.2	31.6	56.2
3	75.9	20.1	4.0				94.6	5.8	

Table VIII

Data from the X-Ray Solid Solution Investigation

Lattice Spacings in kX Units

Pure Al	α Phase Pure In	α Phase + 5% Al	β Phase 23% Sn, 77% In	β Phase + 5% Al
a 2.326	2.691	2.675	2.683	2.691
b 2.021	2.442	2.448	2.410	2.432
c 1.429	2.264	2.275	2.170	2.174
d 1.219	1.668	1.668	1.717	1.725
e 1.167	1.614	1.611	1.621	1.622
f 1.008	1.461	1.459	1.451	1.453
g 0.926	1.389	1.385	1.345	1.341
h .902	1.352	1.350	1.214	1.223
i .824	1.231	1.227	1.109	1.110
j .778	1.145	1.142	1.089	1.091
k .776	1.086	1.083	1.060	1.072
	1.054	1.053	0.998	1.002
	1.039	1.038	.976	0.977
	1.024	1.023	.934	.936
	0.980	0.978	.924	.926
	.944	.944	.905	.903
	.902	.903	.850	.849
	.884	.884	.822	.824
	.840	.840	.816	.815
	.816	.816	.802	.801
	.789	.789	.775	.775

Table VIII (Cont'd.)

Pure Al	α Phase Pure In	α Phase + 5% Al	β Phase 23% Sn, 77% In	β Phase + 5% Al
	.788	.787	.773	.773
	.777	.777		
	.775	.775		a 2.324
				b 2.019
		b 1.992		c 1.429
		d 1.215		e 1.165
		g 0.926		j 0.778
		i 0.824		
		c 1.421		
γ Phase 83% Sn, 17% In	γ Phase + 5% Al	δ Phase Pure Sn	δ Phase + 5% Al	
2.755	2.755	2.823	2.858	
2.022	2.030	2.005	1.996	
1.607	1.609	1.648	1.646	
1.411	1.409	1.475	1.475	
1.385	1.385	1.437	1.438	
1.314	1.314	1.292	1.288	
1.257	1.265	1.198	1.197	
1.093	1.099	1.091	1.088	
1.049	1.053	1.036	1.035	
1.017	1.019	1.022	1.021	

Table VIII (Cont'd.)

γ Phase 83% Sn, 17% In	γ Phase + 5% Al	δ Phase Pure Sn	δ Phase + 5% Al
0.992	0.992	0.978	0.979
.938	.938	.968	.968
.926	.929	.925	.924
.885	.885	.915	.916
.860	.862	.883	.883
.848	.846	.872	.873
.810	.810	.845	.844
.803	.801	.836	.835
.788	.788	.806	.807
.786	.786	.804	.804
.775	.775	.783	.783
.773	.773	.781	.781
		.775	.775
	d 1.219	.773	.773
	h 0.903		

DISCUSSION OF RESULTS

As already outlined, the values obtained in Table I from the isothermal investigation of the Al-In miscibility gap were from analysis of samples withdrawn from alundum crucibles using alundum tubes, the process being performed while the alloy was at the equilibrating temperature. Thus there was no danger of introduction of silicon as Kuzmak had observed, and also the inaccuracies of quenching were avoided. There was always the possibility of the introduction of a small portion of the upper layer into the sampling tube as it was being inserted for the recovery of a sample from the lower layer. For this reason the upper portion of the lower sample was always discarded.

However at 850° difficulty was experienced in withdrawing samples due to the extreme fluidity of the melt. In several attempts metal flowed from the sampling tube as it was being withdrawn from the molten alloy, thus rendering the sample unsuitable for analysis. At 900° a sample could not be obtained by this method for the above reason. Resort was, therefore, made to quenching (see Table III).

Table II gives a summary of Table I in that the various values for a given temperature have been averaged. The averages have been plotted in Figure 14. The miscibility gap curve has not been fully outlined in the region above 800°, since the individual values at 850° are somewhat

THE SYSTEM - AL. - IN.

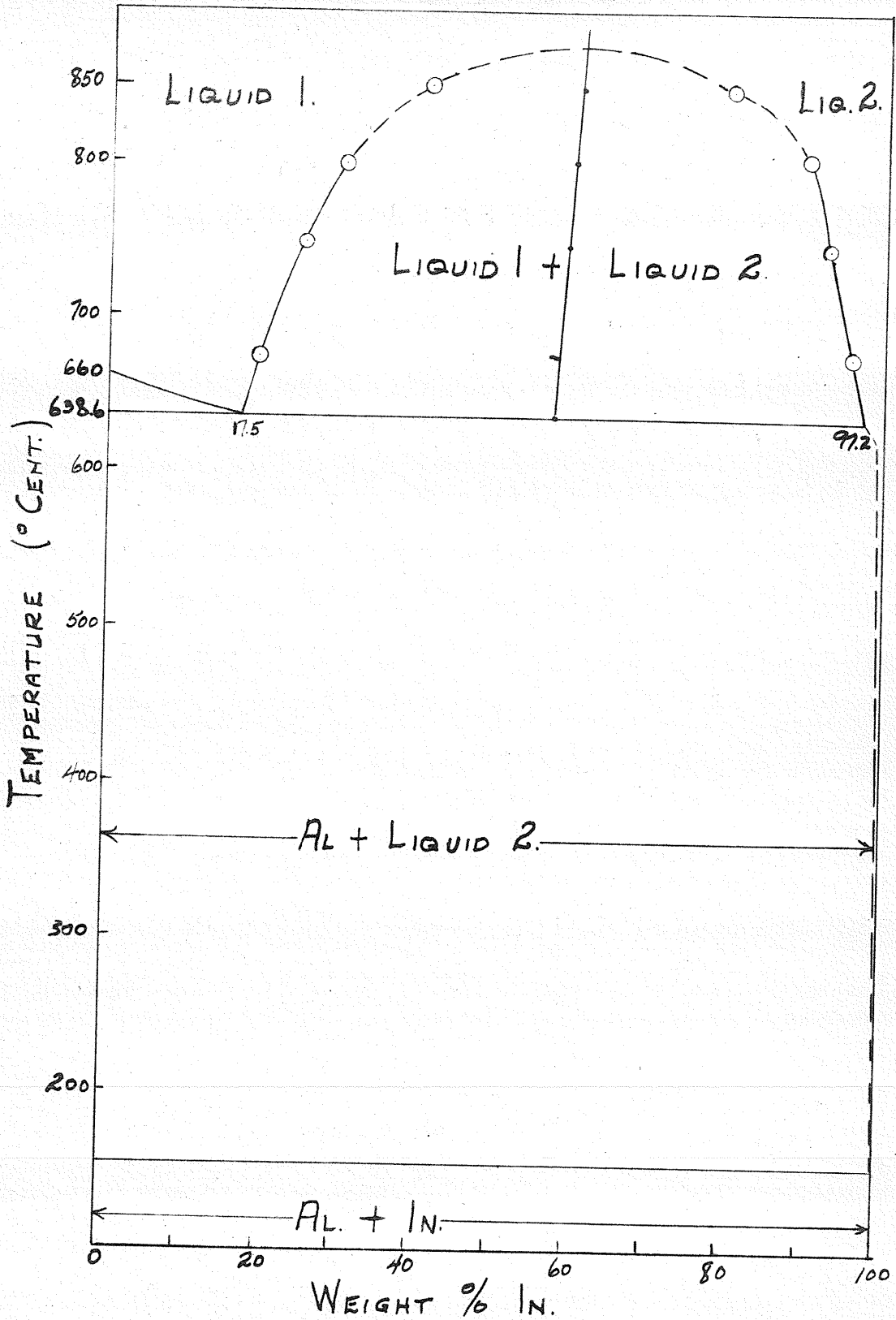


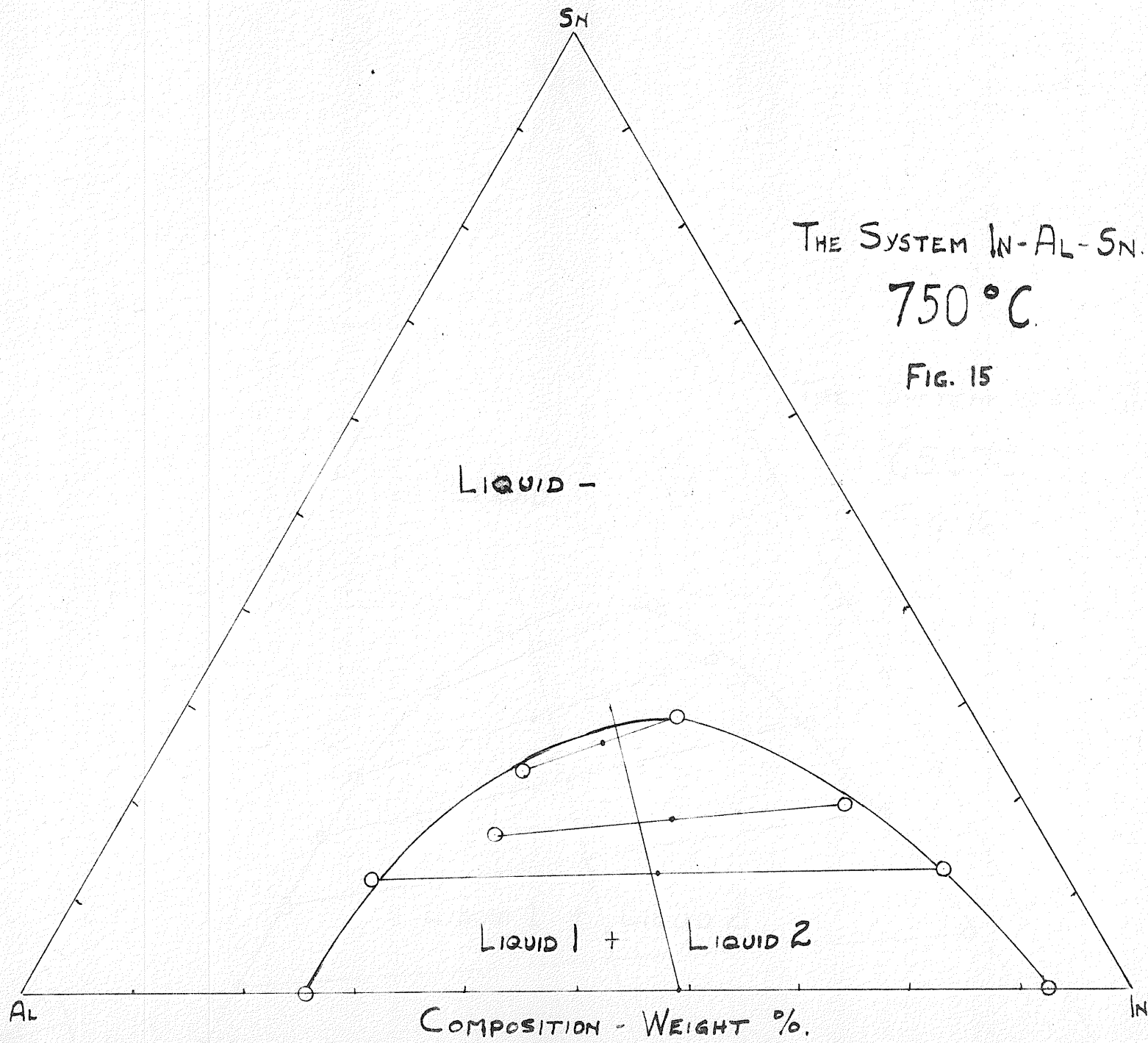
FIG. 14

inconsistent with each other. The extrapolated curve intersects with the extension of the rectilinear diameter to give an approximate upper critical solution temperature and composition of 875° and 61 weight per cent indium, respectively. The values for the lower limits of the miscibility gap have been taken as follows: Al-rich layer, 17.5% In, Raub and Engel (4); In-rich layer, 97.2% In, Buchanan (8). Buchanan's value of 638.6° for the lower limit temperature has been used in the construction of the figure.

The analyses of quenched samples contained in small alundum crucibles placed in sealed copper tubing are given in Table III. The first sample was equilibrated in the Hoskins electric furnace while the last two were heated in the open element furnace. The samples were prepared to contain 61 weight per cent indium, which was the upper critical solution temperature as given above. This composition was used in an attempt to bracket the upper critical solution temperature as the temperature was progressively varied. However, it can be seen from the analyses that the sample appeared to increase in indium content during the heating period. This is most probably due to preferential oxidation of the aluminum at these high temperatures, since some oxygen was sealed in the copper tubing along with the sample. It is obvious that this would render the bracketing process described above less successful, but since the miscibility gap curve is quite flat along its upper boundary, the error would

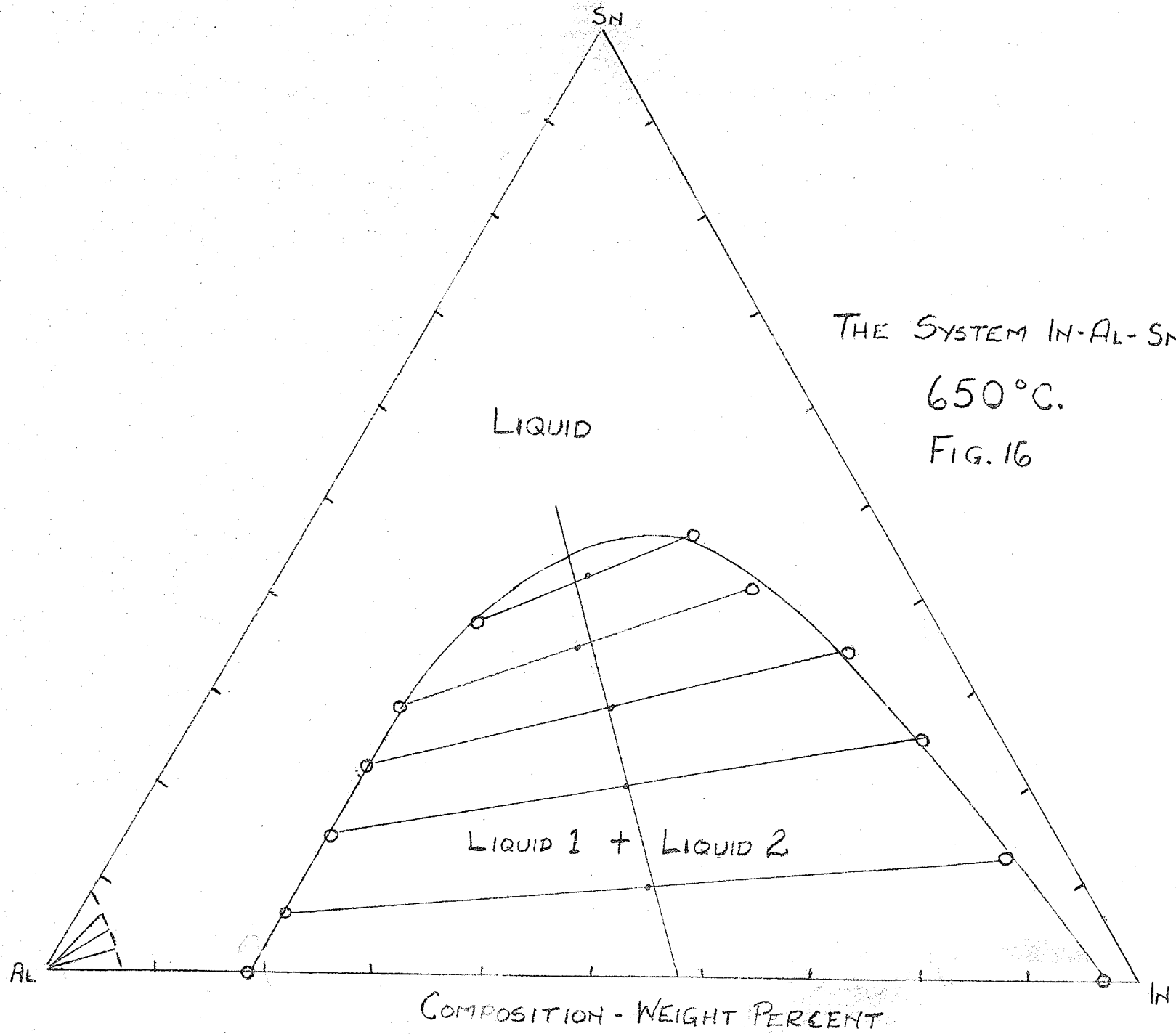
not be appreciable. The first two samples at 926° and 900° , respectively, would tend to indicate that there is complete miscibility at 900° and above, which corroborates the evidence from Figure 14. There is a slight separation of the two metals evident at 926° but this may have been due to liquation during the quenching process. At 850° the metals appear to be much more immiscible than was indicated previously from samples obtained by tube sampling. This was probably due to the presence in the melt of a trace of copper from the container, since a reddish-brown precipitate was left after solution in hydrochloric acid of the top and middle portions. Since previous results indicate immiscibility at 850° and these data indicate miscibility at 900° , the upper critical solution temperature must lie somewhere between the two values. Thus a check is furnished for the value previously given.

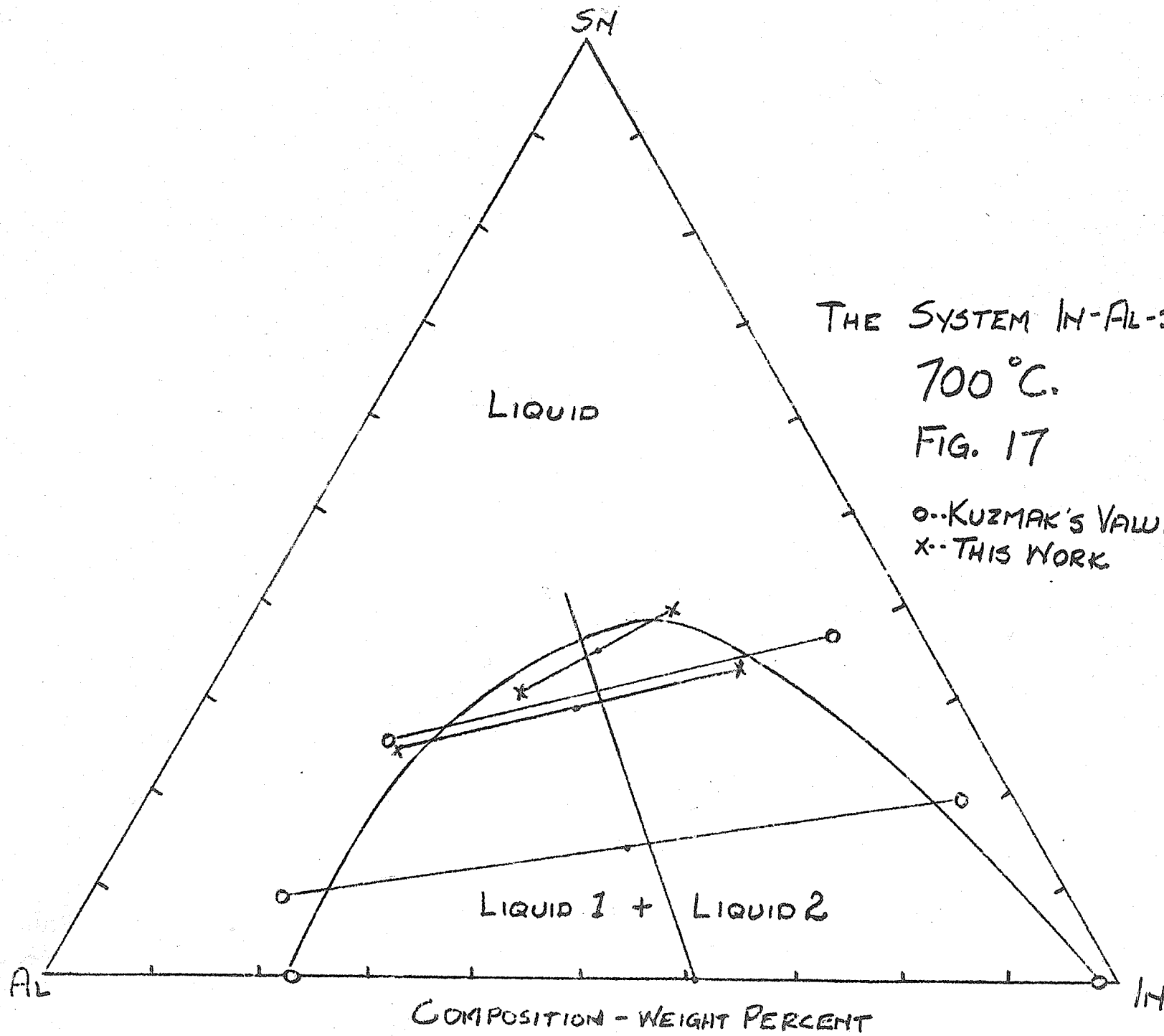
From the two curves given under the heading "Thermal Analysis of the In-Al Miscibility Gap," it can be seen that no significant results were obtained. Thus both curves were linear which, of course, was the requisite for the standard curve, but which is undesirable for the second curve. It was expected for the actual run that the separation of the melt into two liquid layers at the upper critical solution temperature would register as a break in the linearity of the cooling curve. Thus the upper critical solution temperature could be defined more exactly. Such was not the case, however, and the explanation that must be given is that the heat effect



THE SYSTEM IN-AL-SN.
 750 °C.
 FIG. 15

COMPOSITION - WEIGHT PERCENT





THE SYSTEM IN-AL-SN

700 °C.

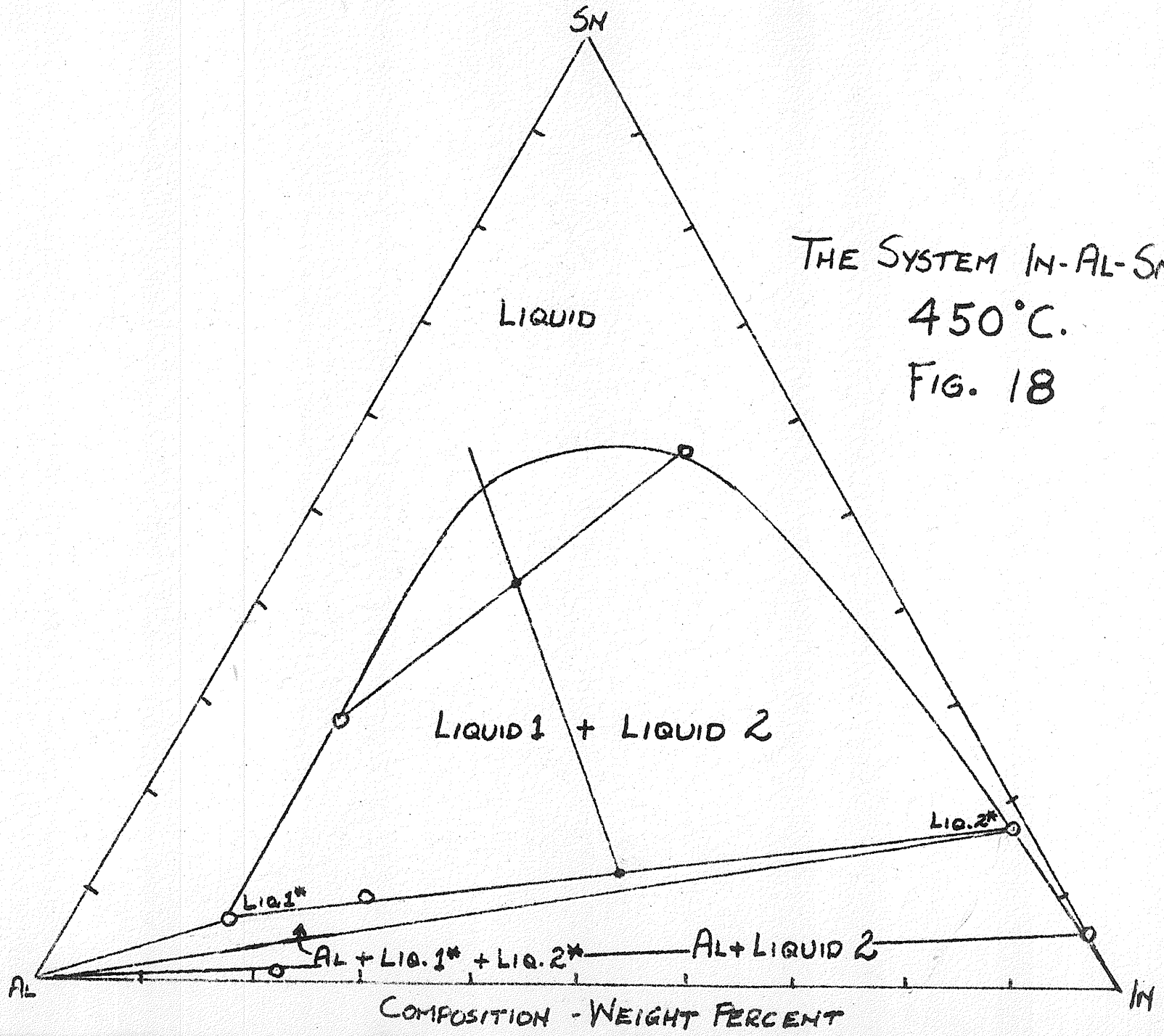
FIG. 17

o..KUZMAK'S VALUES
 x..THIS WORK

accompanying such a separation into two liquid layers is not sufficiently great to be recorded. A slower rate of cooling might be the solution to the problem, but such a procedure would not be practicable. The data, time-consuming as they were to obtain, must be discarded.

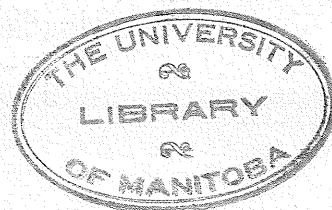
The composition boundaries of the ternary miscibility gaps at 750°, 650° and 700° as given in Tables IV, V and VI were obtained as previously outlined by the analysis of samples obtained by suction into alundum tubes. In most cases the two smallest values of the three obtained as the percentages of the metals in a given sample are given as the more reliable, with the value for the third metal adding to give 100%. In all cases the value obtained by analysis for the third metal added to give a value as close to 100% as experimental conditions would allow.

In Figure 17 for the isotherm at 700° certain values of Kuzmak's (9) are given but those missing have supposedly been improved upon in this later work. This improvement has been termed such, since Kuzmak used quenching techniques in obtaining his values, leading to errors due to liquation. Such errors would cause the miscibility gap to expand so as to enclose a larger area, which this work has shown to be the case. Also the three miscibility gaps obtained are of such a nature as to lie on a smooth surface extending into the ternary solid model from the In-Al side of the triangular prism.



THE SYSTEM IN-AL-SN
 450°C.
 FIG. 18

At 450° it was found for all samples investigated that a layer of solid aluminum sufficiently deep to defy drilling to liquid below had formed at the surface. Recourse was, therefore, had to quenching, so that the results are liable to the errors of liquation. However, quenching from the relatively low temperature of 450° would not cause these errors to be as large as in any previous work cited. The results have been interpreted as shown in Figure 18, i.e., the first sample is assumed to have a composition on, or very close to, the base of the miscibility gap which has now moved into the body of the diagram. Because the temperature is relatively low, equilibration will be much slower, and therefore, the value for the analysis of the middle portion of the first sample which gives a point on the straight line joining points for the upper and lower portions must represent the composition of a mixture of upper and lower portions, this mixture being present due to incomplete equilibration (or perhaps also some liquation in the quenching). Similarly it is assumed that the third sample represents an equilibrium between solid aluminum and an indium-rich liquid, incomplete separation being apparent (the upper portion of the third sample is directly analogous to the sample obtained in Schreinemaker's wet-rest method for the determination of the solid(s) in equilibrium with liquid solutions).



DISCUSSION OF RESULTS

The X-ray data given in Table VIII show that aluminum does not enter into the In-Sn solid solutions to the extent of five per cent and probably not at all, since the lines of the pure phases have not been shifted to any observable extent. Although attempts were made several times, no aluminum lines could be observed when 5% aluminum was added to pure tin (the occurrence of aluminum lines would have indicated the presence of aluminum as an extra phase). These lines should have been observed, since the established diagram for the system Al-Sn denies solid solution. An explanation may be that the aluminum and tin had been but poorly mixed in the preparation of the samples for X-ray purposes. However, sufficient aluminum lines have been observed in the cases of the α , β , and γ solid solutions to indicate the presence of aluminum as a separate phase (five per cent is an average minimum to be equalled or exceeded if a phase is to make any contribution to an X-ray picture).

SUMMARY

SUMMARY

1. The complete diagram for the system In-Al has been completed with the closing of the miscibility gap. The upper critical solution temperature and composition are estimated at 875° and 61 weight per cent indium, respectively.
2. In the ternary system the critical composition at 750° is approximately 39% In, 34% Al, 27% Sn.
3. At 650° the critical composition is approximately 25% In, 30% Al, 45% Sn.
4. At 700° the critical composition is approximately 32% In, 32% Al, 36% Sn.
5. At 450° the critical composition is approximately 15% In, 32% Al, 53% Sn. The lower limits of the miscibility gap are approximated at 15% In, 78% Al, 7% Sn, and 81% In, 2% Al, 17% Sn.
6. An X-ray investigation has shown that the solid solubility of aluminum in the binary solid solutions of indium and tin is not greater than 5%, if indeed there is any such solid solubility.

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