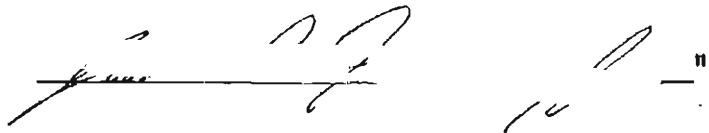


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THE EFFECT OF A TEMPERATURE GRADIENT ON
CONCENTRATION IN SOLID ALLOYS

A THESIS

Presented to
the Faculty of the Graduate Division
Georgia Institute of Technology

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Chemistry

By
James Collier Fanning

June 1956

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THE EFFECT OF A TEMPERATURE GRADIENT ON
CONCENTRATION IN SOLID ALLOYS

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Date Approved by Chairman:

May 3, 1936

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT.	ii
LIST OF TABLES	iv
LIST OF FIGURES.	v
CHAPTER	
I. INTRODUCTION.	1
II. EXPERIMENTAL.	7
Materials	
Apparatus	
Procedure	
Analytical Determinations	
III. DISCUSSION OF RESULTS	20
IV. SAMPLE CALCULATION AND DATA	24
V. SUMMARY	27
BIBLIOGRAPHY	29
APPENDIX I. TABLES.	31
APPENDIX II. FIGURES.	43

LIST OF TABLES

Table	Page
1. Data on Samples Used	32
2. Cu-Ni Data for Film 1238	32
3. Cu-Cr Data for Film 1235	33
4. Cu-Cr Data for Film 1236	33
5. Cu-Cr Data for Film 1237	34
6. Sn-Pb Data	35
7. Zn-Al Data for Rod A	37
8. Zn-Al Data for Rod B	39
9. Zn-Al Data for Rod C	41

LIST OF FIGURES

Figure	Page
1. Zn-Al Phase Diagram	3
2. External view of Apparatus.	4
3. Cu-Cr Alloy	44
4. Sn-Pb Alloy	45
5. Zn-Al Alloy, Rod A.	46
6. Zn-Al Alloy, Rod B.	47
7. Zn-Al Alloy, Rod C.	48

CHAPTER I

INTRODUCTION

THE EFFECT OF A TEMPERATURE GRADIENT ON CONCENTRATION IN SOLID ALLOYS

CHAPTER I

INTRODUCTION

The purpose of this research is to determine the effect of a temperature difference on an alloy's concentration where one portion of the alloy is maintained at a temperature corresponding to an unsaturated solution and the other portion maintained at a temperature which lies below the saturated solution curve. The expected result would be the migration from the region of saturation to that of unsaturation of the solute component, and would occur in alloy systems where the solubility of one of the components increases rapidly with temperature. (See Fig. 1 for example.)

Closely aligned with this problem is the study of thermal diffusion. However, in thermal diffusion there is a non-uniformity of temperature within a mixture and because of this diffusion occurs. Thus, thermal diffusion occurs in a one-phase region whereas in the research presented here diffusion occurs in a two-phase region, with the exception of one alloy. Basically, however, the problems of thermal diffusion, both experimentally and theoretically, are the problems in this research.

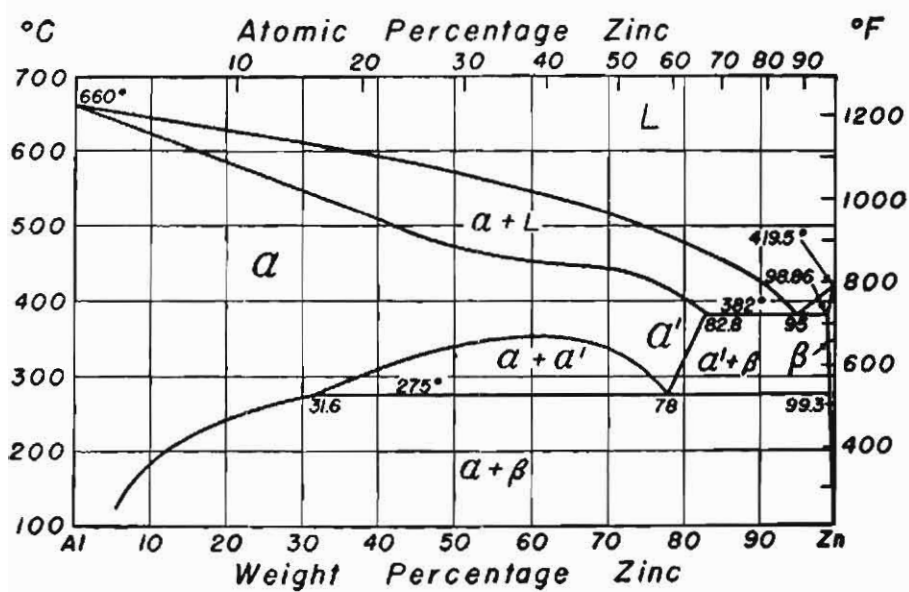


Figure 1. Zinc-Aluminum Phase Diagram

There has been no work done in the past on what might be called "2-phase thermal diffusion." However, in "pure" thermal diffusion much work has been done especially on gases and liquids. Chapman,¹ Jost,² and Grew and Ibbs³ give accounts of the history of thermal diffusion. Briefly though, in 1856 Ludwig found that when he applied a temperature gradient on a vessel containing a sodium sulphate solution, a difference in concentration resulted. Then twenty years later Soret (1879-81) repeated Ludwig's experiment and received better results by using various salt solutions. Thermal diffusion is sometimes given the name Ludwig-Soret effect or Soret effect.

In gases the phenomena of thermal diffusion was predicted theoretically by Enskog (1911, 1912, 1917) and Chapman (1912, 1916, 1917) before being observed experimentally by Chapman and Dootson (1917), and Clusius and Dickel (1938).

In solids, the experimentation has been meager and the theoretical treatment almost non-existent. Reinhold and Schulz (1933) investigated solid ionic crystals. They used mixed crystals of halides and sulfides of copper and silver, but the observed changes in concentration though were not

¹S. Chapman, University of Maryland, The Institute for Fluid Dynamics and Applied Mathematics, Lecture Series, No. 19 (1952).

²W. Jost, Diffusion in Solids, Liquids, Gases, New York: Academic Press Inc., (1952).

³K. E. Grew and T. L. Ibbs, Thermal Diffusion in Gases, New York: Cambridge University Press, (1952).

entirely due to thermal diffusion as deGroot pointed out later. In fact, deGroot⁴ in his monograph on the Soret effect notes that three authors claimed to detect a Soret effect in solids; he himself classes the amorphous solids with the liquids. The results for the crystalline solids he considered unsatisfactory.

Liquid alloy solutions have been investigated to some extent; recently Winter and Drickamer⁵ have published in this field. Only in the past few years has any substantial work been published on thermal diffusion in solid alloys. However, some work was done by Ballay⁶ on the Pb-Tl system. Ballay found that segregation took place when prolonged uneven heating was carried out on a bar. Darken and Oriani⁷ published some results on thermal diffusion in three solid binary alloys, Fe-N, Fe-C, and Au-Cu. They found that the interstitial solutes migrate to the higher temperature region of the specimen as also does copper in the Cu-Au alloy.

The selection of the alloys for this investigation was governed by the nature of the equilibrium diagram. As an example, consider the Zn-Al system shown in Figure 1. The

⁴S. R. deGroot, L'Effect Soret, Thesis, Amsterdam, (1945).

⁵F. R. Winter and H. G. Drickamer, Jour. Phys. Chem., 59, 1229 (1955).

⁶M. Ballay, Compt. rend. 183, 603-4 (1926).

⁷L. S. Darken and R. A. Oriani, Acta Metallurgica, 2, 841-847 (1954).

initial concentration of the alloy was approximately twenty per cent zinc. The lower temperature was ca. 150° C and the upper temperature ca. 300° C. The lower temperature as shown by the diagram for twenty per cent zinc is the alpha plus beta and the upper temperature lies in the alpha region.

The alloy systems which were picked after due consideration with regard to chemical stability, availability, and equilibrium diagram were the Cu-Ni, Zn-Al, Sn-Pb, and Cu-Cr. The ease of analysis was not in all cases a chief factor in the selection of the alloy systems and the analytical methods to be used presented major problems to be overcome.

CHAPTER II

EXPERIMENTAL

CHAPTER II

EXPERIMENTAL

Materials.--The alloys used in this study were, as previously stated, Cu-Ni, Cu-Cr, Sn-Pb, and Zn-Al. The Cu-Ni sample used was Alloy 11 from Driver-Harris Co. and the Cu-Cr was donated by Anaconda Copper Co. The per cent of nickel was 0.4 in the Cu-Ni alloy and since it was used previously as a spectrographic standard it was considered to be free of impurities. The Cu-Cr alloy was 0.5 per cent chromium and the remainder copper. The Zn-Al sample came from the Aluminum Company of America and had approximately twenty per cent zinc. From a semi-quantitative analysis on the spectrograph, the Zn-Al alloy was found to have about 0.1 per cent each of iron, silicon, and magnesium and trace quantities of gallium, vanadium, copper and lead. The Sn-Pb alloy was obtained from the National Lead Co. and contained approximately fifteen per cent tin and the rest lead. It also was checked on the spectrograph and was shown to have only trace quantities of silver, copper, bismuth, and calcium. All of the alloys were obtained in rod form.

Apparatus.--A standard type of apparatus was used to provide the temperature gradient on each sample. Figure 2 pictures the external view of two identical set-ups of the equipment

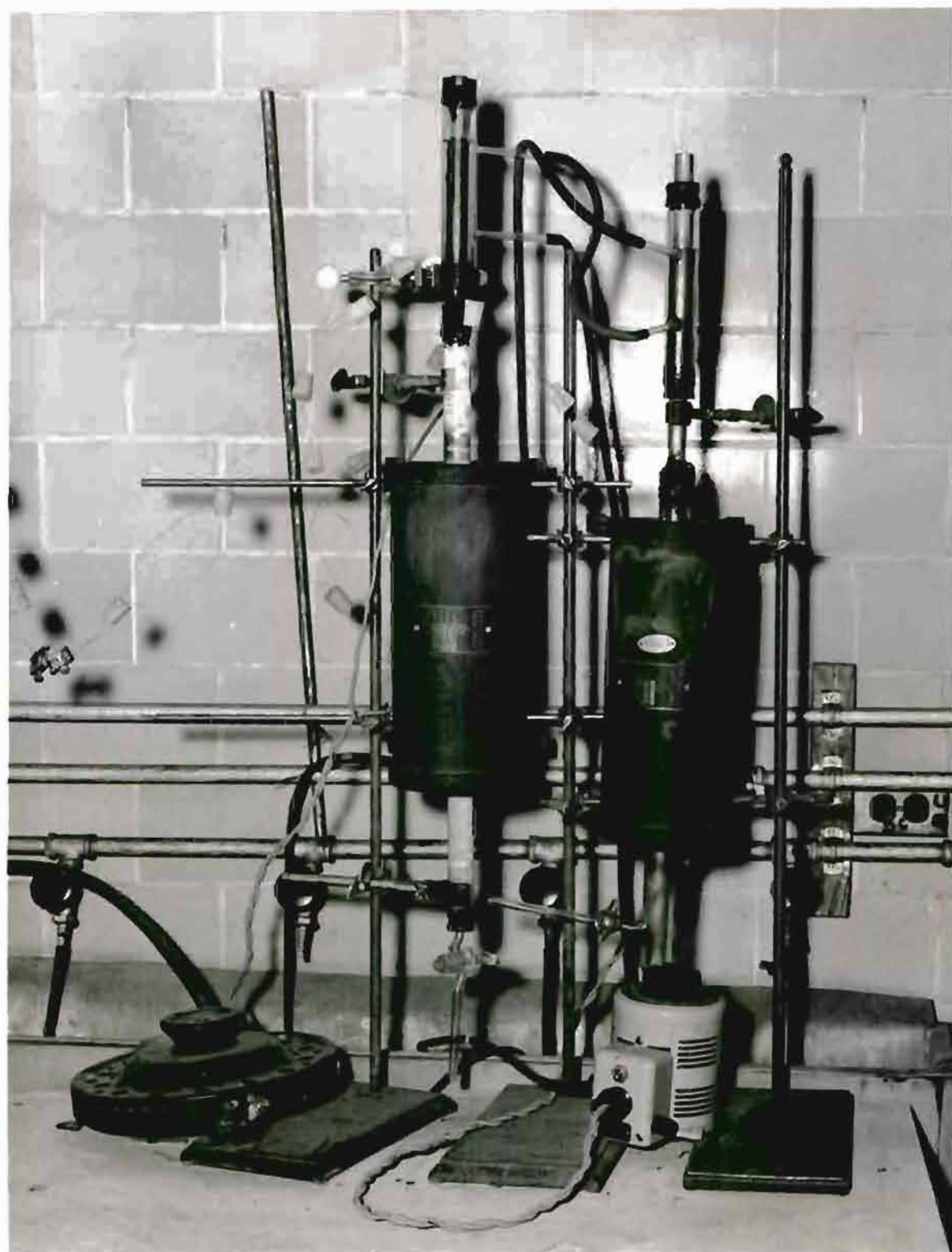


Figure 2. External View of Apparatus

used. The source of heat was a Hoskins electric furnace. Into this furnace was placed a quartz tube of one inch inside diameter and thirty inches in length.

A condenser was made by attaching eight inches of 1/2-inch diameter brass tubing to one end of a one-inch piece of 1/2-inch diameter copper rod by means of silver solder. This copper rod had a 1/4-inch threaded hole 1/4 inch deep drilled on the end away from the brass tube. A rubber stopper was placed on the brass tube and positioned about 3/4 of an inch from the copper rod with the narrow end toward the copper rod. The brass tube then had placed on it another rubber stopper with the narrow end pointing toward the open end of the tube. A glass tube, one inch in diameter and four inches in length, with two smaller 1/4-inch glass tubes attached to its side, was then placed around the brass tube and fitted down on the second rubber stopper. A third stopper was placed on the brass tube and pushed down in order to seal off the glass tube. The small glass tubes provided an inlet and an outlet for water.

For a "heat reservoir" to maintain a constant temperature for the hot end, a 3/4-inch diameter copper rod six inches long was used. The rod had two holes drilled on one end, a 1/4-inch threaded hole of depth 1/4 inch and another of 1/16 inch diameter and 1/2 inch depth.

In order to measure the temperature, thermocouples were required and since the maximum temperatures at which

the samples were to be studied ranged between 200 and 500° C, it was decided that the chromel-alumel thermocouple would be the most satisfactory. A two-foot strand of 28-gauge alumel wire and a two-foot strand of 28-gauge chromel wire were twisted together at one end and welded. For about six inches from the welded end the wires were covered with thin ceramic covering or "spaghetti" which protected the wire from the heat and from touching one another or any other metallic material. The rubber stopper on the brass tube nearest the copper rod was cut down its side to form slits into which the thermocouple wires were placed. The wires from this point led to a normal thermocouple circuit with a cold junction at 0° C.

At this point the sample was shaped to the diameter and length desired (Table 1), then threaded on both ends. The sample was screwed into the "heat reservoir" and then into the condenser. The thermocouple was placed into the 1/16-inch diameter hole on the "heat reservoir" and wires pushed into slits of the rubber stopper.

The Zn-Al sample was prepared in a slightly different manner. The original form of the Zn-Al sample was a 3/4-inch diameter rod 7-1/2 inches in length. On one end of the rod, a 1/4-inch diameter hole was centered, drilled, and threaded. About 1/2 inch from this end a hole of 1/2 an inch in depth and 1/16 inch diameter was drilled into the side of the rod. One-half inch from the 1/16-inch hole, the rod was machined

down to $1/4$ of an inch in diameter. This was done $3-3/4$ inches along the rod away from the threaded hole. About one inch from the other end, a hole of $1/2$ of an inch in depth and $1/16$ inch diameter was drilled on the side of the rod. Instead of a copper rod on the end of the brass tube, the brass tube was closed by means of a stainless steel disc soldered to the brass tube. In the disc was a hole of $1/4$ of an inch in diameter which was threaded and fitted with a double-headed screw. The Zn-Al rod was then screwed to the double-headed screw by means of the threaded hole in one end of the rod. The rubber stopper in this case had four slits cut into it and a thermocouple placed into each of the two $1/16$ -inch holes on the side of the rod and wires were passed through the slits of the stopper.

The sample, together with the condenser, thermocouples, and "heat reservoir" were placed into the quartz tube and pushed down until the "heat reservoir" was centered in the middle of the furnace. The rubber stopper nearest the sample was fitted tightly into the quartz tube. The other end of the quartz tube was fitted with a rubber stopper and a glass stopcock. The connection between all the rubber stoppers, the glass, quartz, and metal were sealed by means of Apiezon wax. With a Welch Duo-Seal High Vacuum Pump, the quartz tube was evacuated and the tube filled with argon then evacuated again. After repeating this "flushing" process several times, the tube was filled with argon and the

stopcock closed. Rubber hose was connected to the small glass tubes on the condenser. Water was allowed to pass through the condenser. About five milliliters of water were poured into the brass tube. The apparatus was then ready for operation.

The equipment used for the measurement of the temperature was a Leeds and Northrup Potentiometer and a standard cell. Weber's⁸ tables were used for the conversion of potentiometer readings to temperature.

Several types of equipment were used for the analytical determinations. An Applied Research Laboratory one and one-half meter grating spectrograph with a dispersion of 7 Å per millimeter was used for the analysis of the Cu-Ni and Cu-Cr samples. A Leeds and Northrup Electrochemograph Model No. 42200-A1 with a Leeds and Northrup Micromax Recorder was used for the analysis of the Zn-Al alloy. The apparatus for the tin determination in the Sn-Pb sample will be described in the analytical section of this chapter.

Procedure.--After the sample had been placed in the tube, argon was passed in; water was turned on to pass through the condenser and water was placed in the brass tube. The sample was ready to be subjected to the thermal gradient. Initially, the Variac was turned on and set at a voltage which

⁸R. L. Weber, Temperature Measurement and Control, Philadelphia: Blakeston Co., P. 388, (1941).

would cause the furnace and the "heat reservoir" to reach the required temperature. After about three hours the temperature was measured and the variac adjusted if need be. The following morning the temperature was recorded and again eight hours later. This procedure was followed for about three or four days after turning on the furnace or until the temperature no longer gave more than a 10° variation. The temperature could not be recorded after the lapse of a week because of the contamination of the thermocouples. The apparatus was then ignored for several months. Occasionally, however, water was placed in the brass tube. For the exact conditions to which each sample was subjected Table 1 may be consulted.

After several months had passed, the furnace was turned off and allowed to cool for about two hours. The sample was then removed from the tube and unscrewed from the "heat reservoir" and its attachment to the brass tube.

In the case of the Cu-Cr and the Cu-Ni samples, the rods were planed down lengthwise in order to give a smooth surface suitable for spectrographic analysis.

The Sn-Pb and Zn-Al were sampled by means of a lathe which cut off samples along the rod at the following intervals: Sn-Pb rod, every 0.06 of an inch; Zn-Al (A and B) rods, every 0.06 inch; and Zn-Al (C) rod, every 0.05 inch. These intervals were chosen in order to get the proper weights for the analytical procedures. Each sample was then

placed into a vial, corked, and weighed as soon as possible. Sample number one for each rod was taken from the hot end and the highest sample number in the group was obtained from the cold end.

Analytical Determinations.--The Cu-Cr and Cu-Ni samples were analyzed by use of the spectrograph. The samples were planed down as previously stated until about one-half of the sample remained thus producing a long, flat surface on the rod. The area immediately beyond the threaded end which had been at a temperature of ca. 100°C was numbered one. Ten such areas were spaced out on the Cu-Cr sample and nine such areas on the Cu-Ni sample. Areas ten and nine were at the hot ends of the Cu-Cr and Cu-Ni samples respectively. Each area was then subjected to a spark from the spectrograph. Thus, by using a spark excitation method the changes in the concentration of the alloy along the rod were detected.

The spectral lines of the sample were recorded on film and with a densitometer the transmission was measured for the following lines: the Cu-Ni sample, Cu-3010.8 \AA and the Ni-3002.49 \AA ; the Cu-Cr sample, Cu-3010.8 \AA and the Cr-2979.7 \AA . From the transmission of these lines the ratio of intensities was calculated. (See Tables 2, 3, 4, and 5 for examples.) It should be pointed out that this was not an absolute method since no standards were available to set a working curve. Only relative changes could be observed by this method.

An iodimetric technique was used for the determination of tin in the Sn-Pb alloy. It was first used by McDow, Furbee, and Clardy⁹ for the analysis of solder bearing material.

The sample was weighed to contain between 0.1 and 0.2 grams of tin into a 300 milliliter Erlenmeyer flask. Ten ml. of concentrated sulfuric acid and about five grams of potassium sulfate were added and then the mixture heated until the lead sulfate turned white. The flask was then cooled and carefully diluted with water to about 100 ml. Ten grams of ten mesh nickel shot were added along with 75 ml. of concentrated hydrochloric acid. The flask was then stoppered with a one-hole rubber stopper fitted with a bent glass tube and rubber tubing that extended to the bottom of a beaker of water. The solution was boiled gently for thirty minutes, transferring the end of the rubber tube to a beaker of ten per cent sodium bicarbonate solution several minutes before the end of the period. Keeping the end of the tube below the surface of the bicarbonate solution, the flask was placed in a suitable container of ice water and allowed to stand until cold. The rubber stopper was then removed and a small piece of dry ice introduced into the flask. Keeping the flask below 10° C by adding more dry ice if necessary, five ml. of

⁹T. B. McDow, K. D. Furbee, and F. B. Clardy, Ind. Eng. Chem. Anal. Ed., 16, 555-6 (1944).

starch solution were added and the solution titrated immediately with standard iodine solution to a permanent blue end-point. The standard iodine solution was prepared by adding 11 grams of iodine to 20 grams of potassium iodide, dissolving both in water, and making solution up to one liter. By subjection of a known volume of a standard tin solution to the method above, the titer of the iodine was calculated in grams of tin per ml. of iodine. The standard tin solution was made by dissolving an accurately weighed amount of pure tin in 100 ml. of concentrated hydrochloric acid and then diluting to one liter in a volumetric flask.

The polarograph was used for the determination of zinc in the Zn-Al alloy. This procedure was devised by Payne,¹⁰ who stated that in his experience the best results for the determination of zinc in the presence of aluminum was by means of a polarographic technique. His procedure was based on the standard addition technique. A theoretical treatment of this technique is given by Meites.¹¹

A 0.1 gram sample of the alloy was weighed and dissolved in five ml. of concentrated hydrochloric acid. When the reaction had ceased, 0.5 ml. of three per cent hydrogen peroxide was added. The solution was evaporated by boiling until solid began to crystallize out, then it was taken up

¹⁰S. T. Payne, Light Metals 15, 152 (1952).

¹¹L. Meites, Polarographic Techniques, New York: InterScience Publishers, Inc. (1955) P. 178ff.

in a little water and evaporated again. Twenty ml. of water and two ml. of ten per cent hydroxylamine hydrochloride were added and the solution allowed to sit on the hot plate for three minutes.

The solution was cooled to room temperature and one ml. of bromocresol green indicator solution added. A quantity of a saturated solution of sodium acetate was then added to the solution until the green end point was reached. This occurs at a pH of about 4.4. Three ml. of a twenty-five per cent potassium thiocyanate solution followed by ten ml. of a freshly prepared suppressing solution (made by dissolving 0.1 gram of sucrose and 30 grams of potassium chloride in 100 ml. of water). Finally the solution was placed into a 100 ml. volumetric flask, made up to volume, and mixed well.

A twenty-five ml. aliquot was removed from the alloy solution. This aliquot was placed into a clean, dry fifty ml. volumetric flask and made up to volume by using a standard zinc solution to be described later.

About ten ml. of the unknown solution was then placed into a polarographic cell and de-aerated with hydrogen for ten minutes. The reference electrode was a mercury pool in the polarographic cell. After the de-aeration, a polarogram was recorded between -0.6V and -1.4V (the half wave potential for zinc is ca. -1.0V). About ten milliliters of the unknown solution with the standard added was placed into the cell and given the same treatment as the first

solution. Thus, two waves were produced, the first being one-half the height of the second, provided the standard zinc solution was made up to contain approximately the same weight of zinc per ml. of solution as did the unknown solution. In making the standard zinc solution, pure zinc sulfate was weighed out and dissolved in one liter of water. The height of the wave of the unknown solution and the height of the wave of the unknown plus the standard solution were measured in centimeters. From the height of the waves, the weight of the sample, and the concentration of the standard solution, the per cent zinc was calculated.

CHAPTER III

DISCUSSION OF RESULTS

CHAPTER III

DISCUSSION OF RESULTS

As was pointed out in Chapter I, one alloy was subjected to conditions which should have given rise to pure thermal diffusion. This alloy was the Cu-Ni rod. The upper and lower temperatures imposed on this rod were bounded in the equilibrium diagram in a solid solution region. From Table 2 it is seen that the ratio of intensities for the rod varies only slightly from the ratio of intensities for the standard. Thus, the nickel does not seem to migrate. This might be expected since the diffusion coefficient of nickel in copper is much lower than that of any other common metal in copper. This last fact was pointed out by Kubachewski and Hopkins,¹² when they stated that the diffusion coefficient of nickel in copper is 0.000089 centimeters per second between 550 and 1050° C.

The Cu-Cr, Zn-Al, and Sn-Pb alloys have their lower temperatures in a region below the saturated solubility curve and their upper temperatures in an unsaturated solution region. From the Figures 3-7, each is seen to have an increase in concentration of the solute component at the hot end.

¹²O. Kubachewski and B. E. Hopkins, Oxidation of Metals and Alloys, New York: Academic Press, Inc., (1953) P. 22.

The chromium content in the Cu-Cr alloy seems to have increased by an appreciable amount as indicated by Tables 3-5 and Figure 3. The standard or untreated sample is seen to have a much lower ratio of intensity than do the positions along the rod. This could be due to oxidation and/or volatilization of the chromium, but there is no proof of this. Again it should be pointed out that the increase in chromium is a relative increase and not an absolute one since no standards were used to set up a working curve.

Table 6 shows the data from which Figure 4 is drawn and from these it is noted that the concentration of the tin increases at the hot end. In this case there is a one per cent increase in tin from the original concentration to the concentration of the heated rod. This change would appear quite significant. Samples 1-9 of this rod came from the threaded end of the rod and probably would be expected to lose some tin due to the "heat reservoir" and the sample.

The three Figures 5, 6, and 7 give the changes in the Zn-Al rods A, B, and C. They are drawn from the data given in Tables 7-9. The great variation of results is due largely to the analytical method. Little credance is held with the results on rod A, since the experimenter had great difficulty getting the polarograph to operate effectively. However, even in that case, as with the other rods, there is evidence of a definite increase in zinc, the solute, at the hot end of the alloy.

No theoretical interpretation of these results shall be attempted here, though this would lead to a fascinating aspect of the problem. Certainly, as was pointed out in the introduction, the results obtained here were to be expected since there is present in the treated alloy a part which is in an unsaturated state and a part which is in a saturated state. The solute would be expected to migrate from the region of saturation to that of unsaturation.

A project which might be undertaken as a further development of this study would be to take an alloy and allow it to be treated for several different periods of time. From this some information as to the kinetics of this process might be gained. A good alloy for this might be the Sn-Pb system. It is easily obtainable, the analysis is very accurate, and the operating temperatures are very low as compared with the other systems.

CHAPTER IV

SAMPLE CALCULATIONS AND DATA

In order to give an example as to how the calculations were made in the determination of the tin in the Sn-Pb sample and the zinc in the Zn-Al samples, a run from each group was picked as being typical of the entire group.

The run for the tin determination is number 20. (See Table 6.) The sample which was taken 1.20 inches from the hot end weighed 0.8917 grams. One ml. of the standard iodine solution was equivalent to $5.6557 \pm 0.0165 \times 10^{-3}$ grams of tin. After being treated according to the procedure, the sample required 23.0 ml. of iodine for titration, therefore 0.1301 grams of tin were present. This gave a per cent of tin in sample 20 of 14.59.

For the Zn-Al alloy run, number 30 of rod C was chosen, the weight being 0.1071 grams (Table 9). The sample was removed 1.50 inches from the hot end. The sample was dissolved and treated according to procedure. Curves were plotted by the automatic recorder, and wave heights measured. The wave height of the sample solution alone was 8.40 centimeters and the wave height of the sample solution plus the standard was 17.70 centimeters. The standard zinc solution was made up to contain 7.220×10^{-4} grams of zinc per ml.

From the following equation the zinc concentration of the sample liquid solution in terms of grams of zinc per ml. was found:

$$X = \frac{hC}{2H-h}$$

where h is the height of the sample solution's wave; H , the height of the sample solution plus standard solution's wave; and C , the concentration of the standard solution. This equation may be verified by referring to any theoretical treatment of the standard addition method of polarographic analysis.¹³

From the above equation the concentration of the sample solution for run number 30 was found to be 2.246×10^{-4} grams of zinc per ml., thus the original solution of 100 ml. contained 0.02246 grams of zinc which gives a per cent in the alloy of 20.97.

¹³L. Meites, loc. cit., P. 178.

CHAPTER V

SUMMARY

CHAPTER V

SUMMARY

Four alloys, Cu-Cr, Cu-Ni, Sn-Pb, and Zn-Al, were subjected to a treatment wherein one end of a rod of each alloy was maintained at a high temperature and the other end maintained at a low temperature. The hot end corresponded to a region of unsaturation and the cold end to a region below the saturated solubility curve in the Cu-Cr, Sn-Pb, and Zn-Al systems. In the Cu-Ni system both ends corresponded to a solid solution region. No migration after many days was found in the case of the Cu-Ni alloy. There is evidence, however, in the case of the other three alloys that migration occurred, for after a long period of time the concentration of the solute component seemed to have been increased in the hot end.

BIBLIOGRAPHY

1. Ballay, M., "The Ludwig-Soret Phenomenon in Alloys." Comptes Rendus 183 (1926), 603-604.
2. Ballay, M., "A Theory of the Ludwig-Soret Phenomenon." Comptes Rendus 186 (1928), 232-234.
3. Ballay, M., "The Ludwig-Soret Effect in Metallic Alloys." Comptes Rendus 25 (1928), 427-454, 509-520.
4. Chapman, S., "Thermal Diffusion." University of Maryland, The Institute for Fluid Dynamics and Applied Mathematics, Lecture Series No. 19 (1952).
5. Darken, L. S., and Oriani, R. A., "Thermal Diffusion in Solid Alloys." Acta Metallurgica 2 (1954), 841-847.
6. Grew, K. Z., and Ibbes, T. L., Thermal Diffusion in Gases. New York: Cambridge University Press (1952).
7. deGroot, S. R., L'Effect Soret. Thesis, Amsterdam: (1945).
8. Jost, W., Diffusion in Solids, Liquids, Gases. New York: Academic Press, Inc. (1952).
9. Kubachewski, O., and Hopkins, H. E., Oxidation of Metals and Alloys, New York: Academic Press, Inc. (1953) P. 22.
10. McDow, T. B., Furbee, K. D., and Giardy, F. B., "Determination of Tin by a Modified Iodometric Method." Industrial and Engineering Chemistry (Analytical Edition) 16 (1944), 555-556.
11. Maties, L., Polarographic Techniques. New York: Interscience Publishers, Inc. (1955).
12. Payne, S. T., "Chemical Analysis of Light Metals and Alloys." Light Metals 15 (1952), 152.
13. Reinhold, H., "Thermal Force and Ludwig-Soret Effect in Solid Salts and Solid Solutions and Their Relation to Electric Conductivity." Zeitschrift Elektrochemie 39 (1933), 555-556.

14. Smithells, C. J., Metals Reference Book. New York: InterScience Publishers, Inc. (1949).
15. Wessels, H., "Thermolysis, The Ludwig-Soret Phenomenon in Solid Substances." Zeitschrift Physikalische Chemie 87 (1914), 215-222.

APPENDIX I

Table 1. Data on Samples Used

Sample	Diameter of rod (in.)	Length of rod (in.)	Temp.		Days in operation	Comp. of untreated alloy
			hot	cold		
Cu-Cr	0.190	2.5	580°C	100°C	289	ca 0.1 %Cr
Cu-Ni	0.250	3.0	540	100	239	ca 0.4 %Ni
Sn-Pb	0.313	3.15	220	100	90	14.79 %Sn
Zn-Al(A)	0.250	3.75	370	210	122	20.90 %Zn
Zn-Al(B)	0.250	3.25	350	180	129	20.90 %Zn
Zn-Al(C)	0.250	3.25	340	150	166	20.90 %Zn

Table 2. Cu-Ni Data for Film 1238

Rod Position	Transmission		Ratio $\frac{Ni}{Cu}$
	Ni-3002.49	Cu-3010.8	
1	27.3	15.1	.72
2	26.7	13.6	.69
3	19.0	10.2	.79
4	21.4	10.7	.70
5	29.4	15.5	.69
6	31.6	16.3	.68
7	28.9	14	.67
8	29	13.9	.66
9	29.8	14.6	.66
Standard	32.5	17.7	.70
Standard	29.1	16.3	.76

Table 3. Cu-Cr Data for Film 1235

Rod Position	Transmission		Ratio $\frac{Cr}{Cu}$
	Cr-2979.7	Cu-3010.8	
1	31.5	28.9	0.945
2	---	---	---
3	28.7	31.8	1.07
4	---	---	---
5	20.7	28.7	1.20
6	---	---	---
7	22.5	25.0	1.10
8	22.6	26.7	1.10
9	---	---	---
10	---	---	---
Standard	34.5	25.0	0.81
Standard	36.0	27.5	0.84
Standard	33.9	27.0	0.86
Standard	30.7	20.5	0.79
Standard	31.7	23.4	0.83
Standard	33.5	24.0	0.81

Table 4. Cu-Cr Data for Film 1236

Rod Position	Transmission		Ratio $\frac{Cr}{Cu}$
	Cr-2979.7	Cu-3010.8	
1	39.5	38.0	0.97
2	45.7	47.5	1.03
3	45.7	55.0	1.18
4	27.5	46.2	1.18
5	23.5	50.0	1.70
6	23.0	46.0	1.60
7	36.5	56.1	1.43
8	25.9	48.5	1.55
9	15.4	38.2	1.70
10	---	---	---
Standard	36.0	31.9	0.91
Standard	39.0	34.0	0.91
Standard	25.7	26.2	1.01
Standard	34.0	28.9	0.90

Table 5. Cu-Cr Data for Film 1237

Rod Position	Transmission		Ratio $\frac{Cr}{Cu}$
	Cr-2979.7	Cu-3010.8	
1	23.7	27.3	1.08
2	31.2	30.2	0.98
3	30.2	40.0	1.22
4	19.6	33.5	1.39
5	15.7	32.0	1.51
6	13.0	29.5	1.57
7	25.3	34.7	1.23
8	23.1	27.3	1.10
9	22.4	25.2	1.07
10	12.0	19.0	1.26

Table 6. Tin-Lead Alloy Change

Sample No.	Weight in grams	Ml. of iodine solution	Percentage of Sn
1(Hot end)	0.3822	7.6	10.23
2	0.3646	7.1	11.00
3	0.4044	9.1	11.52
4	0.4034	8.6	10.97
5	0.4054	9.3	11.81
6	0.1904	4.6	12.43
7	0.4464	12.2	14.06
8	0.5233	14.3	14.09
9	0.7673	21.7	14.52
10	0.8582	25.2	15.11
11	0.9000	26.9	15.36
12	0.8875	26.7	15.48
13	0.9108	27.8	15.71
14	0.9482	28.6	15.52
15	0.9112	27.1	15.30
16	0.8273	24.3	15.12
17	0.9207	24.3	14.93
18	0.8511	22.5	14.95
19	0.8727	23.0	14.91
20	0.8917	23.0	14.59
21	0.9505	24.8	14.76
22	0.8445	21.7	14.53
23	0.8552	21.9	14.48
24	0.9106	23.3	14.47
25	0.7525	19.5	14.51
26	0.8544	21.7	14.37
27	0.9385	23.9	14.40
28	0.7253	18.8	14.66
29	0.8800	23.3	-----
30	0.8787	23.0	14.80
31	0.9118	23.8	14.76
32	0.8353	21.6	14.62
33	0.8766	22.5	14.52
34	0.8990	23.0	14.47
35	0.9163	23.6	14.57
36	0.8477	22.9	15.26
37	0.8812	22.7	14.42
38	0.8457	21.8	14.43
39	0.8730	22.4	14.36
40	0.9367	23.9	14.28

Table 6. (Continued)

Sample No.	Weight in grams	Ml. of iodine solution	Percentage of Sn
41	0.8832	22.2	14.07
42	0.8545	22.2	13.84
43	0.8976	22.9	14.28
44	0.8899	22.8	14.52
45 (Cold end)	0.8324	21.6	14.52

Notes.--Samples No. 1 through 8, 41, and 42 boiled over during analysis.

Sample No. 29, end-point was overrun.

Samples No. 1 through 8 came from the threaded end of rod.

Between samples 1 through 16 standard iodine solution was equivalent to 5.146×10^{-3} g. of Sn/ml.

Between samples 17 through 36 standard iodine solution was equivalent to 5.6557×10^{-3} g. of Sn/ml.

Between samples 37 through 45 standard iodine solution was equivalent to 5.5960×10^{-3} g. of Sn/ml.

Table 7. Zinc-Aluminum Alloy Chanse Rod A

Sample No.	Weight in grams	\bar{h} in cm.	\bar{h} in cm.	Percentage of Zn
1(Hot end)	0.1028	7.95	17.25	21.16
2	0.1026	7.05	15.10	23.00
3	0.1015	7.60	17.05	20.62
4	0.0877	5.55	13.40	21.70
5	0.1006	5.20	11.05	22.00
6	0.1044	7.75	16.70	21.30
7	0.1080	7.05	14.30	21.10
8	0.1080	7.35	14.90	21.32
9	0.1046	7.10	14.70	21.91
10	0.1020	7.45	16.10	21.68
11	0.1037	7.60	16.00	21.23
12	0.1019	6.65	14.35	20.97
13	0.1028	7.20	15.70	20.55
14	0.1051	7.50	15.85	21.15
15	0.1011	6.85	15.30	20.13
16	0.1020	7.05	15.80	20.69
17	0.0792	5.80	15.60	20.27
18	0.1021	7.40	16.95	21.44
19	0.1048	8.10	16.25	22.88
20	0.1052	6.50	14.00	21.62
21	0.1036	6.80	13.60	23.23
22	0.1059	6.95	14.35	21.79
23	0.1057	5.80	10.65	25.57
24	0.1057	5.95	12.80	21.09
25	0.1073	6.30	14.85	18.12
26	0.1049	6.25	13.50	20.74
27	0.1052	6.10	13.95	19.23
28	0.1018	6.40	12.50	21.90
29	0.1055	8.00	17.25	20.69
30	0.1080	8.45	18.15	21.72
31	0.1037	7.70	16.60	21.06
32	0.1037	7.60	17.10	19.92
33	0.1048	7.85	16.90	20.87
34	0.0851	6.35	15.90	21.20
35	0.1013	7.45	16.70	20.49
36	0.1064	7.70	16.70	20.37
37	0.1049	7.60	16.60	20.46
38	0.1050	6.90	15.00	20.57
39	0.1009	7.50	16.60	20.96
40	0.1027	7.00	15.65	20.28

Table 7. (Continued)

Sample No.	Weight in grams	\bar{h} in cm.	\bar{H} in cm.	Percentage of Zn
41	0.1018	6.85	15.55	20.07
42	0.1023	7.10	15.25	21.45
43	0.1068	7.00	15.25	20.18
44	0.0886	5.90	15.05	19.90
45	0.1054	7.10	15.50	20.38
46	0.1019	6.95	15.30	20.05
47	0.1045	6.90	15.60	19.65
48	0.1024	6.85	14.90	21.08
49	0.1004	6.70	15.05	20.62
50 (Cold end)	0.1065	7.20	15.30	20.85

Notes.--Standard zinc solution used for samples 1 through 26 had a zinc concentration of 7.222×10^{-4} g/ml.

Standard zinc solution used for samples 27 through 50 had a zinc concentration of 7.231×10^{-4} g/ml.

Table 8. Zinc-Aluminum Alloy Change Rod B

Sample No.	Weight in grams	<u>h</u> in cm.	<u>H</u> in cm.	Percentage of Zn
1(Hot end)	0.1038	6.90	15.40	20.20
2	0.1088	7.00	14.60	21.05
3	0.1088	7.05	14.80	20.87
4	0.1046	6.95	14.25	22.39
5	0.1056	6.00	13.00	20.63
6	0.1063	6.35	13.80	20.41
7	0.1061	6.20	14.15	19.20
8	0.1060	6.75	14.50	20.78
9	0.1084	6.95	14.95	20.29
10	0.1058	6.75	13.10	23.82
11	0.1058	6.85	14.15	21.92
12	0.1067	6.80	14.75	20.39
13	0.1036	6.60	14.70	20.29
14	0.1070	7.70	16.70	20.33
15	0.1081	7.95	16.95	20.58
16	0.1036	7.50	16.65	20.38
17	0.1062	7.95	16.65	21.44
18	0.1048	7.75	17.00	20.46
19	0.1045	7.60	16.85	20.24
20	0.1046	7.80	17.00	20.67
21	0.1087	7.40	16.40	19.46
22	0.1060	7.65	16.95	19.96
23	0.1058	7.85	16.80	20.92
24	0.1077	7.90	16.95	20.49
25	0.1045	7.95	17.05	21.13
26	0.1082	7.95	17.75	19.32
27	0.1073	8.20	17.50	20.70
28	0.1061	7.90	17.05	20.64
29	0.1070	8.00	17.35	20.34
30	0.1079	8.00	17.00	20.58
31	0.1037	7.60	17.20	19.73
32	0.1058	7.55	16.55	20.15
33	0.1048	7.50	16.65	20.01
34	0.1090	7.75	16.60	20.16
35	0.1071	7.65	16.60	20.17
36	0.1064	7.70	16.75	20.23
37	0.1035	7.65	16.65	20.79
38	0.1035	7.90	16.85	21.34
39	0.1042	8.25	17.85	20.81
40	0.1054	8.10	17.90	20.02

Table 8. (Continued)

Sample No.	Weight in grams	\bar{h} in cm.	\bar{H} in cm.	Percentage of Zn
41	0.1065	8.15	18.25	19.47
42	0.0968	7.70	17.25	21.35
43	0.1037	8.25	18.00	20.68
44	0.1064	7.95	17.25	20.30
45	0.1052	8.30	17.95	20.62
46 (Cold end)	0.1042	7.60	16.75	20.31

Notes.--Standard zinc solution used for samples No. 1 through 46 had a zinc concentration of 7.262×10^{-4} g/ml.

Table 9. Zinc-Aluminum Alloy Change Rod C

Sample No.	Weight in grams	\bar{h} in cm.	\bar{H} in cm.	Percentage of Zn
1(Hot end)	0.1119	8.80	18.30	20.41
2	0.1119	8.95	18.15	21.10
3	0.1101	8.85	18.40	20.75
4	0.1025	8.65	18.70	21.33
5	0.1079	9.05	18.80	21.20
6	0.1011	8.50	18.50	21.28
7	0.1084	8.45	17.75	20.79
8	0.1049	8.35	17.70	21.23
9	0.1083	8.25	17.60	20.39
10	0.1108	9.20	17.15	25.87
11	0.1046	7.95	16.65	21.63
12	0.1036	7.30	16.20	20.25
13	0.1097	7.40	16.10	19.62
14	0.1074	7.40	15.90	20.37
15	0.1039	7.05	15.70	20.10
16	0.0806	5.65	14.90	20.96
17	0.1084	7.50	16.40	19.74
18	0.1032	7.55	16.60	20.59
19	0.1092	7.90	16.65	20.57
20	0.1045	7.30	15.85	20.67
21	0.1076	7.60	16.10	20.73
22	0.1089	7.85	16.80	20.21
23	0.1128	8.50	16.65	21.94
24	0.1103	7.90	16.90	19.97
25	0.1118	8.20	16.40	21.53
26	0.1087	7.90	16.70	20.58
27	0.1115	8.45	17.45	20.69
28	0.1059	8.00	17.60	20.05
29	0.1048	8.25	17.80	20.78
30	0.1070	8.40	17.70	20.97
31	0.1046	8.00	17.50	20.55
32	0.1072	7.90	17.30	19.93
33	0.1085	7.60	17.90	17.93
34	0.1092	8.45	17.75	20.66
35	0.1124	8.35	17.00	20.91
36	0.1075	8.00	18.35	18.72
37	0.1122	8.55	17.75	20.41
38	0.1063	8.15	17.80	20.47
39	0.1125	8.35	17.95	19.45
40	0.1061	8.40	17.75	21.09

Table 9. (Continued)

Sample No.	Weight in grams	\bar{h} in cm.	\bar{H} in cm.	Percentage of Zn
41	0.1052	8.40	18.00	20.89
42	0.1072	8.50	17.95	21.05
43	0.1070	8.40	17.40	21.47
44	0.1095	8.10	17.30	20.16
45	0.1096	8.25	17.65	20.09
46	0.1048	8.05	17.50	20.58
47	0.0927	7.40	17.10	21.51
48	0.1097	8.35	17.70	20.32
49	0.1064	7.90	16.95	20.62
50	0.1087	8.20	17.40	20.40
51 (Cold end)	0.1047	8.05	17.65	20.37

Notes.--Standard zinc solution used for samples No. 1 through 15 had a zinc concentration of 7.262×10^{-4} g/ml.

Standard zinc solution used for samples No. 16 through 51 had a zinc concentration of 7.220×10^{-4} g/ml.

APPENDIX II

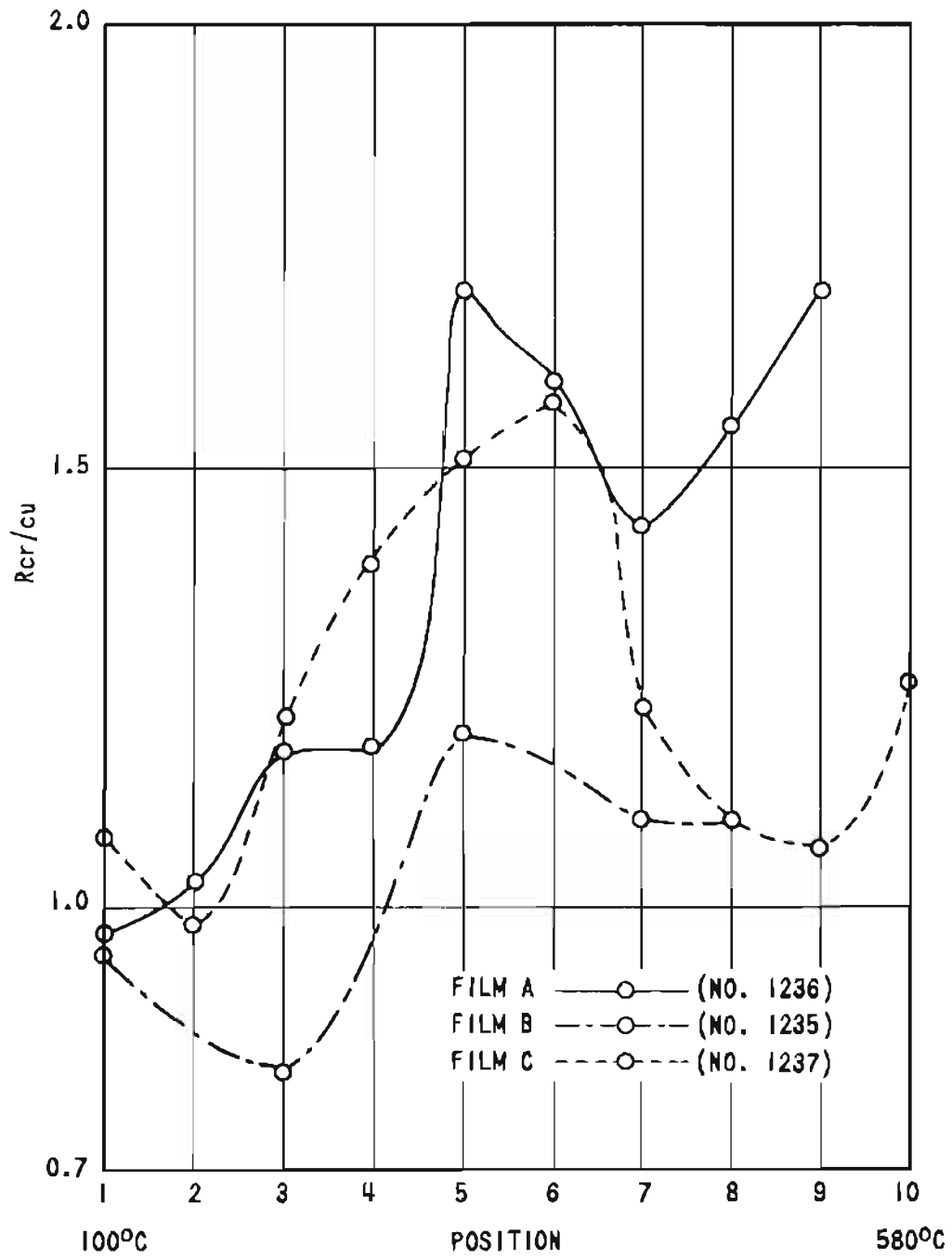


Figure 3. Copper-Aluminum Alloy

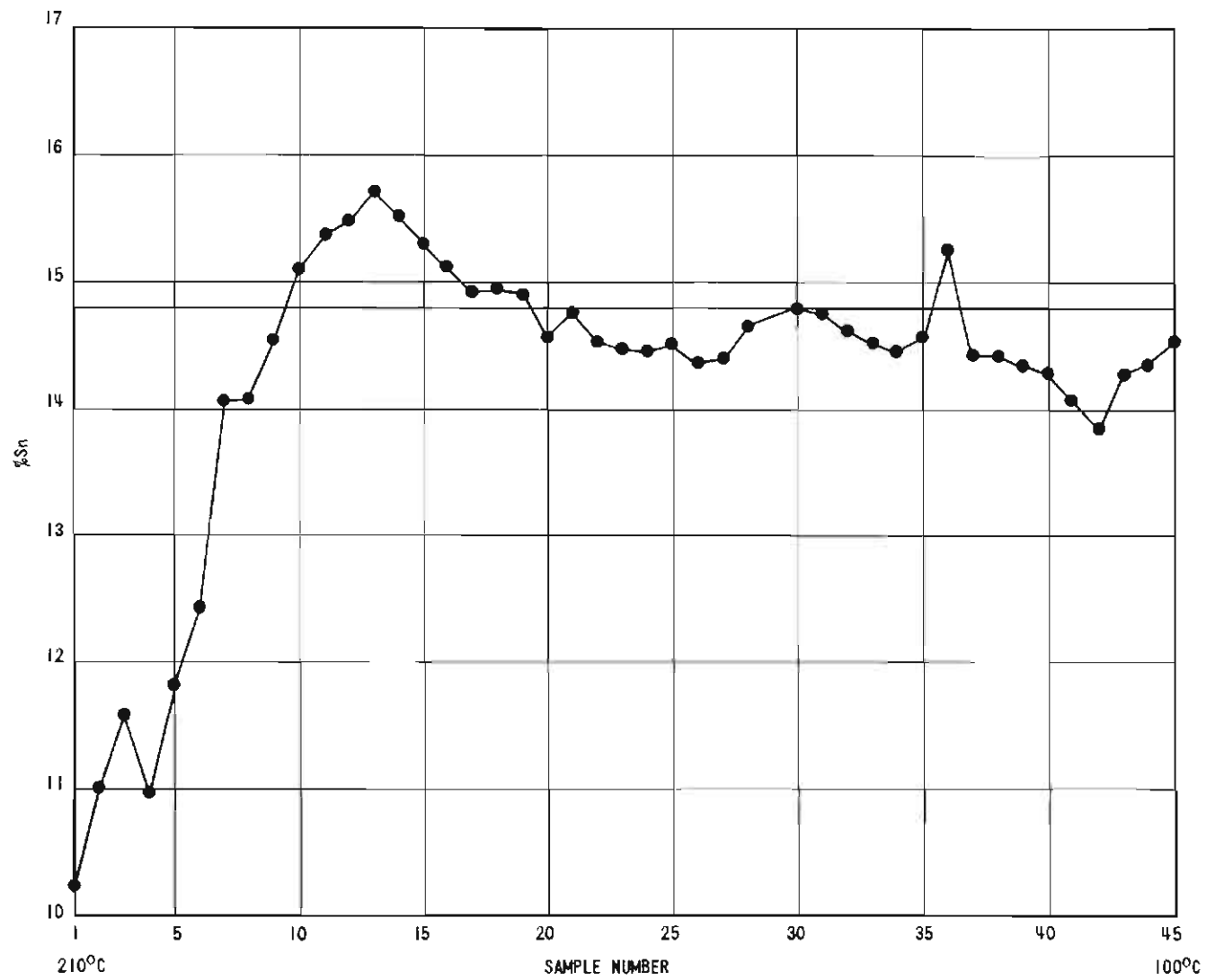


Figure 4. Tin-Lead Alloy

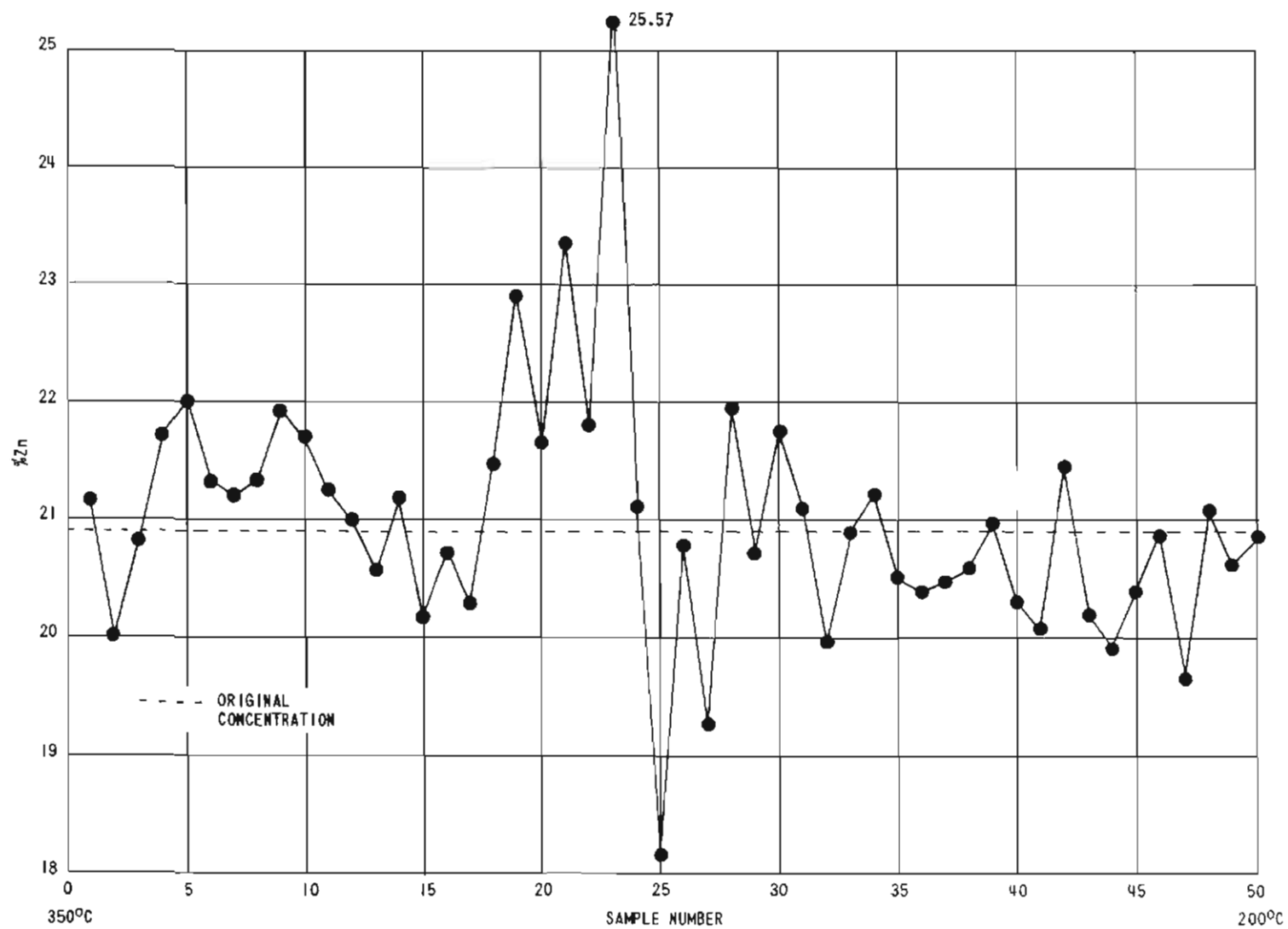


Figure 5. Zinc-Aluminum Alloy, Rod A

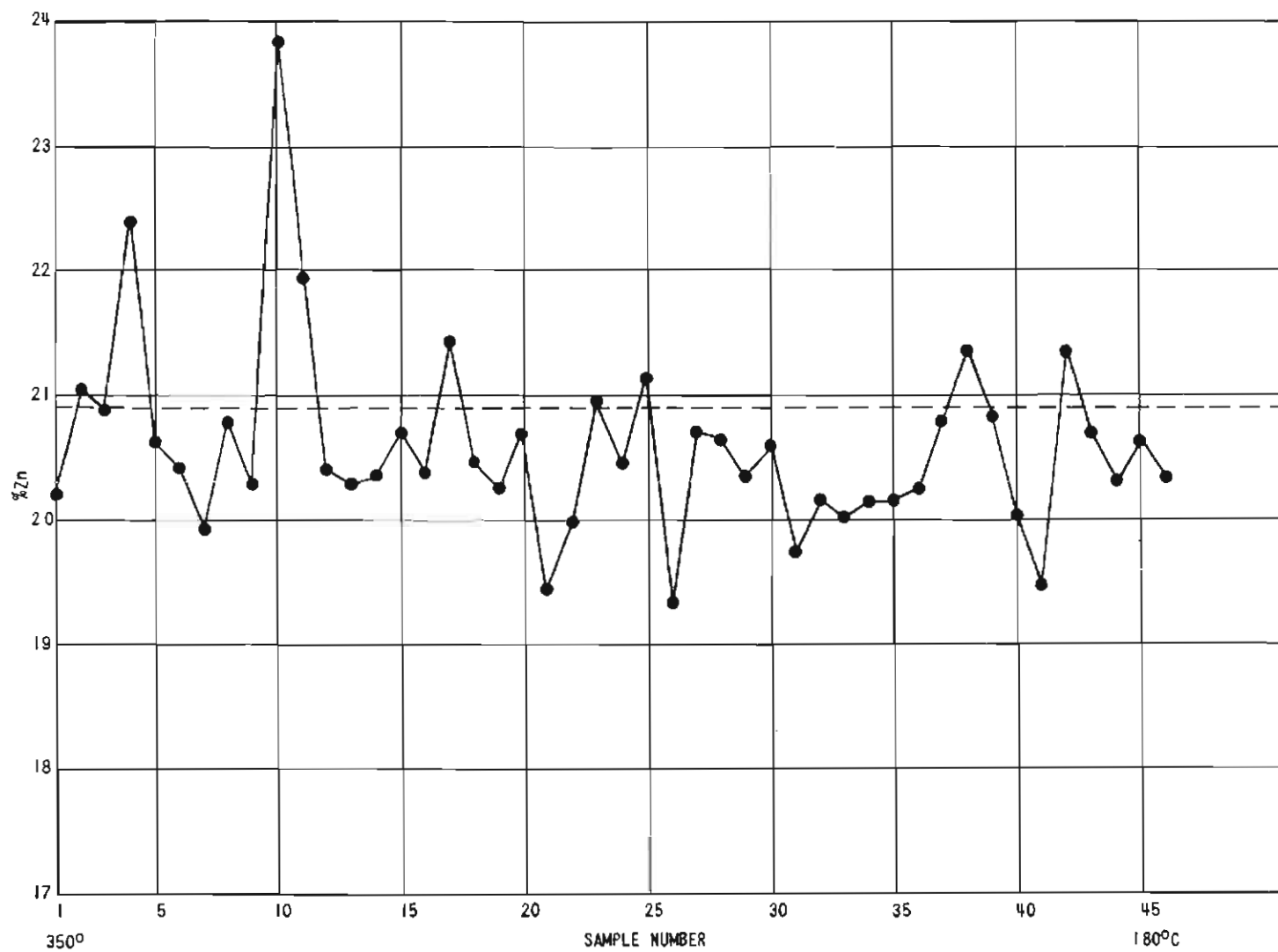


Figure 6. Zinc-Aluminum Alloy, Rod B

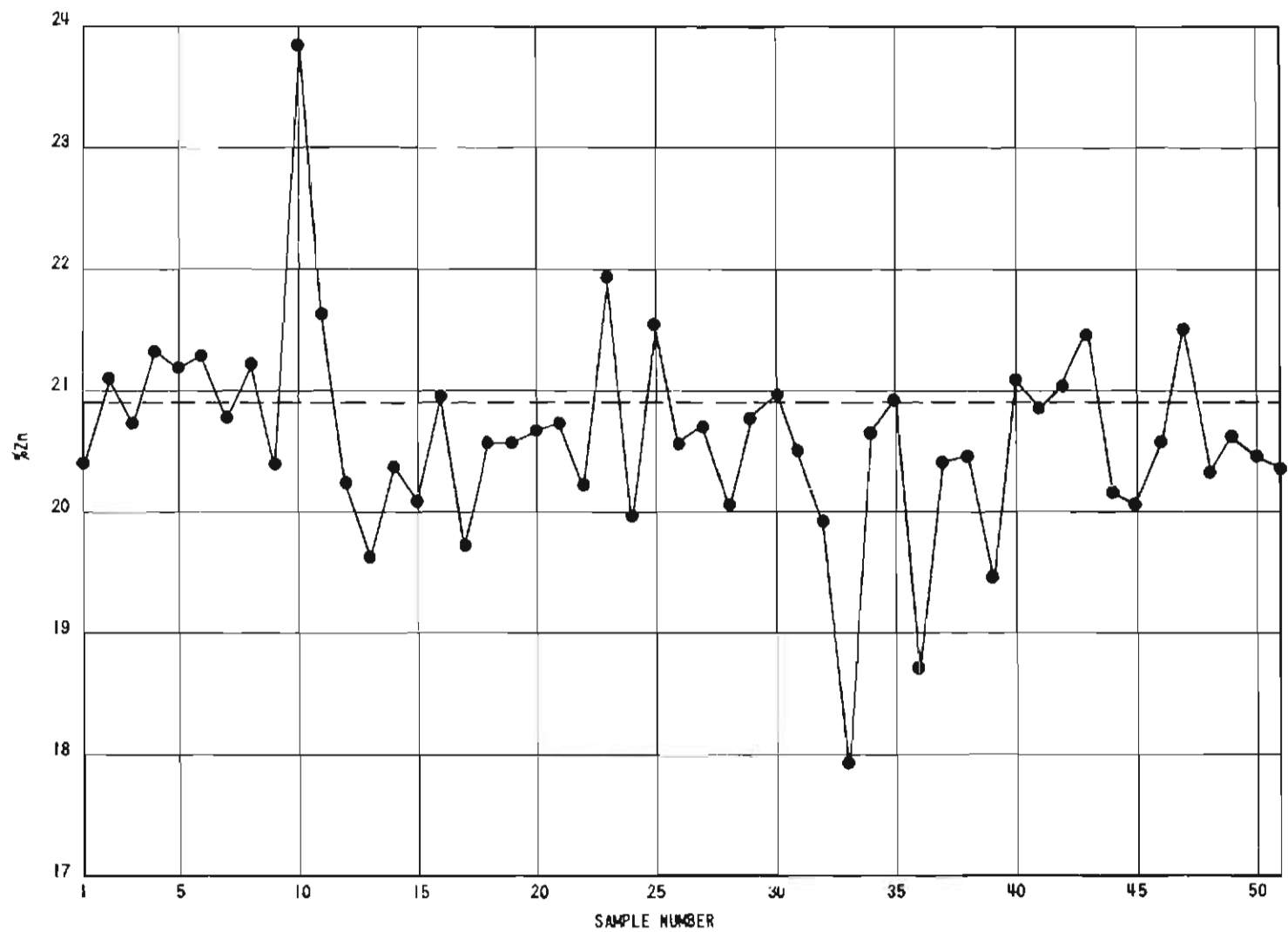


Figure 7. Zinc-Aluminum Alloy, Rod C