THE SYSTEM ALUMINUM-INDIUM-TIN

by

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To Dr. A. N. Campbell
who patiently and helpfully
guided me in this, my first venture
into the field of research

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THE SYSTEM ALUMINUM-INDIUM-TIN

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INTRODUCTION

INTRODUCTION

The study of the system aluminum-indium-tin was begun by Mr. L.B. Buchanan at the University of Manitoba in the fall of 1948 as a result of the interest shown by the Consolidated Mining and Smelting Co., Ltd. in alloys of indium and other metals. Indium, a comparatively rare metal, which occurs in zinc-blende, is being refined as a by-product by the Consolidated Mining and Smelting Company.

The above mentioned company was particularly interested in the system indium-aluminum, which, it was learned, was being investigated by Valentiner in Germany. Buchanan checked certain portions of this binary system, including the extent of the miscibility gap, and then proceeded to investigate the ternary system Al-In-Sn. He determined the ternary eutectic, and began an isothermal investigation of the miscibility gap.

It was felt that a more thorough isothermal investigation of the ternary miscibility gap should be carried out, beginning at 700°C and going up to higher temperatures. There is, of course, the possibility that some new aspect of the problem might be revealed in the process of carrying out the above isothermal investigation. If this should happen, and if it should appear more significant as far as the problem as a whole is concerned, then an investigation of this new aspect would be pursued.

TECHNIQUES

TECHNIQUES

A review of only those considerations which have a bearing on the immediate problem will be given here. In the study of this system, the aim is the construction of a phase diagram for the system. A phase diagram, or equilibrium diagram, indicates the various phases present in equilibrium for different composition-temperature relationships; pressure is not a variable in an open system. The four principal methods of determining phase diagrams are thermal analysis, isothermal analysis, microscopic analysis and X-ray diffraction analysis and the most accurate information is obtained when all four methods are used to supplement one another. A brief discussion of isothermal analysis, microscopic analysis and X-ray diffraction analysis will now be given, since these are the methods that will be used in the present investigation.

Isothermal Analysis

Isothermal analysis has been sparingly used in the construction of phase diagrams for alloys, although it has been the main method for the investigation of systems of salts and water. The method can be applied to alloy systems, because the liquidus curve of an alloy system is actually a solubility curve. The alloy is kept at a constant temperature for a length of time sufficient to ensure the attainment of equilibrium. There are two methods that are usually used to obtain portions of the phases in equilibrium for analysis. By one method, the whole sample is quenched, then it is cut vertically in two, and a portion is taken using a drill large enough to give a representative sample. By the other method, a portion for analysis is removed from the molten alloy by using a pipette.

A little more should be said about quenching. When a liquid phase is slowly cooled, the solid phase that is obtained generally does not have the same composition as the liquid phase had at the temperature from which it was cooled. For example, if a liquid phase at 700°C containing 50% tin and 50% aluminum by weight were slowly cooled, the first solid phase to appear would be pure aluminum. Aluminum would continue separating out until the eutectic (2% Al and 98% Sn) was reached, then this tin-rich eutectic would solidify out. The more rapid the cooling, the smaller will be the crystals that separate out; if the cooling is rapid enough, the particles first separating out will not have time to rise, or settle, depending on their density, before the whole mass is solid. Thus, quenching, which is a rapid cooling that does not allow the particles separating out to rise or settle, preserves the composition of the liquid phase. It should be noted that the structure of the quenched solid is not the same as that of the molten liquid; it is only the composition of the solid which is the same as that of the liquid. The method of quenching can obviously be used to study a miscibility gap, since the composition of a liquid consisting of two layers of different composition, will be retained. The quenching must be very rapid if the desired results are to be obtained, since the slower the quenching, the greater will be the tendency for the particles to rise or settle out as in the case of slow cooling.

The method of Alexejeff (1) is also suitable for the investigation of systems having two liquid layers. In this case a series of samples of varying composition are brought to equilibrium at the same temperature and then quenched. Some of these will show the presence of two layers, while others will not, and thus the composition boundary between the one homogeneous liquid phase and the liquid composed of two layers could be determined. The disadvantage in using this method is the large number of samples required to obtain only a few points.

Microscopic Analysis

Microscopic examination consists of examining a polished and etched plane surface of the sample under a reflecting microscope. The structure of the quenched sample shows the phases present, and is useful in determining the boundary between two layers, if they exist.

X-ray Analysis

X-rays are diffracted from atoms in a crystal in a manner dependent on the type of atom and the spatial arrangement of the atoms. A study of the X-ray diffraction pattern enables one to identify the crystal. X-rays have a further use than the mere identification of crystals, but, since in this investigation they will probably not be used for more than identification, a further discussion will not be given here. The one disadvantage of the X-ray method is the fact that in many cases it cannot detect the presence of a new phase until it is present to the extent of at least 5% of the whole.

PREVIOUS INVESTIGATIONS

PREVIOUS INVESTIGATIONS

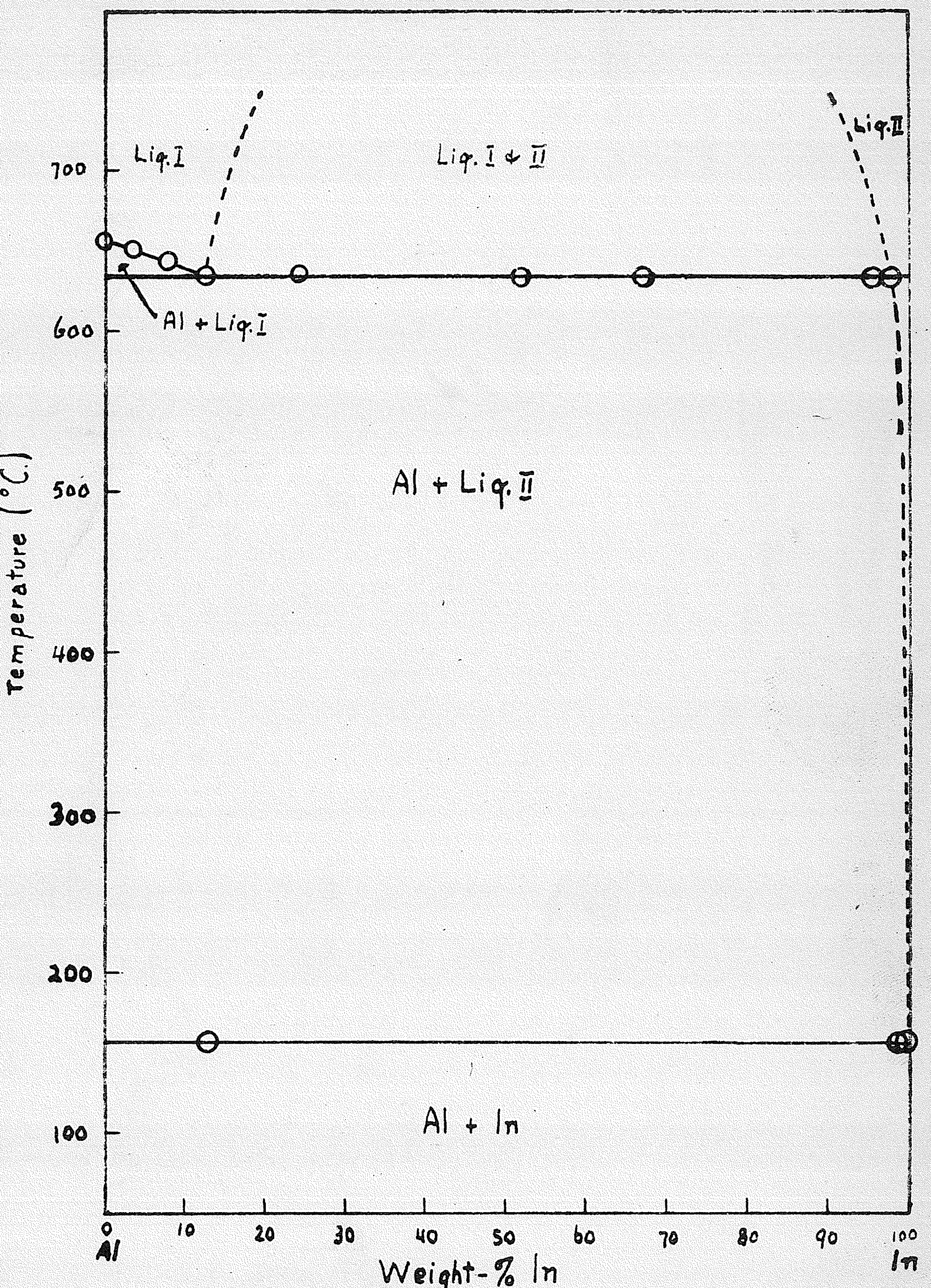
A considerable amount of experimental work has been done on the binary systems Al-In, Al-Sn and In-Sn. A review of this work will appear in Buchanan's thesis. Therefore, a brief outline of only the Al-In and the Al-Sn systems will be given here, since they have a bearing on the present investigation; the In-Sn system will not be reviewed at this time.

The System Al-In

The first published paper available on this system was that of Valentiner (17). He obtained his results by thermal analysis supplemented by X-ray analysis and electrical resistance measurements. The diagram (Fig. 1) shows the eutectic, containing a very small percentage of aluminum, occurring at about 156°C. It also indicates a miscibility gap extending from 13 to 98 weight percent indium at 634°C. He states further that the solubility of indium in aluminum and of aluminum in indium in the solid state can be only slight. The limits of the gap were obtained by the extrapolation of the thermal analysis points on the high aluminum end, and on the low aluminum end the limit was taken as the last alloy that showed a gap halt. It should be noticed that he obtained no points on the miscibility gap itself, and no points on the liquidus in the high indium end of the diagram.

E. Raub and M. Engel (13) claim that the miscibility gap extends from 17.3% indium to almost pure indium (no more than 2% Al. by weight). They used aluminum of 99.99% Al. and indium of a commercial degree of purity. Their method of investigation was thermal analysis amplified by microscopic and X-rays diffraction investigation. The thermal analysis was carried out on alloys melted under argon in pythagoras pots. The results of their thermal analysis appear in Table I., and the equilibrium

The System Al-In



(Valentiner)

Fig. 1

diagram constructed on the basis of these figures is shown in Fig. 2. They take 634°C as the invariant temperature.

TABLE I

THERMO ANALYSIS OF ALUMINUM-INDIUM ALLOYS

Indium (Wt.%)	Halt points on the cooling curves		
	T_1(°C)	T_2(°C)	T_3(°C)
2.5	655	633	
5.0	647	632	
7.5	644	634	
10.0	642	635	
12.5	640	635	
15.0	635	634	
20.0	---	634	158
50.0	---	634	156
80.0	---	640	156
90.0	---	630	156
95.0	---	641	156
97.5	---	640	155

Raub and Engel state that aluminum has no influence on the melting point of indium, and that the freezing temperatures determined thermoanalytically lie as the mean of slight variations at 156°C They practically coincide with the melting temperature of pure indium at 156.4°C. Also, the solubility of indium in solid aluminum was investigated microscopically and by X-rays. The results of the investigation by both these methods showed that it was extremely small.

Buchanan found the limits of the gap in this system to be 14.0% indium and 97.2% indium. He obtained the value 14.0% indium by the extrapolation of his points derived by thermal analysis but, by isothermal

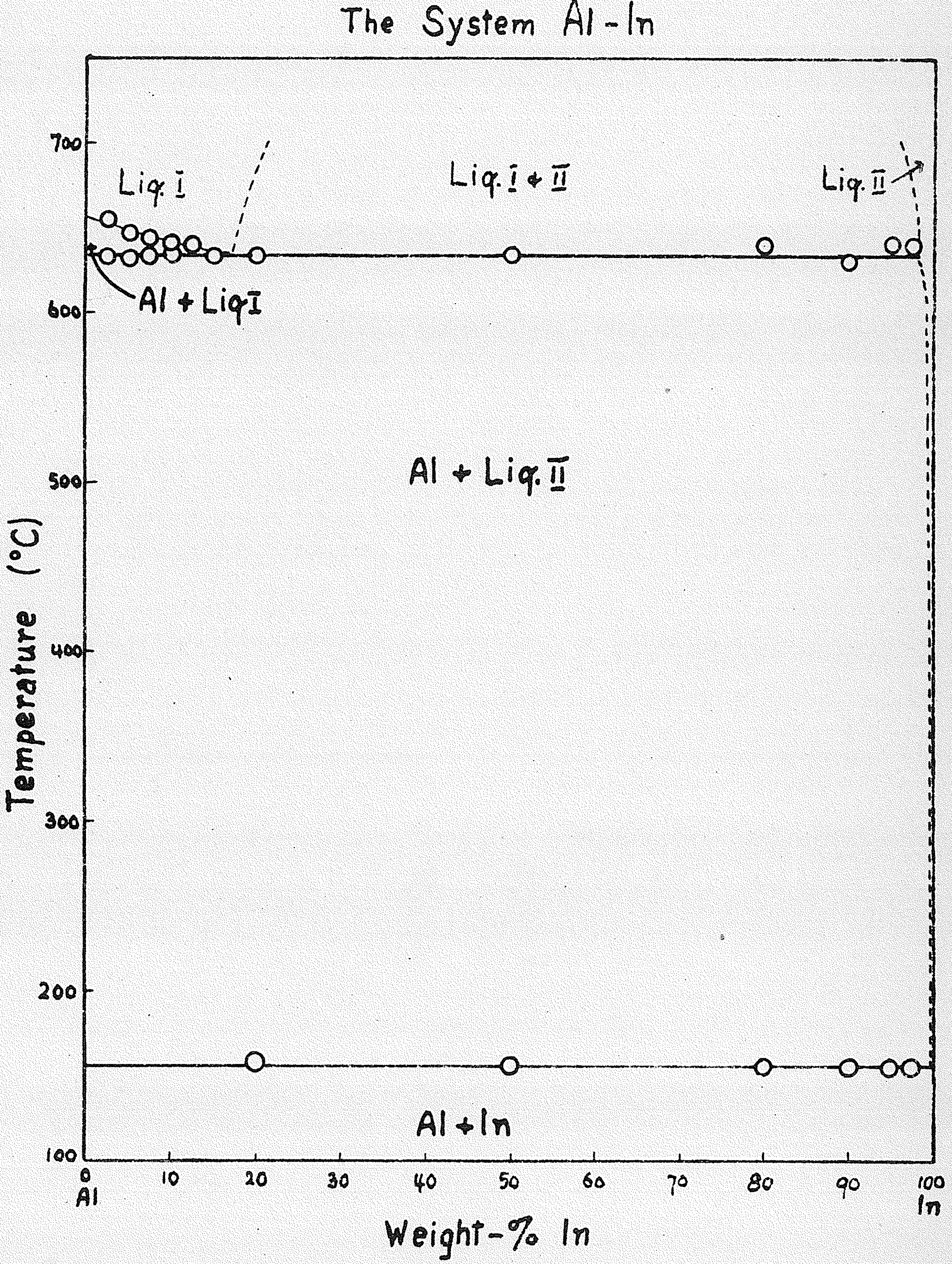

The System Al - In
Liq. I
Liq. I + II
Liq. II
Al + Liq I
Al + Liq. II
Al + In
Temperature (°C)
700
600
500
400
300
200
100
0
Al
10
20
30
40
50
60
70
80
90
100
In
Weight-% In

Fig. 2

analysis he got 20.6% indium. His extrapolated value of 14.0% indium is questionable. In Fig. 3 his results have been plotted and using his differential thermal analysis points, which he considers to be the more accurate, the extrapolated value is found to be about 20.5% indium. Fig. 4 shows the results he obtained by the method of isothermal analysis in the region beyond the indium-rich gap limit. The value 97.2% indium was obtained by extrapolating to the gap halt temperature of 638.6°C. Thus Buchanan's investigation indicates the limits of the gap to be 20.5% indium and 97.2% indium which is different from that found by Raub and Engel. His value of 638.6°C for the gap halt temperature does not agree with the value of 634°C claimed by Raub and Engel.

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

The System Al-Sn

Heycock and Neville (6), in 1890 showed that the freezing point of tin was regularly lowered by the addition of aluminum, up to 0.48% Al. Addition of aluminum beyond this amount did not lower the freezing point further and they gave the maximum as 3°C. Thus, they gave the eutectic as occurring at 228.8°C and 0.48% Al.

In 1896 Gautier (4) published his freezing point curve for the system. His curve indicated a maximum at 81% tin and a temperature of 580°C. This corresponds to a compound of the composition Al Sn. He had a minimum occurring at 78% tin and a temperature of 550°C. Eutectic halt points were not given.

Campbell and Matthews (3) arrived at very similar results, but made the further observation, using a microscope, that the aluminum con-

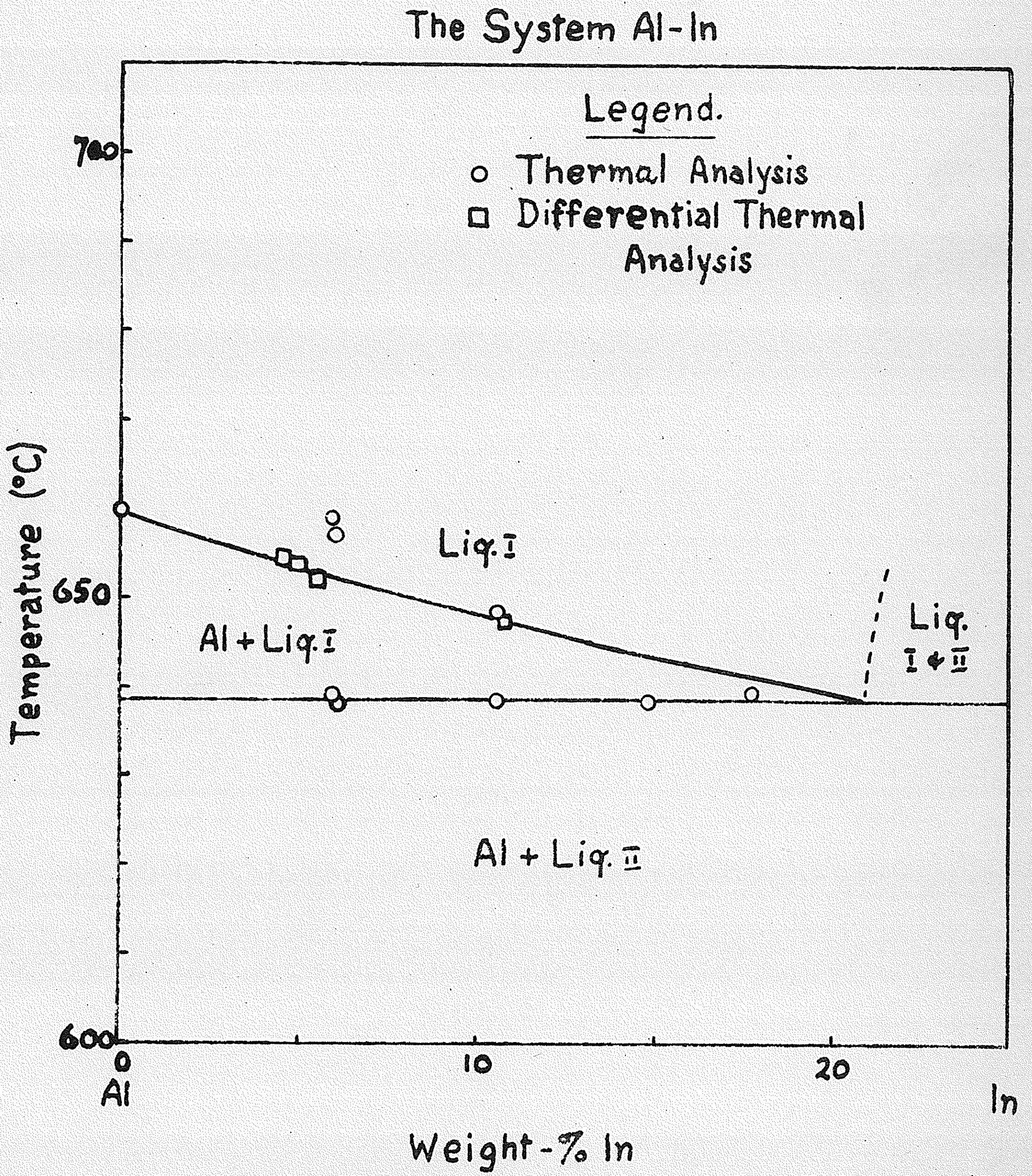

The System Al-In
Legend.
○ Thermal Analysis
□ Differential Thermal Analysis
700
650
600
Temperature (°C)
Liq. I
Al + Liq. I
Liq. I + II
Al + Liq. II
0
Al
10
20
In
Weight-% In

Fig.3

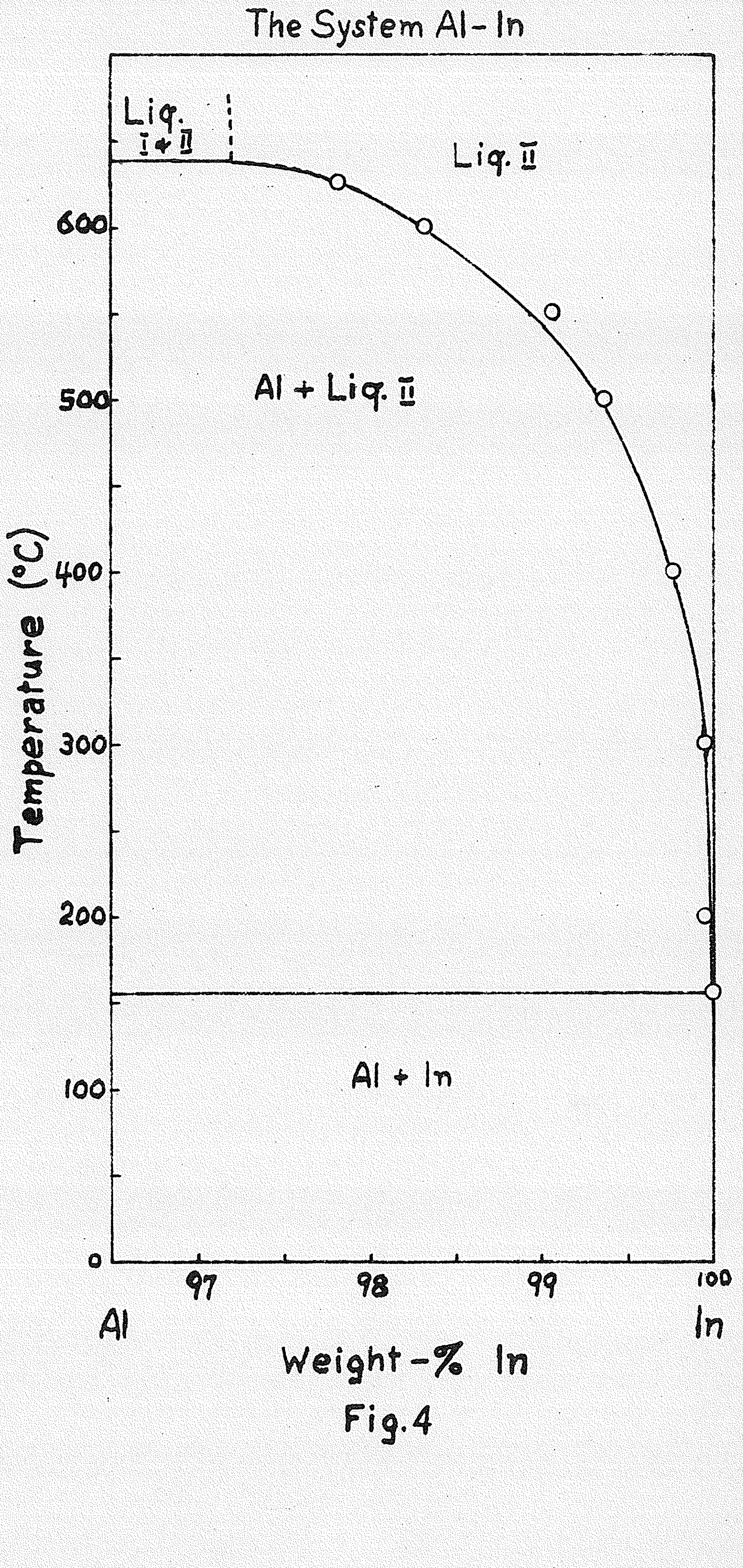

The System Al-In
Liq. I + II
Liq. II
Al + Liq. II
Al + In
Temperature (°C)
600
500
400
300
200
100
0
97
98
99
100
Al
In
Weight-% In

Fig. 4

tained the tin in solid solution, and that the eutectic at that time was not resolvable into two constituent metals, but seemed to be a solid solution.

Anderson and McLean (2) in their diagram gave the same constant temperature for the beginning of crystallization of all alloys of 75 to 83% tin, thus indicating the possible existence of a miscibility gap in this system.

No compound, AlSn, could be found by Shepherd (14) who claimed that there was a solid solution of the composition 20% tin and 80% aluminum.

Gwyer (5) carefully and accurately determined the eutectic halt time for each of the various compositions for increasing amounts of tin. He found that the freezing point curve fell continuously from the melting point of pure aluminum to the eutectic (see Fig. 5). By heating the appropriate mixture of aluminum and tin for a period of five hours with constant stirring at 710°C, he ruled out the possibility of a slow formation of the compound AlSn, that is, under the above conditions he obtained no evidence for the existence of the compound.

An investigation of this system by Lorenz and Plumbridge (12) published in 1913, gave results essentially the same as those of Gwyer. The freezing point curve fell continuously from the melting point of pure aluminum to the eutectic. Furthermore, these authors used microscopic techniques of investigation which revealed that all alloys of 0 to 98% tin consisted of a primary separation of aluminum crystals in a tin-rich eutectic. These results are shown in Fig. 5.

The System Al- Sn

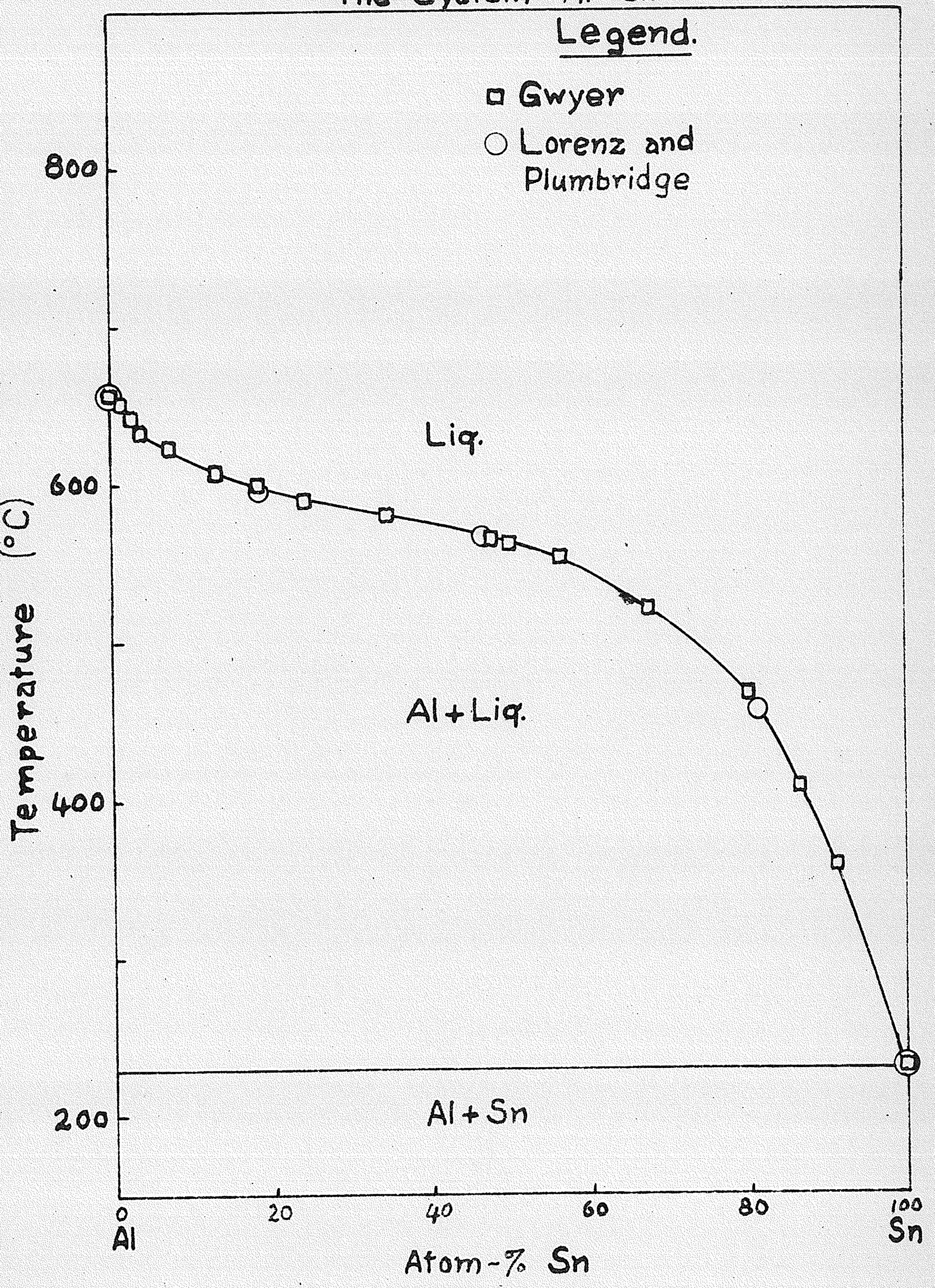


Fig.5

CONSIDERATION OF THE PROBLEM

CONSIDERATION OF THE PROBLEM

The study of the system Al-In-Sn will include the following:

(1) Isotherms for the ternary system will be plotted thus mapping out the extent of the miscibility gap in the liquid state. If it is indicated that the gap is closing up at not too high a temperature, several isotherms will be determined in an effort to establish whether the critical point is, or is not, a true ternary critical point. The isotherms will be used to construct a solid model.

(2) The miscibility gap in the Al-In system will be isothermally investigated at higher temperatures, and the critical solution temperature will be determined, if it does not occur at too high a temperature.

(3) The ternary liquidus will be mapped out using thermal analysis.

(4) The solid phase regions in the ternary system should be investigated using X-ray or microscopic analysis.

EXPERIMENTAL

EXPERIMENTAL

Purity of Metals Used

The experiments throughout this investigation were performed using aluminum, indium and tin which had analyses supplied as follows:

Aluminum (from the Aluminum Co. of America 2# notch bar ingot, 99.995% Al)

Si	0.0019%
Fe	0.0007%
Cu	0.0004%
Mg	0.0008%
Na	0.0005%

Indium (from The Consolidated Mining and Smelting Co., Ltd.) Lot No. 10.

Cu	0.001%
Pb	0.003%
Fe	0.001%
Zn	0.002%
Tl, Ca, Mg	low
Al, Si, Ag, Mn	trace

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

Fe	0.0020%
Pb	trace
Sb	0.0023%
Cu	trace
Sn . (by difference)	99.9957%

Methods of Chemical Analysis

Two methods were used in determining the amount of aluminum present in a given sample. By the first method the solution containing not more than 0.1 gm. aluminum per 100 ml. of solution (the indium and tin are removed by methods to be described later) is treated as follows: The solution is made just slightly acidic, and then warmed to 50 to 60°C. To it is then added an excess of oxine solution (about 10 ml.). The oxine solution consists of 5% 8-hydroxyquinoline in 2N acetic acid and is prepared as described by Kolthoff and Sandell (10). To the solution containing the excess oxine a 2N ammonium acetate solution is added drop by drop until a permanent precipitate appears, and then 20 to 25 ml. more ammonium acetate is added to ensure the complete precipitation of the aluminum. The precipitate of Al-8-hydroxyquinoline is allowed to settle for approximately half an hour, then the liquid is filtered through a tared sintered glass crucible and the precipitate is washed with cold water, and finally dried at 120 to 140°C for two hours and weighed.

By the second method the amount of aluminum present was determined by finding the density of the alloy sample. When the metals in an alloy form a mixture, the density of the alloy is an additive property, and hence by knowing the amount of any one of the three metals present in the alloy the other two can be calculated, if the density of the alloy is known also. It is therefore also true that the volume of the alloy is the sum of the volume of aluminum, the volume of indium and the volume of tin present in the alloy. The amount of aluminum was determined by the following calculation:

$$V = V(In) + V(Sn) + V(Al)$$

where V = the volume of the alloy

$V(In)$ = the volume of the indium

$V(Sn)$ = the volume of the tin

$V(Al)$ = the volume of the aluminum

$$V = \frac{x}{d_{In}} + \frac{y}{d_{Sn}} + \frac{z}{d_{Al}} \text{ - - - - - - - - - - } (1)$$

where x = weight of indium in the alloy

y = weight of tin in the alloy

z = weight of aluminum in the alloy

d_{In}, d_{Sn} and d_{Al} are the densities of indium, tin and aluminum respectively

The amount of one of the metals present must be known. Let x, the weight of indium, be known since it can be determined polarographically. Also the volume, V, is measured using a pyknometer, and the weight of the alloy, W, is found using a balance.

Therefore, $y = W-x-z$

Equation (1) may now be written in the form

$$V = \frac{x}{d_{In}} + \frac{W-x-z}{d_{Sn}} + \frac{z}{d_{Al}} \text{ - - - - - - - - - } (2)$$

Now all the quantities except z in equation (2) are known, and hence z can be evaluated. Equation (2) may be written in the form

$$z = \frac{\left\{\left(V - \frac{x}{d_{In}}\right) d_{Sn} - W + x\right\} d_{Al}}{d_{Sn} - d_{Al}} \text{ - - - - - - - - - } (3)$$

The volume of the alloy was determined using a 10 ml. pyknometer which was calibrated using pure boiled water. The drillings from the alloy were placed in the pyknometer and weighed. The fineness of the drillings used ensured that no air holes were present in the alloy. The pyknometer containing the alloy was then filled with acetone, the density of which was known by a former determination, and the pyknometer was tapped while under suction to remove any bubbles of air trapped in the pyknometer. All the determinations using the pyknometer were made at a constant temperature of $29.1 \pm .03^{\circ}C$, that is, the pyknometer was calibrated at this temperature by placing it in a thermostatted bath of $29.1 \pm .03^{\circ}C$ and allowing it to attain equilibrium at this temperature; also the pyknometer containing acetone and the alloy was kept in this same constant temperature bath until equilibrium was reached. The pyknometer containing the acetone and the alloy was removed from the bath and weighed. The volume of the acetone could now be ascertained, since from the foregoing measurements its weight could be found. Subtracting the volume of the acetone from the volume of the pyknometer gave the volume of the alloy. At this point the volume of the alloy and the weight of the alloy are known, and therefore, it is now necessary to determine the weight of the indium by the polarographic method and substitute in equation (3) to obtain the weight of the aluminum. The density of the acetone was found to be 0.7809 g./ml. and that of indium, tin and aluminum were found to be 7.284, 7.275 and 2.703 g./ml. respectively. The literature values are 7.31, 7.29 and 2.703 g./ml. respectively.

The amount of indium present in a sample was determined using a Sargent-Heyrovsky polarograph. The polarographic method of analysis was invented by Heyrovsky (7) and the theory of the method is discussed by Kolthoff and Lingane (9).

This method is based on the interpretation of current-voltage curves obtained by electrolyzing solutions of electroreducible or electroxidizable substances. The solution is placed in a cell in which one electrode consists of mercury falling slowly in small drops, and the other electrode consists of a stationary mercury pool. The current at any point is solely a function of the potential of the dropping electrode, and is independent of the previous course of the electrolysis. Furthermore, the dropping mercury electrode quickly attains complete polarization and has a high hydrogen over voltage, thus making possible the deposition of the alkali and alkaline-earth metals. The mercury pool electrode maintains a virtually constant potential independent of the applied e.m.f. It remains practically depolarized when the solution contains ions which form insoluble salts with mercury; such ions are the halide ions. The addition of potassium chloride, or other chlorides having high decomposition potentials, makes the resistance of the solution to be analyzed negligibly small. Since there is no polarization of the mercury pool electrode, the resistance of the cell is due almost entirely to the processes taking place at the dropping electrode and solution interface. In view of the fact that oxygen present in the solution is easily reduced, it is removed by bubbling hydrogen through the solution for from five to ten minutes.

Fig. 6 is a schematic diagram showing the principle of the polarographic method of analysis. The dropping electrode is connected through the potentiometer bridge to the negative pole of the polarizing e.m.f. and hence positive ions are reduced at this electrode. The motor moves the drum and the bridge simultaneously. The current at any instant is traced on the photographic paper by a light beam from the galvanometer. The sensitivity of the galvanometer is adjusted by means of the Ayrton shunt connected in parallel.

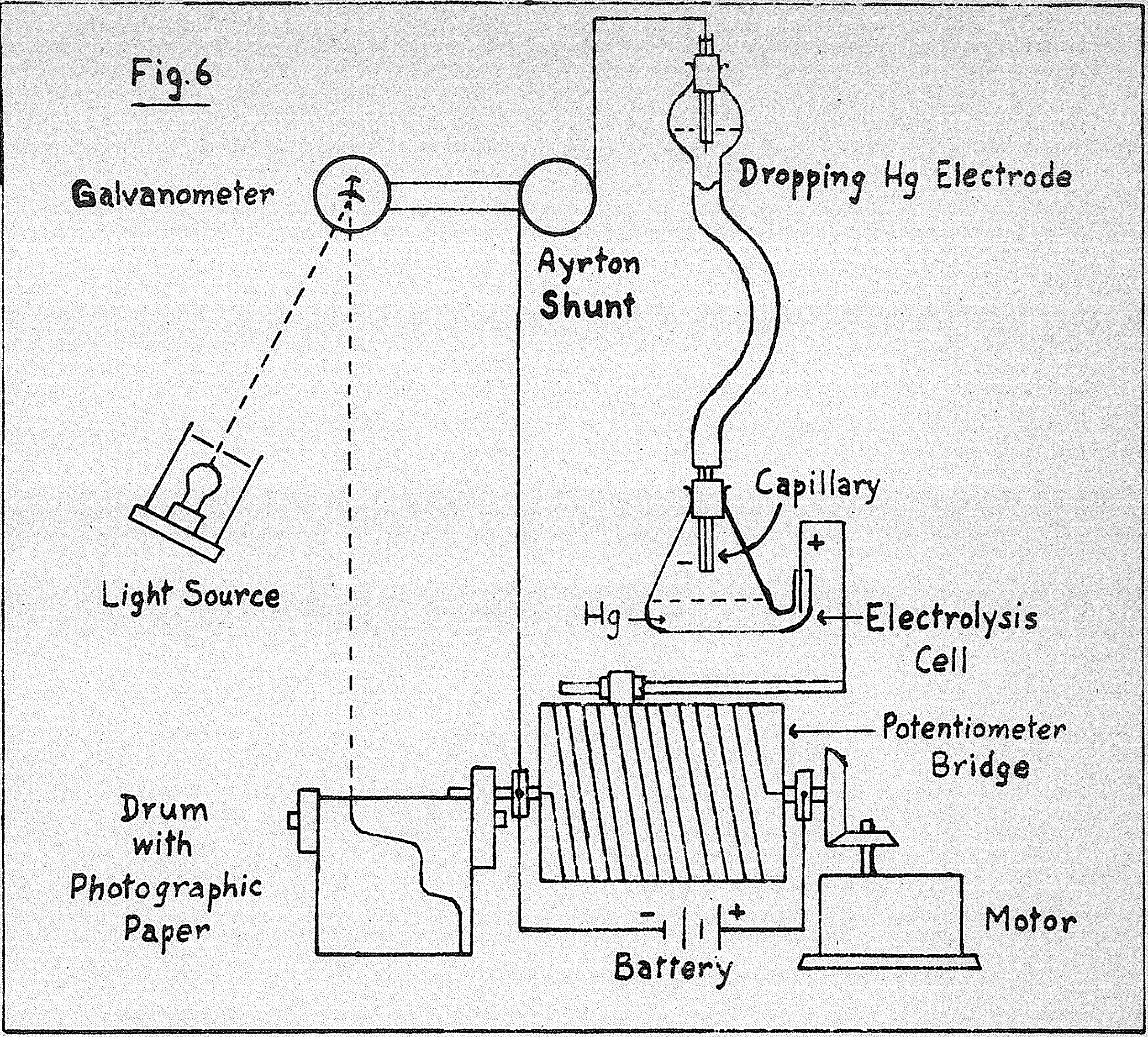


Fig. 6
Galvanometer
Dropping Hg Electrode
Ayrton Shunt
Capillary
Light Source
Hg
Electrolysis Cell
Potentiometer Bridge
Drum with Photographic Paper
Battery
Motor
+
-
-
+

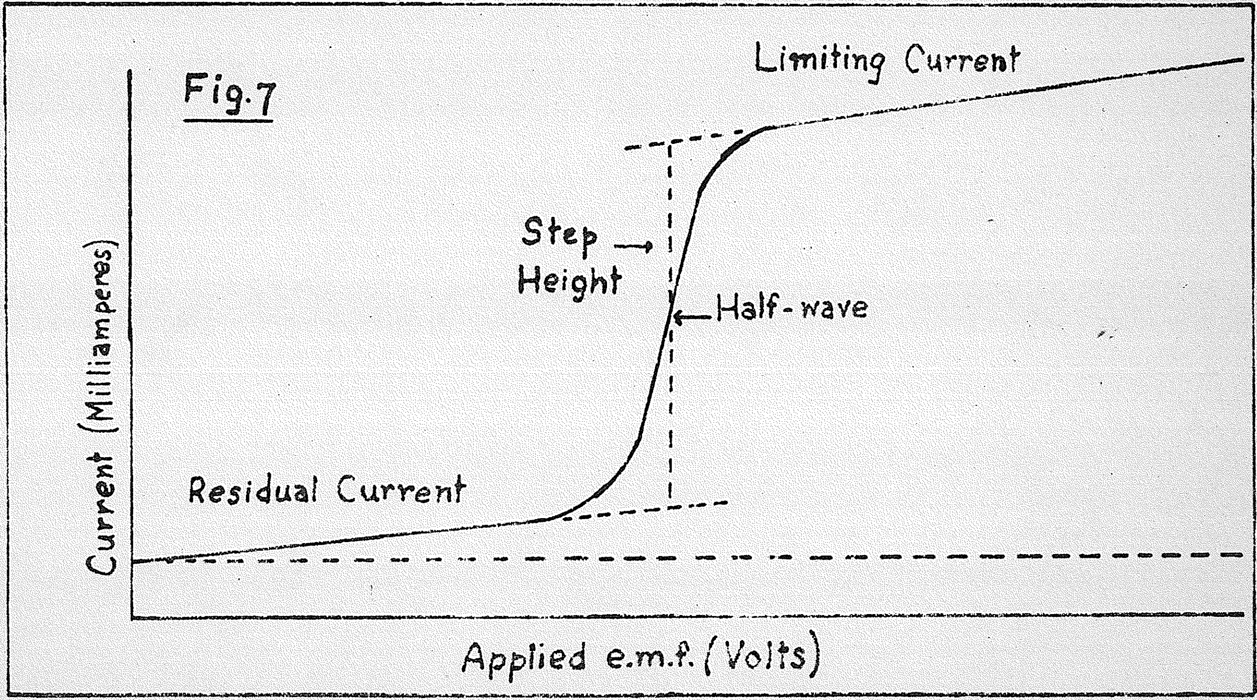


Fig. 7
Limiting Current
Step Height
Half-wave
Residual Current
Current (Milliamperes)
Applied e.m.f. (Volts)

A curve similar to that shown in fig. 7 is obtained when the current is plotted against the applied e.m.f. Due to the cathodic effects or to the traces of other materials, a small residual current flows at first. When the decomposition potential of an ion in solution is reached, electrolysis begins, and there is a rapid increase in the amount of current flowing for a comparatively small increase in the applied e.m.f. During electrolysis the cathode surface is constantly being renewed as the drops form and fall. At the same time, the positive ions are being discharged at the cathode. Mercury from the mercury pool anode passes into solution and reacts with the chloride ions to form calomel. Since only the ions in the immediate vicinity of the drop are removed by being discharged, the concentration of ions in this vicinity is reduced to zero. This results in concentration polarization. At this stage, to reach the electrode, the ions must diffuse through the solution; they do not move due to a potential gradient. As the e.m.f. is further increased, the current becomes constant, because the rate at which the ions diffuse through the solution is constant and equal to the difference between the concentration of ions in the solution and their zero concentration at the electrode. This final constant current is called the "limiting current", and is dependent on the rate of diffusion of the ions in question, and hence on the concentration of the ions in the solution. The relationship between the limiting current and the concentration of the ions being discharged is the basis for quantitative analysis. A solution of known concentration is prepared and a curve of the type shown in Fig. 7 is obtained, and from it the diffusion current is calculated. The basis of a quantitative determination lies in the fact that, if the diffusion current for an unknown concentration is twice as great as that for the known solution, then its concentration is twice as great also, etc.

The half wave potential is constant and characteristic for a particular ion; on a curve such as that showen in Fig. 7, it occurs at the mid point or inflection point of the current rise. Since the half wave potential is constant and characteristic for a particular ion, it can be used for qualitative analysis.

Because only the ions in the neighborhood of the drop are removed, the concentration of the solution as a whole is but slightly altered in obtaining a polarogram. Therefore, it is possible to obtain more than one polarogram, agreeing within the limit of error, from one solution in the cell. The main source of error in a polarographic determination is that introduced in "measuring up" the polarogram, that is, measuring the step height. This error varies from 1.5 to 1.0% depending on the step height. In addition to the advantage that the same solution can be used for more than one determination, there is the further advantage that only a small quantity of metal is necessary for an analysis (0.001 to 0.00001 M).

The actual experimental procedure in the analysis for indium consisted of the following: The drillings (about 1.0 g) from the alloy were dissolved in dilute hydrochloric acid, and this solution was then diluted to 500 ml. in a volumetric flask. Of this 500 ml. of solution, a known portion, the amount depending on the concentration of indium in solution, was removed using a pipette and placed in a 250 ml. volumetric flask. Twenty-five ml. of concentrated hydrochloric acid and 25 ml. of 1.0 N potassium chloride were added, and then the volume of the solution made up to 250 ml. Ten ml. of this solution were then saturated with hydrogen and electrolyzed using the polarograph. From the polarogram obtained the amount of indium present was determined by referring to the calibration curve derived using a solution of known concentration.

It was observed that sometimes there was a falling off of the diffusion current following the completion of the indium wave. This phenomenon has been observed by other investigators, and as yet, according to the literature, the cause is not known. It was found that this falling off could be prevented if the concentration of the indium was kept low enough and the acidity high enough. The solution should not be made too acidic however, because the limiting current, instead of being nearly horizontal on the polarogram, tends more and more toward the vertical. This is caused by the increasing deposition of hydrogen with increasing applied e.m.f., thus decreasing the accuracy of the measurements.

The amount of tin present was determined at first by volumetric analysis. The drillings were dissolved in hydrochloric acid in a 400 ml. Erlenmeyer flask fitted with a rubber stopper carrying an inlet tube for carbon dioxide and an outlet tube. When the sample was dissolved, 50 ml. of concentrated hydrochloric acid and about one gram of antimony powder were added. This was diluted to 200 ml. A slow current of carbon dioxide was passed through the flask, and the solution was boiled briskly for 30 minutes. It was then cooled by placing the flask in cold water, while passing a rapid current of carbon dioxide through the flask. When the solution had cooled, starch solution was added and the solution titrated with 0.01 N iodine. Carbon dioxide was passed through the flask throughout the titration, and the stopper was lifted only far enough to permit the burette tip to be introduced into the flask. Antimony does not interfere with the end point when the solution is cold and strongly acid.

The results obtained by this method were inconsistent, and hence the gravimetric method was adopted. About one gram of the alloy was dissolved in 25 ml. of nitric acid (1:1), and the solution was then evaporated on a steam bath to a volume of 10 ml. This was then diluted to 50 ml., digested at 80 to 90°C, and then filtered while hot. The precipitate was washed ten times with hot nitric acid (1-20) and transferred to a porcelain crucible where it was ignited to a constant weight, and weighed as stannic oxide. This method, though more laborious, gave satisfactory results. Tin could not be determined polarographically due to insufficient equipment.

At this point some information about the necessity for and the methods of separating the aluminum, indium and tin from one another should perhaps be given. The tin analyses could be carried out in the presence of the other two metals; likewise, indium could be determined in the presence of aluminum and tin. However, in order to determine the amount of aluminum using 8-hydroxyquinoline it was necessary to remove the indium, since indium, as well as aluminum, was precipitated by oxine. The indium was removed by electrolysis (8). To an aliquot portion of the solution sulphuric acid was added, and evaporated until dense white fumes of sulphur trioxide appeared. This was done to get rid of the hydrochloric acid, which, if present during the electroysis,produced chlorine gas. This solution was diluted, neutralized with ammonium hydroxide, and then buffered with Rochelle salt. The above solution was electrolyzed in a platinum dish (cathode) using a platinum coil as anode. The current employed was four amperes, and the time for complete deposition of indium was found to be 2.5 hours. The platinum dish was now dried and weighed; the gain in weight would be due to the indium plated out, and this information was utilized as a check on the polarographic determination of indium. It was learned from Dr. N.O. Smith, Associate Professor of Chemistry at the University of Manitoba, that Rochelle salt interfered with the precipitation of the aluminum by the oxine. Two different precipitations under these conditions, however, were made, but there was some doubt as to their accuracy in view of the above information. The Assay Office of the Consolidated Mining and Smelting Co., Ltd. suggest that aluminum be determined by precipitating it as aluminum phosphate, after removing the indium and tin.

To avoid using Rochelle salt the solution, after being neutralized with ammonium hydroxide, was made slightly acidic with acetic acid and buffered with ammonium acetate. This produced a very viscous solution, which, when electrolysis was attempted, produced a very firm foam which rose to a considerable height above the platinum dish and eventually overflowed. Attempts to reduce the viscosity by adding dilute sulphuric acid were unsatisfactory, because the increased acidity was too great to permit the deposition of the indium. More time could not be spent perfecting this technique, and it was therefore discarded in favor of the determination by density already discussed.

Isothermal Analysis

(a) Introduction

For isothermal analysis it is necessary to have some means of controlling and maintaining a constant temperature. Since ordinary mercury regulators are not suitable for controlling high temperatures, the method usually employed involves the use of a thermocouple. The thermocouple is connected to a galvanometer. A light shines on the galvanometer mirror and is reflected back on a photoelectric cell, which in turn is connected to an electronic control. The electronic control operates a relay which regulates the amount of current delivered to the furnace.

Mr. K.I. Roulston, Assistant Professor of Physics at the University of Manitoba, designed the electronic control which was used throughout this investigation.

(b) Apparatus

Fig. 8 schematically illustrates the electronic control. The parts in the circuit and their values are as follows:

R_1 - - - - - 10K
R_2 - - - - - 200K
R_3 - - - - - 200K
R_4 - - - - - 30M
R_5 - - - - - 200K
R_6 - - - - - 250K
R_7 - - - - - 200K
R_8 - - - - - 5K
R_9 - - - - - 7.5K
R_{10}- - - - - 200K
R_{11} - - - - - 100K

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 any impulse from the photo-cells
6N7 - - - - - a duo triode type tube used to operate the relay
5Y4G - - - - a full wave rectifier duo diode type tube
Two 927 photocells

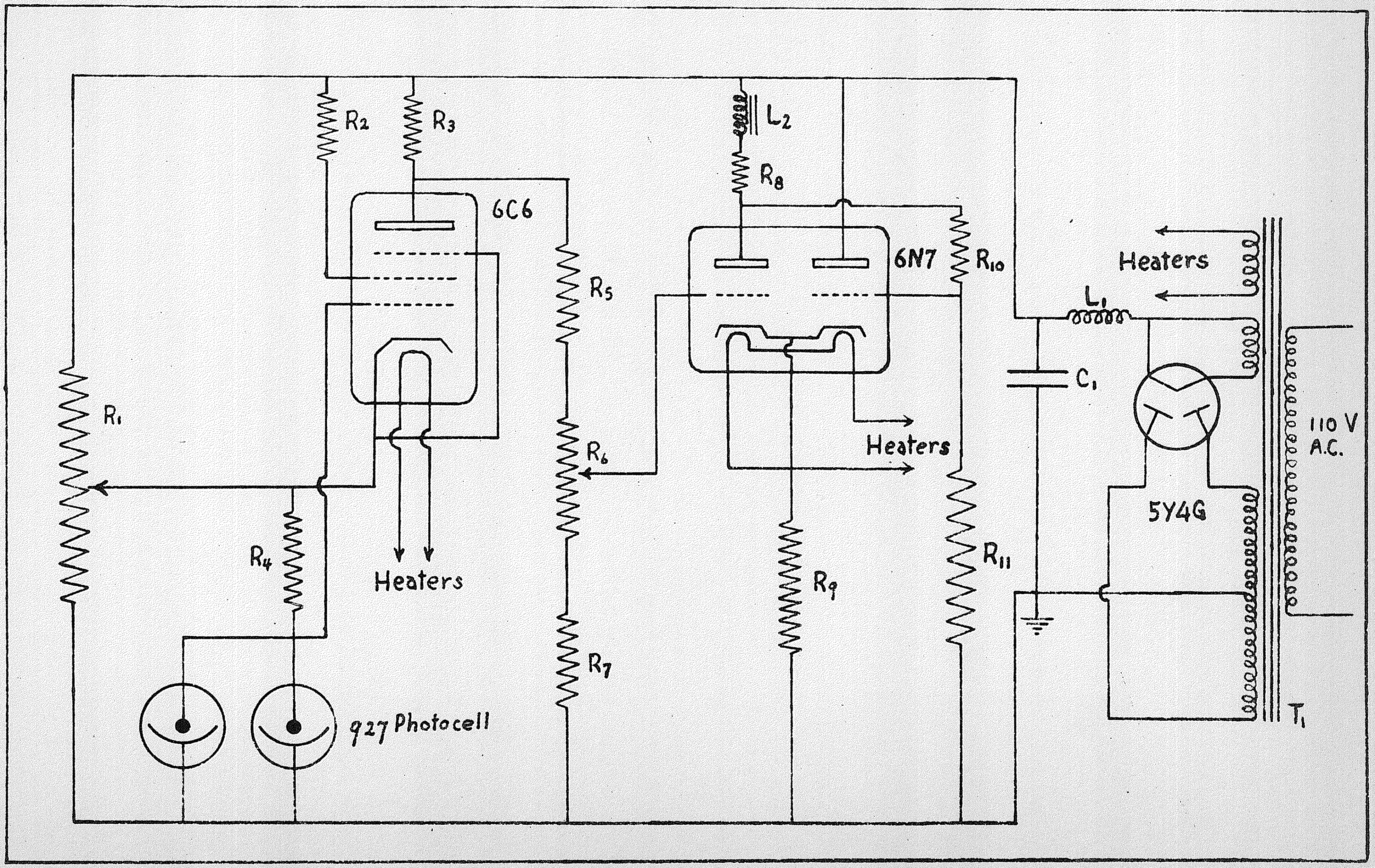
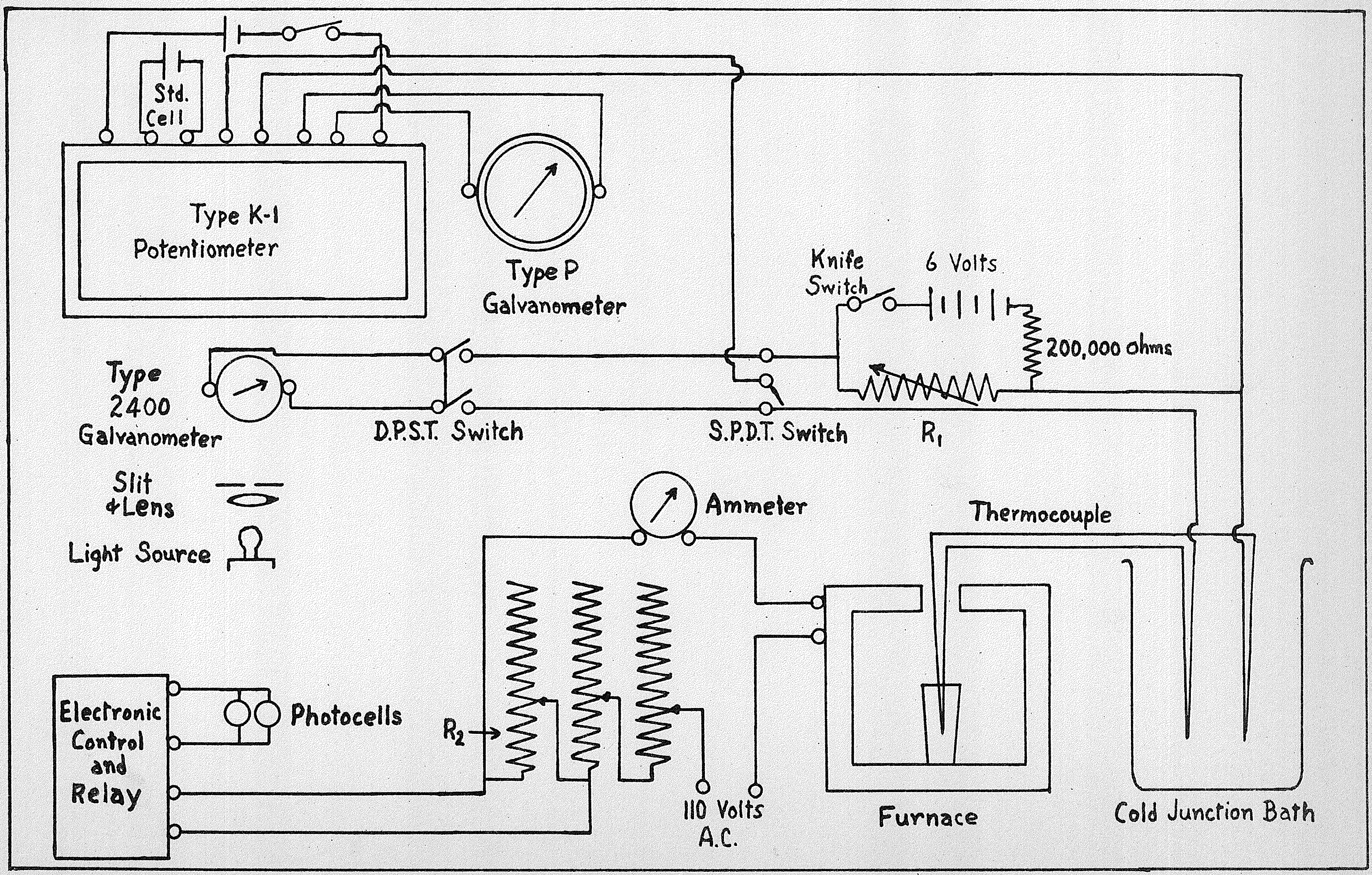

R₁
R₂
R₃
6C6
R₄
Heaters
927 Photocell
R₅
R₆
R₇
L₂
R₈
6N7
R₁₀
Heaters
R₉
R₁₁
Heaters
L₁
C₁
110 V A.C.
5Y4G
T₁

Fig.8

When the beam of light from the galvanometer mirror falls on the photo-cells, which are connected in parallel, the potential, where the resistor, R_4, is connected to the cells, is lowered. Hence, the potential of the number one grid of the 6C6 tube is lowered and the anode potential raised. This then raises the potential at the sliding contact of resistor, R_6, and this in turn causes the potential of the left grid of the 6N7 tube to increase. As the grid potential increases, the anode potential decreases until the relay, L_2, releases. This condition is maintained as long as the light falls on the photocells. When the beam of light moves off the cells, the action is the reverse of that just described. The function of the 5Y4G tube, the transformer T_1, the inductance L_1 and the capacitance C_1 is to convert the A.C. input into D.C. and to supply the proper voltages to the various parts of the circuit.

The control was mounted on a metal chassis and the leads to the photocells were of metal-sheathed cable. The sheath as well as the chassis were grounded. The entire circuit used for the temperature control is shown in Fig. 9. The desired temperature was obtained by adjusting the various parts in the circuit. A certain e.m.f. would be produced by the thermocouple with the cold junction at one fixed temperature and the hot junction at another fixed temperature. This e.m.f. was set on the potentiometer, and, with the knive switch closed, the S.P.D.T. switch was thrown to close the circuit between the backing e.m.f. and the potentiometer. Any desired backing e.m.f. was produced by a six-volt lead stor-



Std. Cell
Type K-1 Potentiometer
Type P Galvanometer
Knife Switch
6 Volts
200,000 ohms
Type 2400 Galvanometer
D.P.S.T. Switch
S.P.D.T. Switch
R_1
Slit & Lens
Light Source
Ammeter
Thermocouple
Electronic Control and Relay
Photocells
R_2
110 Volts A.C.
Furnace
Cold Junction Bath

Fig. 9

age battery with a 200,000 ohm resistance connected in series, and a dial resistance box, R_1, connected in parallel. Now, with the circuit between the potentiometer and the backing e.m.f. closed, the resistance, R_1, was adjusted until the backing e.m.f. was balanced against that set on the potentiometer. The backing e.m.f. now has the desired value. The circuit is so arranged that, when the S.P.D.T. switch is open and the D.P.S.T. switch is closed, the e.m.f. of the thermocouple is opposed by that of the backing e.m.f. With the backing e.m.f. set at the desired potential, the S.P.D.T. Switch was opened and the D.P.S.T. switch closed. As the temperature in the furnace rises, the e.m.f. produced by the thermocouple increases, thus causing the light beam from the galvanometer mirror in the electronic control circuit to move toward the photocells. When the temperature in the furnace reaches the point where it causes the thermocouple e.m.f. across the resistance, R_1, to equal that of the backing e.m.f., there will be no current flowing in the circuit, and, therefore, the galvanometer will not be deflected; the light will fall on the cells. The electronic control then trips a relay which throws extra resistance, R_2, into the furnace heating circuit. The furnace cools slightly causing the e.m.f. of the thermocouple to decrease, and, since the two opposing e.m.fs. are no longer equal, a slight current flows in the circuit, thus causing the galvanometer to deflect off the cells. As soon as the light falls off the cells, the relay is tripped the other way, the resistance, R_2, is cut out of the circuit, and the furnace begins to heat up again. The process keeps repeating, thus maintaining a constant temperature.

The S.P.D.T. switch can be thrown, either to close the circuit between the backing e.m.f. and the potentiometer, or to close the circuit between the thermocouple and the potentiometer. With the latter circuit the e.m.f. of the thermocouple can be determined directly, and hence the temperature of the furnace can be ascertained.

The Leeds and Northrup galvanometer, Type 2400, had a sensitivity of 0.003 microamperes per mm. at one metre. The leads to this galvanometer were shielded in grounded metal casings to avoid any possible interference with the current in them. Fig. 10 shows the galvanometer, lens, light source and photocells. These were mounted in a box six feet long, six inches wide and a foot high; their relative positions were as indicated in the diagram. The light source was a Mazda #2330 automobile headlight bulb which was operated on a 6-volt alternating current. The purpose of the slit was to reduce the light to a narrow parallel beam. The interior of the box was painted black to minimize internal reflection of light. The two photocells were arranged in such a manner that, if the light beam moved past the first, it would strike the second. As a further precaution, a mirror of polished nickel was placed beside the cells at such an angle that the light beam, if it moved past the second cell, would be reflected on the cells, thus still maintaining control. In practice, when the heating circuit was carefully adjusted, the beam did not move beyond the second cell.

It was found that at 700°C the temperature could be controlled to within ± 1.°C, while at 900°C it could be controlled within ± 2°C. The limiting factor that determined how accurately the temperature could be controlled was the voltage of the power source. It varied considerably during the day, thus making better control impossible. With the power source voltage constant, the power input would be constant resulting in more accurate control.

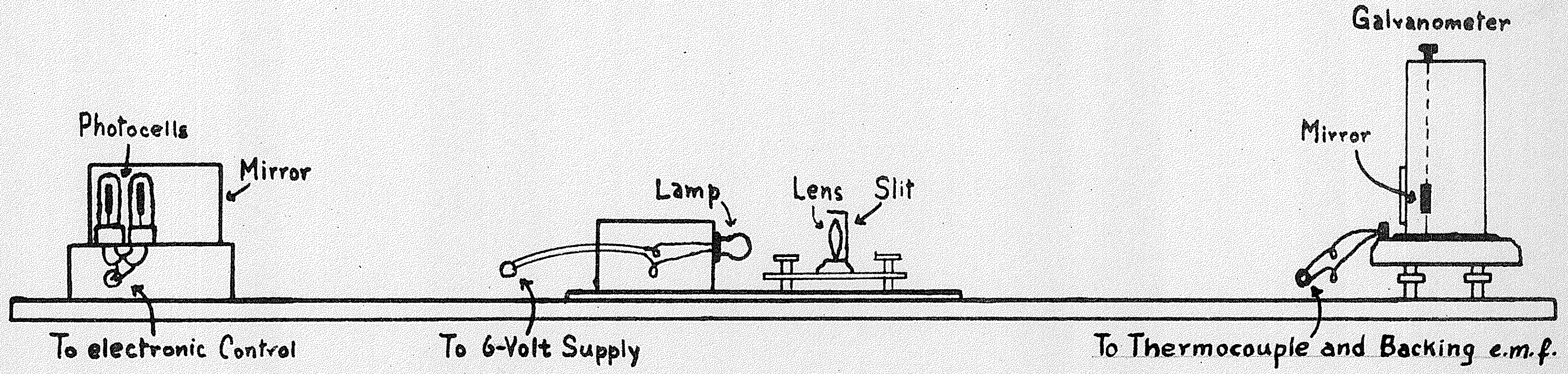

Photocells
Mirror
To electronic Control
Lamp
Lens
Slit
To 6-Volt Supply
Galvanometer
Mirror
To Thermocouple and Backing e.m.f.

Fig.10

The furnace used was constructed in the laboratory in the following manner: Two pieces of rubber tubing with an external diameter of five-sixteenths of an inch were wound parallel to one another twice around a cylindrical cardboard box four inches in diameter. The pitch of the winding was about two inches per turn, so that the two turns extended a total distance of four inches up the side of the box. The two pieces of rubber tubing had a common starting point at the top and a common ending point at the bottom, but elsewhere in the spiral the distance between them was one inch. The box with the tubing wound around it was placed vertically in the centre of a galvanized thin sheet iron cylinder, five inches in height and seven inches in diameter. A fifty-fifty mixture of "Insalute" cement and sand with water was poured into the space between the cardboard box and the iron cylinder. This was allowed to set by placing it in a large drying furnace for two days during which time the temperature was raised gradually from 50°C to 150°C. When the furnace block had hardened, the iron cylinder was taken off, the box was removed by collapsing it, and the rubber tubing was removed leaving behind grooves to support the heating elements. Two holes were drilled in the side of the furnace block to admit copper terminals five-sixteenths of an inch in diameter. Two nichrome heating elements of 1700 watts each were wound in parallel inside the furnace block and connected to the terminals.

The furnace, four inches in internal diameter and five inches in height, was placed on a circular piece of asbestos board, one quarter of an inch in thickness, which rested on a mortar stand, two inches in height. The stand was in the centre of the base of a galvanized thin sheet iron cylinder, seventeen inches in diameter and nine inches in height. The furnace terminals protruded through two holes in the galvanized iron cylinder. The space between the furnace block and the iron cylinder was insulated by filling it with asbestos powder. A lid containing the necessary holes for the thermocouple, etc. was made of transite, one quarter of an inch thick.

A chromel P-Alumel thermocouple was used, and arranged as shown in Fig. 9. The Chromel and Alumel ends in the cold junction bath were attached to copper wires; this did not affect the thermocouple e.m.f. (Law of Successive Contacts).

The e.m.f. of the thermocouple was measured by means of a Leeds and Northrup Type K-1 potentiometer along with a Leeds and Northrup Type P wall galvanometer of sensitivity 0.0015 microamperes per mm. Because the uncertainty in any e.m.f. reading was less than 10 microvolts, which corresponds to about 0.25°C, it was possible to measure any temperature to within ±0.5°C.

The cold junction ends of the thermocouple were placed in two 20 ml. test tubes dipping into a two-litre beaker of water thermostatted at 29.1 ± .03°C. The tops of the test tubes were filled with insulating material to prevent convection currents. A mercury regulator in the water bath was connected through a relay to the heating element which consisted of a 40 watt light bulb.

The thermocouple was calibrated using the following points:

Sn - - - - - Freezing Point 231.9°C
Al - - - - - " " 659.9°C
Ag - - - - - " " 960.5°C

A curve showing the variation of e.m.f. with temperature of a standard Chromel P-Alumel thermocouple was plotted on a large scale using the data given in "Temperature - Its Measurement and Control in Science and Industry" (16). The calibration point e.m.fs. were plotted on the same graph, to allow the shape of the standard curve to be used as a guide in drawing the calibration curve. The calibration point e.m.fs. were obtained by adding the e.m.f. for 29.1°C to the observed e.m.f. for the known hot junction temperature.

To prevent oxidation of the alloys at high temperatures the ammonia cracker, designed after that of Larson (11) and built by Skinner (15), was used to produce a reducing atmosphere consisting of a mixture of hydrogen and nitrogen gases. A current of 7 amperes was necessary to operate the cracker at about 600°C. For a complete description and set up of this part of the apparatus, Skinner's thesis (15) should be consulted. Some of the metal joints had to be brazed to prevent leaks, and a new heating coil and new gaskets were necessary before the cracker was put into operation.

(c) Procedure

Various procedures were used in an effort to eliminate the difficulties as they arose. In the early part of the work the metals were cut into small pieces, placed in 20 ml. Pyrex test tubes and melted down in the induction furnace. The composition of the alloy was made such that it fell well within the miscibility gap region. In order to reduce oxidation to a minimum the test tube was sealed off just above the surface of the alloy. The test tube containing the sample was inserted in a snugly fitting cylindrical brass crucible, four inches in height, and placed in the furnace. The furnace was then heated to, and maintained at, any desired constant temperature for as many hours as necessary by the method already described. The sample was then quenched by quickly but carefully removing the brass crucible from the furnace and plunging it into ice water. Care had to be exercised to ensure that the crucible always remained vertical, that the water did not flow over the top of the crucible and hence into it, and that the crucible was not shaken or unduly jarred. These precautions were necessary in order to preserve the separation of the two immiscible layers. The quenching time was five to six minutes. Drillings for analyses were taken from the top and bottom layers of the sample which, after being removed from the crucible and test tube, had been sawed vertically in two. The composition of each of the two layers was plotted on an equilateral triangle graph (see Fig. 12), and these two points were joined by a "tie line".

It was noticed near the beginning of this work that, when the drillings from the layer rich in aluminum were dissolved in hydrochloric acid, a black insoluble residue appeared. This was thought to be stannic oxide and it was taken into account as such when making the calculations. The appearance of this same precipitate in the binary alloy, Al-In, revealed that it was not a tin compound. The results, when an x-ray powder photograph of this substance was measured up, were as shown in Table II. Thanks are due to Dr. R.B. Ferguson, Assistant Professor of Mineralogy, University of Manitoba, who assisted in obtaining the powder photograph shown in Fig. 11. The measured values of d in Table II checked with those for crystalline silicon, thus showing that silicon had been introduced into the system. The silicon was produced by the reduction of silica in the glass test tube by the molten aluminum; therefore, glass test tubes could not be used.

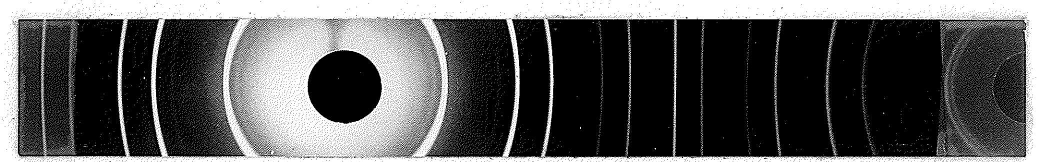


Fig. 11

X-ray powder photograph of Silicon taken with copper radiation nickel filter

Alundum (aluminum oxide) crucibles would not react with any of the metals in the system, but their shapes were not what was required in order to secure good quenching, but, since nothing else was available, two sizes of these were tried. The first, one and three-eighths inches wide and three and three-eighths inches high was unsatisfactory, since the sample in it was too bulky to allow proper quenching. The second type, one inch in diameter at the top, half an inch in diameter at the bottom, and one and one-eighth inches in height, was then used. The procedure in this case was the same as that used with the test tubes, except that now, since no air tight lids for these crucibles were available, oxidation could not be prevented to the same extent as formerly. However, a few trials indicated only very slight oxidation at the temperature that was being used, so that air tight lids were not really an essential. Quenching, on the other hand, was a serious problem. The ice water could not be any more than an inch and a half deep owing to the height of the brass molds that were made to hold the crucibles when placed in the ice water. The use of molds was in itself an undesirable feature, yet the hot Alundum crucibles themselves could not be plunged into cold water. In many cases it took as long as ten minutes for the alloys to cool to about 50°C when quenched, using the technique just described.

Liquation is very rapid in this system, and it was found that its effects were vitiating the results of the investigation.

It was decided to try the following method: A clay tube was inserted into the upper layer, and a portion drawn into the tube by suction. Solidification occurred in the tube as the Liquid came in contact with the cooler upper part of the tube. In a few cases, at 700°C, a little of the liquid ran out of the tube as it was being withdrawn from the furnace.

This happened in every case at 800°C, and was due, evidently, to the fact that the aluminum had separated out on the walls of the tube, and the indium had run out.

In view of the above, it was necessary to analyze the whole portion withdrawn. Because of the separation of the aluminum and indium, the portion near the top of the tube contained much more aluminum than the portion near the bottom; this could be observed by the fact that the upper portion was much harder than the lower. The analysis of the total sample that entered the tube was essential, since what entered the tube was necessarily the required upper layer. In the instances when some of the indium ran out, the analyses would indicate less indium in the upper aluminum-rich layer than was actually present. Also, at 800°C a small amount of a blackish precipitate, insoluble in hydrochloric acid, was present; this could be silicon reduced from the clay tube.

Attempts to draw off the bottom indium-rich layer in this manner were unsuccessful, owing to the fact that the liquid flowed out of the tube when it was withdrawn.

To obtain the composition of the lower layer, the method adopted consisted of quenching the sample which was contained in a thermocouple guard tube sawed off to the required length, and sealed off at one end by fusing it in an oxygen gas flame. This tube was inserted into a brass tube which was closed by pinching the ends in a vise. The diameter of the tube was about a quarter of an inch, and with the above arrangement the quenching time was approximately one minute. In order to get the metals into the tube, the pieces had to be quite small. This was undesirable, because a layer of oxide would form on the metals, expecially on the aluminum, thus preventing the mixing of the aluminum with other metals.

One of the Al-Sn samples, No. 13, was subjected to the Brinell hardness test. Thanks are due to Mr. D. Thompson, of the Engineering Faculty, who carried out this test. Two series of hardness reading were taken in a line from top to bottom using the Rockwell E Scale. These readings are given in Table III.

The microscope was used in this work also. Some of the samples were polished, etched with 0.5% hydrofluoric acid, and examined under the microscope. A sample was first filed roughly flat, and then a plane surface was obtained using abrasive powders. Next, the sample was polished successively on 0, 2/0, and 3/0 abrasive papers, using a solution of paraffin in kerosene as a lubricant. The sample was washed in hot kerosene when changing from one paper to the next. The final polish was applied using jewellers' rouge and a suspension of magnesium oxide in distilled water on a cloth lap.

RESULTS

RESULTS

TABLE II

X-RAY POWDER PHOTOGRAPH DATA FOR SILICON REDUCED FROM PYREX GLASS BY ALUMINUM

R	L(or centre)	2S	S = θ	d(meas)
58.40	29.80	28.6	14.30	3.1121
67.90	20.40	47.5	23.75	1.9087
72.20	16.10	56.1	28.05	1.6347
78.80	44.15	----	34.65	1.3520
82.30	"	----	38.15	1.2444
88.25	"	----	44.10	1.1046
91.75	"	----	47.60	1.0410
97.60	"	----	53.45	0.9569
101.30	"	----	57.15	0.9150
107.90	"	----	63.75	0.8571
112.50	"	----	68.35	0.8270
117.60	"	----	73.45	0.8019
123.50	"	----	79.35	0.7822

TABLE III

BRINELL HARDNESS TEST TAKEN FROM TOP TO BOTTOM ON ALLOY NO.13 USING THE ROCKWELL R SCALE

(The alloy was 7.0 cm.long, 2.5 cm. wide at
the top and 1.5 cm. wide at the bottom)

First series	Second series
92.2	98.8
100.7	101.4
101.1	101.8
101.0	101.5
99.9	100.6
100.0	101.3
99.9	101.5
99.9	102.0
99.8	

TABLE IV

COMPOSITION BOUNDARIES OF THE TERNARY MISCIBILITY GAP AT 700°C

(The samples were contained in Pyrex glass test tubes)

Alloy No.	Time in furnace (hours)	Approximate total composition			Al-rich layer			In-rich layer		
		%Al	%In	%Sn	%Al	%In	%Sn	%Al	%In	%Sn
1	48	60.	29.	11.	73.0	16.8	10.2	4.1	80.8	15.1
2	48	55.	27.	18.	71.5	14.4	14.1	8.4	63.8	27.8
3	48	45.	25.	30.	74.2	8.2	17.6	6.3	47.1	46.6
4	48	43.	27.	30.	53.6	20.0	26.4	4.6	51.2	44.2
5	48	32.	30.	38.	58.2	14.5	27.3	8.1	44.6	47.3
6	48	70.	30.	--	75.2	24.8	---	1.9	98.1	---
7	72	28.	24.	48.	31.0	21.5	47.5	26.6	25.3	48.1
8	72	21.	20.	59.	61.4	4.4	34.2	8.7	24.7	66.6
9	72	65.	28.	7.	76.9	17.2	5.9	2.4	83.4	14.2
10	144	70.	30.	--	79.6	20.4	---	1.9	98.1	---

TABLE V

COMPOSITION BOUNDARIES OF THE ALUMINUM-TIN MISCIBILITY GAP AT 700°C

(Alloy No. 11 and alloy No. 12 were contained in Pyrex glass test tubes, and alloy No. 13 and alloy No. 14 were contained in Alundum crucibles)

Alloy No.	Time in furnace (hours)	Al-rich layer		Sn-rich layer	
		%Al	%Sn	%Al	%Sn
11	72	43.8	56.2	20.1	79.9
12	72	(no two layers)		top	63.6% Sn
				middle	64.3% Sn
				bottom	65.2% Sn
13	72	(no two layers)		top	68.3% Sn
				Middle	71.7% Sn
					72.5% Sn
				Bottom	71.8% Sn
14	72	(no two layers)		Top	65.6% Sn
				Bottom	70.0% Sn

TABLE VI

COMPOSITION BOUNDARIES OF THE TERNARY MISCIBILITY GAP AT 700°C

(The samples were contained in Alundum crucibles)

Alloy No.	Time in furnace (hours)	Approximate total compositions			Al-rich layer			In-rich layer		
		%Al	%In	%Sn	%Al	%In	%Sn	%Al	%In	%Sn
15	72	39.	32.	29.	55.7	19.2	25.1	8.7	54.6	36.7
16	72	70.	30.	---	77.1	22.9	---	2.0	98.0	---
17	72	45.	42.	13.	74.0	17.3	8.7	4.9	75.5	19.6
21	72	31.	29.	40.	44.7	20.7	34.6	6.9	43.6	49.5
22	72	26.	24.	50.	32.2	22.0	45.8	23.5	24.7	51.8

TABLE VII

COMPOSITION BOUNDARIES OF THE ALUMINUM-INDIUM MISCIBILITY GAP

(The samples were contained in Alundum crucibles)

Alloy No.	Time in furnace (hours)	Temperature of furnace (°C)	Al-rich layer		In-rich layer	
			%Al	%In	%Al	%In
18	72	700	78.8	21.2	2.9	97.1
19	72	700	81.6	18.4	2.6	97.4
20	60	700	78.8	21.2	---	---
20	108	700	77.5	22.5	---	---
20	132	700	77.1	22.9	---	---
23	36	650	81.7	18.3	---	---
23	60	650	81.4	18.6	---	---
24	24	800	71.6	28.4	---	---
24	60	800	66.6	33.4	---	---
25	24	800	---	---	3.9	96.1
25	24	800	---	---	2.9	97.1
26	3	800	79.9	20.1	---	---
26	20	800	74.4	25.6	---	---
27	48	800	---	---	7.8	92.2
28	48	800	72.6	27.4	---	---
28	84	800	69.6	30.4	---	---
28	90	800	67.9	32.1	---	---

TABLE VIII

COMPOSITION BOUNDARIES OF THE ALUMINUM-INDIUM MISCIBILITY GAP

(The samples were contained in Alundum crucibles)

Temperature (°C)	Al-rich layer %In	In-rich layer %In
650	18.6	---
700	22.7	96.6
800	32.0	92.2

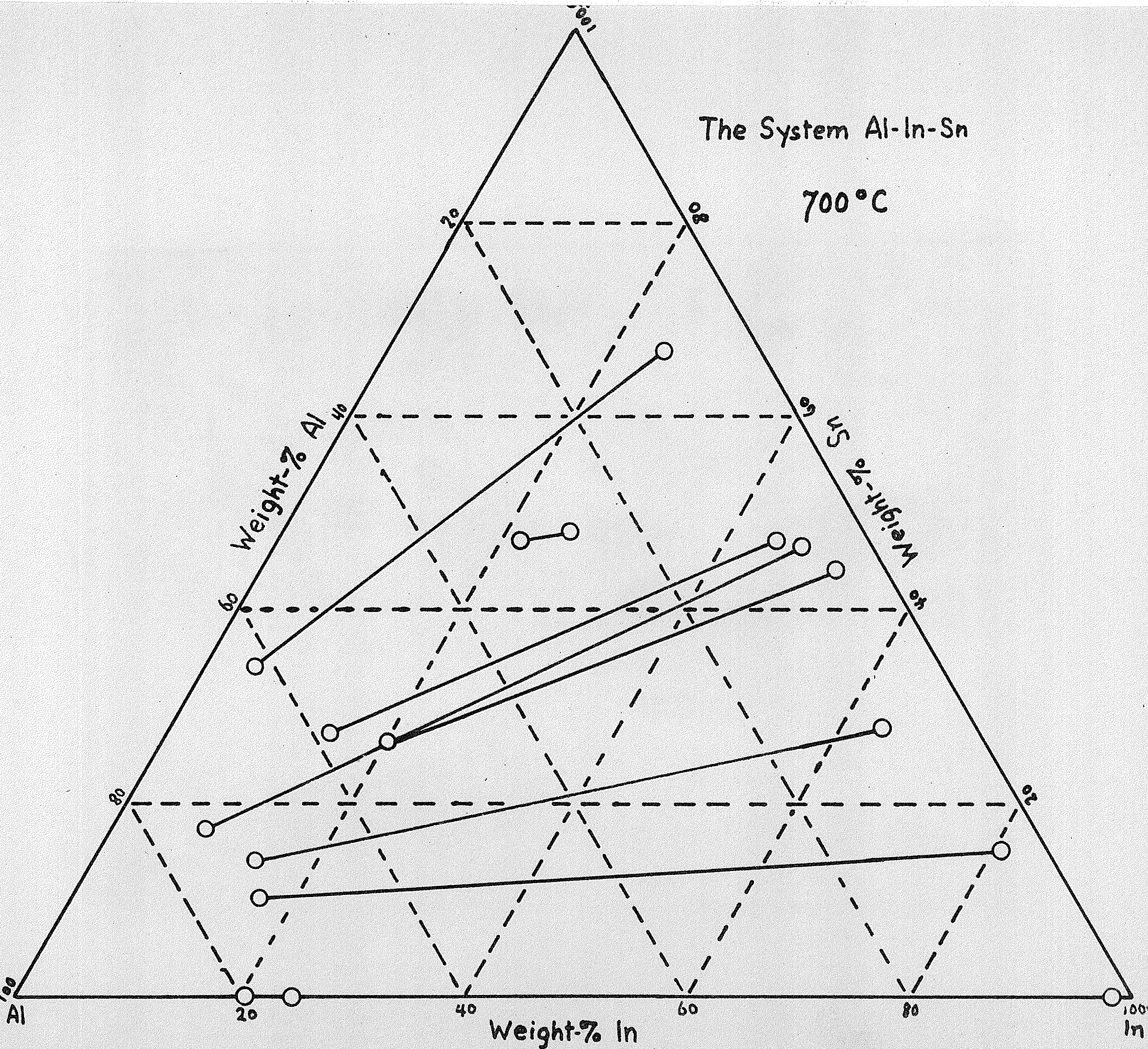
DISCUSSION OF RESULTS

DISCUSSION OF RESULTS

Although the values given in Table IV are obviously faulty owing to the presence of silicon in the system, they are, nevertheless, plotted in Fig. 12 to illustrate their erratic nature. As elsewhere pointed out, silicon was identified by means of the X-ray powder photograph shown in Fig. 11. Fig. 13, a photomicrograph of a section of alloy No. 12, shows a silicon crystal magnified 200 times its original size.

Before the silicon was detected as such, the position of the tie lines indicated that there probably was a miscibility gap in the Al-Sn system. Such a gap had been indicated by some of the earlier investigations. A check on this system seemed to indicate that there indeed was a gap, but the gap observed at this temperature would have been a gap in the ternary system Al-Sn-Si. The presence of this gap is not a certainty because at this time the alloys were being quenched in Alundum crucibles for which the quenching time was often about ten minutes. The results obtained during this investigation are given in Table V, and these, except the result for alloy No. 11, do not indicate a gap.

The expected boundary between the two immiscible layers was absent in sample No. 22, at least it could not be seen with the naked eye. To be sure that no boundary existed the sample was polished, etched and examined under a microscope. No boundary could be found, but there was a gradual change in



The System Al-In-Sn

700 °C

Fig. 12

Fig. 13

(x200) Photomicrograph showing silicon crystal imbedded in an aluminum-indium-tin matrix. Silicon reduced from Pyrex glass the relative amounts of the phases present from top to bottom. A photomicrograph of a section of the top part and one of a section of the bottom part of the sample were taken, and these are shown in Figs. 14a and 14b respectively. These photomicrographs clearly indicate the difference in the relative amounts of the phases.

The results of the Brinell hardness test taken on sample No. 13, in view of their agreement, indicate that the sample is homogeneous. This is in good agreement with the evidence presented by the analysis result for sample No. 13 given in Table V.

The validity of the results listed in Table VI and plotted in Fig. 15 are questionable, for although no silicon was present in these samples, the rate of quenching was comparatively slow, and consequently liquation would be extensive. It was found later, during the investigation of the Al-In system, that use of small thermocouple guard tubes as crucibles gave results more in agreement with what was expected, and different from those obtained when the larger Alundum crucibles were used. The percentage of aluminum in the indium-rich layer was observed to be higher when the guard tubes were used. This could be attributed to the fact that, with the better quenching obtained by using the small tubes, liquation was considerably reduced. Although it was known that there was some liquation, the extreme rapidity with which it occurred was not discovered until work at 800°C on the Al-In system was begun. Both objections already raised are applicable to the results in Table V.

Fig. 14a

(x200) Photomicrograph of alloy No. 22

Al = aluminum - rich layer   In = indium-rich layer

Fig. 14b

(x200) Photomicrograph of alloy No. 22

Al = aluminum-rich layer In = indium-rich layer

The System Al-In-Sn

700°C

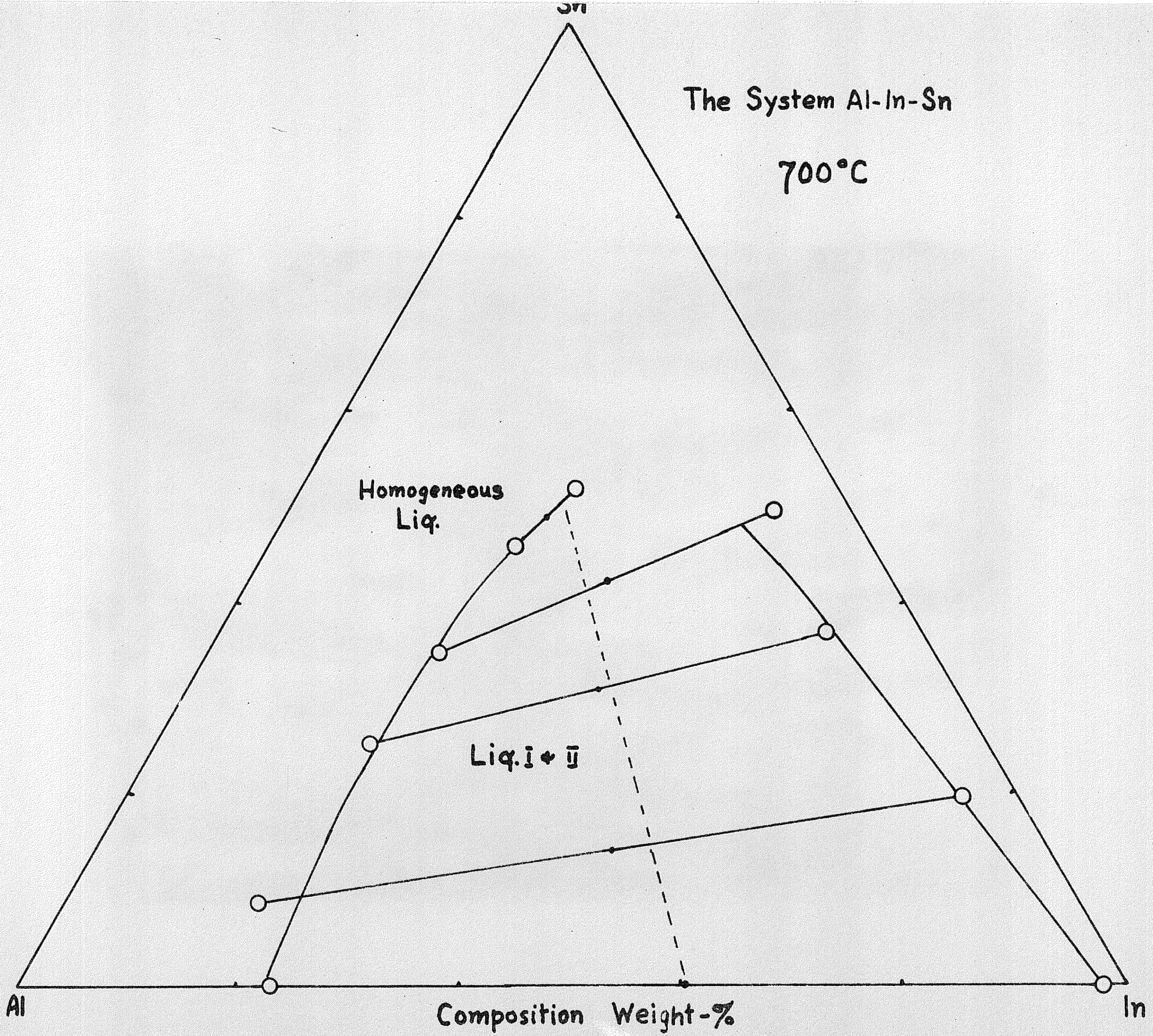


Fig. 15

More accurate values are given in Table VII. The quenching time for these determinations was approximately one minute and hence liquation was reduced to a minimum. In two or more instances the quenched samples indicated that the mixing of the metals had not been complete, owing to oxidation. The results of these analyses were discarded. At 800°C the thermocouple guard crucible was attacked by the alloy, thus making the result at this temperature doubtful. The fact that, at 800°C, some of the alloy ran out of the clay tube into which it was drawn was also an objectionable factor. The clay tube had to be broken to remove the solidified sample, and those samples drawn off at 800°C contained small amounts of a blackish precipitate, insoluble in hydrochloric acid. This precipitate, not present in the samples drawn off at 650 to 700 degrees C, and as yet unidentified, is probably silicon reduced from the clay tube. Those points which are considered to be the best values, or mean value, in Table VII, are given in Table VIII and plotted in Fig. 16.

If the above mentioned precipitate is silicon, it could be eliminated by using alundum instead of clay tubes. Furthermore, in view of the fact that some of the sample always ran out of the tube at higher temperatures, it may be necessary to use a mechanical device made of Alundum to remove a portion for analysis. An Alundum tube having a removable bottom, cap or plug, could be lowered into the desired layer, the cap could then be removed allowing the liquid to flow into the tube, the cap would then be replaced, and thus a portion withdrawn. A tube of this type would have to be specially made. Another and

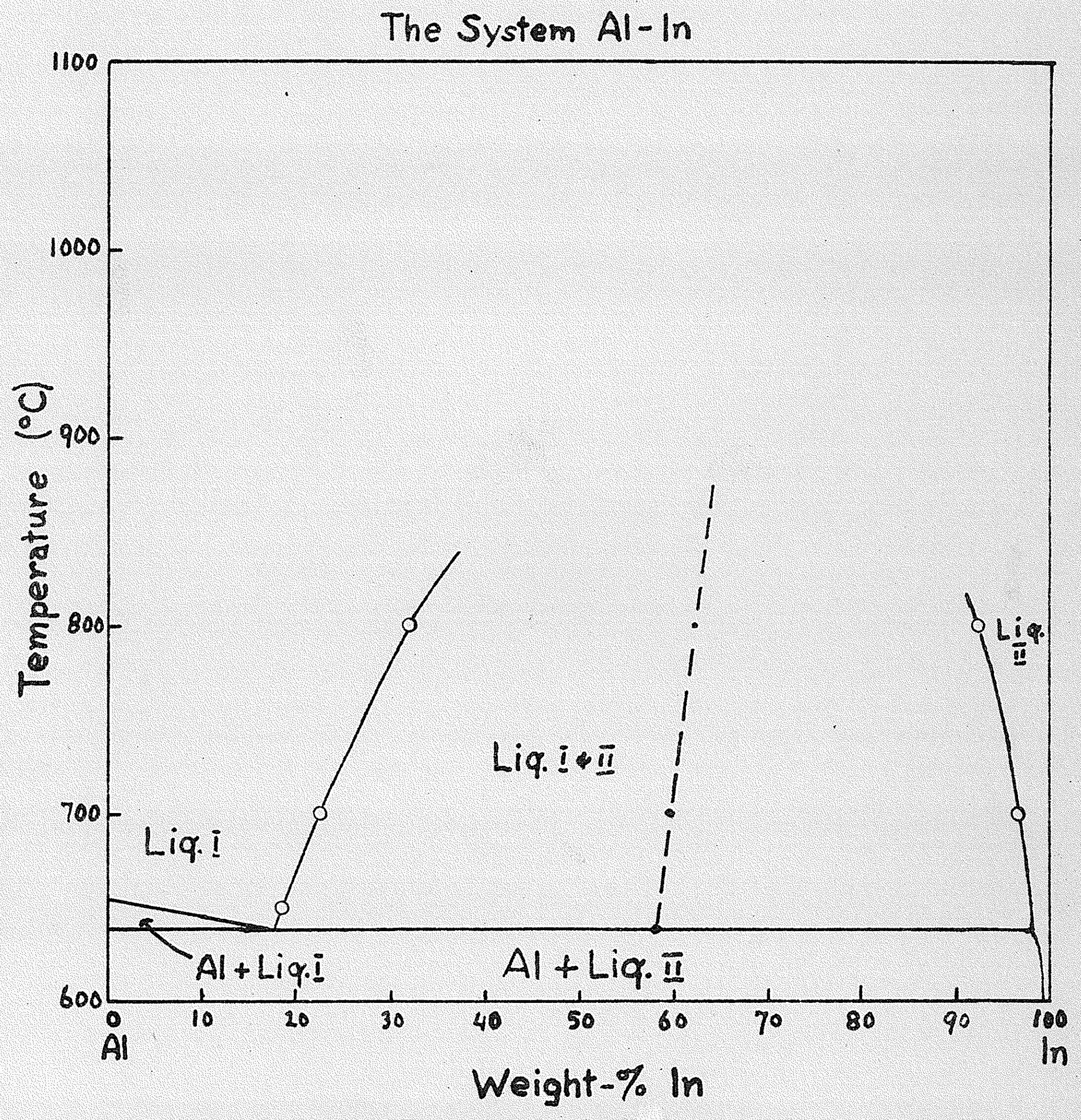

The System Al - In
1100
1000
900
800
700
600
Temperature (°C)
Liq. II
Liq. I + II
Liq. I
Al + Liq. I
Al + Liq. II
0
10
20
30
40
50
60
70
80
90
100
Al
In
Weight-% In

Fig. 16

simpler alternative is to quench the sample. It should be pointed out that the composition of the alloy could be made such that, at the equilibrium temperature, there was either a large upper layer or a large lower layer, depending on whether the overall composition was just inside the gap on the aluminum-rich side, or just inside on the indium-rich side. This is actually what was done in the Al-In investigation, and hence two different samples were used, one to give the upper layer and another to give the lower layer in equilibrium with it at a certain temperature. For example, when the points at 650°C and at 700°C were plotted and joined in Fig. 16, it was estimated from the slope of the composition boundary that one sample containing 45% indium and another containing 80% indium would be well within the gap at 800°C. Therefore a sample containing 45% indium was placed in an Alundum crubible in the furnace at 800°C and portions of the top layer were withdrawn by suction and analyzed. At the same time a sample containing 80% indium was placed in a guard tube in the furnace. This sample was quenched and drillings from the lower indium-rich layer were analyzed. These analyses gave the two points at 800°C shown in Fig. 16.

The fact that in several cases the amount of indium or aluminum in a layer was not as large as expected indicated that the metals were separating very quickly as the alloy cooled. For example, when alloy No. 27 was not quenched rapidly enough the analysis gave about 4.0% aluminum instead of 7.8% aluminum as given in Table VII.

SUMMARY

SUMMARY

1. The binary miscibility gap of the system Al-In is closing in with rising temperature more rapidly than might have been expected (Fig. 16).

2. In the ternary system (Fig. 15) the indications are that the critical composition at 700°C is approximately 26% aluminum, 24% indium and 50% tin.

3. The possibility of a gap in the system Al-Sn was investigated. The results are not conclusive.

4. It has been established that the metals separate very rapidly when the alloy is cooled.

5. A method of analysis has beem perfected. It consists of determining the amount of aluminum by density, the amount of indium polarographically and the amount of tin gravimetrically. When the quantity of a sample was too small for a density determination, the amount of indium and the amount of tin was determined, and the amount of aluminum was taken as the difference.

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BIBLIOGRAPHY

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Fig.6

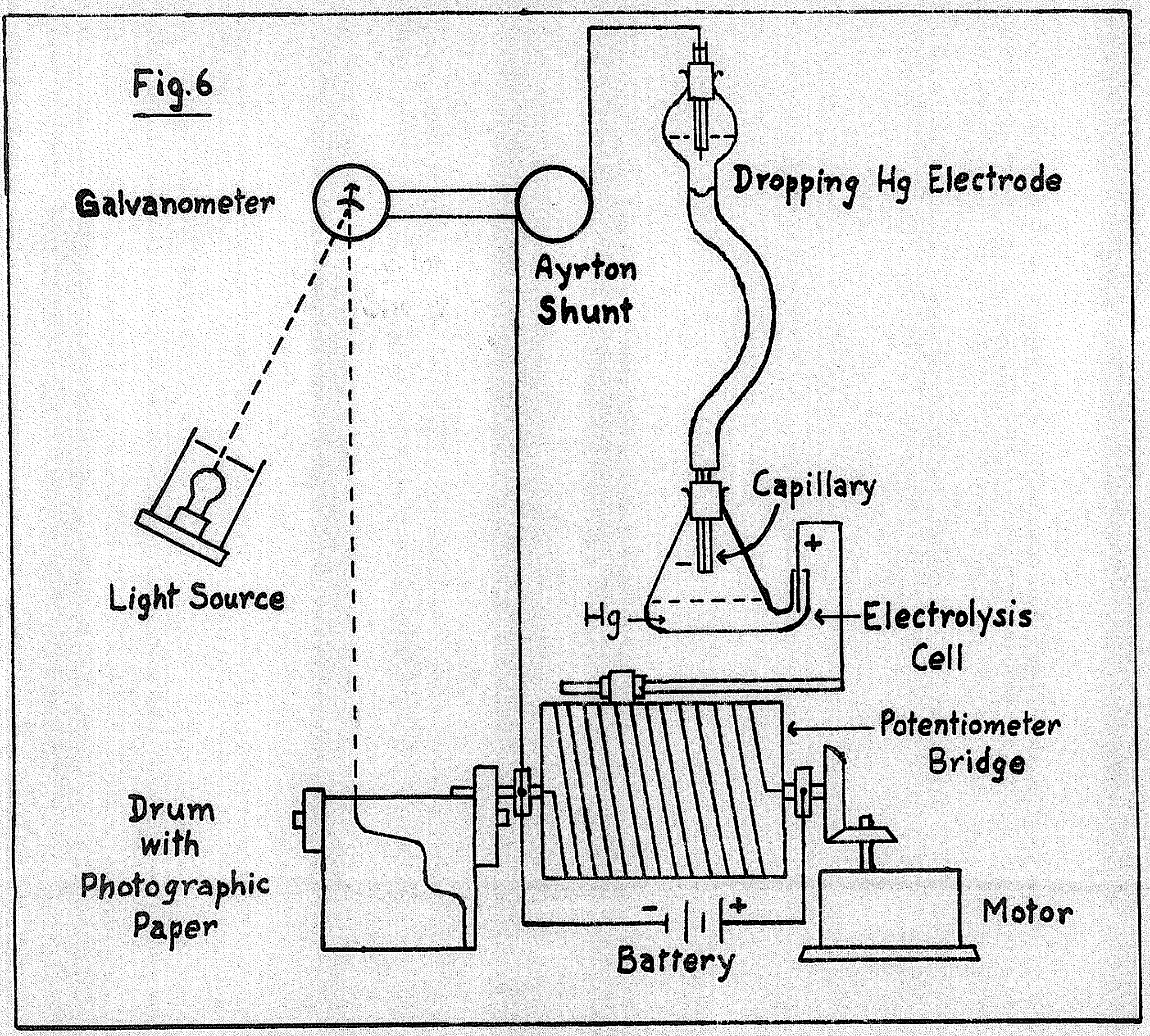
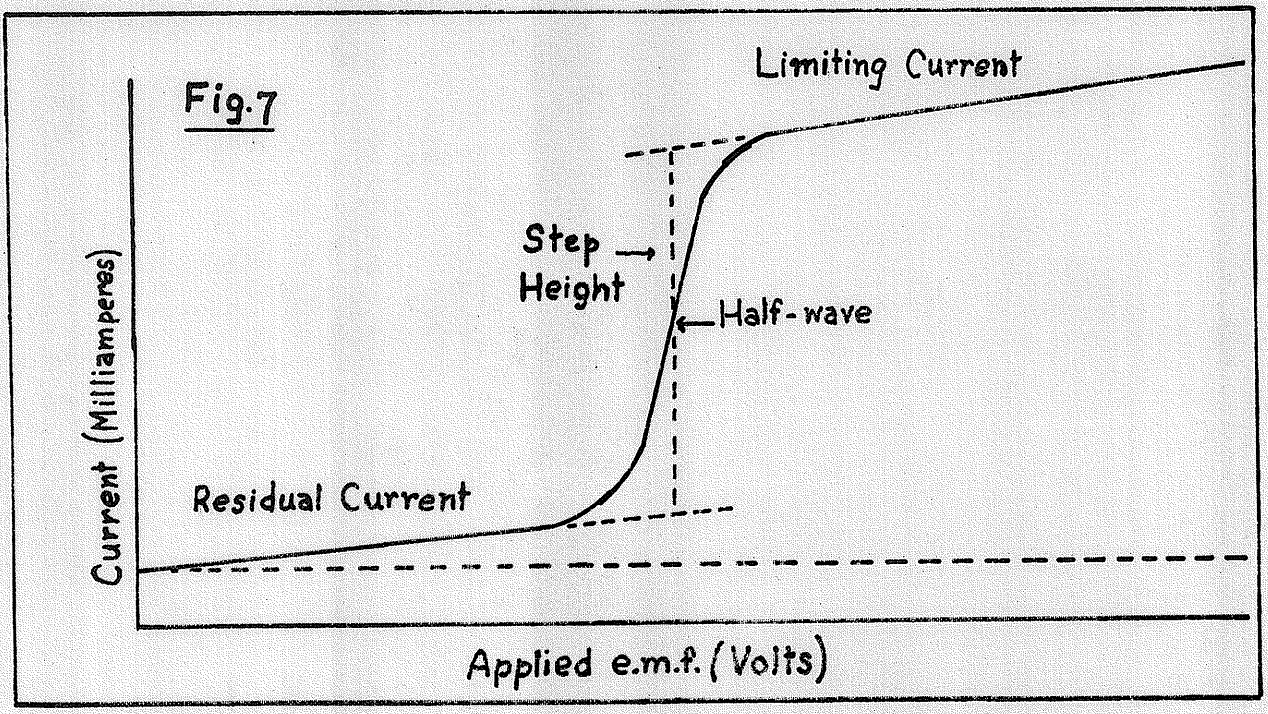

Galvanometer
Ayrton Shunt
Dropping Hg Electrode
Light Source
Capillary
+
-
Hg
Electrolysis Cell
Potentiometer Bridge
Drum with Photographic Paper
-
+
Battery
Motor

Fig.7


Limiting Current
Step Height
Half-wave
Residual Current
Current (Milliamperes)
Applied e.m.f. (Volts)

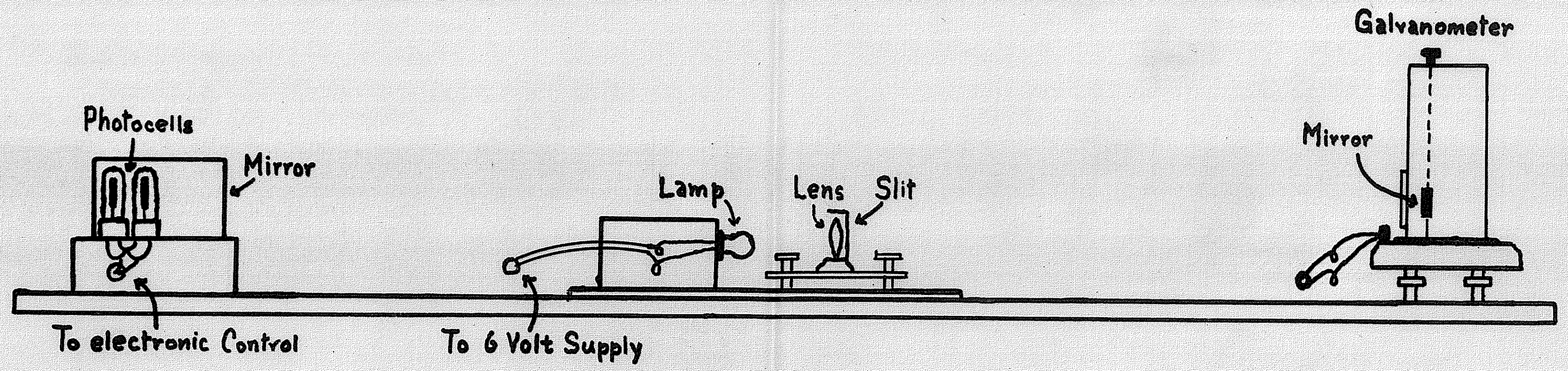

Photocells
Mirror
To electronic Control
To 6 Volt Supply
Lamp
Lens
Slit
Galvanometer
Mirror

Fig.10

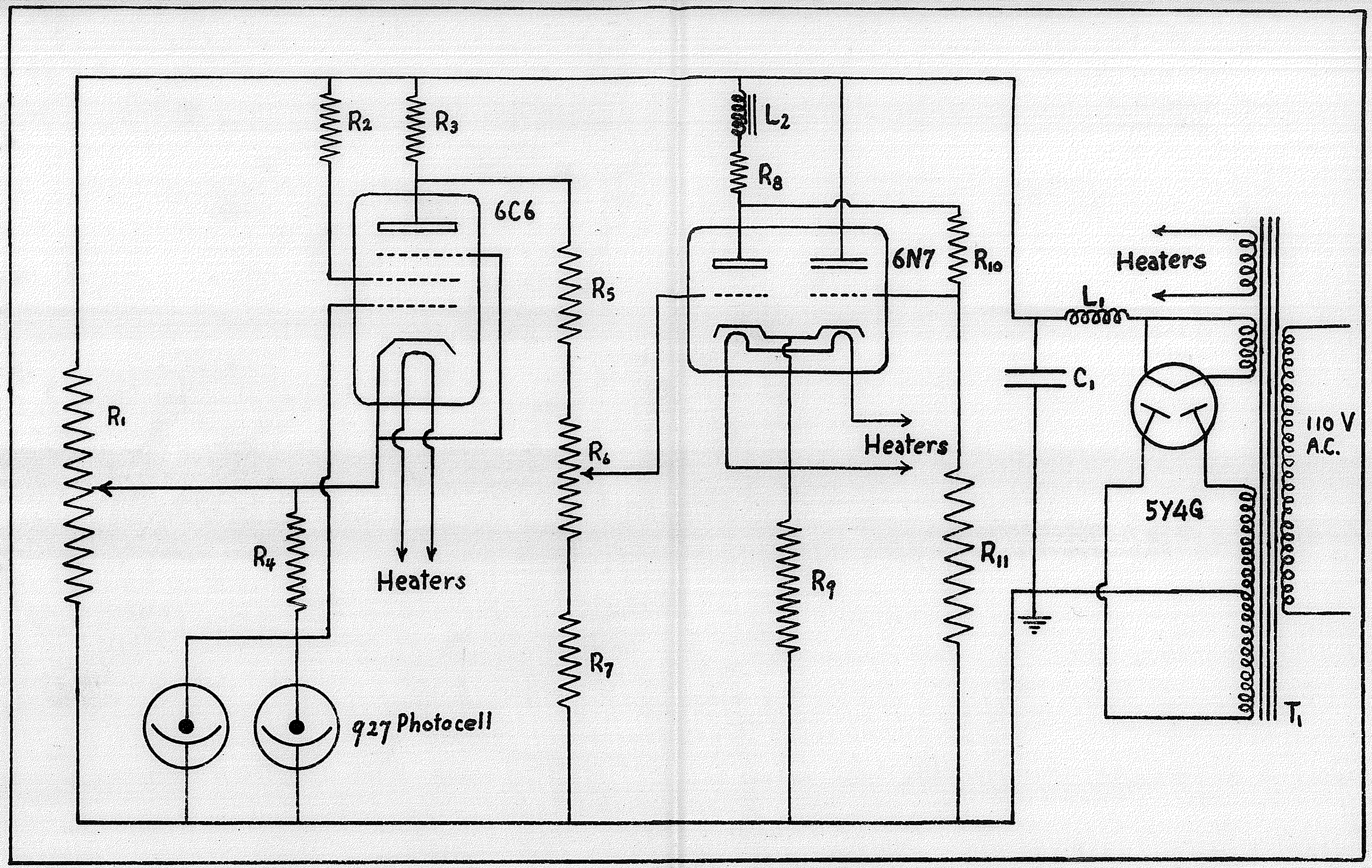
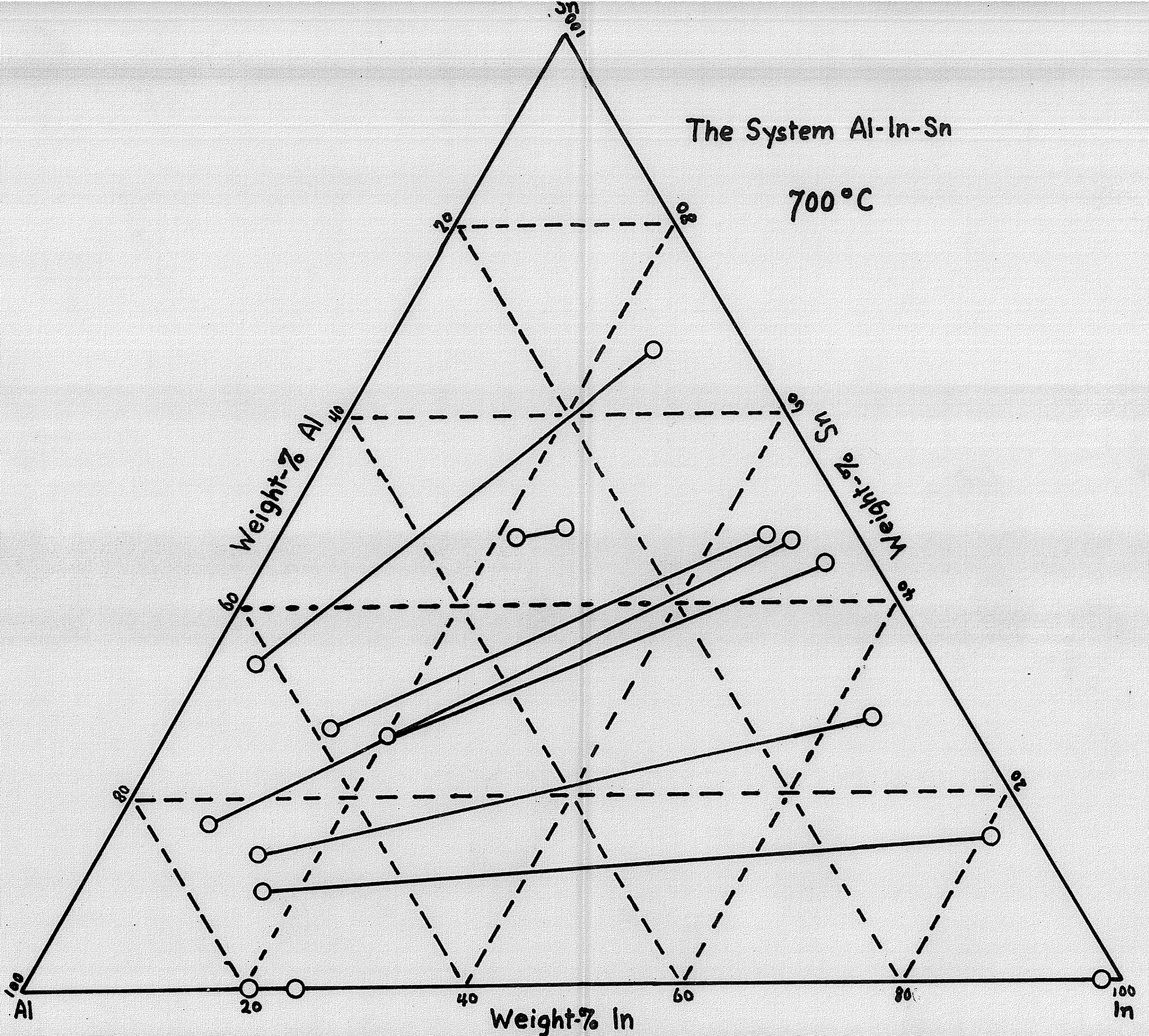

R₂
R₃
L₂
R₈
6C6
6N7
R₁₀
Heaters
L₁
R₅
C₁
R₁
R₆
110 V
A.C.
Heaters
5Y4G
R₄
Heaters
R₁₁
R₉
R₇
927 Photocell
T₁

Fig.8


The System Al-In-Sn

700 °C

Fig. 13

The System Al-In

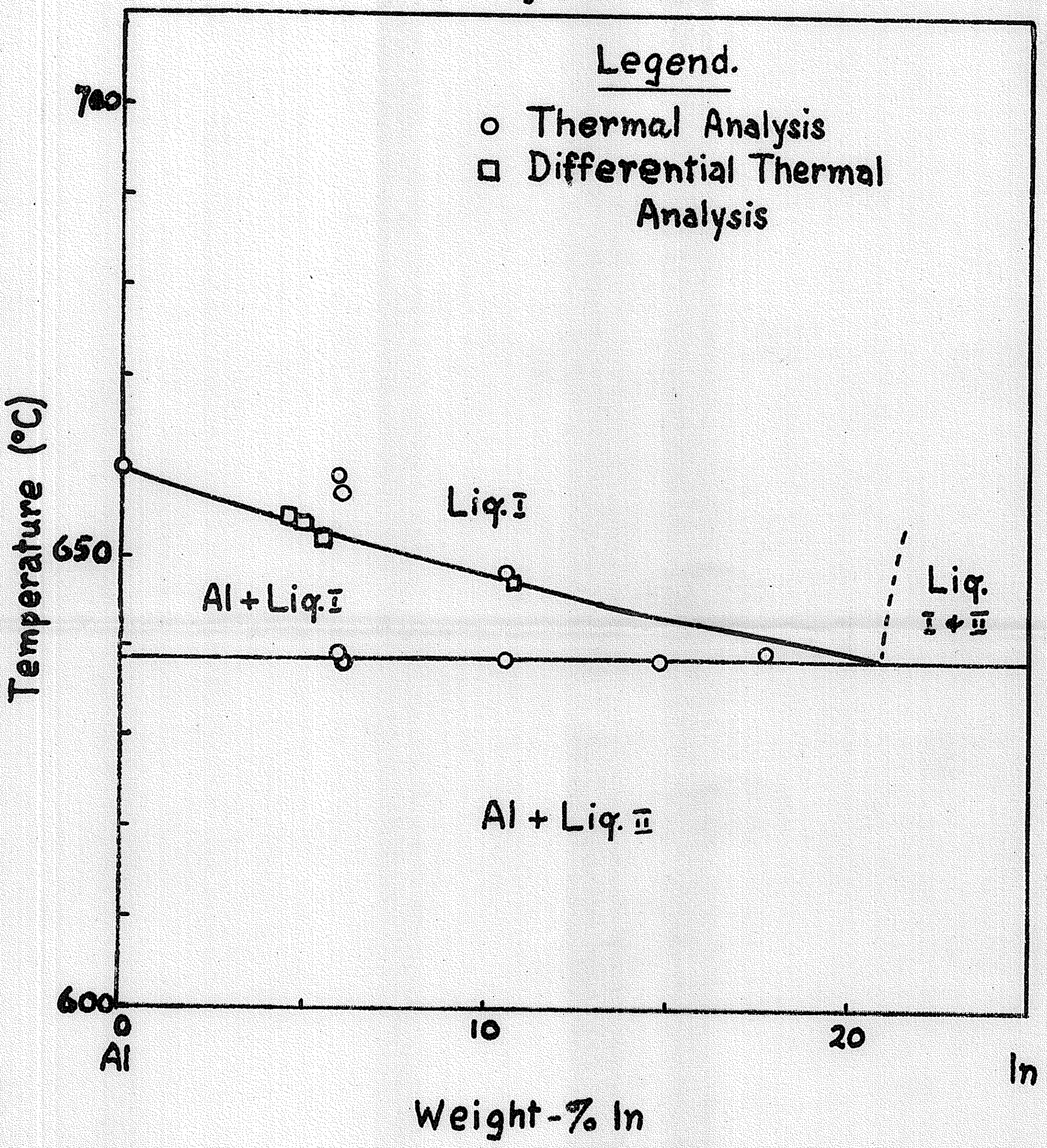


Fig.3

The System Al-In

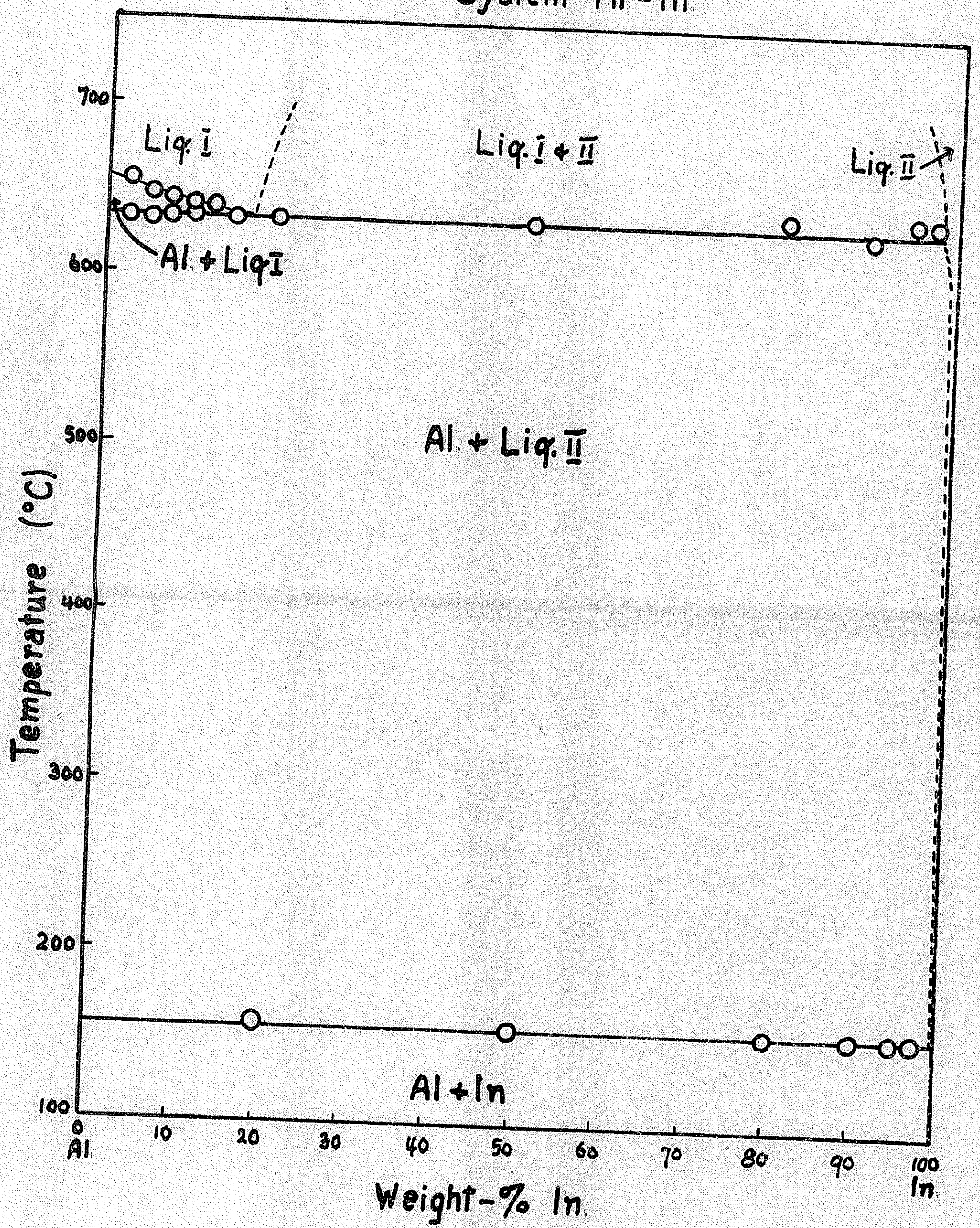
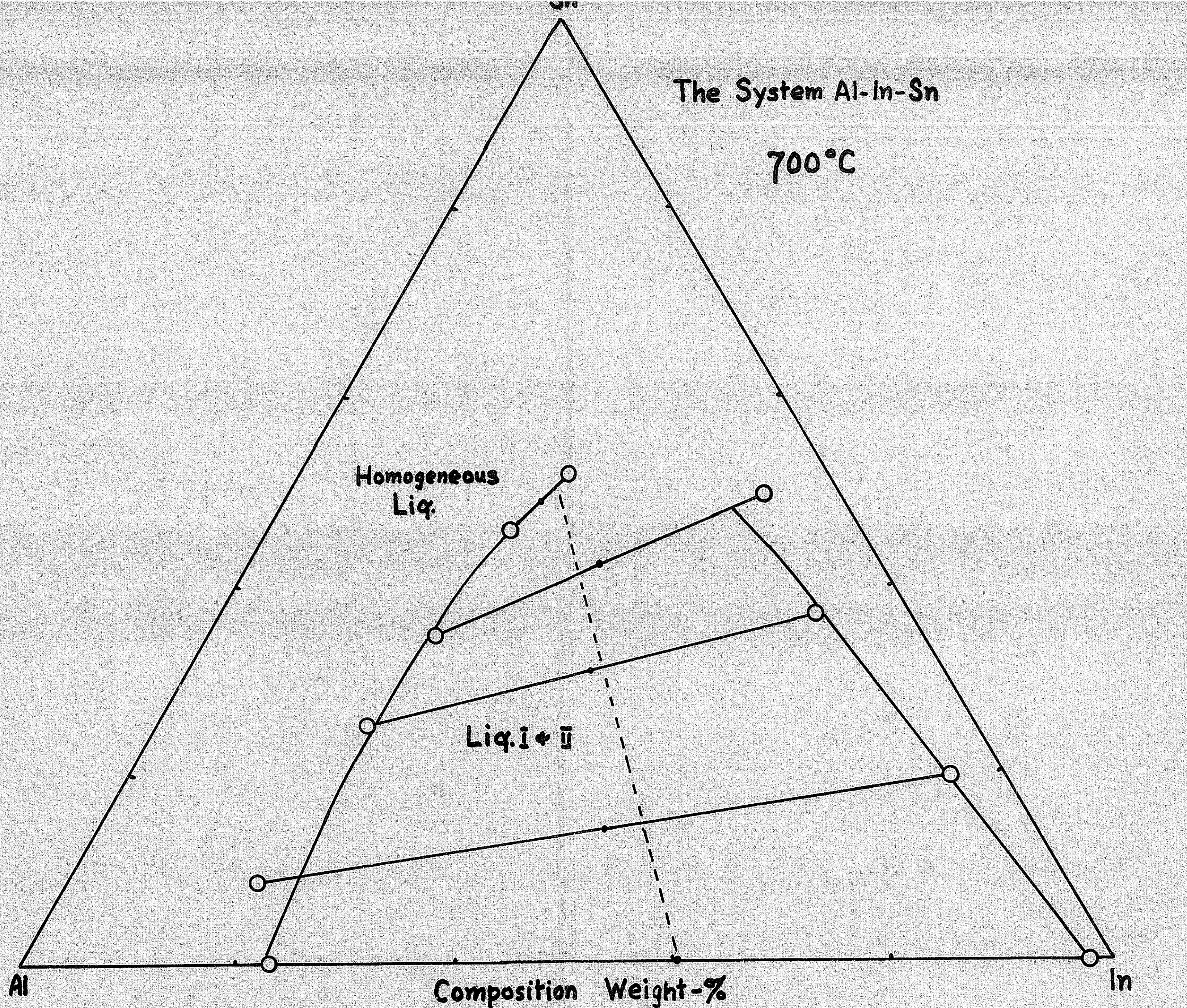


Fig. 2



The System Al-In-Sn
700°C
Homogeneous Liq.
Liq. I + II
Al
In
Composition Weight-%

Fig. 14

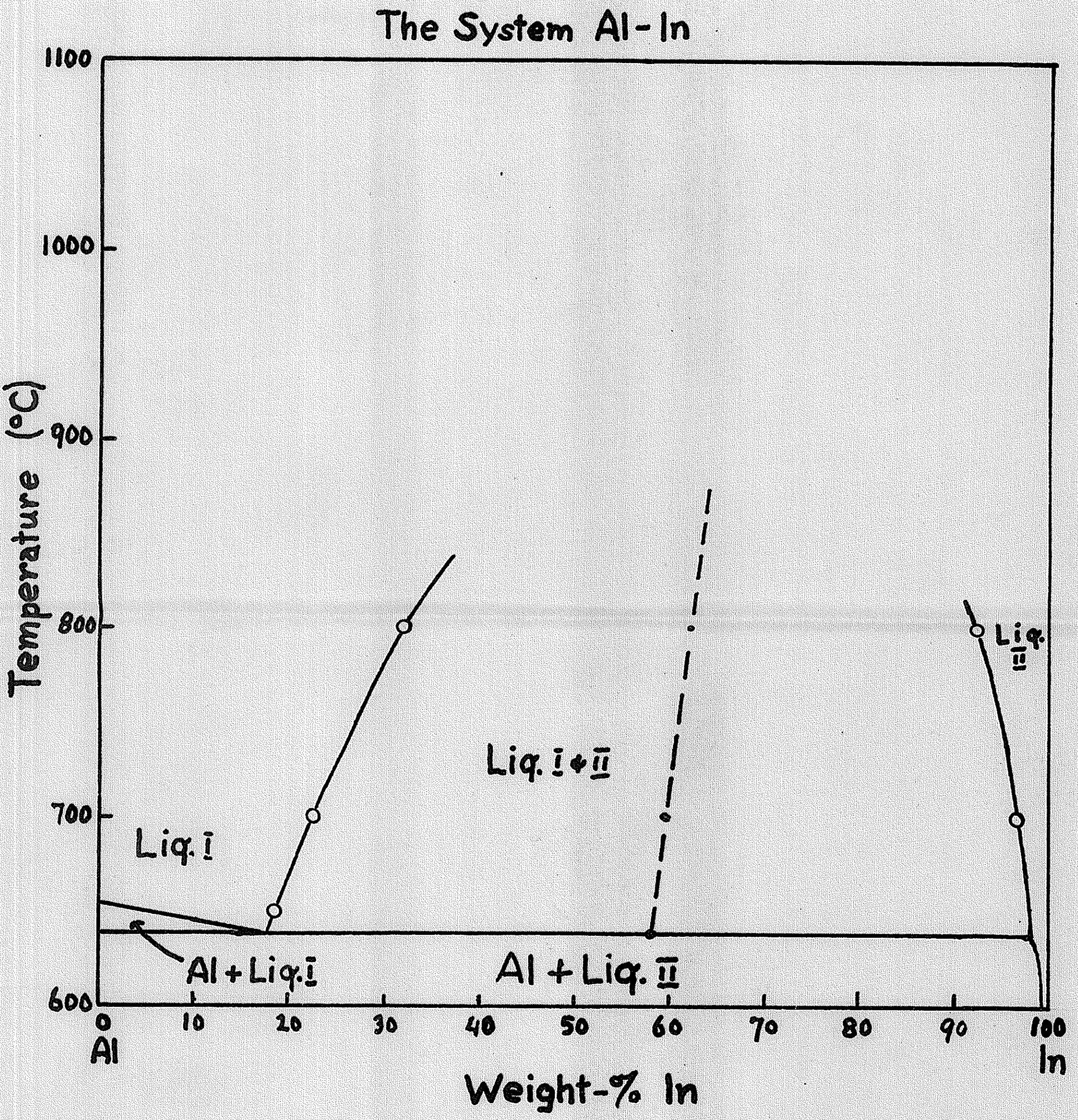

The System Al-In

Fig.15

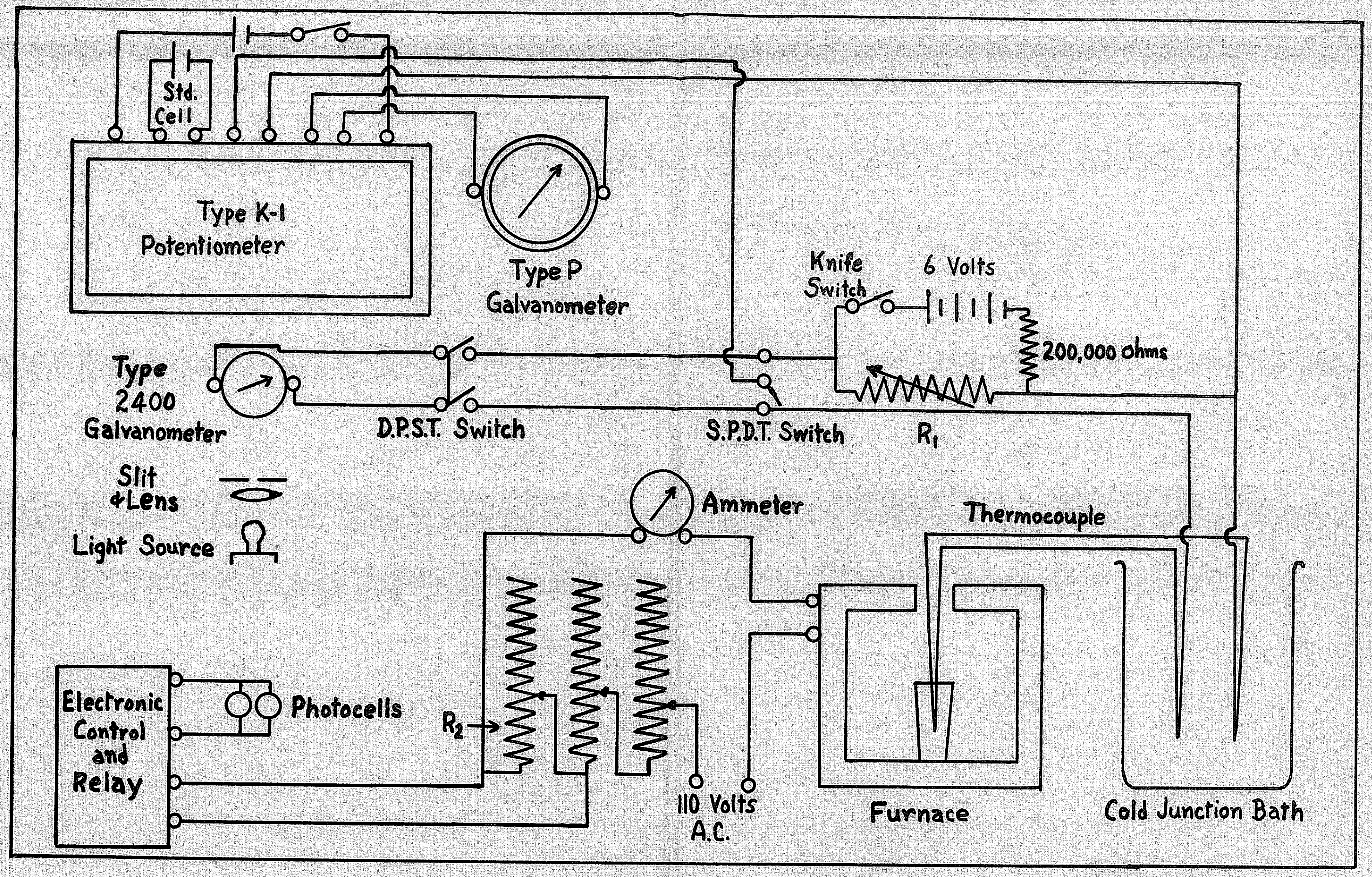

Std. Cell
Type K-1 Potentiometer
Type P Galvanometer
Knife Switch
6 Volts
200,000 ohms
Type 2400 Galvanometer
D.P.S.T. Switch
S.P.D.T. Switch
R_1
Slit & Lens
Light Source
Ammeter
Thermocouple
Electronic Control and Relay
Photocells
R_2
110 Volts A.C.
Furnace
Cold Junction Bath

Fig. 9