

THE SYSTEM IRON-TIN

To Dr. A. I. Daybell,
who patiently and helpfully
guided me in this, my first venture
into the study of research.

Gordon B. Skinner

A thesis presented to the Committee on
Graduate Studies, University of Manitoba,
in partial fulfillment of the requirements
for the degree of Master of Science.

August 1948



ACKNOWLEDGMENTS

The author wishes to express his appreciation to the
University of Illinois, and particularly to the Department of
Geology, for the facilities provided for his work, and for the
extra grant for the purchase of special equipment.

To several people who assisted in various stages of
the work, the author wishes to express his sincere appreciation.

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Engineering, who did most of the work on the design and construction

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To Mr. George Russell of the Department of Geology, who supervised
the author in the method of pollarding septines, and who took
the photomicrographs.

To Mr. J. Illingworth and other members of the University Training
staff, who assisted in obtaining a good deal of the material used
in the cracker.

To Mr. Robert Bird, University Technician, and his assistants,
Gordon Trider and Sam Marshall, who gave valuable advice and
assistance in the construction and maintenance of the equipment
used.

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to the Consolidated Mining and Smelting Company Limited, of Trail, B. C., for their generous Fellowship grant to the author, and for their extra grant for the purchase of special equipment.

To several people who assisted in various phases of the work, the author wishes to express his sincerest appreciation:

To Mr. J. J. Paterson, Assistant Professor of Agricultural Engineering, who did most of the work in building the ammonia cracker. Without his skilled assistance, this useful piece of equipment could never have been built.

To Mr. George Russell of the Department of Geology, who instructed the author in the method of polishing sections, and who took the photomicrographs.

To Mr. J. Illingworth and other members of the University building staff, who assisted in obtaining a good deal of the material used in the cracker.

To Mr. Robert Bird, University Technician, and his assistants, Gordon Trider and Cam Turnbull, who gave valuable advice and assistance in the construction and maintenance of the equipment used.

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INTRODUCTION

The study of the system iron-tin at the University of Manitoba was begun in the fall of 1946 by John H. Wood, at the request of Dr. C. H. Wright, research director of the Consolidated Mining and Smelting Company of Canada, who was interested in the solubility of iron in liquid tin in connection with the tin smelting operations of the company at Kimberley, B. C. Wood made a thorough survey of the literature on the system, and determined the solubility curve for iron in tin from 232° to 900° C. (1).

This curve, however, was known to continue to temperatures somewhat above 1100°C, while at still higher temperatures (and higher iron content) there was a region where conditions had not yet been determined. The presence of a miscibility gap was suspected but neither proved nor disproved.

Thus it was considered highly desirable to continue work on the system, with a view to completing the liquidus curve, and settling the question of the miscibility gap. The work may thus be considered a continuation of that begun by Wood.

PREVIOUS INVESTIGATIONS

A considerable amount of experimental work has been done on this system. A review of this work was made by Todd for this reason, only those data relating to the phase diagram investigated in the present program will be mentioned here. The composition of liquids on the tin-rich side of the diagram will be reviewed here.

The first constitutional diagram for the arsenic-tin system was that published by Irwin and Tarver (1) in 1907 (see Figure 1). It was determined by micro-analysis and magnetometric study. Their diagram showed a eutectic at 21.4% tin and 83 to 100% tin. They made no attempt to trace the solubility gap, but stated that it exists because they observed two layers in cooled samples. The only figures they give for the liquidus curve are:

Irwin	Temperature °C.
10	1154
1.5	1050
5	964
2.5	833

These points cannot be considered to be very accurate, since thermal analysis is not very sensitive in determining a liquidus curve.

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PREVIOUS INVESTIGATIONS

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The first constitutional diagram for the iron-tin system was that published by Isaac and Tammann (2) in 1907 (see Figure 1). It was determined by microscopic and magnetometric study. Their diagram showed a miscibility gap at 1140°C and stretching from 50 to 89% tin, and a steep liquidus curve from 89 to 100% tin. They made no attempt to trace the miscibility gap, but stated that it exists because they observed the presence of two layers in cooled samples. The only figures they give for the liquidus curve are:

% Iron	Temperature °C.
10	1134
7.5	1050
5	968
2.5	833

These points cannot be considered to be very accurate, since thermal analysis is not very sensitive in determining a steep curve.

Wever and Reinecken (3) also investigated the system

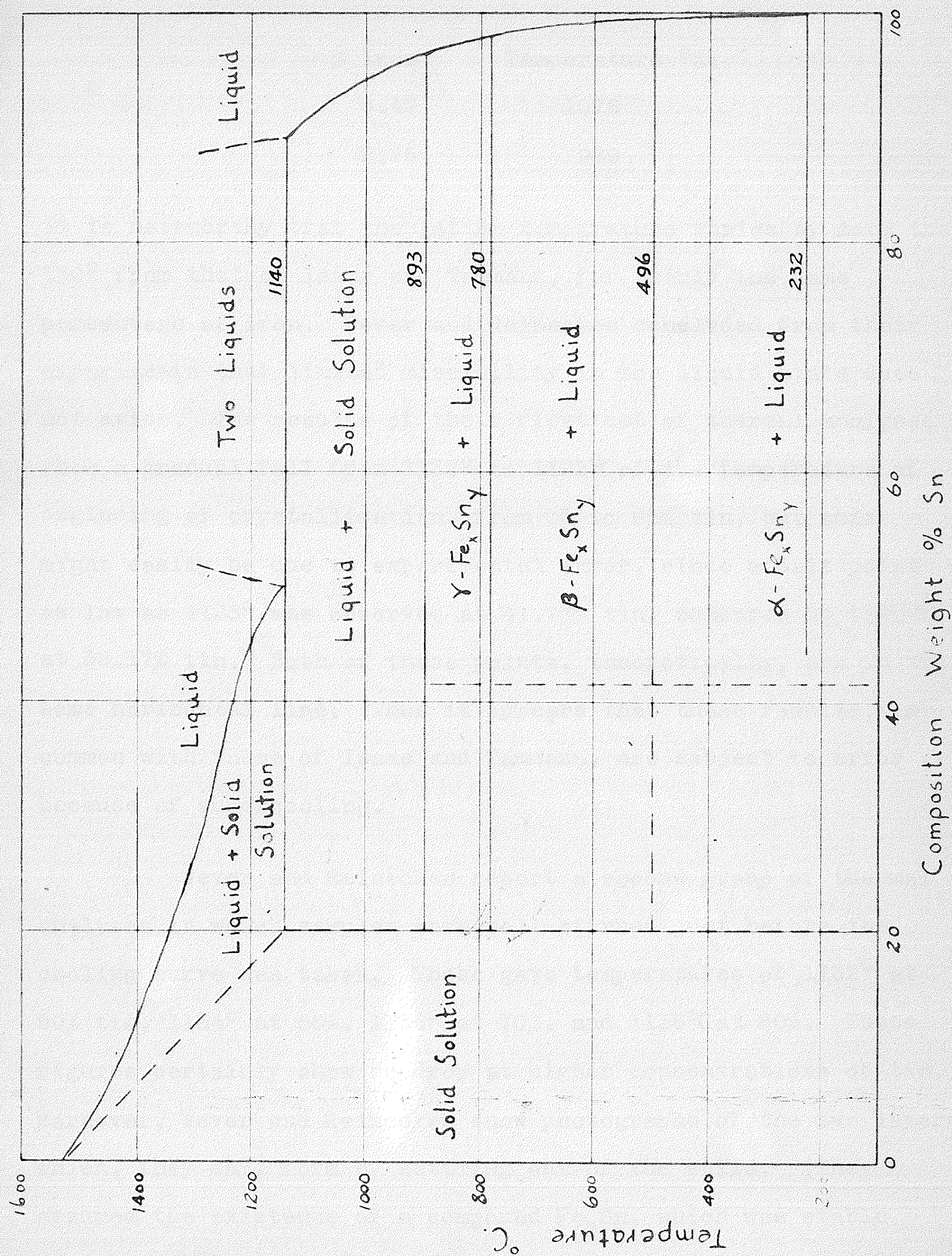


Figure 1.
Equilibrium Diagram according to Isaac and Tammann.

by thermal analysis and microscopic examination of rapidly cooled samples. They gave only two values on the liquidus curve:

% Iron	Temperature °C.
5.47	1076
2.45	989

It is noteworthy that the latter temperature varies by more than 150° from that of Isaac and Tammann, for nearly the same percentage of iron. Wever and Reinecken concluded from their experiments that limited miscibility in the liquid state does not exist. The results of their first set of thermal analyses show a gradual fall from 1132° to 1122° of the temperature of beginning of crystallization, from 55 to 85% tin, but this might easily be due to experimental error, since a halt point as low as 1123° was observed at 41.77% tin, compared to 1130° at 38.17% tin. Both of these points, theoretically, are on the same horizontal line. Thus it appears that these results, in common with those of Isaac and Tammann, are subject to error because of supercooling.

Wever and Reinecken report a second group of thermal analyses in which samples were well stirred just before the cooling curve was taken. These gave temperatures of 1132° at 50% tin, 1134° at 60%, 1134° at 70%, and 1136° at 80%. These figures certainly show no drop at higher concentrations of tin. Moreover, Wever and Reinecken show photographs of the two layers which, they say, form by settling out of the solid. (They assumed the existence of a compound Fe_3Sn , which was stable between 890° and 1136° , but later x-ray work (4) has shown that

this compound does not exist, and it is not included in present day diagrams.) They remark on the sharpness of the line of separation.

The denial of the existence of two liquid layers was really based on rapid quenching experiments. For instance, one sample containing 70% tin was heated at 1400° , well stirred, then "slowly" cooled to 1160°C , kept at that temperature for 15 minutes, and then quenched in water. The lower part of the sample was richer in iron than the top, but no distinct layers were observed. This would suggest that the rapid cooling prevented the solid from settling out, but it may be that fifteen minutes was not long enough for the two layers to separate out.

Ruer and Kuschmann (5) challenged this point of view. They showed a photomicrograph of the boundary between the two layers, and stated that such a clear-cut boundary could never be caused by liquation. Their picture showed droplets of the bottom layer suspended in the top layer, the presence of which, they said, was certain proof of the existence of two liquid layers.

Edwards and Preece (6) were the next to investigate the system. By thermal analysis they obtained a horizontal line at 1110°C . Their points, however, varied from 1095° to 1120°C , and the method was such that the samples may have been contaminated with carbon.

An experiment was carried out to try to show whether two layers were actually present in the liquid state. A sample containing 59.5% tin, and covered with graphite, was heated in a

long, narrow crucible at 1320°C for one and a half hours, then at 1220°C for two hours. A little of the top portion was then poured off into water, and the rest of the sample poured in a long strip onto a sheet of iron. The last portion to come out of the crucible was considered representative of the bottom layer, if any. Analysis showed 70% tin at the top and 56% at the bottom. Edwards and Preece considered this to be conclusive evidence for the existence of a miscibility gap, but they did not pursue the question further.

Further work has been concerned mainly with the structure and composition of solid forms, and need not be considered here. However, the data obtained in the most recent work, that of Wood, are given in the section under experimental results.

CONSIDERATION OF THE PROBLEM

As seen from the previous section, the problem has two parts - the determination of the liquidus curve from 400°C . up, and investigation of the miscibility gap. These parts are somewhat similar in that they both involve the composition of liquid solutions. In view of the difficulties reported by the previous investigators, thermal analysis could not be expected to be satisfactory for the liquidus curve, while they did not obtain any noticeable heat effects indicating separation into two layers.

In view of this, Wood adopted an isothermal method. He heated iron with **CONSIDERATION OF THE PROBLEM** equilibrium was established, and then quenched the sample in cold water. An analysis near the top of the sample gave the composition of the liquid.

A word might be said about quenching. When a liquid solution is cooled we do not obtain in general a solid solution of the same composition. For instance, in cooling a solution containing from 60 to 97% tin, the first solid to separate from the solution is a solid solution containing from 15 to 18% tin. Other solid phases will form as the temperature falls; the last will be practically pure tin, forming at 432°C . The more rapid the cooling, the smaller will be the crystals of solid that crystallize out. If the cooling is rapid enough, the crystals formed first will not have had time to get out appreciably before the whole mass is solid. It may be also said the solid first formed (solid solution) which are not thermodynamically

CONSIDERATION OF THE PROBLEM

As seen from the previous section, the problem has two parts - the determination of the liquidus curve from 900° up, and investigation of the miscibility gap. These parts are somewhat similar in that they both involve the composition of liquid solutions. In view of the few scattered results of the previous investigators, thermal analysis could not be expected to be satisfactory for the liquidus curve, while they did not obtain any noticeable heat effects indicating separation into two layers.

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stable at room temperature, may be found because the rapid cooling does not allow a transformation into the stable solid forms to occur.

Thus, although the structure of the quenched sample in no way resembles that of the liquid solution, the composition, when determined by analysis of a portion taken by a drill large enough to give a representative sample, is the same. This method could also be used to show the boundary of a miscibility gap, since, if the solids do not separate out, there will be an abrupt change of composition at the interface between the layers. Needless to say, one must be sure of heating long enough before quenching, and of quenching rapidly enough, to obtain the required result.

Another method of obtaining the composition of a liquid solution is to draw off a portion while the sample is maintained at the required temperature. This has an advantage in that it avoids any doubt as to the rapidity of cooling.

The method of Alexejeff (7) is suitable for an investigation of a system having two liquid layers. Here a series of samples of varying composition would be heated to the same temperature, and then quenched. Some would show two layers, while others would not. Thus the boundary of the region of two solutions would be determined. This is simple but requires the use of many samples to obtain only a few points.

In view of the conflicting reports of Isaac and Tammann and Edwards and Preece on the one hand, and of Wever and Reinecken on the other, the first thing to ascertain was, whether

two layers were present at any points in the temperature - composition area. It might be found whether the two layers observed in chilled samples were due to separation of solid, by quenching a sample from a moderate temperature (say 1200°C) to obtain two layers, and then quenching one of similar composition from a higher temperature, after stirring it up. Assuming that the rates of cooling are the same, then if two layers are not found in the second sample, the idea of Wever and Reinecken would appear to be mistaken, while the presence of two layers in both samples would support their view.

The method of taking portions from the hot sample should be useful here also. Portions taken from the top and bottom of the liquid would not only indicate whether there was a difference in composition, but also give the composition of each layer. This should be a definite answer to Wever and Reinecken's theory, since it allows no opportunity for the settling out of solids, but it has certain practical difficulties which will be discussed later.

EXPERIMENTAL

INTRODUCTION:

The experimental methods followed along the lines suggested in the previous section. The method of taking portions from the hot samples was used successfully for the liquidus curve. It proved unsuccessful in investigating the miscibility gap, so that the method of Alexejeff had to be used there.

PURITY OF MATERIALS USED:

The tin used in all the work was obtained from the Vulcan Detinning Works in Sewaren, N. J. This was termed "Commercial" tin, batch #73, and an analysis supplied with it was as follows:

Fe	.0020%
Pb	trace
Sb	.0023%
Cu	trace
Sn (by difference)	99.9957%

For the determination of the liquidus curve, Merck iron wire (at least 99.8%) and Cenco wire (at least 99.7%) were used. The Merck wire was very fine, while the Cenco wire was heavier and came in three-inch lengths. For the investigation of the miscibility gap, Wemco research iron, obtained through the Canadian Westinghouse Company, was used. No batch analysis was available, but the purity of the iron was guaranteed to be at least 99.95%. This iron came in rods 15 cm. long and 5 mm. diameter.

APPARATUS:

The method of measuring and controlling the temperature was the same as that used by Wood in his work on this system. Temperatures were measured with a platinum - platinum-10%-rhodium thermocouple. This was protected from injury by a sillimanite tube. The cold junction was a large beaker of water kept at a temperature of 31.7°C , and the voltage of the thermocouple was measured with a Leeds and Northrup Type K-1 potentiometer, and a Leeds and Northrup Type P wall galvanometer of sensitivity 0.0015 micro-ampere per millimeter. This gave an uncertainty in e.m.f. readings of less than 5 microvolts, corresponding to about 0.5° .

The thermocouple was calibrated using the following points:

Sn	Freezing Point	231.9°C .
Pb	" "	327.4
Zn	" "	419.4
Al (99.95%)	" "	659.9
NaCl	Melting Point	800.4
Ag	Freezing Point	960.5

The variation of the e.m.f. of a standard Pt - Pt-10%-Rh thermocouple^{with temperature} was plotted on a large scale using the data given in "Temperature - Its Measurement and Control in Science and Industry" (8). The calibration point e.m.f.'s 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 did not change noticeably with time. It

It was not necessary to calibrate each time using all the points, because if one point remained constant all the others would also. No suitable substance was available for calibrating at a high temperature, but since the curve varied very little from the standard - about one degree at the lowest calibration point and two degrees at the highest - the extrapolation was not likely to result in an appreciable error.

The method of temperature control, in brief, consisted in opposing the thermocouple voltage by a voltage equal to that which the thermocouple should generate when the hot junction was at the desired temperature, and using the off-balance current when the hot junction was not at the desired temperature to deflect a galvanometer. A beam of light shining on the mirror of the galvanometer was thus reflected onto one or other of two photo-electric cells, which then acted through an electronic circuit to increase or decrease the current in the heating coil of the furnace. For a complete description, Wood's thesis should be consulted, and also his published paper (9). By this means it was possible to maintain temperatures constant to within 3° .

The furnace was designed to fulfil two conditions:

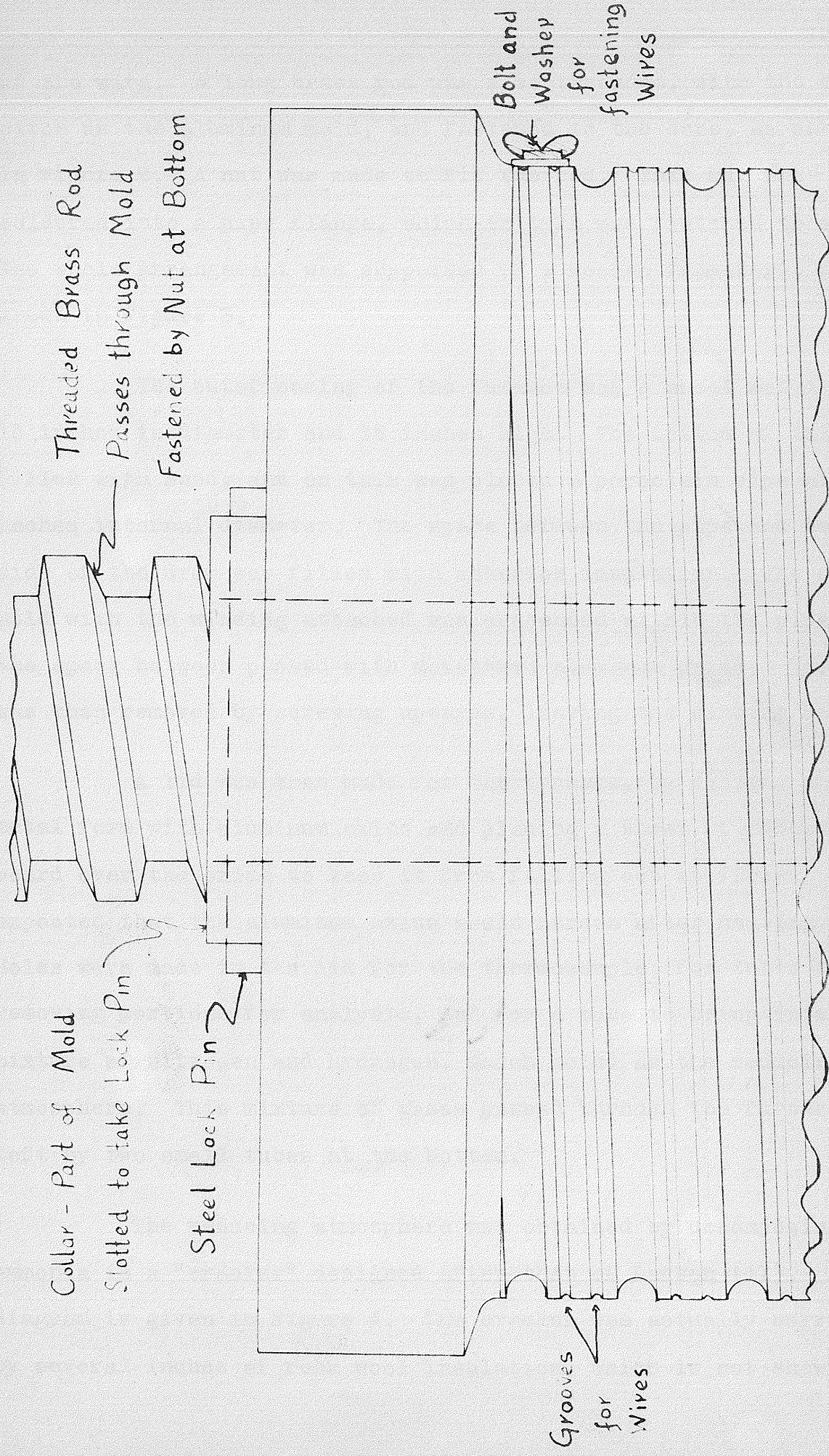
- (1) The furnace itself should be able to maintain a temperature of at least 1200°C .
- (2) The sample being heated should be protected from oxidation.

Wood's furnace did not fulfil these conditions. It had a chromel heating coil, covered with furnace cement, and the

sample was protected from oxidation by being sealed in vacuo in a pyrex test tube. The furnace could not maintain a temperature of even 1000°C , while pyrex appeared to become too fluid above 900°C to form a satisfactory protective covering. The use of silica tubes was suggested, but apart from the expense, they were not used because with samples completely enclosed in this manner, portions for analysis could not be taken in situ, and it would be necessary to rely entirely on results from quenching, which was not considered to be desirable.

For these reasons it became necessary to construct a vacuum furnace, or one in which the air could be replaced by an inert or reducing atmosphere. An inner wound furnace with tungsten wire as heating element was constructed, after the design of Fehse (10). Such a furnace requires a reducing atmosphere inside, to prevent oxidation of the tungsten wire. This would serve equally well to prevent oxidation of the sample. While this furnace was not successful in operation, it could have been improved so as to make it work. Therefore a description of the method of construction is given.

The method was, essentially, to wind the tungsten wire on an aluminum mold, pack moistened aluminum oxide around it, and then remove the mold. The aluminum mold was of cylindrical shape and slightly tapered to make it easier to remove from the "cast" of aluminum oxide. It was approximately eight inches long and four inches in diameter. A double thread, to take two heating wires in parallel, was cut on the cylinder, with a pitch of 0.4 inch. The wires were wound on at a red heat, to prevent cracking



Collar - Part of Mold

Slotted to take Lock Pin

Threaded Brass Rod

Passes through Mold

Fastened by Nut at Bottom

Steel Lock Pin

Grooves
for
Wires

Bolt and
Washer
for
fastening
Wires

Figure 2

of the wire. A long brass rod was also threaded, with the same pitch as the aluminum mold, and fastened to the core, as shown in Figure 2. A nut was made to fit the rod. This nut was soldered into a pipe flange, which in turn was fastened to a board. The whole arrangement was supported by a wooden framework, as shown in Figure 3.

The outer casing of the furnace was a sheet metal drum 15 inches in diameter and 16 inches high. The bottom of this was filled with sand, and on this was placed a porcelain pipe of 8 inches internal diameter. The space between the pipe and the side of the drum was filled with asbestos insulation. The aluminum mold with the winding attached was suspended within the pipe, and the space between packed with moistened aluminum oxide. The mold was then removed by screwing upwards, leaving the winding behind.

A lid was then made for the furnace, by filling a sheet metal form with aluminum oxide and placing a sheet of asbestos board over the oxide to keep it from falling out at first. It was expected that the aluminum oxide would harden after heating. Holes were made in the lid for the thermocouple, for tubes for removing portions for analysis, and for a tube to bring in a mixture of nitrogen and hydrogen, which acted as the reducing atmosphere. This mixture of gases passed through the furnace and left by two small tubes at the bottom.

The reducing atmosphere was obtained by decomposing ammonia in a "cracker" designed after that of Larson (11). A diagram is given in Figure 4. The cracker was actually surrounded by several inches of rock wool insulation, which is not shown in

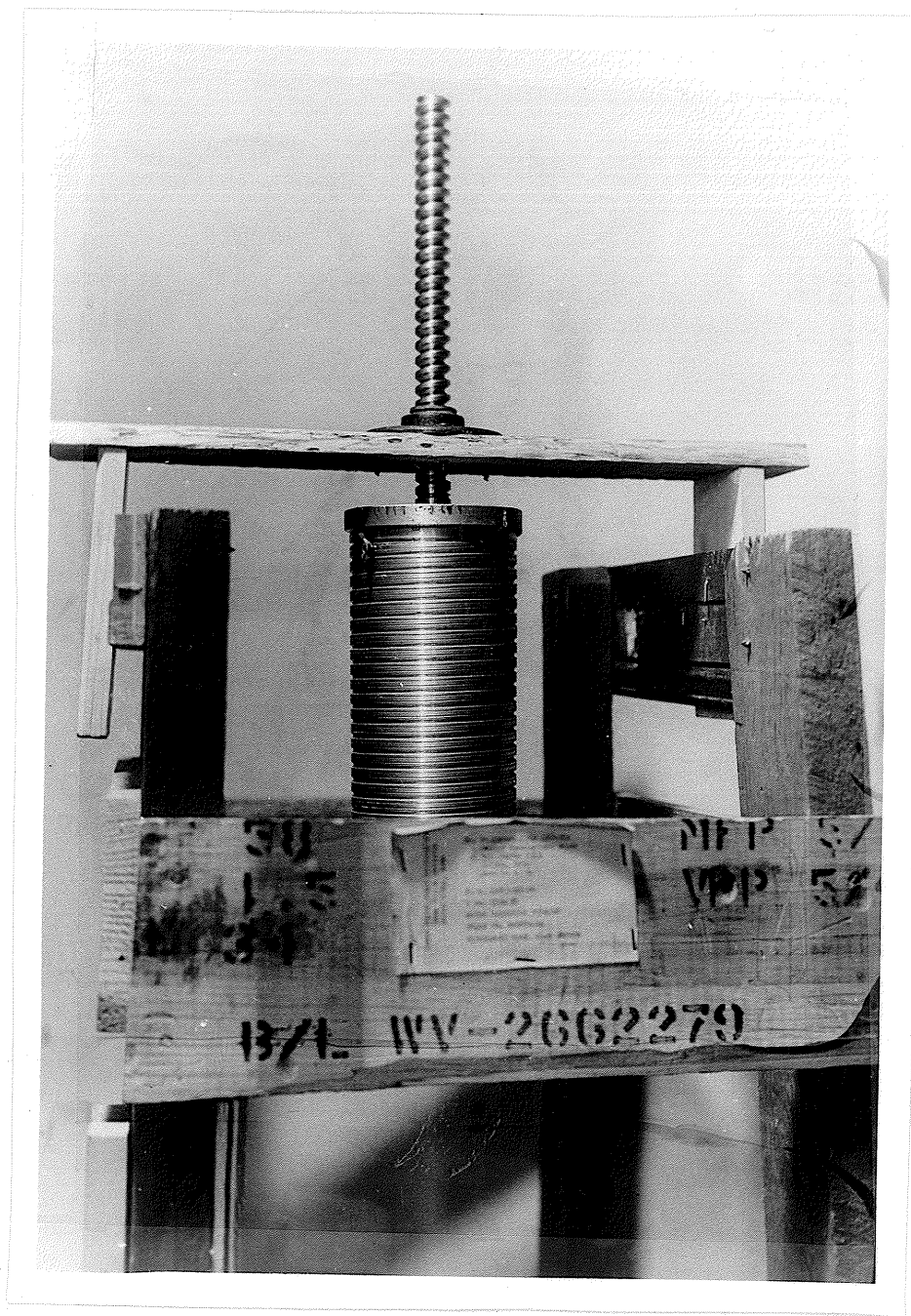


Figure 3.

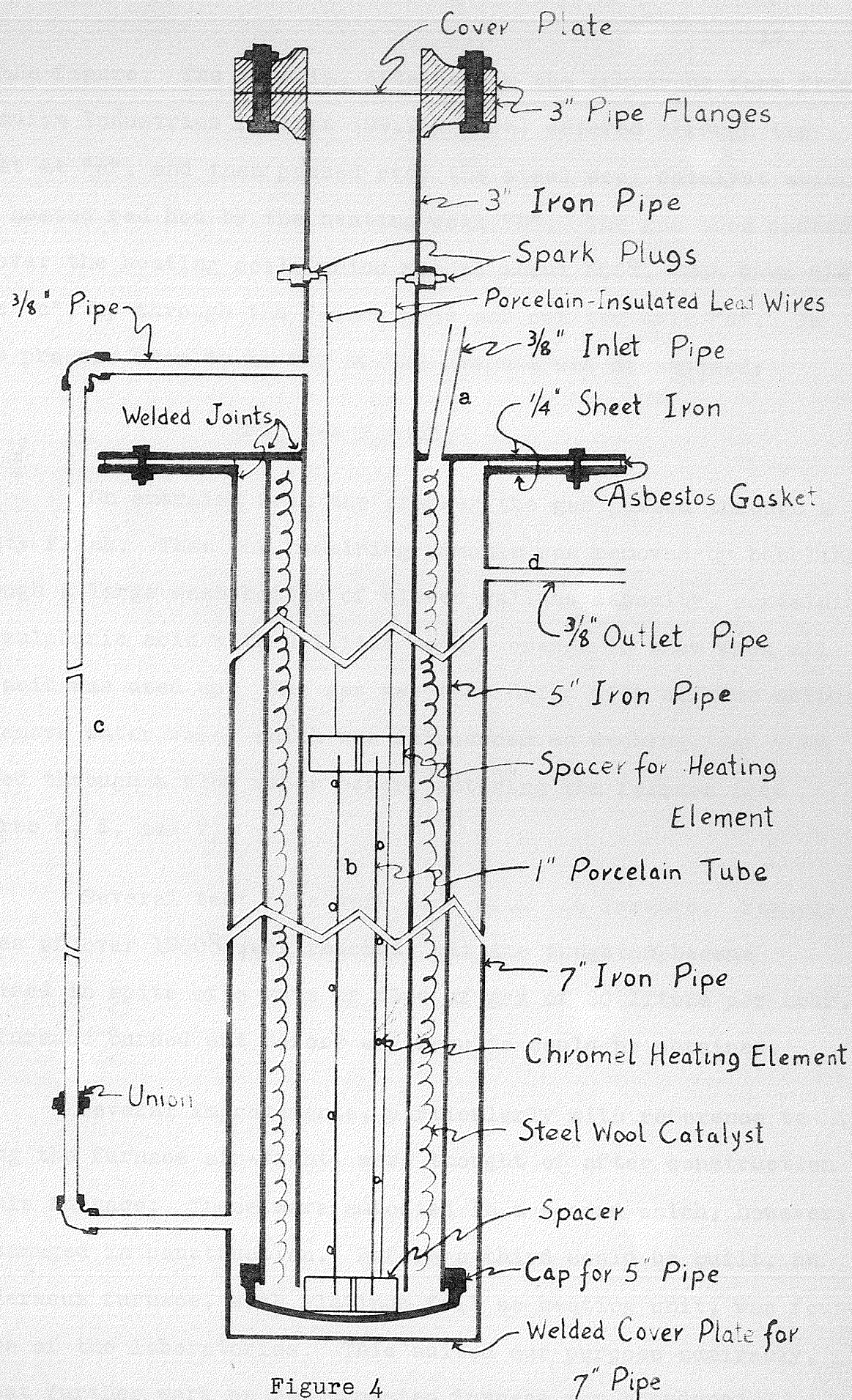
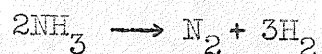


Figure 4

7" Pipe

in the figure. The ammonia, obtained in the anhydrous form from Canadian Industries Limited (99.98% pure) entered through the inlet at "a", and then passed over the steel wool catalyst which was heated red hot by the heating coil "b". The gas then passed up over the heating coil, which was at about 600°C, then down the pipe "c", up through the 7-inch pipe and out the exit "d". In this process from 80 to 90% of the ammonia was decomposed:



On emerging from the cracker the gas passed through a safety flask. Then the remaining ammonia was removed by bubbling through a large wash bottle of eleven gallons capacity, containing 10% sulphuric acid with a little methyl orange to show when all the acid was used up. The gas was then dried with calcium chloride to remove water vapor which was introduced on washing, and then passed through a flow meter before entering the furnace (see Figures 5, 6, and 7).

Several test runs were made with the furnace. Temperatures of over 1200°C were reached, but the tungsten became oxidized in spite of a rate of flow of gas of 80 liters per hour. The furnace burned out before any results could be obtained.

Several improvements, particularly with reference to making the furnace air-tight, were thought of after construction of this furnace. These were embodied in a second which, however, was damaged in construction. Before a third could be built, an old Heraeus furnace, with platinum foil as heating unit, was found in one of the laboratories. This suited our purpose admirably, so that further work on the tungsten furnace was abandoned.



Figure 5.

1. Thermostatted cold junction for thermocouple
2. Rheostats for furnace
3. Outlet from cracker
4. Calcium chloride bottles
5. Safety flask
6. Tube to flow meter
7. Flow meter
8. Rheostats for cracker
9. Cracker
10. Regulating valve on ammonia inlet
11. Inlet to cracker
12. Cooling coil
13. Ammonia cylinder
14. Wash bottle

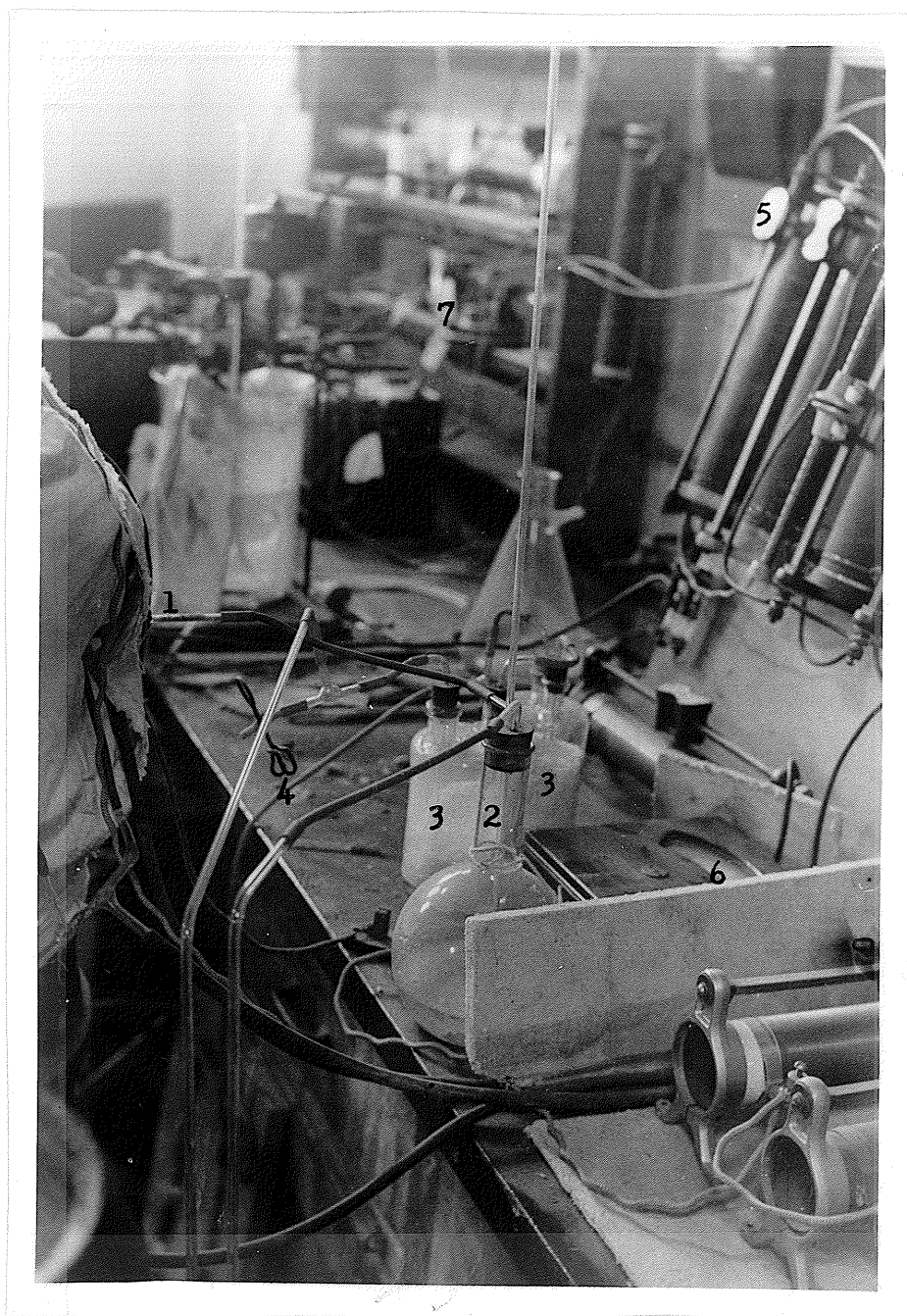


Figure 6

1. Outlet from cracker
2. Safety flask
3. Calcium chloride bottles
4. Tube to flow meter
5. Rheostats for controlling furnace
6. Ammeter in furnace circuit
7. Relay switch to shunt part of external resistance in furnace circuit

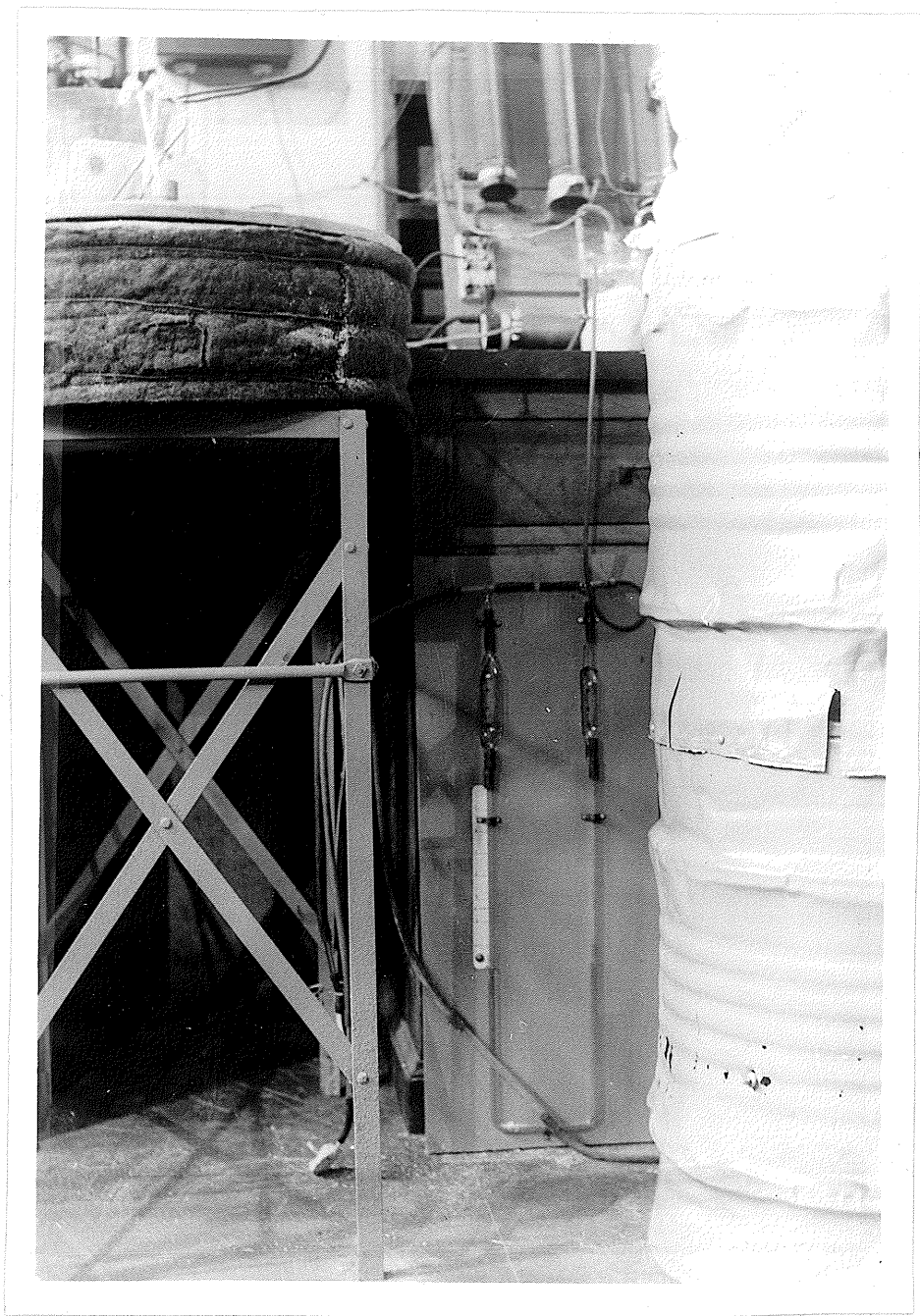


Figure 7.
The Flow Meter

The Heraeus furnace had the platinum foil wound on the outside of a sillimanite tube about 12 inches long, with an inside diameter of $1\frac{1}{4}$ inches. By providing inlet and outlet tubes at the ends, it was possible to pass the hydrogen-nitrogen mixture through the inside of the furnace, thus protecting the samples from oxidation, while at the same time the platinum was exposed to the air as it should be. The furnace had a resistance of about 0.4 ohm at room temperature, and required about 16 amperes current for a temperature of 1150°C . The furnace was operated with the tube in a vertical position, and with the crucible supported on a silica tube, to keep it at the center of the furnace.

After the liquidus curve had been completely investigated and some work done on the miscibility gap region, the tube of this furnace broke and the platinum was damaged. In view of difficulties incurred in the suction method of taking samples, it was decided not to repair this furnace, but to revert to the quenching method.

The common type of small laboratory furnace at the University consists of a muffle four inches high, four inches in inside diameter, and with a wall thickness of a little over an inch. This has a roughly spiral groove on the inside, to take a chromel heating element, usually of 850 watts. At the ends of the groove are holes through the furnace wall, through which bolts pass to bring in the current. For his work Wood covered the heating element with furnace cement.

It was found that an 850-watt chromel element could

give temperatures of 1150° and even 1200°C , in this type of furnace, if the coil was not covered at any points, but completely exposed to the air. The type of cement in the laboratory furnaces melted at these temperatures, however, and it was necessary to mold another muffle, with a groove to take the heating wire, from "Plicast 27", a refractory cement obtained from the Winnipeg Supply and Fuel Company. This appeared quite capable of standing these high temperatures. The only difficulty then was oxidation of the lead bolts. These were of mild steel and oxidized rather badly. However it was not difficult to replace them. The furnace was placed on several thicknesses of asbestos board, and surrounded by several inches of asbestos insulation.

For a higher temperature, a tube was made of Alundum cement, three inches in inside diameter, $\frac{1}{4}$ inch wall thickness, and four inches high. This was fired at 1100°C in the chromel furnace, and a platinum foil heating element wound onto it. A plain muffle of "Plicast 27", of four inches inside diameter and about one inch wall thickness, was made to surround this, and the whole surrounded with asbestos as before. This furnace could maintain a temperature of 1300°C with a current of 18 amperes.

In connection with these furnaces a 3-kilowatt Ajax-Northrup induction furnace was used to homogenize the samples. It could heat them above the melting point of iron in about 15 minutes, and in addition had a pronounced stirring action, due to the fact that the sample acts as the secondary coil of a transformer, the coil of the furnace being the primary.

GENERAL PROCEDURE:

For the earlier part of the work, samples were contained in alundum (aluminum oxide) crucibles, one and three-eighths inches outside diameter and three and three-eighths inches high. The iron of whichever type was being used was first polished with emery cloth. The Wemco iron was cut using a clean hack-saw blade into pieces one to two inches long, Cenco iron into somewhat shorter pieces, while the Merck wire was coiled up before using. For the liquidus an amount of iron was taken sufficient to give a sample richer in iron than the liquid was expected to be. A check was always made to see that this had actually been the case. For the miscibility gap compositions were chosen that fell within the range where it was expected to be. The tin was melted and poured over the iron.

The sample was then placed in the furnace, and most of the air was displaced by the hydrogen-nitrogen mixture before the current was turned on. The sample was kept at the desired temperature for two days as a rule, in order to allow complete solution of the iron. In several cases, however, after a sample had been taken, the furnace would be thermostatted at a higher temperature for a day, and another portion taken, so that more than one point could be determined using one sample.

A sillimanite tube was then inserted into the upper part of the solution, and a portion drawn into the tube by suction. Solidification occurred in the tube as the liquid came into contact with its cooler upper part. Thus the tube had to be broken to recover the sample for analysis. In a few cases,

some liquid appeared to have run out of the tube as the tube was being withdrawn from the furnace. In such cases unusually high percentages of iron were found, presumably because high-melting solid solutions had separated on the walls of the tube and tin-rich liquid had flowed out.

For similar reasons, it was necessary to analyze the whole portion withdrawn. Because of separation of solid solutions, the portion near the top of the tube contained much less iron than the part near the bottom. By taking the total analysis, of course, this was not important, since what entered the tube was necessarily the required solution.

Portions from near the bottom of the crucible were taken in a similar manner. Care was taken to avoid contamination with solution from the top by closing the top end of the tube and allowing the thermal expansion of the air in the tube to force out any top layer which had entered while the tube was being inserted into the melt. Samples from the bottom were taken only in the region where limited liquid miscibility was suspected.

In several cases where limited miscibility was expected, samples were quenched. This was done by rapidly removing the sample from the furnace and placing it in a close-fitting copper mold surrounded by cold water. Solidification required two to three minutes. More rapid cooling would have been desirable, but the insulating nature of the crucibles made this difficult to obtain without pouring the samples, which would have ruined any boundary between two layers. These quenched samples were hacksawn in half vertically and drilled for analysis at various points.

Two other methods were used in examining the samples. Several samples were polished, and etched with dilute hydrochloric acid. The samples were first filed roughly flat, and then a plane surface was obtained by grinding on a steel grinding wheel with carborundum powder. The sample was next polished successively on 0, 2/0, and 3/0 polishing papers, using a solution of paraffin in kerosene as a lubricant, and they were carefully washed in warm kerosene when changing from one paper to the next. The final polish was applied using a suspension of soap and Norton's levigated aluminum oxide in water, on a cloth lap. Various concentrations of acid and various times of etching were tried, but the etching process did not seem to be of great importance, since the great difference in hardness between the two main phases present allowed them to be distinguished very easily even without etching. These polished specimens were examined under a microscope, and photomicrographs were taken.

Also, a sample was tested for hardness using a Rockwell machine. Thanks are due to Mr. Donald Thompson, of the Engineering faculty, who carried out this test.

Following the failure of the Heraeus furnace, and the partial failure of the suction method of sampling (as will be described below) the method of Alexejeff was adopted. The method was briefly to melt the tin and iron together in the induction furnace, then maintain it at some constant temperature in the muffle furnace for some time to allow separation of liquid layers if this was to occur, and then to quench the sample and examine it for the presence of two layers.

A good deal of trouble was experienced in obtaining something to hold the sample. It was found that alundum crucibles cracked in the severe temperature gradient in the induction furnace. Nickel crucibles melted. Graphite crucibles were found to be satisfactory. They became very hot and burned somewhat, but not seriously. Also it was found that samples sealed in glass under vacuum were able to stand very high temperatures. The method was to place the glass-covered sample in the graphite crucible, and fill in the space between sample and crucible with dry alundum cement. This hardened in the intense heat of the induction furnace, while the glass melted and formed a remarkably good protective covering over the sample. Thus there was no necessity for an atmosphere of hydrogen, which was impossible to sustain when transferring the sample from the induction furnace to the muffle furnace.

It was found that an hour and a half was sufficient time in the muffle furnace to show the presence of two layers. In those samples near the iron-rich side of the gap, the division between the layers was easily seen, but with samples near the tin-rich end it was necessary to polish the samples and examine microscopically for droplets of the bottom layer suspended in the top. Samples were chosen so that the sides of the gap were bracketed - one sample showing two layers and another of slightly different composition only one layer, at a given temperature.

METHOD OF CHEMICAL ANALYSIS:

The method of analysis for iron in the samples was standard, and very simple. Solutions of potassium dichromate of approximately 0.01, 0.02, 0.05, and 0.1 N were made up. These were standardized using Merck iron wire. A suitable amount of iron was weighed, and dissolved in 10 cc. of concentrated hydrochloric acid contained in a 500 cc. Erlenmeyer flask.

The solution was heated to boiling and 15% stannous chloride solution added drop by drop until the yellow color of the ferric iron disappeared. The solution was then cooled and diluted to 300 cc.; 10 cc. of 3% mercuric chloride solution, 10 cc. of syrupy phosphoric acid and 6 drops of 0.2% solution of barium diphenylamine sulphonate were added. The solution was titrated with the potassium dichromate to the violet end point. According to Kolthoff and Sandell (12), for this amount of indicator, a correction of 0.24 ml. must be subtracted from the titration as an indicator blank for 0.01N potassium dichromate, and corresponding amounts for the other concentrations.

The phosphoric acid was added to reduce the oxidation potential of the iron. The dilution was necessary to reduce the chloride ion concentration to less than 2N. At higher concentrations, chloride ion is oxidized by dichromate.

For the samples, the method was essentially the same, except that after the sample had all dissolved, the tin, which dissolved as stannous chloride, was oxidized to stannic chloride by bubbling chlorine through the solution until the yellow color

of ferric iron was observed. The solution was then heated and the stannous chloride reduction carried out. Here the stannous chloride reduced not only ferric iron, but also any free chlorine left in solution. The analysis then proceeded as described above.

Hydrolysis of the stannic chloride sometimes occurred during titration, but this did not affect the end point, as was found by adding pure tin solutions to weighed amounts of iron.

The burette was calibrated to ensure accurate volume readings.

12-5411-15

The solubility, eutectic and liquidus curves, determined by both Wood and myself, are listed below in Table I.

Table I

Atom percent of tin in equilibrium with solid phase

Temperature (C.) Weight % Iron

200	0.017
240	0.070
280	0.201
300	0.270
305	0.280
310	0.285
315	0.290
320	0.295
325	0.300
330	0.305
335	0.310
340	0.315
345	0.320
350	0.325
355	0.330
360	0.335
365	0.340
370	0.345
375	0.350
380	0.355
385	0.360
390	0.365
395	0.370
400	0.375
405	0.380
410	0.385
415	0.390
420	0.395
425	0.400
430	0.405
435	0.410
440	0.415
445	0.420
450	0.425
455	0.430
460	0.435
465	0.440
470	0.445
475	0.450
480	0.455
485	0.460
490	0.465
495	0.470
500	0.475
505	0.480
510	0.485
515	0.490
520	0.495
525	0.500
530	0.505
535	0.510
540	0.515
545	0.520
550	0.525
555	0.530
560	0.535
565	0.540
570	0.545
575	0.550
580	0.555
585	0.560
590	0.565
595	0.570
600	0.575
605	0.580
610	0.585
615	0.590
620	0.595
625	0.600
630	0.605
635	0.610
640	0.615
645	0.620
650	0.625
655	0.630
660	0.635
665	0.640
670	0.645
675	0.650
680	0.655
685	0.660
690	0.665
695	0.670
700	0.675
705	0.680
710	0.685
715	0.690
720	0.695
725	0.700
730	0.705
735	0.710
740	0.715
745	0.720
750	0.725
755	0.730
760	0.735
765	0.740
770	0.745
775	0.750
780	0.755
785	0.760
790	0.765
795	0.770
800	0.775
805	0.780
810	0.785
815	0.790
820	0.795
825	0.800
830	0.805
835	0.810
840	0.815
845	0.820
850	0.825
855	0.830
860	0.835
865	0.840
870	0.845
875	0.850
880	0.855
885	0.860
890	0.865
895	0.870
900	0.875
905	0.880
910	0.885
915	0.890
920	0.895
925	0.900
930	0.905
935	0.910
940	0.915
945	0.920
950	0.925
955	0.930
960	0.935
965	0.940
970	0.945
975	0.950
980	0.955
985	0.960
990	0.965
995	0.970
1000	0.975
1005	0.980
1010	0.985
1015	0.990
1020	0.995
1025	1.000
1030	1.005
1035	1.010
1040	1.015
1045	1.020
1050	1.025
1055	1.030
1060	1.035
1065	1.040
1070	1.045
1075	1.050
1080	1.055
1085	1.060
1090	1.065
1095	1.070
1100	1.075
1105	1.080
1110	1.085
1115	1.090
1120	1.095
1125	1.100
1130	1.105
1135	1.110
1140	1.115
1145	1.120
1150	1.125
1155	1.130
1160	1.135
1165	1.140
1170	1.145
1175	1.150
1180	1.155
1185	1.160
1190	1.165
1195	1.170
1200	1.175
1205	1.180
1210	1.185
1215	1.190
1220	1.195
1225	1.200
1230	1.205
1235	1.210
1240	1.215
1245	1.220
1250	1.225
1255	1.230
1260	1.235
1265	1.240
1270	1.245
1275	1.250
1280	1.255
1285	1.260
1290	1.265
1295	1.270
1300	1.275
1305	1.280
1310	1.285
1315	1.290
1320	1.295
1325	1.300
1330	1.305
1335	1.310
1340	1.315
1345	1.320
1350	1.325
1355	1.330
1360	1.335
1365	1.340
1370	1.345
1375	1.350
1380	1.355
1385	1.360
1390	1.365
1395	1.370
1400	1.375
1405	1.380
1410	1.385
1415	1.390
1420	1.395
1425	1.400
1430	1.405
1435	1.410
1440	1.415
1445	1.420
1450	1.425
1455	1.430
1460	1.435
1465	1.440
1470	1.445
1475	1.450
1480	1.455
1485	1.460
1490	1.465
1495	1.470
1500	1.475
1505	1.480
1510	1.485
1515	1.490
1520	1.495
1525	1.500
1530	1.505
1535	1.510
1540	1.515
1545	1.520
1550	1.525
1555	1.530
1560	1.535
1565	1.540
1570	1.545
1575	1.550
1580	1.555
1585	1.560
1590	1.565
1595	1.570
1600	1.575
1605	1.580
1610	1.585
1615	1.590
1620	1.595
1625	1.600
1630	1.605
1635	1.610
1640	1.615
1645	1.620
1650	1.625
1655	1.630
1660	1.635
1665	1.640
1670	1.645
1675	1.650
1680	1.655
1685	1.660
1690	1.665
1695	1.670
1700	1.675
1705	1.680
1710	1.685
1715	1.690
1720	1.695
1725	1.700
1730	1.705
1735	1.710
1740	1.715
1745	1.720
1750	1.725
1755	1.730
1760	1.735
1765	1.740
1770	1.745
1775	1.750
1780	1.755
1785	1.760
1790	1.765
1795	1.770
1800	1.775
1805	1.780
1810	1.785
1815	1.790
1820	1.795
1825	1.800
1830	1.805
1835	1.810
1840	1.815
1845	1.820
1850	1.825
1855	1.830
1860	1.835
1865	1.840
1870	1.845
1875	1.850
1880	1.855
1885	1.860
1890	1.865
1895	1.870
1900	1.875
1905	1.880
1910	1.885
1915	1.890
1920	1.895
1925	1.900
1930	1.905
1935	1.910
1940	1.915
1945	1.920
1950	1.925
1955	1.930
1960	1.935
1965	1.940
1970	1.945
1975	1.950
1980	1.955
1985	1.960
1990	1.965
1995	1.970
2000	1.975

RESULTS

Wood showed also that the eutectic at the tin-rich end of the diagram contains $0.002 \pm 0.001\%$ iron.

RESULTS

The solubility values for the liquidus curve, obtained by both Wood and myself, are listed below in Table I.

Table I

Iron content of solution in equilibrium with solid phase

Temperature °C.	Weight % Iron
270	.0047
329	.0073
382	.023
389	.029
394	.022
451	.046
454	.043
483	.070
502	.087
548	.141
576	.169
594	.222
606	.221
637	.322
654	.32
700	.75
746	.96
773	1.24
775	1.31
787	1.36
795	1.56
801	1.61
826	1.72
846	2.02
857	2.11
895	2.73
916	2.88
938	3.08
962	3.60
1008	4.31
1045	5.19
1065	6.27
1125	11.10
1128	12.00

Wood showed also that the eutectic at the tin-rich end of the diagram contained $0.003 \pm 0.001\%$ iron.

Data on the miscibility gap are given in Table II.

Table II

Boundaries of the miscibility gap

Temperature °C.	Iron rich boundary	Tin rich boundary	Mean
	Weight % Iron	Weight % Iron	Weight % Iron
1150	40.1	17.4	28.8
1200	40.8	17.0	28.9
1300	41.2	16.8	29.0

The temperatures given in Table I are assumed to be the equilibrium temperatures of the system. The values of the equilibrium constants K are calculated from the data in Table I. The values of K are plotted against $1/T$ in Figure 1. The straight line obtained from the data in Figure 1 is shown in Figure 1. The slope of the line is -1.1×10^4 K. The intercept of the line on the $1/T$ axis is 1.1×10^4 K. The value of ΔH° is -1.1×10^4 K. The value of ΔS° is 1.1×10^4 K.

It is seen from Figure 1 that the equilibrium constants K are plotted against $1/T$ in Figure 1. The straight line obtained from the data in Figure 1 is shown in Figure 1. The slope of the line is -1.1×10^4 K. The intercept of the line on the $1/T$ axis is 1.1×10^4 K. The value of ΔH° is -1.1×10^4 K. The value of ΔS° is 1.1×10^4 K.

DISCUSSION OF RESULTS

The equilibrium constants K are plotted against $1/T$ in Figure 1. The straight line obtained from the data in Figure 1 is shown in Figure 1. The slope of the line is -1.1×10^4 K. The intercept of the line on the $1/T$ axis is 1.1×10^4 K. The value of ΔH° is -1.1×10^4 K. The value of ΔS° is 1.1×10^4 K.

The question of the equilibrium of the system is discussed in this section. The equilibrium constants K are plotted against $1/T$ in Figure 1. The straight line obtained from the data in Figure 1 is shown in Figure 1. The slope of the line is -1.1×10^4 K. The intercept of the line on the $1/T$ axis is 1.1×10^4 K. The value of ΔH° is -1.1×10^4 K. The value of ΔS° is 1.1×10^4 K.

DISCUSSION OF RESULTS

The temperatures given in Table I are accurate to $\pm 3^\circ$. The accuracy of the analyses varies with the percentage of iron in the samples. The values for points above 900°C , obtained by the volumetric method, are accurate to one part in 300, while Wood's values, obtained colorimetrically for samples containing very little iron, are not so accurate.

If there were any errors in sampling they could not be estimated directly. They would be random errors, and could be estimated by observing how well the points fell on a smooth curve. From Figure 13 it may be seen that these errors are small. Examination of a large scale graph showed that only one of the eight points above 900°C lies farther from a smooth curve than could be expected from the errors in temperature and analysis.

The question of attainment of equilibrium was investigated by Wood. It is generally considered desirable in work of this kind to approach the equilibrium condition from both sides. In this case, that would mean to do one set of experiments as we have, heating iron in contact with liquid tin at the desired temperature; and another set of experiments in which the iron and tin are heated at a high temperature, and then cooling to the desired temperature, in which process solid phase would separate until a saturated solution is again obtained. Identical values for the compositions of these two solutions could be considered proof of a true equilibrium condition.

Wood found that this process was not practicable in our case, since the solid phase did not settle to the bottom of the crucible on cooling, but remained in suspension. Wood therefore did the next best thing. By heating samples at the same temperature for different lengths of time, he found that, using Merck or Cenco wire, at temperatures above 600°C , samples heated a day or more all had the same composition of solution: presumably that of the saturated solution.

No experiments of this sort were done by myself, but, as stated previously, several portions were often taken from the same sample at different temperatures. Usually a day was allowed for the new equilibrium to be established. Some of the melts, therefore, were heated for several days and some for only one, but all the points so obtained lie on a smooth curve.

In the miscibility gap region, there was no doubt as to whether the iron was all dissolved, since it was actually melted in the induction furnace, and well mixed with the tin by the stirring action of the furnace.

The presence of two liquid layers was proved beyond reasonable doubt. One sample was heated to the melting point of iron^(1535°C) in the induction furnace, and then allowed to cool in the furnace with the power off. It required about forty minutes to cool to 200°C . The original sample contained 28.0% iron. Drillings for analysis were taken at four points spaced equally from top to bottom. From top to bottom the analyses were:

23.5 Weight % Iron

27.2 "

28.7 "

31.5 "

In addition, no discontinuity was visible to the eye. Another sample containing 24.4% iron was similarly heated in the induction furnace, but quenched rapidly (two minutes to room temperature). This sample likewise showed no separation into layers. These experiments showed that the layers observed in other cases were not due to the rapid settling out of solid, as Wever and Reinecken had suggested.

On the other hand, many samples containing from twenty to forty percent iron were heated above 1140°C . in the resistance furnaces, the temperature being kept constant for one to **forty-eight** hours before quenching. In these cases quenched samples always showed a distinct line of separation between two layers. Thus the behavior observed was the very opposite to that which Wever and Reinecken's theory would suggest, and points definitely to the existence of a miscibility gap.

The structure of the quenched samples is very interesting to observe. Figures 8 to 12 are photomicrographs of a sample containing 27.6% iron, quenched from 1166°C . These are all at a magnification of 100 diameters. This sample shows a sharp division into two layers. Figure 8 shows part of the dividing line. Each of the layers has a typical structure. The upper has a light colored continuous component which from Figure 1 is seen to be practically pure tin (.003% iron) with a small amount of the various intermetallic compounds, and a dark



Figure 8

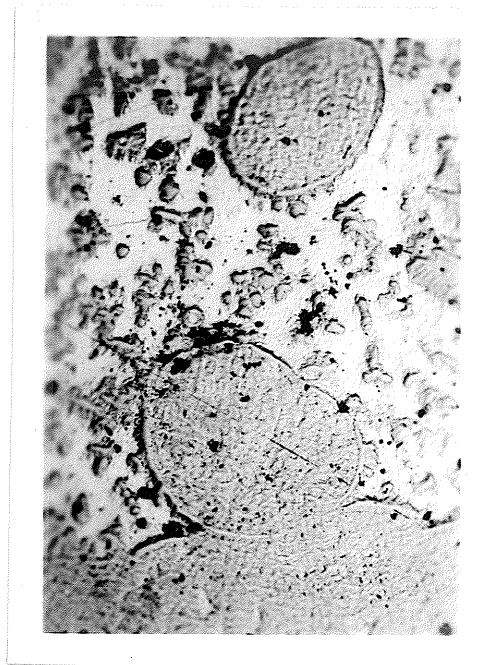


Figure 9

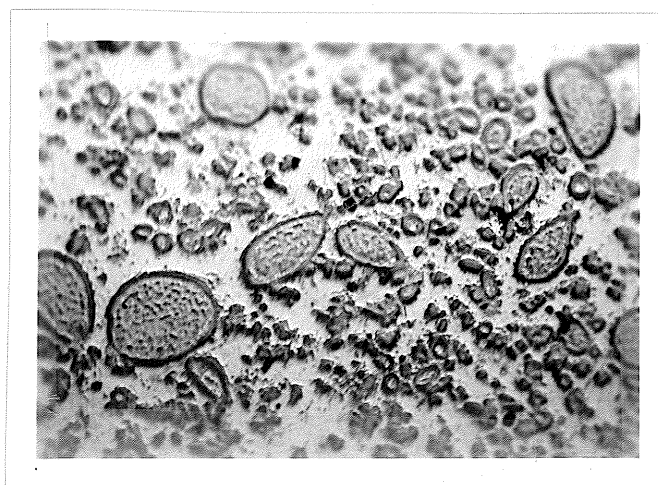


Figure 10

component scattered through it which is a solid solution, shown by Wever and Reinecken to contain about 82% iron. This latter is very hard compared to the tin, as the tin has been removed in polishing, leaving the solid solution in relief. In the bottom phase the solid solution is much more prominent. Actually in both layers the solid solution shows up too much, on account of its hardness. In the lower layer the solid solution appears to be continuous: in hacksawing the sample in half before taking the pictures the lower half was found to be much harder than the top.

In Figure 9 are shown two large (0.2 - 0.3 mm. diameter) drops of lower layer suspended in the top layer. The lower drop is resting on the body of the lower layer. Notice the clear line of separation around each drop. Figure 10 shows a number of smaller drops which are, however, in the center of the upper layer. An analysis of this part of the sample would give a high value for the iron content of the upper layer.

Figures 11 and 12 are both of the bottom layer. The first is near the center of the layer, the second near the edge. The difference in structure must be due to different rates of cooling in the two parts of the layer.

The Rockwell hardness test was carried out on a sample containing 29.8% iron, and quenched from 1176°C. This sample was cut down the center and filed flat, and a series of hardness readings were taken in a line from top to bottom. The readings, on the "B" Rockwell scale, are:

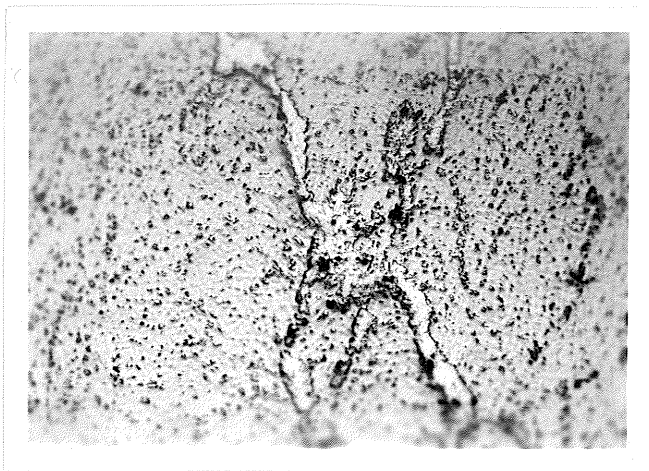


Figure 11

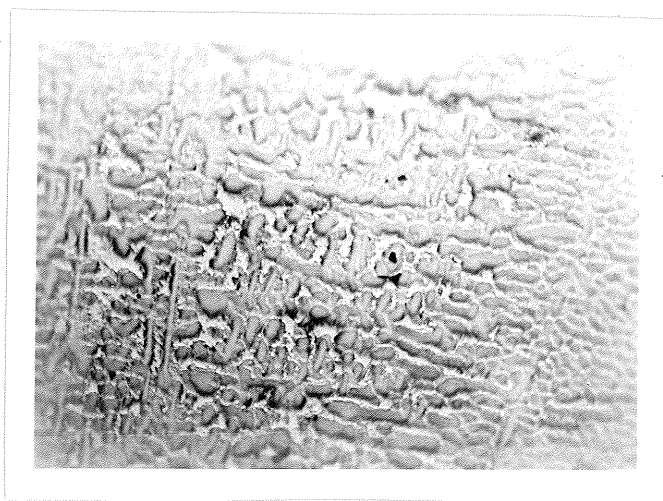


Figure 12

22	the composition of the layers
19	the ball samples were not uniformly
23	between 15.4% and 23.1% values for the upper layer
21	and for the lower layer, from
45	(on line between layers)
99	and then at the top. This is
100	direct experimental evidence of the layer,
100	for which is as possible in this method of
100	sampling.

The figures for the top layer may be high since the 1/16" ball used for the "B" scale sank so deeply into the top layer that its support touched the sample. A separate set of values using a 1/4" ball ("L" scale*) was taken on the top layer. These gave, from top to bottom:

91
98
89

However the bottom layer was too hard to give readings with such a large ball. Figures in Table II were obtained by examination

of 10 samples, using the method of Alexander. The figure can be considered accurate only to $\pm 0.5\%$, since a moderate amount of are present, with a sharp break between them. The very great difference in hardness is not due only to a larger amount of solid solution in the lower layer, but also to a difference in structure which is shown well in Figure 8. In the upper layer the soft tin phase is continuous, while the hard solid solution is not, and hence contributes little to the hardness. In the lower layer the solid solution is fairly continuous, and thus the hardness observed approximates to that of the solid solution.

* "B" scale - 1/16" ball, 100 kg. major load.
 "L" scale - 1/4" ball, 60 kg. major load.

Attempts to determine the compositions of the layers by withdrawing portions from the hot samples were not entirely successful. Between 1140° and 1200°C , values for the upper layer ranged from 19.0% to 31.2% iron, and for the bottom layer, from 30.6% to 48.8% iron. Nevertheless it may be seen that the melts were richer in iron at the bottom than at the top. This is direct experimental evidence for the existence of two layers, for there is no possibility of liquation in this method of sampling.

The reasons for this erratic behavior are not entirely understood. One of them, illustrated in Figures 9 and 10, is that droplets of the bottom layer were suspended in the top layer. The reason that the method worked so well for the curve below the gap is that in that case there was a heavy solid solution in equilibrium with the liquid, and the solid solution kept out of the way at the bottom of the crucible.

The figures in Table II were obtained by examination of 19 samples, using the method of Alexejeff. The values can be considered accurate only to $\pm 0.5\%$, since a moderate amount of each layer had to be present before it could be noticed. Samples containing less than 20% of iron appeared homogeneous to the eye, but the limits could be established by microscopic examination for drops of bottom (i.e. iron-rich) layer. For some reason, whenever there was only a little of the top layer, it all collected at the top of the sample, and could be seen with the naked eye.

It would have been desirable to have traced the gap to the bottom layer, from which the solid solution

higher temperatures, but this was impossible with the equipment available. A sample containing 29.0% iron (i.e. at the center of the gap to give equal amounts of the layers) was heated in the induction furnace to a temperature above the melting point of iron - probably about 1600°C. On examination after quenching, large droplets of one layer in another were observed. By means of an optical pyrometer the temperature was read at about 1400°C, but with a shining liquid surface in the open, temperature readings are low by this method. For steel the correction is about 125°. Here it would be even more because the sample had no oxide coating since it was protected by a pyrex glass tube. All that can really be said from this experiment is that two layers are present at a high temperature, probably about 1600°C.

To complete the liquidus curves, two other points should be settled - the temperature of the base of the gap, and the position of the liquidus curve on the iron rich side of the gap. No experimental work was done on these, but the data obtained have some effect on their probable values.

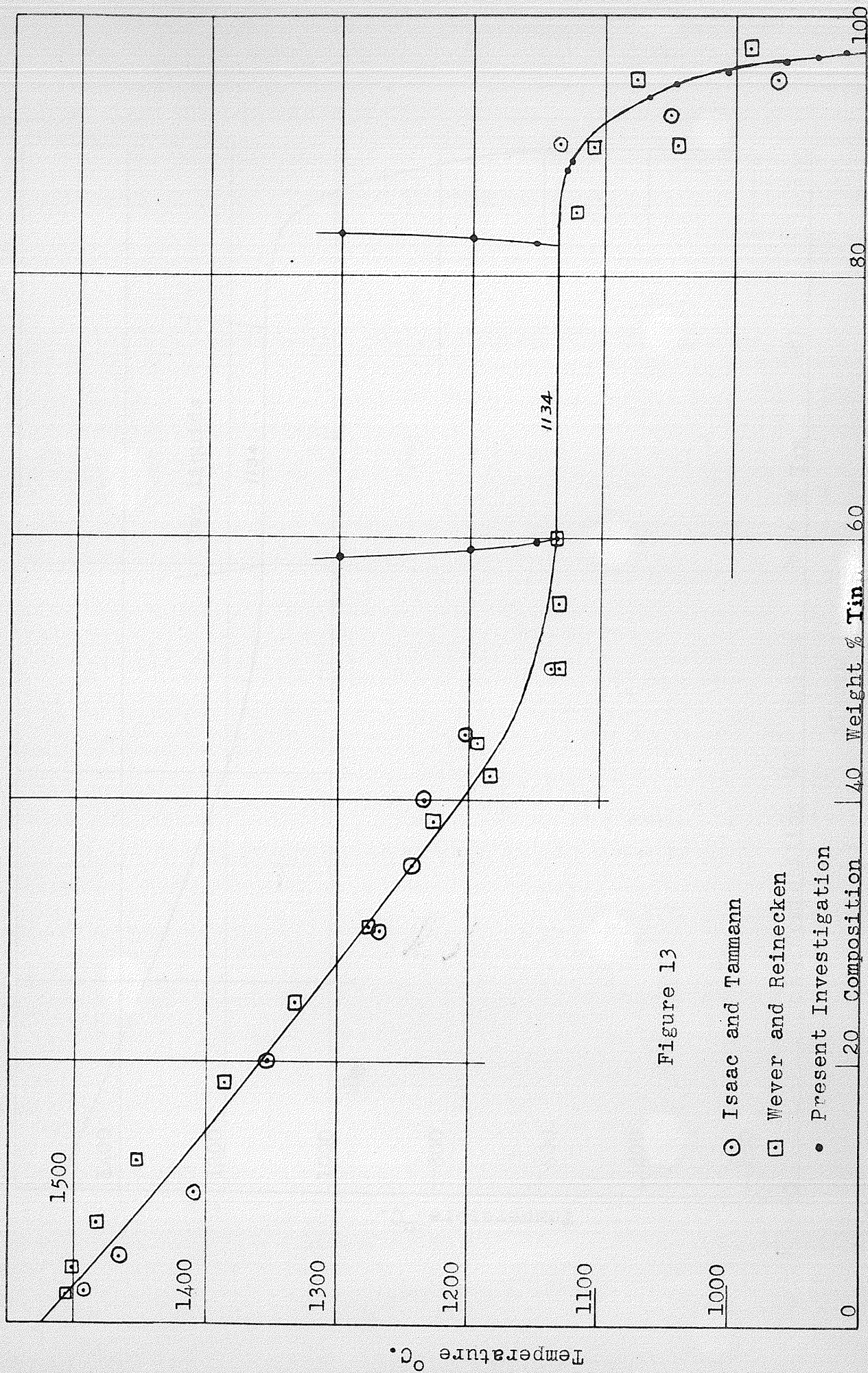
The figures in Table II coupled with the last two points in Table I show that the base of the gap is higher than 1128° and lower than 1150°C. Thus it is seen that Edwards and Preece were in error in placing the horizontal at 1110°C. Of the other two pairs of workers, Wever and Reinecken appear to have had the most refined technique and the purest materials. The average of their second set of thermal analyses - 1134°C - is probably better than any of their first set (which are lower) because of the presence of the two layers. In the first set, with no stirring, the bottom layer, from which the solid solution

actually formed first, was mostly at the bottom of the crucible, while the thermocouple was likely half way up. Thus supercooling was more likely to occur than in the second set, where the solid solution separated throughout the solution.

A considerable amount of personal opinion enters into such a choice. Others might choose the highest temperature in the set - 1136°C . - on the theory that no thermal effect can be observed until some solid has separated, and that therefore the highest temperature will be the most nearly correct, and the lower ones show the effect of varied amounts of supercooling. It is seen that there is the possibility of a few degrees error in any figure assigned.

The previous workers had all assumed that the high-iron liquidus curve came down to about 1140°C . by the time the composition was 50% iron. However, it is shown here that the curve terminates at 1134°C , and 40.0% iron. In Figure 13 a plot of some of the data of Isaac and Tammann, Wever and Reinecken, and myself is given. The extension of the curve does not seem to do too great violence to the experimental points, although it is not clear why the previous investigators did not notice that it was prolonged to 40% iron. The curve must approach the horizontal, so that the thermal effect would be combined with that occurring at 1134°C .

A complete diagram of the liquid curves is given in Figure 14. This is also based on the results obtained in the three investigations mentioned in the preceding paragraph.



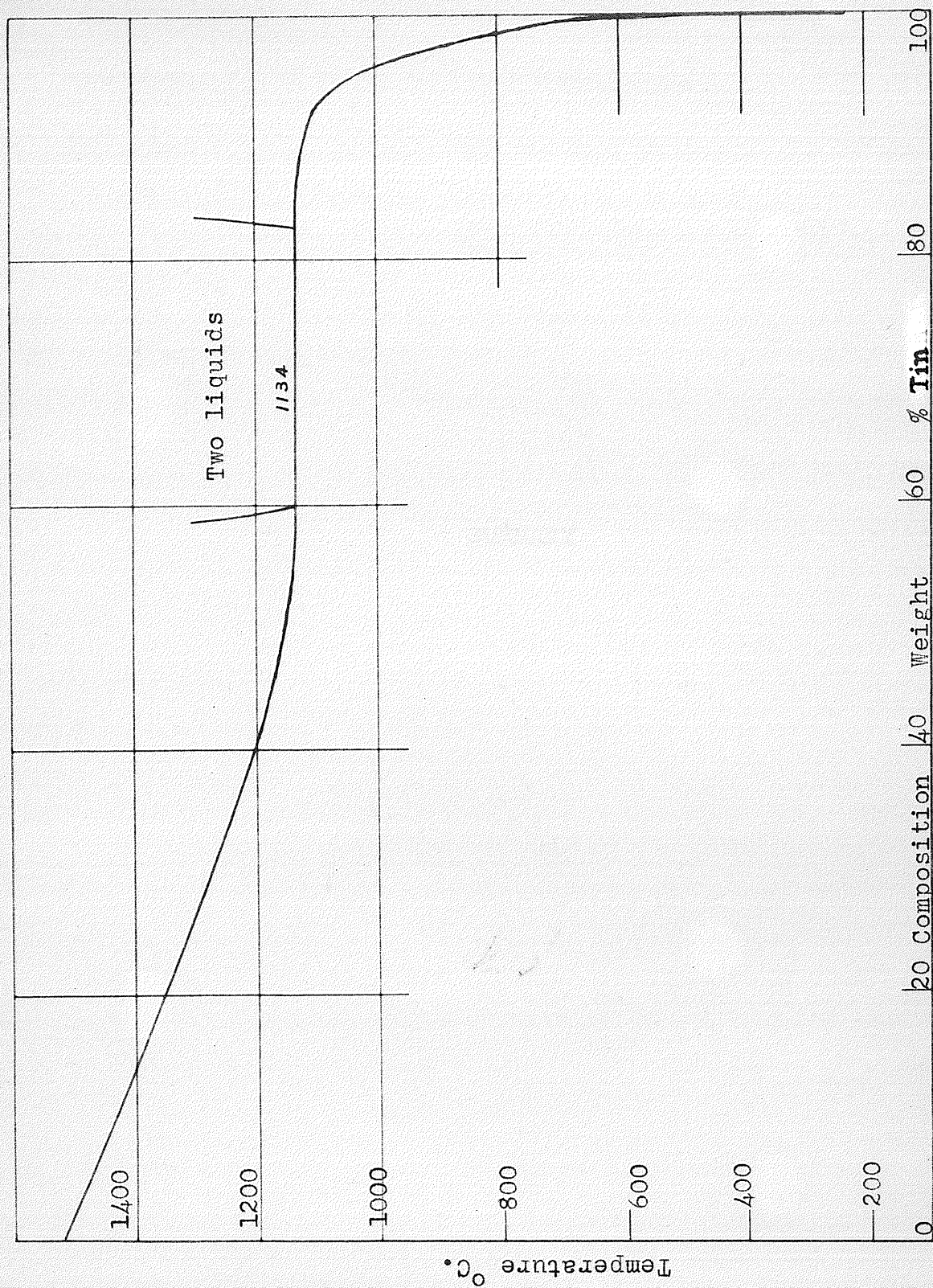


Figure 14

Liquid Curves for the System Iron-Tin

1. The liquidus curve of the Fe-Ni system has now been determined from the melting point of Fe at 2232°C . through to 1134°C . (see Table I).

2. The solubility of a miscibility gap has been proved, and the solubility determined from 1134°C . up to 1700°C . (see Table II).

SUMMARY

SUMMARY

1. The liquidus curve of the iron-tin system has now been determined from the melting point of tin at 232°C . through to 1134°C . (see Table I).
2. The existence of a miscibility gap has been proven, and its limits determined from 1134°C . up to 1300°C . (see Table II).

1. J. H. Wood, The History of the ... of ... (1911)

2. W. L. ... and ... (1912)

3. ... (1913)

4. ... (1914)

5. ... (1915)

6. ... (1916)

7. ... (1917)

8. ... (1918)

9. ... (1919)

10. ... (1920)

11. ... (1921)

12. ... (1922)

13. ... (1923)

14. ... (1924)

15. ... (1925)

16. ... (1926)

17. ... (1927)

18. ... (1928)

19. ... (1929)

20. ... (1930)

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