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I. THE EFFECT OF A TEMPERATURE GRADIENT UPON  
CONCENTRATION IN BINARY ALLOYS

II. THE EFFECT OF A PRESSURE GRADIENT UPON  
CONCENTRATION IN BINARY 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

Gilbert LaRue Steiner, Jr.

June, 1957

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Date Approved by Chairman: May 30, 1957

### ACKNOWLEDGMENT

The writer wishes to acknowledge his indebtedness to his thesis adviser, Dr. William M. Spicer for his suggestion of the problem, for his help in execution of the program and for his securing of an Air Force sponsored research fellowship for the writer, under which most of the work was done.

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## SUMMARY

## PART I

In a binary alloy system having a terminal solid solution, the extent of which decreases with decreasing temperature, the solubility of the metal of smaller percentage, that is, the solute, is obviously greater at a higher temperature than at a lower one. The purpose of this work is to determine experimentally whether in a chemically homogeneous specimen of such a binary alloy, having appropriate composition and being subjected to an appropriate temperature difference so that one part is of one-phase structure and one part is of two-phase structure, the chemical composition of the specimen will in time become inhomogeneous due to diffusion of solute toward the part that is a one-phase structure, i.e., the higher temperature region.

The method employed was to subject homogeneous specimen of Pb-14%Sn, Al-24%Zn, Cu-5%Ag and Cu-0.1%Cr alloys, while protected by inert atmospheres, to controlled temperature gradients for long periods of time, after which the chemical compositions of all parts of the specimen were checked for any changes.

It was found that, in addition to the unavoidable experimental errors in the analyses, inhomogeneities in chemical composition appeared in the specimen, there being a large migration of solute, theoretically from the two-phase region to the one-phase region, in practice from the cooler portion of the specimen to the hotter portion. This is in accord

with a theoretical prediction based upon the phase rule. Superimposed upon this larger effect of migration of solute toward the hotter portion of the specimen was a similar migration of smaller extent that was confined entirely within the region of the one-phase solid solution. This smaller effect is believed to be the Soret effect; its direction of migration is found to be in accord with that reported by others for the Soret effect acting alone in completely one-phase alloys. It is recommended that more work be done on this whole problem, refining it by incorporating several new important experimental procedures which the present work emphasized as being needful. These improvements will eliminate areas where the findings were doubtful.

## PART II

It is proposed to answer by both theoretical and experimental means the following question: Will there be non-uniform chemical composition formed as a result of a portion of an alloy specimen of uniform chemical composition being maintained at a pressure different from that of the remainder of the alloy specimen?

The complete theoretical foundation of the solution is presented, which, by means of sound mathematical and physical chemical concepts, shows the feasibility of this pressure effect. The basis of this theoretical proof is the utilization of the concept of fugacity and the fact that under conditions of equilibrium the fugacities of a particular component in each of two adjoining portions of an alloy specimen are equal, even when the two portions are subjected to different pressures. There is also attached theoretical importance to the difference in the

partial molal volumes of the component in question when this component is present in different concentrations in the same binary alloy system. It is calculated that, starting with an alloy specimen of copper and tin with a mole fraction of tin of 0.5 and subjecting two portions of it to a pressure difference of 10,000 atmospheres, having the lower pressure portion of the alloy specimen being so large in size that there will be only a negligible change in its composition, the higher pressure portion will have a mole fraction of tin of 0.37 at equilibrium.

In performing experiments to test this theory, there was at first developed a screw-type pressure-exerting apparatus exerting approximately 25,000 atmospheres, but due to inconstancy of pressure it finally proved to be unsatisfactory and had to be abandoned. A more satisfactory apparatus which was developed derived its force from the weight of a steel ingot acting downward on a portion of an alloy specimen, subjecting it to a pressure of approximately 550 atmospheres. Assuming again the same copper-tin alloy and theoretical calculations used above, this pressure gives an equilibrium value of the mole fraction of tin of 0.486.

Chemical analysis of various copper-tin alloy specimens, after treatment in the screw-type apparatus at elevated temperatures, gave some results that did and some that did not show the proposed effect. Spectroscopic analysis of copper-phosphorous, copper-lead and copper-tin alloys, treated at elevated temperatures in the weight-type apparatus, showed in only one run of one alloy the proposed effect. Thus the experiments failed to unquestionably demonstrate the theory which seems sound.

PART I

THE EFFECT OF A TEMPERATURE GRADIENT  
UPON CONCENTRATION IN BINARY ALLOYS

## CHAPTER I

## INTRODUCTION

Proposal.—If a piece of solid binary alloy originally having the same chemical composition throughout is subjected to a temperature gradient by having one location in the alloy at a certain temperature and another location in the alloy at a different temperature, will the chemical composition of the alloy specimen become inhomogeneous? To find the answer to this question is the purpose of this investigation.

Migration due to different solubilities of solute in two-phase and one-phase regions.—Assume the composition of an original alloy specimen is such that when it is subjected to a temperature gradient, one location in the alloy specimen is at a certain temperature and is by microscopic structure a single phase, that is, a solid solution. Also assume another adjacent location in the same alloy at the same time but at a lower temperature is by microscopic structure two phases, one the same solid solution, the other, a phase richer in solute, ideally being the pure solute. To illustrate this condition, consider an alloy specimen having the composition 7.5% copper and 92.5% silver, ordinary sterling silver, and having one location at 800°C. and another location in the same specimen at 700°C. with all regions lying between having temperatures between these extremes. The American Society for Metals (1) copper-silver phase diagram, Figure 1, shows that these assumed conditions are fulfilled since the 800°C. location would be in the  $\alpha$ , or single-phase solid solution

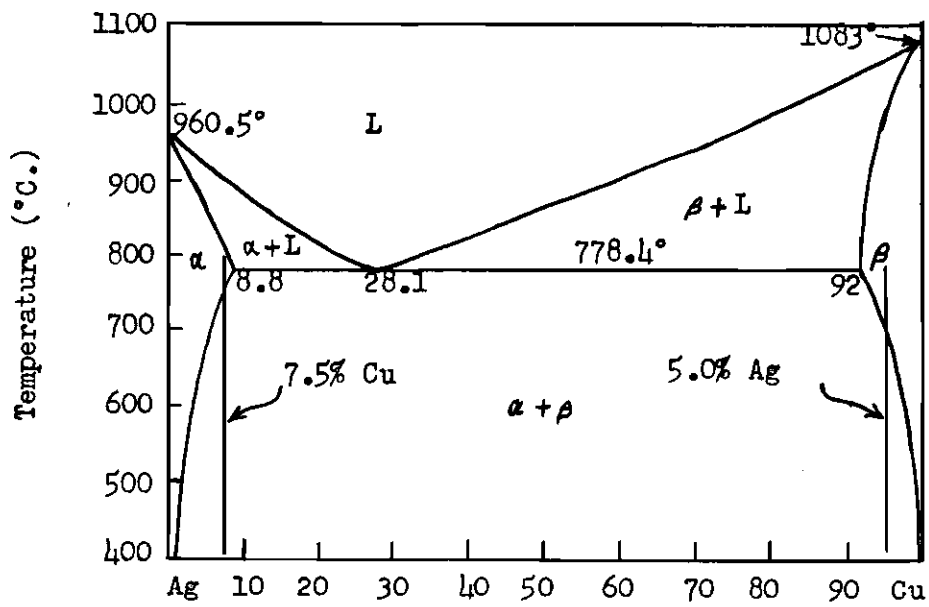


Figure 1. The Copper-Silver Phase Diagram

region, the 700°C. or lower temperature location would be in the  $\alpha + \beta$  or two-phase region. Now at the particular point in the  $\alpha$  region under consideration, that is 7.5% copper and 800°C.,  $\alpha$  is unsaturated with respect to copper, being able to hold in solid solution at this temperature about 8% copper. Also the compositions and proportions of the  $\beta$  and  $\alpha$  phases in the  $\alpha + \beta$  region at the point 7.5% copper and 700°C. are readily found by the tie-lines. The  $\beta$  phase is found to be of very small amount, since its ratio to the  $\alpha$  phase is inversely proportional to the ratio of the lengths of the long tie line to the short one. However, the  $\beta$  phase is found to be very rich in copper, in fact, it is very nearly pure copper. Therefore one might expect for an alloy of overall, homogenous chemical composition 7.5% copper and 92.5% silver, subjected to a temperature gradient of 800°C. to 700°C. or lower, that in order for the system to move toward equilibrium, the unsaturated hotter  $\alpha$  phase must become more nearly saturated with copper by dissolving copper from the  $\beta$  phase of the adjoining colder  $\alpha + \beta$  region. As a result the hotter pure  $\alpha$  one-phase location of the alloy becomes richer in copper.

The same kind of reasoning can be applied to any binary metallic system that has a terminal solid solution of limited solubility and whose solid solubility decreases with decreasing temperature. Evidently this is the first time that this particular qualitative approach has been used to predict the unmixing and the direction of unmixing of the type of alloys mentioned above.

Secret Effect.—The phenomenon of the unmixing of a solution of homogeneous chemical composition, that is, the formation of a concentration gradient

in a solution, by the application of a temperature gradient, is called the Soret effect or sometimes the Ludwig-Soret effect. It was discovered by Ludwig in 1856 and was rediscovered and investigated more fully by Soret in 1879-81. In both cases liquid solutions were studied. The Soret effect is also called "thermal diffusion." In a brief history of the Soret effect in gases, Grew and Ibbs (2) state that thermal diffusion of gases was predicted theoretically by Enskog in 1911-17 and by Chapman in 1912-17 and was experimentally found by Chapman and Dootson in 1917. The Soret effect in liquid alloys was investigated by Ballay in 1926-28 and a measurable separation due to thermal diffusion was found. An attempt was made by Ballay to see if a thermal diffusion separation could be effected in solid alloys, but the results were inconclusive (3, 4). Reinhold found in 1929-33 that thermal diffusion takes place in crystalline solid solutions of Cu Br - Ag Br and  $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}$  (5, 6). It is possible that the reason the concentration difference was large was that the hot and cold regions of the sample belonged to different phases, somewhat like the assumed alloy specimen described in the previous section. This fact is shown diagrammatically in the original articles by Reinhold, as well as being emphasized later by Jost (7) and de Groot (8). Darken and Oriani in 1954 definitely produced the unmixing of solid binary alloys by the use of a temperature gradient (9). The alloys with which they dealt,  $\alpha$  Fe-N,  $\alpha$  Fe-C and Au-Cu, were, at all the concentrations and temperatures employed, completely single-phase solid solutions, either interstitial or substitutional. Therefore they were studying exclusively the Soret effect in solid alloys.

It is doubtful if the experimentally found direction of migration of the so-called solute for systems of one type (metal, salt, etc.) or

state (solid, liquid, gas) of matter would be of any use to predict the direction of migration for matter of a different type or state. Therefore the direction of thermal diffusion found for gases, aqueous liquids, liquid alloys and solid salts shall not be discussed in this paper, which deals only with solid alloys. In the work of Darken and Oriani on the Soret effect in single-phase solids it was found that in both the interstitial alloys ( $\alpha$  Fe-N and  $\alpha$  Fe-C) and the substitutional alloys (Au-Cu), the solute migrates toward the higher temperature region of the specimen (9).

In addition to the experimental work mentioned, there have been several publications which have dealt with the completely theoretical aspects of the Soret effect in condensed systems. Since the first theory by Van't Hoff in 1887 (10) there have been many others including those by Eastman in 1926-28 (11, 12), Bružs in 1931-32 (13, 14), de Groot in 1942, 1945 and 1951 (16, 8, 15), Jost in 1952 (7), Grew and Ibbs in 1952 (2), Darken and Oriani in 1954 (9), Dougherty and Drickamer (17), and others, but it is believed that the application of these theories would add little to this investigation.

Plan of attack.—It is seen from the previous two sections that there are two possible mechanisms by which one may hope to effect a thermal unmixing of a solid alloy. The first is that explained in connection with the silver-copper phase diagram and requires a terminal solid solution of decreasing solid solubility with decreasing temperature. The second is the Soret effect and needs no particular composition or temperature. In this work the first mechanism is to be sought by using appropriate alloys and

temperatures; the Soret effect is to be only incidental to the experiment since it is impossible to prevent it. The Soret unmixing effect will therefore be, it is hoped, if present at all, superimposed upon the unmixing effect of the first mechanism. The experimentally detected unmixing will be the resultant of the two.

There are apparently a very large number of suitable systems from which to choose the terminal solid solution alloy, but there are several other practical and general requirements in addition to the right general type of binary phase diagram. The range of solid solubility should be large enough so that, if there is a measurable increase of the per cent solute in the higher temperature or one-phase region of the alloy sample, the increase will still not be enough for the new composition coordinate to be in the liquidus region at the highest temperature used. The diffusion coefficient, as defined by the well-known Fick's Law, should preferably be high. This would tend to give a greater diffusion of metallic atoms for a given time, temperature gradient and unmixing force. The melting point of the alloy, that is, the temperature at which the rising temperature reaches the solidus, should be high, as should also be the temperature of transition between the two-phase and one-phase region. This allows one to employ high temperatures and take advantage of the fact that the rate of diffusion increases with rising temperature. The alloy, that is, the metals in the alloy, should have very low vapor pressures at the temperatures employed to prevent erroneous results due to preferential vaporization of one metal and also to prevent the ruining of the specimen due to complete sublimation at the hotter region or contamination of cooler regions of the specimen or apparatus by the condensed

metallic vapors. Chemical properties of the metals and alloys employed should be such that they are not so active that they will react with the atmosphere and corrode at room temperature, thus making their fabrication difficult. The alloys should also not react with fused silica if the sample is to be in contact with this material at the temperature of the experiment. Other practical requirements sought in selecting a binary alloy are that it is not too rare and expensive, that the alloy specimen is easily made and has a macroscopically homogeneous chemical composition, and above all, that at least one of the metals, preferably the one in smaller concentration, lends itself to very accurate determination by analytical procedures.

It is planned to create a temperature gradient in the alloy by holding opposite ends of the cylinder-shaped specimen at different temperatures, keeping the individual temperatures constant to within a few degrees. The chemical composition changes in different macroscopic regions of the alloy specimens, if there are any changes, will be detected by analyzing small pieces or slices of the alloy from these regions, employing chemical methods, or by spectrographically analyzing small spots along the length of a polished specimen.

It is possible by metallographic examination of an alloy to ascertain whether it is structurally composed of a single-phase or a mixture of two phases. By quickly cooling a specimen of long heat treatment to room temperature, one usually preserves in a metastable condition the phases that were present before the specimen was quickly cooled; thus by metallography one can find the structures actually present during the heating of an alloy specimen. In this work an attempt will be made to

find simultaneously in the same specimen the single-phase structure in the higher temperature portion of the sample and the mixture of two phases or the two-phase structure in the lower temperature portion of the sample as would be expected from the equilibrium diagram.

After considering theoretical factors mentioned above concerning choosing of the binary systems for the unmixing experiments and also after performing certain tests to check the practicality of certain materials for use, it was decided to employ the four different alloys whose nominal compositions are: lead - 11% tin, aluminum - 24% zinc, copper - 5% silver and copper - 0.1% chromium. The phase diagrams of these binary systems are all shown in Appendix F, with the exception of the copper-silver diagram which has previously been used in this chapter. The straight vertical lines in the diagrams are to mark the composition of the alloys used in this study. It is seen that these lines cover the range of temperature in their vertical lengths which puts them partly in the two-phase and partly in the one-phase regions, as it is hoped to do with actual alloy specimens of this composition.

## CHAPTER II

## INSTRUMENTATION AND EQUIPMENT

Alloy Specimens.—Based on the theoretical and practical considerations of the previous chapter, the first alloy chosen to study in the temperature gradient were composed of 14% tin and 86% lead. J. T. Baker's Chemical Reagent Grade shot tin and shot lead were weighed in amounts that would by synthesis give this desired composition, assuming no melting and casting changes. Using a Bunsen burner, the lead and tin were melted together in pyrex glass under commercially pure argon gas. The melting temperature was raised to about 400°C. and the molten alloy was thoroughly mixed by a glass rod for a few minutes. The alloy was now cast into rods by quickly pouring into preheated nearly horizontal pyrex glass tubes, Figure 2, by means of elbows or vertical bends, bent up at each end of the tube, the alloy being poured into one opening with air escaping and metal overflowing from the other. The alloy solidified within 15 seconds of being cast due to cooling of the tube by air currents. It is hoped that there was no segregation of the chemical components of the alloy during solidification. Upon cooling the tube to about 0°C., the metallic alloy contracted more than the glass, thus becoming freed from the glass, after which it was removed by breaking the glass with a hammer. By heating in an oven at 150°C., a temperature a little below the solid solution temperature of 170°C., for approximately 24 hours, the alloy became by structure two-phase (as seen by metallographic examination)

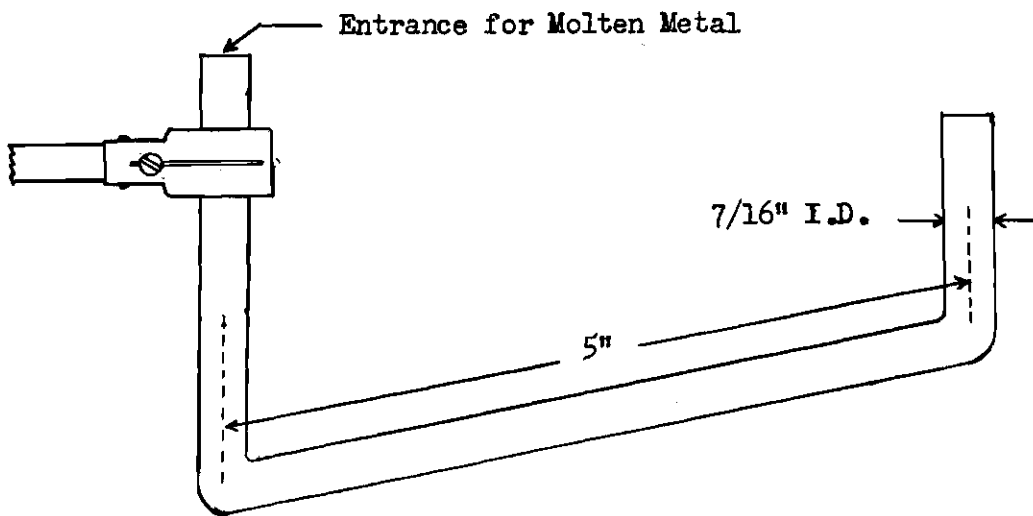


Figure 2. Pyrex Glass Tube for Lead-Tin Alloy Rods

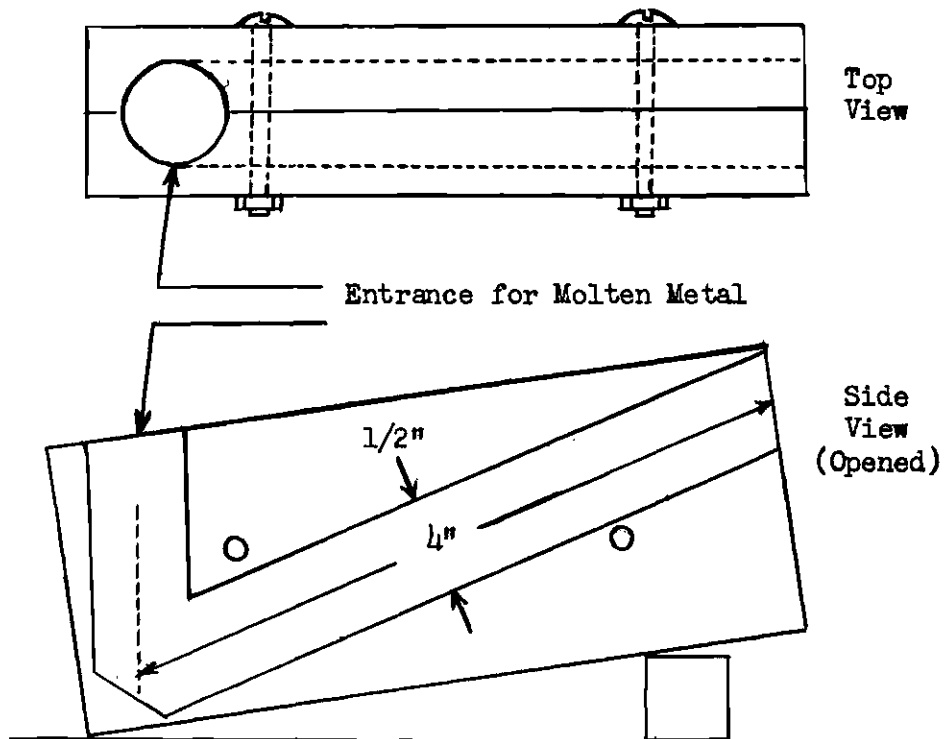


Figure 3. Permanent Graphite Mold for Copper-Base and Aluminum-Base Alloy Rods

and possibly became a little better homogenized. Alloy specimens were made by simply sawing pieces approximately 7.5 inches long from these rods, cleaning the surface with dilute hydrochloric acid and threading each end approximately 1/2 centimeter, leaving the remainder of the rod the original diameter. Small pieces from each end of the remainder of the casting from which the specimen was sawed were saved for future chemical analysis.

Other alloy specimens prepared by casting at Georgia Tech were those composed of 24% zinc and 76% aluminum and those composed of 5% silver and 95% copper. These two types were prepared similarly. The 24% zinc - 76% aluminum alloy was made by melting together the calculated amounts of J. T. Baker's pellet zinc and Sargent's pellet aluminum to give the right composition synthetically. The melting was done by an induction furnace; machined, graphite, cylinder-shaped crucibles were used to eliminate silicon contamination from clay crucibles and the contents of the crucibles were kept covered by powdered carbon during melting to prevent oxidation of the metals. A long graphite rod was used to stir the very red hot molten alloy for about a minute. The alloy was now quickly poured into a graphite mold, Figure 3, which mold had shortly preceding this casting been heated red hot by an induction furnace to remove adsorbed water vapor. Unremoved water would have caused the mold to explode upon pouring in the molten alloy. The rods all solidified within a few seconds and were removed and heat treated at 238°C. (which is a little below the solid solution temperature of about 255°C.) for approximately 24 hours giving the whole alloy what was seen microscopically to be a two-phase structure. According to

Fink and Willoy (18) this state, being the one present at equilibrium at room temperature, could have been reached completely by aging a few days at room temperature only. One of these rough rods, which was approximately 1/2 inches in diameter and 4 inches in length, was machined into a test-bar shaped specimen, that is, with a neck in the central section and coarse threads at each end, the neck itself being 1.0 centimeters in diameter and 4.0 centimeters long. Another rod was machined into a similar specimen but with no reduced diameter neck.

The 5% silver - 95% copper alloy specimens were made in a manner similar to that of the aluminum base alloys, the only difference being that the ingredients of the copper-base alloy were melted in a Denver Fire Clay crucible. The copper used was J. T. Baker's shot copper; the silver was fine sterling silver rod given by the General Plate Division of Metals and Controls Corp. Calculation was made to account for the copper and silver in the sterling so as to give a synthetic composition of exactly 5% silver. The powdered carbon covering and the graphite mold also were used as before. The artificial aging was done by heating the rods in a muffle furnace to 500°C. (the solid solution temperature being 700°C.) for 3 hours to give a completely two-phase structure. The rods were pickled to remove the oxide and machined into test-bar shaped specimens similar to those of the aluminum-base alloys. All other alloy specimens used in this work besides those already described as being prepared here were acquired in rod form from manufacturers. A long rod, having a chemical composition of approximately 0.1% chromium with the remainder copper and a diameter of one-inch, was given to this project

by Anaconda Copper Corporation. From this rod a special shaped specimen to be described later was machined.

Magnesium-base alloys containing 1.1% manganese and in the form of 0.75 inch diameter extruded rods from the Wrought Section, Metallurgical Laboratories, Dow Chemical Company were tried. These were found to completely sublime at the temperature and during the time necessary for an unmixing experiment.

Apparatus for thermal diffusion.—After the failure of several attempts to create the desired controlled temperature gradient in 14% tin - 76% lead alloy specimens by various methods, a final apparatus to be used was designed. This apparatus is shown in Figure 4, and is amply described by the labels.

A temperature gradient apparatus for use with aluminum-zinc alloys is shown in Figure 5. This was used for the temperature gradient treatment of one of the recorded aluminum-zinc specimens; another was treated in the apparatus shown in Figure 6 in which also was treated simultaneously a specimen of 5% silver - 95% copper alloy.

An approximately 0.1% chromium - remainder copper alloy specimen was machined into a short-necked shape as shown in Figure 7. It was then soft soldered to the cooling water chamber of its special temperature gradient apparatus (shown in Figure 7). This apparatus is described by the labeled figure as are the other apparatus.

Temperature control.—The temperatures of the hot ends of the specimens treated in any apparatus of the type shown in Figures 4, 5 and 7 are obtained by simply raising the voltage of the variable transformer a

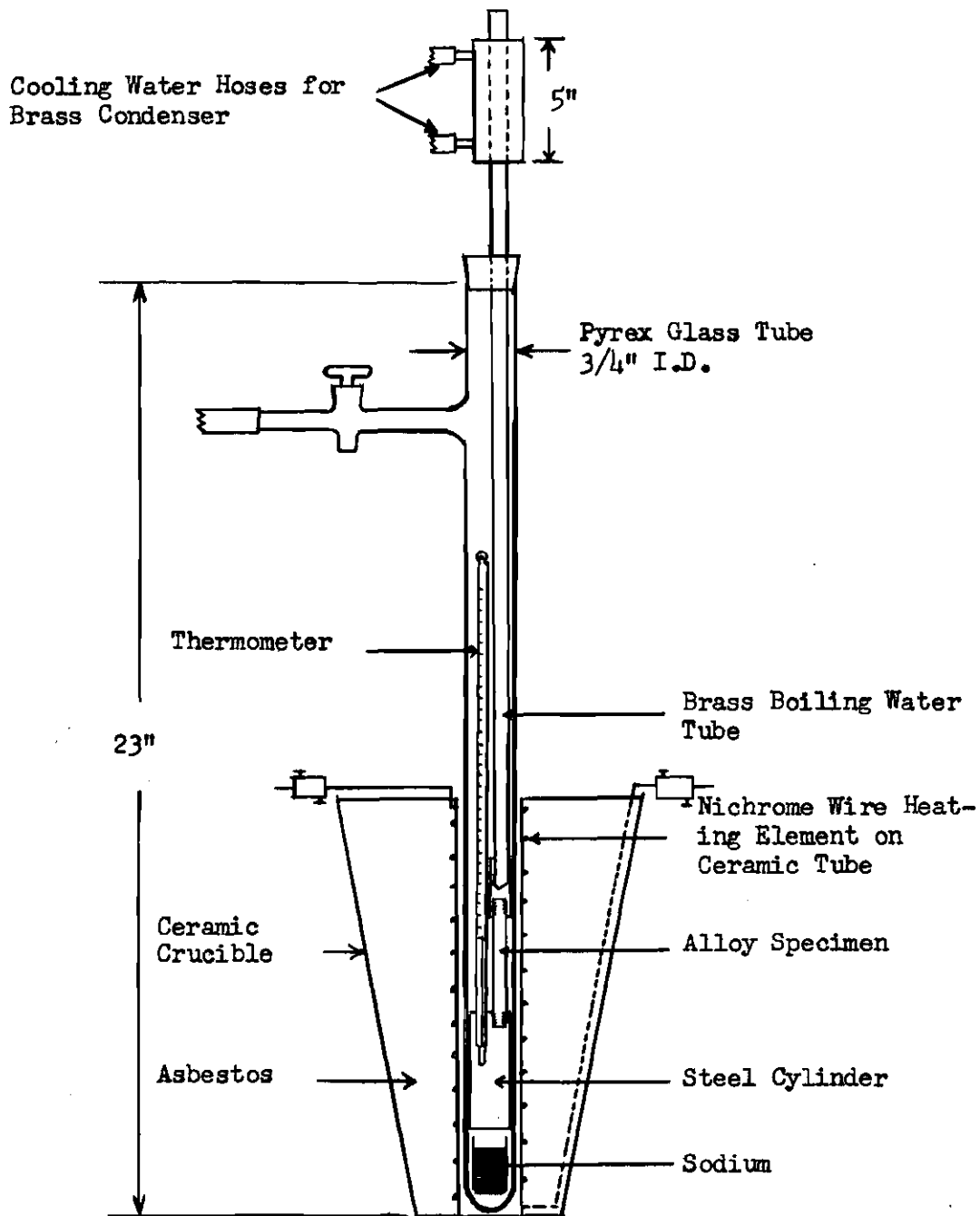


Figure 4. Temperature Gradient Apparatus for Tin-Lead Alloys

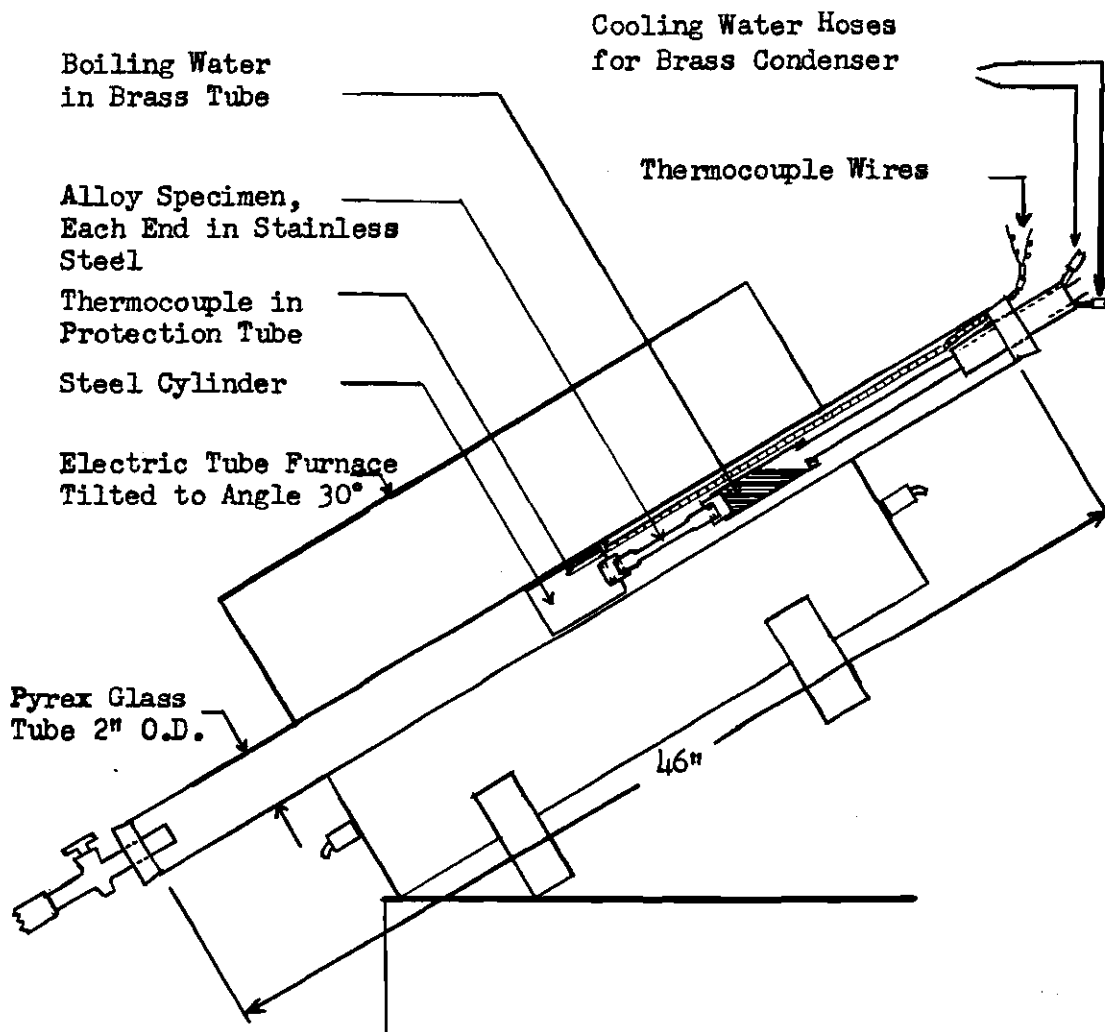


Figure 5. Temperature Gradient Apparatus  
for Aluminum-Zinc Alloys

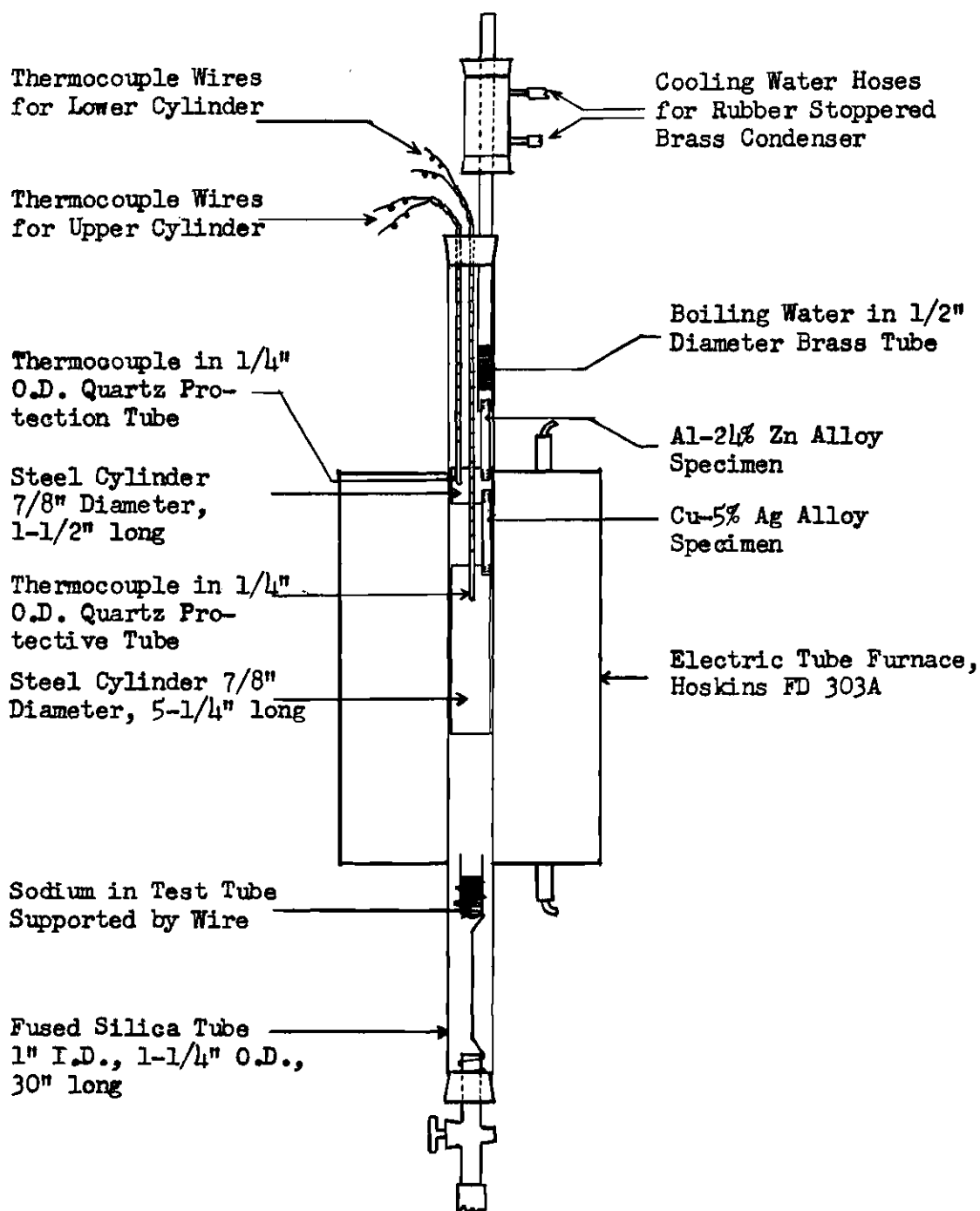


Figure 6. Temperature Gradient Apparatus for Aluminum-Zinc and Copper-Silver Alloys

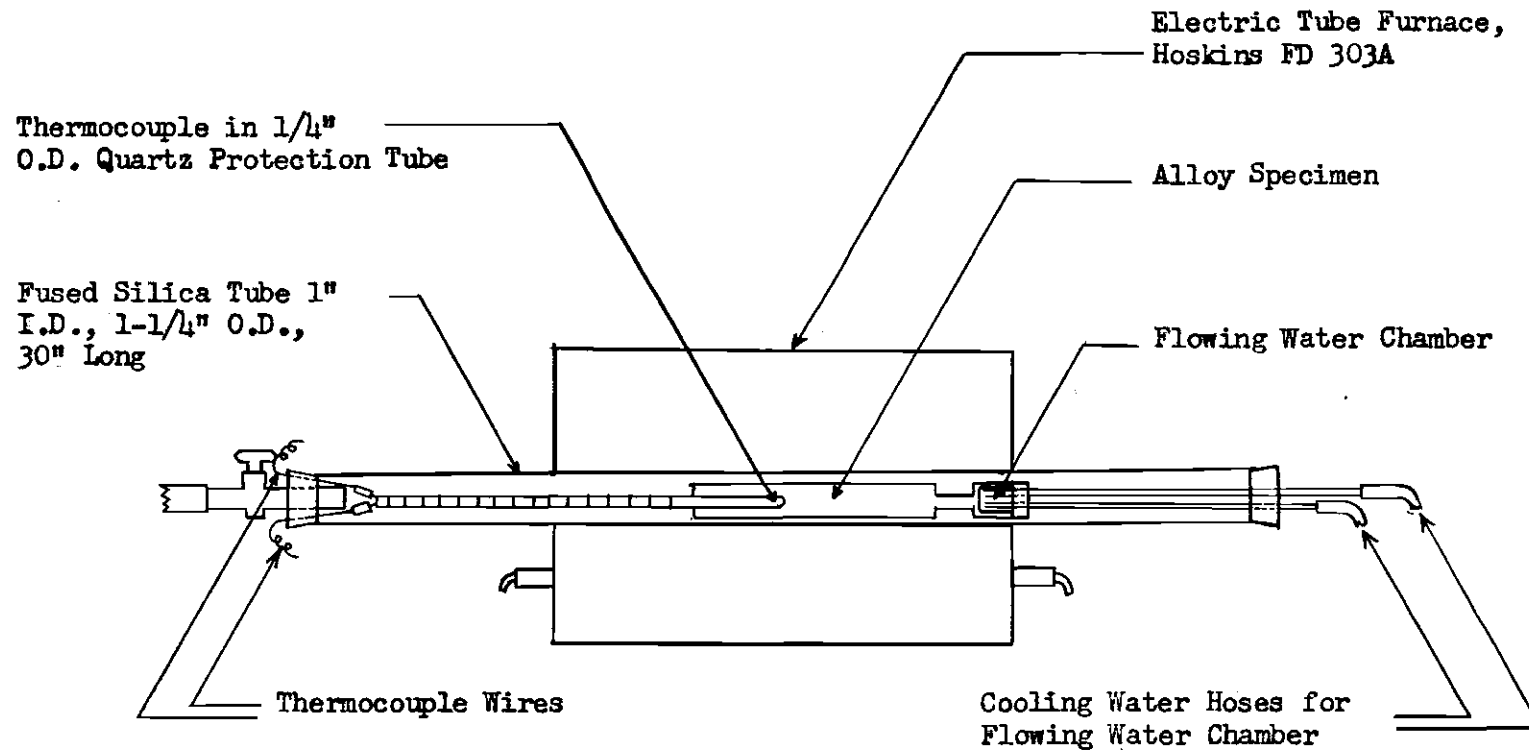


Figure 7. Temperature Gradient Apparatus for the 0.1% Chromium-Remainder Copper Alloy

few volts, waiting for a temperature steady state, checking the temperature and repeating until the desired temperature is reached. To obtain the desired temperatures for the cold end of the 5% silver - 95% copper alloy and also the desired temperature for the hot end of the 24% zinc - 76% aluminum alloy simultaneously (using the apparatus shown in Figure 6), the position within the furnace heating zone occupied by the block joining the two alloys must be adjusted, as well as the voltage of the variable transformer. This adjustment of depth within the furnace heating zone is made by lowering, one inch at a time, the quartz tube with all its contents. This is effective in varying the temperature of the cold end of the 5% silver - 95% copper specimen while the voltage remains constant and also while the hot end temperature of this alloy remains nearly constant.

The temperature of the boiling water ends of the apparatus is supposed to remain constant near 100°C. throughout the experiment and did so to within the accuracy needed, that is, 1 or 2 centigrade degrees.

For all the set ups used, after the desired temperatures are obtained, the temperatures are checked at intervals of about 12 hours for several days. If found to be maintained, the temperatures of the furnaces are then assumed to remain constant to within the accuracy needed for this experiment, that is, 1 or 2 centigrade degrees. This constancy is due mainly to the action of the constant voltage transformer. However, because of temperature changes in the room, changes in the diameter and thus resistance of the heating element with age and other factors, the temperature are not as constant as those of an automatically controlled furnace, but are sufficient. Also the measurements of the temperatures

may have been inaccurate due to unknown factors such as thermocouple contamination, thus making in vain any refinement in control. For this reason the end temperatures used in the plots in Chapter IV are the simple, unweighted averages of the different temperatures in the tables of temperature control data, using all temperatures recorded after the initial heating up of the apparatus.

Temperature measurements.—All thermocouples used for measuring temperatures in the previously described temperature gradient apparatus are of the chromel - alumel type. They were made by welding a No. 28 B. and S. gauge chromel wire to a No. 18 B. and S. gauge alumel wire using a borax flux and an oxygen-natural gas flame as described by Weber (19). Each of the temperature measuring hot junctions is in series with its two cold junctions, one cold junction being copper versus chromel and the other alumel versus copper. These cold junctions are in glass tubes and are kept at 0°C. during temperature measurements by surrounding the glass tubes with a Dewar flask of crushed ice and water in equilibrium. The effective thermal e.m.f. produced by the difference in temperature of the hot junction of a thermocouple and the 0°C. temperature of the cold junction is a measure of the temperature of the hot junction. This thermal e.m.f. is measured by means of a Leeds and Northrup Company K-3 potentiometer. Potentiometer accessories include an Eppley Laboratories, Inc. standard cell for initial balancing of the potentiometer, a 6-volt storage battery in series with a Leeds and Northrup Company resistance box, against which the standard cell and thermal e.m.f. are measured in turn, and a Leeds and Northrup Company galvanometer for indicating the

null point. The chromel and alumel wire used for the thermocouples is from Leeds and Northup Company, and assumed to be of standardized composition. Therefore, for the purpose of relating e.m.f. to temperature there was employed a table of the thermal e.m.f.'s produced by Leeds and Northup chromel - alumel thermocouples at temperature intervals of 2 centigrade degrees and a temperature range of  $-100^{\circ}\text{C}.$  to  $1400^{\circ}\text{C}.$ , the cold junctions being at  $0^{\circ}\text{C}.$  (19). The temperatures are found by simple, straight line interpolation within the 2 centigrade degree temperature intervals, although a formula is available for more exact interpolation. A thermocouple was standardized by getting its e.m.f. at several fixed points, that is, the freezing points of different pure metals, and a deviation curve was drawn showing the error in e.m.f. at different temperatures. It was found that the greatest deviation was 0.037 millivolts, corresponding to about 0.6 centigrade degrees so the curve was not used, this temperature error being well within the limits for this experiment of 1 or 2 centigrade degrees.

The hot end temperature of the apparatus for the 14% tin - 36% lead experiment, Figure 4, is measured with a mercury-in-glass thermometer of the  $360^{\circ}\text{C}.$  type which is left in the apparatus, thus making direct reading possible for this lower temperature alloy.

The temperatures of the boiling water in the boiling water tubes are all measured by a long  $0^{\circ}\text{C}.$ - $100^{\circ}\text{C}.$  mercury-in-glass thermometer that has a scale marked in 0.1 centigrade degrees. This long thermometer is inserted in a boiling water tube only when a temperature reading is wanted and it may be read while the bulb is under the boiling water.

Determination of composition.—Since all alloys used in these experiments are composed nominally of two metals only and since the effect upon the experiments of possible traces of impurities is unknown, there could be no advantage in analyzing for trace elements so this was not done, but it is believed that impurities are lower than in most commercial nominally binary alloys. The metal determined in any one binary alloy is usually the one in least percentage, but sometimes both may be determined to advantage. As stated before, the alloys chosen were those whose solute, that is, element in the least percentage, is determined without difficulty. Exact procedures of chemical analysis are in Appendix B. Tin was determined in the presence of lead by the method described by McDow, Furbee and Clardy (20), their method not being changed in any way. In this method the tin is determined by titrating the stannous ion with a standard iodine solution, the stannous ion being oxidized to the stannic ion. The titration is carried out under a protective covering of carbon dioxide (gas from dry ice). The stannic tin is reduced to stannous by boiling the strongly hydrochloric acid sample solution in the presence of nickel shot. This reaction may be stopped by cooling the solution to  $+10^{\circ}\text{C}.$ , therefore the nickel shot need not be removed to titrate the stannous ions. Lead is prevented from interfering by having an excess of sulfate ion present, the source of which is the potassium sulfate and sulfuric acid with which the alloy sample was put into solution. Lead sulfate precipitates and stays insoluble throughout the determination. The method is very accurate according to McDow, Furbee and Clardy. The difference between the percentage of tin found by the average of six determinations and the true amount of tin present is only 0.01% for a

solder containing 34.88% tin and 0.00% for a lead-base metal containing 10.91% tin. The tin equivalents of the iodine solutions used are determined by titrating solutions containing known weights of tin that have been carried through exactly the same preliminary treatment as the unknown.

In the 24% zinc - 76% aluminum alloys, the zinc was determined in the presence of aluminum by an electrolytic method. The method chosen is very simple and is a combination of those described by Sard (21) and the Association of Light Metal Refiners (22). It consists essentially of the electrolysis of a strongly alkaline solution of the sample. The zinc plates out upon a copper plated platinum electrode and is weighed. Having cyanide ion present in the solution helps give a better zinc plate. Aluminum, of course, is not deposited from an aqueous solution under any conditions, therefore the current density need not be accurately controlled. The sample is dissolved in dilute sulfuric acid to prevent spray after which an excess of sodium hydroxide is added. The main possible source of error is the loss incurred upon the removal of the cathode from the strong alkali and washing and drying it, but if these operations are performed carefully, it was found that the cathode should not weigh low by more than about 0.2 milligrams.

The 5% silver - 95% copper alloy was analyzed by a combination of the chloride separation method of the A.S.T.M. (23) and the electrolytic methods of Mahin (24) and Sand (21). None of the electrolytic separations were necessary. The filtered silver chloride was redissolved by boiling in concentrated sulfuric acid to drive off all chlorides. The solution was then made strongly basic by adding sodium hydroxide after which 3

grams of potassium cyanide were added. The silver was electroplated and weighed. The copper was determined also, as a check, by evaporating the filtrate from the first chloride separation, doing this in the presence of sulfuric acid, thus removing all chloride ions here also. After adding a little nitric acid and urea the copper was electroplated and weighed. Unfortunately, the analyses where both elements were determined did not add up to within 1% of the 100% needed to be correct. The 5% silver - 95% copper results were poor because of this.

The approximately 0.1% chromium - remainder copper alloy was analyzed at selected spots by a spectrographic method using a large grating spectrograph. In this method the density of the 2979.7<sup>o</sup>Å chromium line was compared with the density of the 3010.8<sup>o</sup>Å copper line, the ratio of the chromium density to the copper density being an indication of the concentration of chromium. The percentage of copper (almost 99.9%) is considered constant since a small change in its absolute concentration would not change its relative line density appreciably. Excitation is by the spark method, the sparking time and voltage being controlled. Many spots on the surface of the specimen to be tested were sparked and data taken as one set of congruent data. Standard copper-chromium alloys, that is, pieces of the original bar of 0.1% chromium - remainder copper alloy, were sparked identically as the sets of unknown spots and were included within these sets. This is useful in telling whether the chromium concentration of the unknown is higher or lower than that of the standard and also in relating any one particular set of results with any other set as several sets of results are obtained. See Appendix E for

this calculation relating one set to another). Two of the sets of results or spectroscopic data were obtained without a standard chromium-copper alloy being sparked along with the unknowns. These two sets were related to the others by finding spark locations in these two sets identical to spark locations in the others and considering all the sparked points that have common locations to have identical compositions. This makes it possible to find factors relating these two sets to the others. (See page 73, Appendix E also for this calculation for relating one set of results to another). By these methods, all points plotted in Figure 15 are on exactly the same scale and can, therefore, be put into the same plot and one curve drawn from all the points, thus giving a better average. The indications of chromium concentration cannot, however, be changed to absolute composition percentages by any kind of calculations, except at one concentration, that of the standard. This is because only one concentration of standard was used and therefore there is no way to get the slope of an actual known percentage composition versus transmission ratio plot.

The instrument used was a one and one-half meter, Applied Research Laboratory grating spectrograph with a controlled spark excitation source. An external standard, and iron-iron arc, was used to identify the lines of standard wave length in the sample. A maximum of 15 separate spectrograms could be taken on a single photographic film. The counter electrodes employed in the spark excitation of the alloy specimen were of pure graphite.

Metallography.—All metallographic examinations were of water quenched alloy specimens which were at room temperature when examined. Bausch and

Lomb research metallographic equipment, having binocular eye pieces and a ribbon filament lamp, was used to visually find the different phases. The kind of preparation given the quenched specimens was governed by the chemical composition of a particular specimen and also by the fact that, for all specimens, only the distinguishing of the phases was sought and not the crystal structure nor the grain size.

The 14% tin - 86% lead specimens were prepared in the manner prescribed by Woernley (25) with only one step changed; the sample was not microtoned prior to etching but was left whole. It is well known that the surface of cut lead alloys, even if microtoned, is worked and if the true structure is to be seen the worked layer would have to be etched off. In this etching process the whole specimen was immersed in a solution at 42°C. and containing 15 milliliters of glacial acetic acid, 20 milliliters of concentrated nitric acid and 80 milliliters of water. At frequent intervals the specimen is removed from the etching solution, rinsed with cold water, swabbed with cotton while under cold water and the etching repeated until the crystals appear mirrorlike when viewed with the naked eye. The drying of lead alloys after etching presents a special difficulty in that unless certain precautions are taken the surface will oxidize before it can be viewed through the microscope. This is prevented by quickly rinsing the etched specimen first in tap water and then distilled water, placing it in a 130 milliliter bottle having enough acetone to cover the specimen, stoppering the bottle with a one-hole rubber stopper to which is connected an aspirator or water pump, pumping the air and acetone vapor out for a short time, tilting the bottle so that all the liquid acetone is pumped out, allowing the

specimen to dry in an atmosphere of acetone vapor and finally allowing it to dry further in a vacuum. Thereafter the lead alloy surface remains unoxidized, even in the air for several days, and the phases can be seen readily at a magnification of 250 X.

For the 24% zinc - 76% aluminum alloys, the preparation method for specimens for metallographic examination is similar to those employed by Hanson and Gaylor (26) and Fink and Willey (18). One whole side of the specimen, is abraded flat upon a fast moving wet band of emery cloth, the flat plane being parallel to the axis of the specimen. This flat surface, extending from end to end of the specimen, is now polished, first on successively finer emery paper wheels and then on wet cloth wheels, using successively finer grained aluminum oxide suspensions. After the final polishing, by simply rinsing the specimen in distilled water and in methyl alcohol and then drying in a current of air, one may see the phases present at a magnification of 500 X, but by also giving the polished specimen an etch for about 15 second in 25% nitric acid at 70°C. it is easier to ascertain whether there is one phase or two.

The alloy specimens of the copper-silver system are prepared for metallographic examination in a manner like that described for the 24% zinc - 76% aluminum alloy with the exception that the etching step is different. Silver-rich copper-silver alloys are etched according to Stockdale (27), that is, by swabbing on a mixture of chromic acid and sulfuric acid in dilute aqueous solution. This same method is better described by the American Society for Metals (1). Using this etch, and a magnification of 150 X, the  $\beta$  phase appears as dark areas along the

grain boundaries; the  $\alpha$  phase is the white matrix. Copper-rich copper-silver alloys must be etched by a different method. For very small amounts of  $\alpha$  phase, an ammoniacal solution of cupric chloride, called "copper ammonium chloride" is used and is the one recommended by Smith and Lindlief (28). This is also the etchant used by Stockdale (27), with which the  $\alpha$  phase appears white in a dark matrix at a magnification of 150 X. For larger amounts of silver in copper-rich, copper-silver alloys, ammonium persulfate solution is used, this being also recommended by Smith and Lindlief (28). With this etchant the  $\alpha$  phase appears as white globules very clearly.

The 0.1% chromium - remainder copper alloy was not examined metallographically.

## CHAPTER III

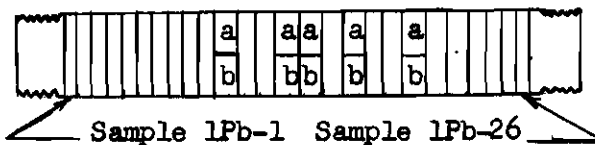
## PROCEDURE

Chemically analyzed specimens.—The apparatus shown in Figure 4 was assembled, using one of the 14% tin - 86% lead alloy specimens already described. The pyrex glass protection tube was evacuated by a mechanical vacuum pump, commercial grade argon gas was let in to atmospheric pressure, the tube was evacuated again, about 1/3 atmosphere of argon gas was then let in, and the stopcock was closed. The voltage of the variable transformer was slowly increased until the higher temperature end of the specimen was at approximately 210°C., the temperature of the lower temperature end rising to a constant 101°C. (Appendix A shows the temperatures maintained during the treatment of all the alloy specimens). After being kept in this temperature gradient for 90 days, the specimen was quenched by allowing cold kerosene to flow into the recently evacuated pyrex glass protection tube. The specimen was removed from the apparatus, washed in benzene, prepared for metallographic examination as described previously under "Metallography," and then examined at a magnification of 250 X. The alloy specimen was now sectioned for chemical analysis as shown in Figure 8. The slices were of only approximately equal thickness. The sectioning was done by a large hinged knife used ordinarily to cut metallic sodium. Individual samples were weighed, and stored in stoppered vials until they were chemically analyzed. The samples were chemically analyzed by the methods described previously under "Determination of Composition," and the results are shown in Appendix C.

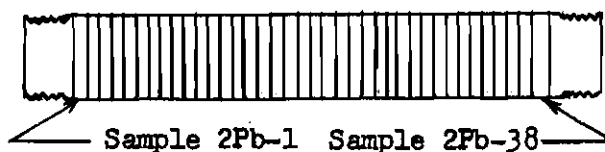
Identification

Cross-Sectional View (Actual Size)

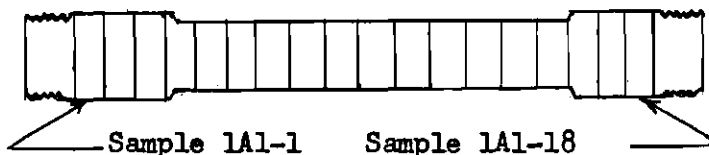
Specimen 1Pb



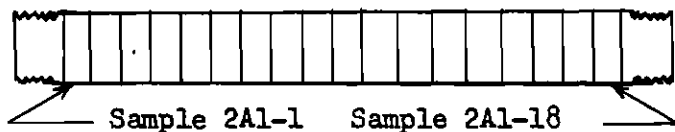
Specimen 2Pb



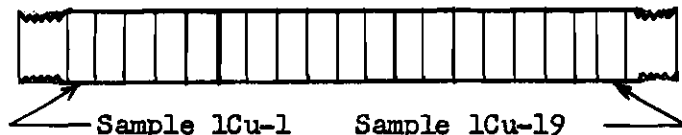
Specimen 1Al



Specimen 2Al



Specimen 1Cu



(The higher temperatures of the above five specimens are toward the left; the lower temperatures are toward the right)

Specimen 2Cu

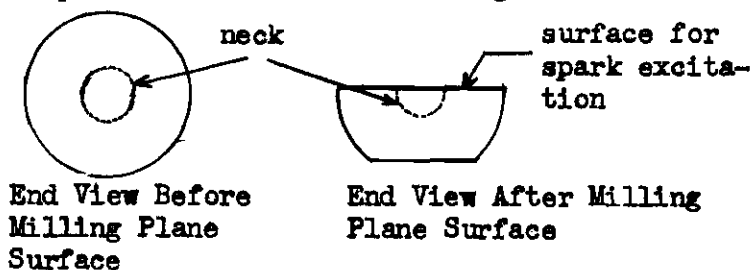


Figure 8. Sectioning of Chemically and Spectroscopically Analyzed Specimens

Chemically analyzed specimens are all given a code name according to the major metal and order of treatment. The chemical analysis samples of the sectioned specimens are numbered according to their distance from the higher temperature end of the specimen rod, the lower numbers being nearer the higher temperature end. As an example the chemical analysis sample nearest the higher temperature end of this first treated 14% tin - 86% lead alloy is called 1 Pb - 1.

Another specimen of the 14% tin - 86% lead alloy of exactly the same size and shape as 1 Pb, and denoted by the code name 2 Pb, was later treated in the same apparatus and in the same way as 1 Pb except that the temperature gradient was maintained for 67 days, the higher temperature end of the specimen was at approximately 225°C. and the specimen was not examined metallographically. (See Appendix A for the temperatures maintained and Appendix C for the results of chemical analysis).

An alloy specimen of approximately 24% zinc and 76% aluminum and with the code name 1 Al was maintained for 148 days in a temperature gradient in the apparatus depicted in Figure 5, the higher temperature remaining approximately 475°C. and the lower temperature at 100°C. as shown in Appendix A. The final protective atmosphere of about 1/3 atmosphere of argon gas, when at room temperature, was put into the pyrex glass tube in the same way as it was with previous apparatus. The quenching was done by quickly removing, while at treatment temperatures, the entire assembly from the pyrex glass tube and immediately plunging into cold water. The specimen was now disconnected from the apparatus, prepared for metallographic examination as described previously under "Metallography," examined at a magnification of 500 X, and then sectioned

for chemical analysis. The sectioning was done with an ordinary hack saw with the slices as shown in Figure 8. The sample slices were weighed individually, stored in stoppered vials until they were chemically analyzed and finally chemically analyzed by the method previously described under "Determination of Composition." The results are shown in Appendix C.

Another alloy specimen of approximately 24% zinc and 76% aluminum and an alloy specimen of approximately 5% silver and 95% copper were simultaneously treated in the temperature gradient apparatus shown in Figure 6. Unwanted diffusion between the two iron cylinders and the specimens was prevented by heating the iron cylinders only in air to red heat before assembling. This forms a coating of  $Fe_2O_3$  on the iron threads. The higher temperature end of this 24% zinc 76% aluminum specimen, 2 Al, was maintained at approximately  $475^\circ C.$ ; the lower temperature end of 2 Al, was at  $100^\circ C.$  The higher temperature end of the 5% silver - 95% copper specimen, denoted by the code name 1 Cu, was maintained at approximately  $887^\circ C.$  The lower temperature end of specimen 1 Cu was at the same temperature as the higher temperature end of specimen 2 Al or approximately  $475^\circ C.$  The protective atmosphere of hydrogen was put into the fused silica tube by simply evacuating the tube and heating the piece of commercially pure sodium (which always contains hydrogen) shown in the pyrex test tube by applying a Bunsen burner flame to the outside of the apparatus. The dropping temperature readings for a particular furnace voltage, shown for the apparatus in Appendix A, are believed to be due to contamination of the thermocouple by the reducing atmosphere, although it is unknown if this contamination actually happened. The

temperature gradient treatment was terminated by quenching the specimens. This was done by evacuating the fused silica tube and then allowing cold kerosene to rush in and fill the evacuated tube. The specimen was removed and washed with benzene. The surface of specimen 1 Cu was found to be covered with a network of cracks due to the hydrogen reacting with occluded copper oxide and releasing water vapor as explained by Smith and Hayward (29). The specimens were prepared for metallographic examination and examined as described previously under "Metallography." Both specimens were sectioned by hack saw, as shown in Figure 8, and the slices weighed and analyzed by the methods previously described under "Determination of Composition" with the results of the analysis in Appendix C.

Spectroscopically analyzed specimen.—The one specimen to be spectrographically analyzed, the previously described approximately 0.1% chromium - remainder copper alloy denoted by 2 Cu, was treated in the temperature gradient in the apparatus shown in Figure 7. After assembling the apparatus and allowing the shellaced stoppers to dry, the fused silica tube used for protecting the specimen was evacuated, and while still being pumped by a mechanical vacuum pump, the furnace was turned on to a temperature of approximately 500°C. for about 1 hour in an attempt to out-gas the metal specimen. Argon gas of commercial purity was now allowed to fill the tube to a pressure of about 1/2 atmosphere at this temperature and the stopcock was closed for the remainder of the treatment time. The variac volts and thus the furnace temperature was gradually raised and the temperatures were maintained as shown in Table 5, Appendix A. The same difficulty with dropping temperature readings was encountered here also and is believed

to be due to contamination of the thermocouple wires in the closed tube by metal vapors although, again, there is no certainty that this happened. The rate of flow of the cooling water was kept at about 2 liters per minute. After heating for 59 days the specimen was quenched by quickly removing the alloy specimen and its attached metal parts from the hot fused silica furnace tube and immersing immediately in cold water. The reason for this quick cooling was not for preserving the phases for metallographic examination but to eliminate the very slow (approximately 12-hour) cooling of the sample which would take place if the furnace was simply turned off and allowed to naturally cool while containing the specimen. It was feared that the very slowly dropping, but still high temperature, cooling of the specimen upon which there was not at the same time maintained a temperature gradient, could possibly result in ordinary concentration-type diffusion causing a remixing of any previously unmixed material. This quenched specimen, appearing quite bright and with no cracks, was unsoldered from the other metal parts. A small amount of chromium-colored material was seen on the cooler parts of the specimen, particularly the neck. This is believed to be sublimed and condensed chromium from the hotter parts of the specimen. By means of a milling machine the specimen was cut so that a plane surface parallel to the specimen axis was formed along its entire length. This plane side was further ground, first by a wet band sander, next by successively finer emery paper wheels and finally by wet cloth wheels using successively finer grained aluminum oxide suspensions. Figure 8, page 29, shows the sectioning of this specimen. In order to get the 8-1/2 inch long specimen into the light-tight enclosure used for excitation, it was cut into two pieces,

each exactly  $\frac{1}{4}$  inches long. The specimen thus prepared was spectrographically analyzed at different spots over the plane surface, employing the principles and methods described under "Determination of Composition." The entire plane surface was now reground and repolished to remove the burned metal and the analysis repeated at a different set of locations. These spark locations are all shown in Figure 9, page 35. Upon analyzing the first set of spark locations it was seen that along the neck where the chromium-colored metal was deposited, some of the individual analyses indicated unusually high chromium content, due to this extraneous material. This material was filed off the specimen before subsequent sets were analyzed. All the data obtained and all the indications of composition for the location are shown in tabular form on pages 68 to 72, Appendix E, and graphically in Figure 15, page 42.

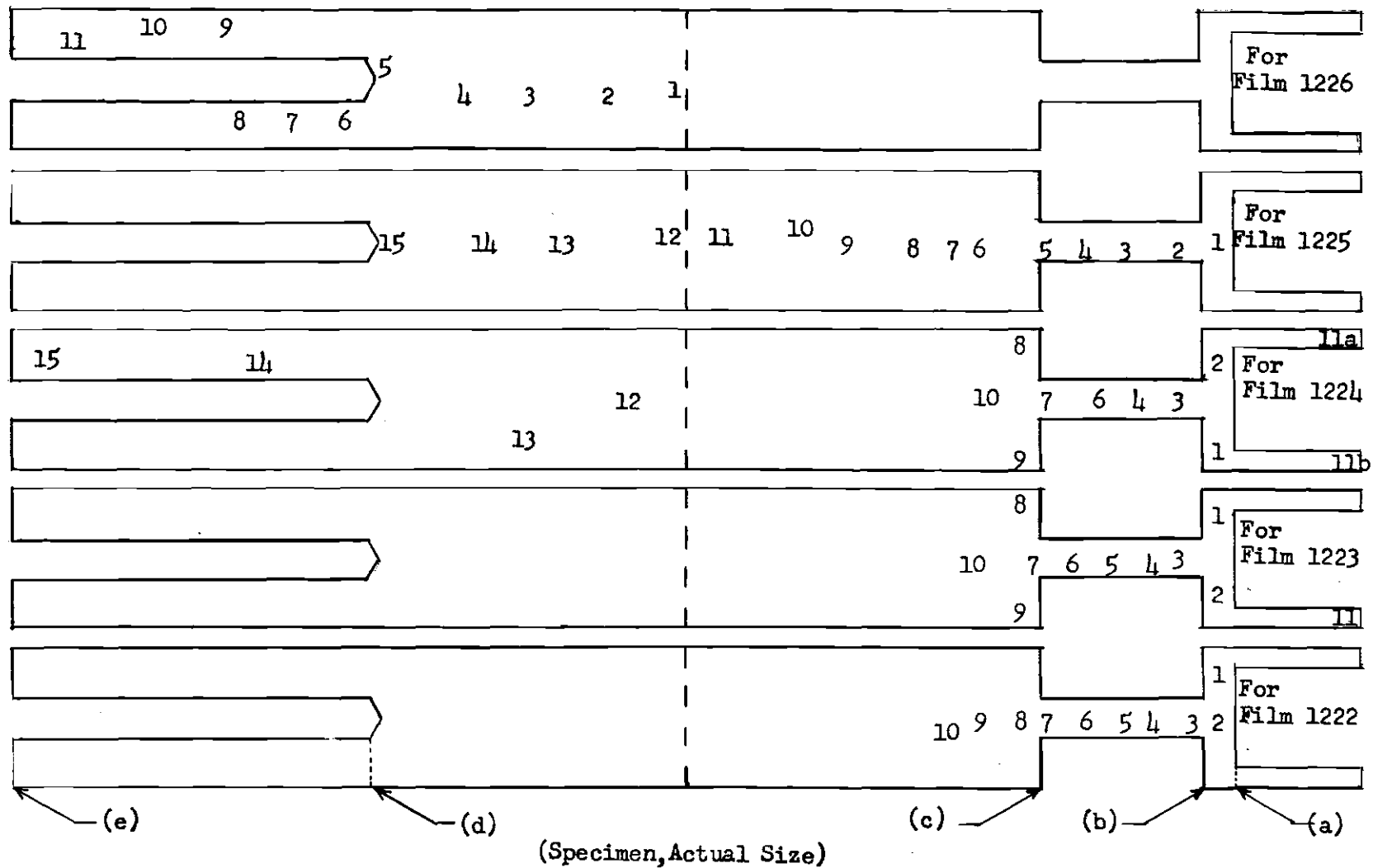


Figure 9. Spark Excitation Locations on the Spectroscopically Analyzed Specimen

## CHAPTER IV

## DISCUSSION OF RESULTS

Graphical Presentation.---It is believed that the best way to envision what has happened to the alloy specimens is to plot the compositions found, that is, the percentages of solute for the final unmixed alloys versus the temperatures maintained in each individual sample during the heating. The plots which may be seen on the next six pages make use of the experimental data in this way. The only temperatures used here that are measured directly are the average terminal temperatures of the specimen rods; the others are estimated. Since the thicknesses, or lengths along the axes of each chemically analyzed sample of alloy cut from these specimen rods, are directly proportional to the sample weights and the temperatures maintained are assumed to be directly proportional to the lengths along the axes from the cold end (the specimen rods being uniform in diameter), the sample weights are used directly to find the temperatures which are shown along the abscissae of these plots. (Sample calculations used to find these temperatures are in Appendix D, page 65). The curves themselves were drawn where they are for no particular reason except that they are roughly the simple averages of the plotted points. The unmixing of the formerly homogeneous alloys is strongly suggested by these plots. It appears that for some of the plots there is not a material balance. By this is meant that the total amount of solute gained by all regions which have a greater concentration

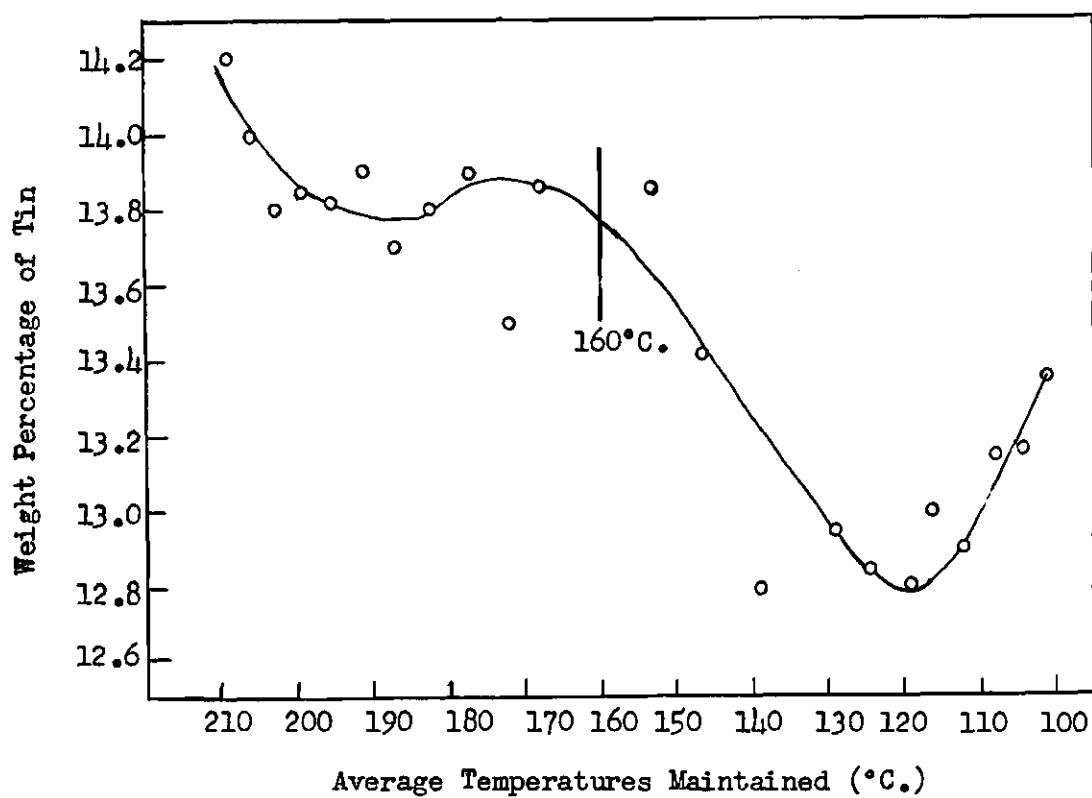


Figure 10. Final Compositions versus Temperatures for Specimen 1Pb

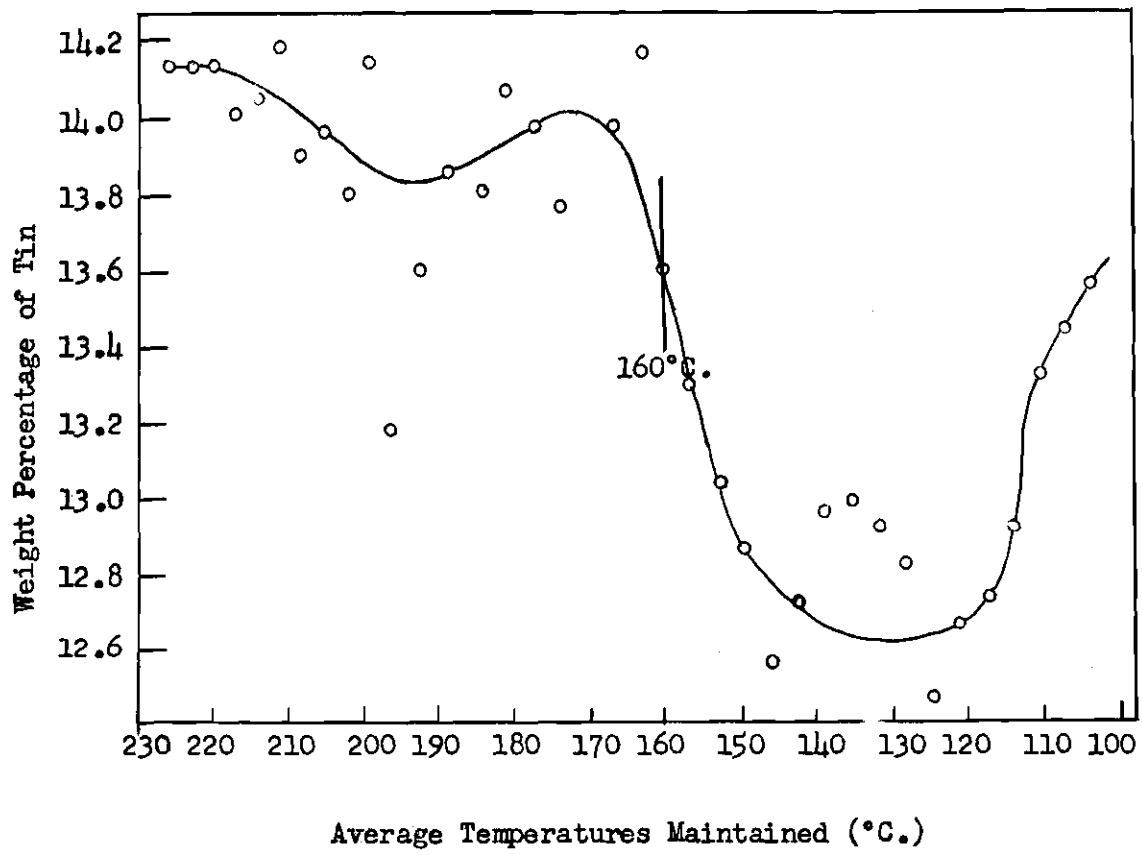


Figure 11. Final Compositions versus Temperatures for Specimen 2Pb

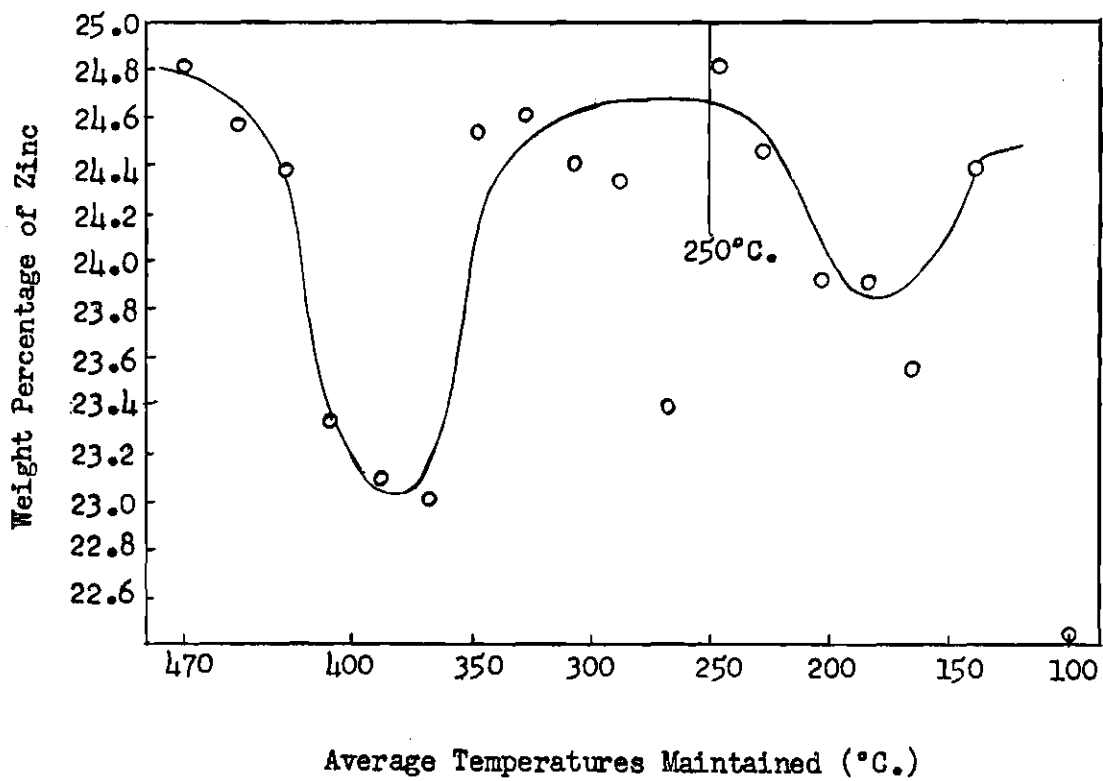


Figure 12. Final Compositions versus Temperatures for Specimen 1A1

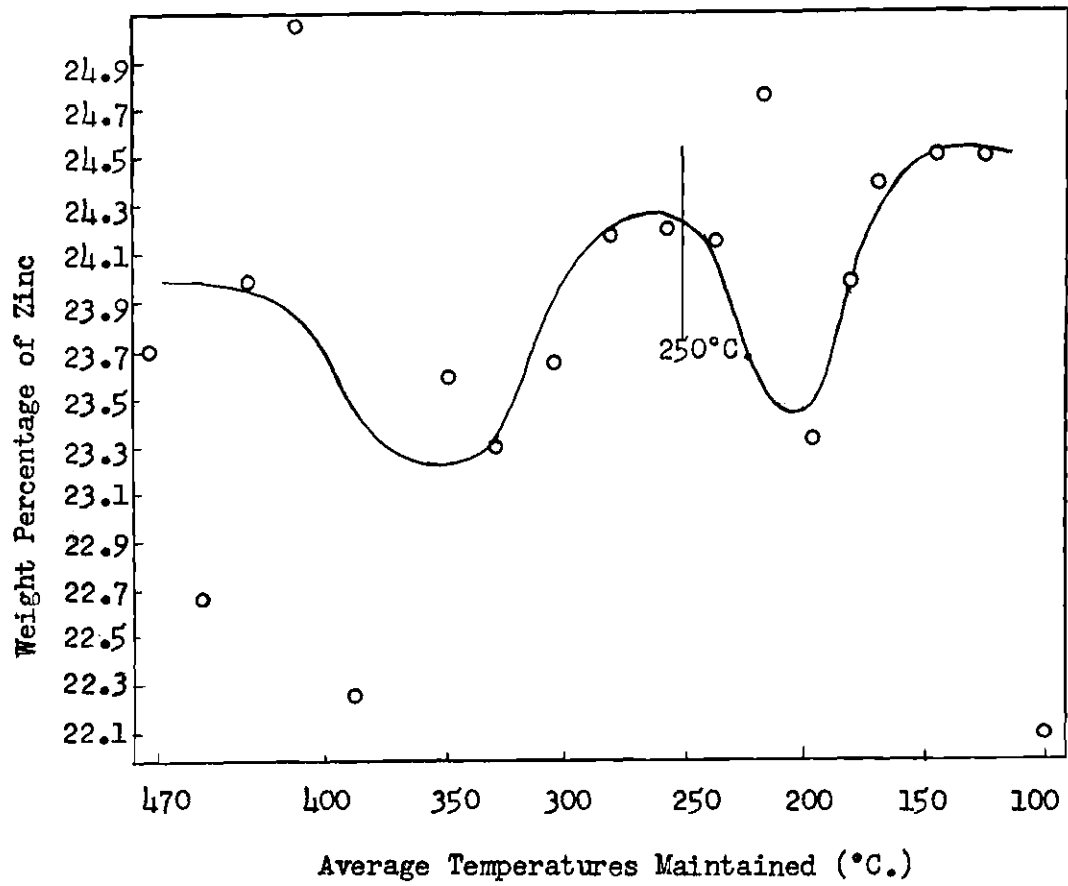


Figure 13. Final Compositions versus Temperatures for Specimen 2A1

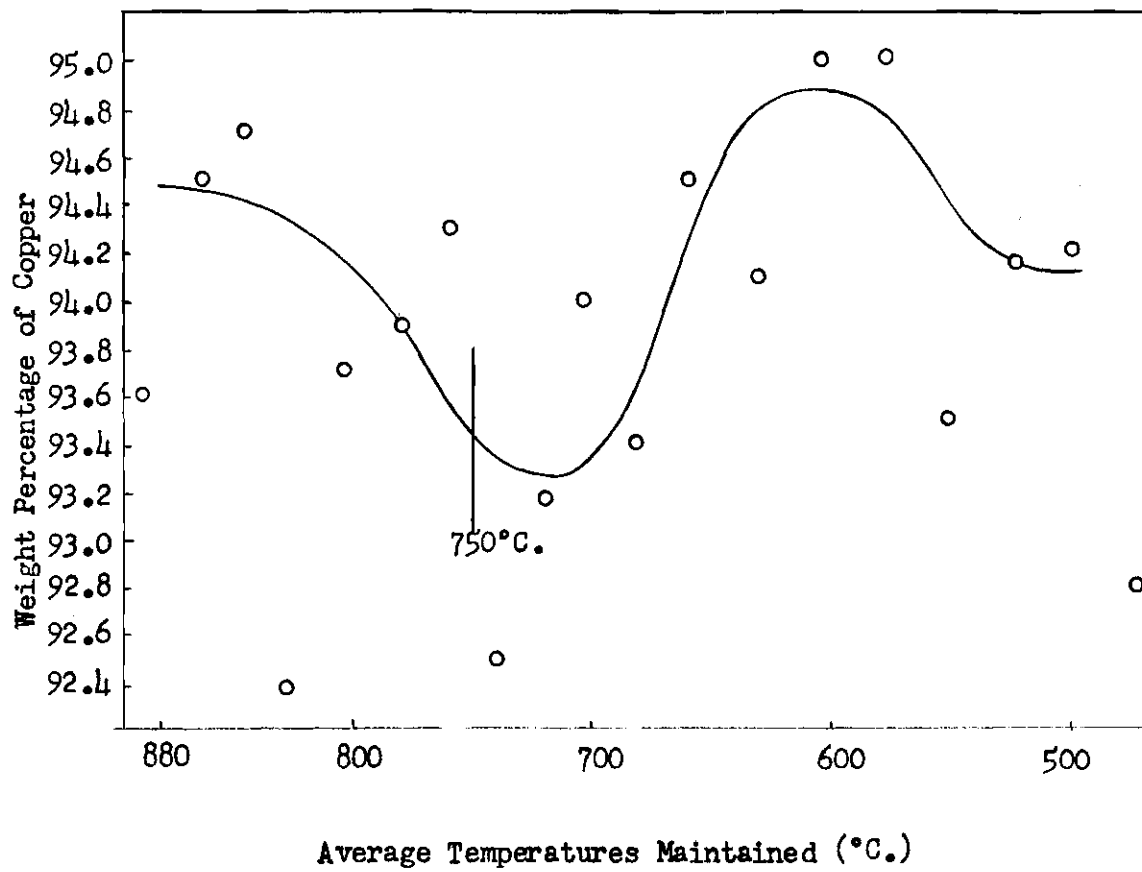


Figure 14. Final Compositions versus Temperatures for Specimen 1Cu

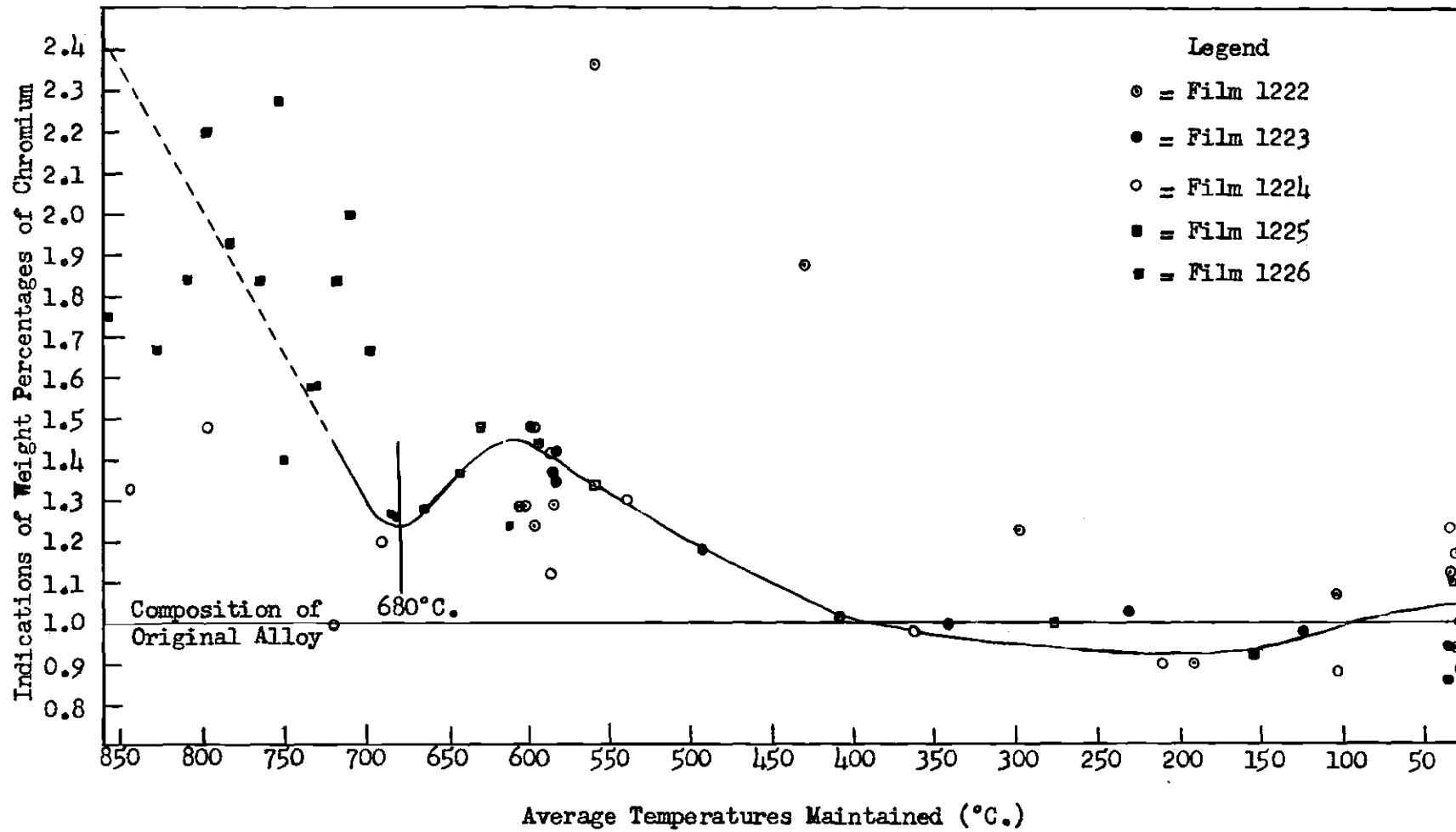


Figure 15. Final Composition Indications versus Temperatures for Specimen 2Cu

than that of the original alloys is not equal to the total amount of solute lost by all regions which have a lesser concentration than that of the original alloy. This paradox could possibly be true for the analyzed portion of the sample only, since the threaded portions of the specimens were not analyzed and their loss might have caused the discrepancies. Nevertheless, the entire specimens definitely should show material balances for the diffusion process. Other possible explanations for the unbalances of material are: firstly, the data are accurate enough to show the general trends of a rise or fall in solute composition but not accurate enough for the material balance to show; secondly, there may have originally been small inhomogeneities in the cast alloy specimens; thirdly, there may have been some diffusion between the specimens and the structural material and; fourthly, there is the possibility of a loss or gain of volatile material at the specimen surfaces considering the high temperatures employed. In the special case of specimen 2 Cu, the plot of which is shown in Figure 15, the apparent lack of material balance is due to the non-uniform diameter of the specimen. In Figure 14, page 41, representing specimen 1 Cu, the 5% silver - 95% copper alloy, the usual representation of the composition is reversed, the major component, copper, being used as the ordinate. This is because the determination of the copper is believed in this case to be more accurate than that of the silver. In all of the graphical presentations, but not in all of the tables, the numerical values of the compositions are rounded off to one decimal place.

Qualitative interpretation.—Upon observing the results of analysis of the two Pb - 14% Sn alloy specimens, 1 Pb and 2 Pb, as shown graphically

in Figures 10 and 11, and also observing in the phase diagrams shown in Appendix F, it is seen that the temperature at which this alloy in its original overall composition changes from a two-phase to a one-phase structure is approximately 160°C. It is also seen that in general for both these specimens there is an overall movement of solute, that is tin, from the two-phase to the one-phase region. This is expected from previous theory. These theoretical locations of the crossing of the phase borderline temperature (160°C.) on both of the plots are also near the locations in which the major unmixing has taken place experimentally and is approximately on the main point of inflection for each of the plots. For clarity these points have been shown by the short, straight vertical lines crossing the curves in Figures 10 and 11. It is reasoned that as the region of the alloy located on the higher temperature or one-phase side of this overall dividing line becomes during the experiment increasingly more rich in solute, that is, tin, the line theoretically dividing the two-phase and one-phase regions gradually moves to a lower temperature. This would necessitate the continual shifting of the line over which the movement of solute occurs toward the tin-enriched one-phase region, that is, toward the higher temperature end of the specimen rod. The experimental effect of this principle is not definitely discernible from the curves. As explained in Chapter I, the true Soret effect, when in operation in a completely substitutional, completely one-phase solid alloy, such as Au - Cu, gives a diffusion of solute toward the higher temperature portion of the specimen. In these specimens, considering the one-phase regions of the specimen as a different specimen for applying this rule, there should be an enrichment

of solute at the extreme higher temperature end of the specimen at the expense of the nearby region. This is possibly the reason there is a small but definite dip found in the curves within the long region of general tin enrichment between  $160^{\circ}\text{C}$ . and the highest temperature. Also this is probably the reason that there is found at the extreme highest temperature of the specimens a short region of tin enrichment greater than at any other place. The pure Soret effect operates best in this region above  $160^{\circ}\text{C}$ . for two reasons; first, the region is all one-phase solid substitutional alloy and second, diffusion rates in solids are always higher at higher temperatures. Equilibrium was not reached here and since time is constant for all the effects, the rate of diffusion is important in determining the final quantities. It is probable that the two effects took place simultaneously, the Soret effect taking place in the one-phase region and the effect due to the differences in solubility of solute in the different phases taking place only at the borderline of the two-phase and one-phase regions, that is, at approximately  $160^{\circ}\text{C}$ .

The shape of the plot of the results of analysis of the Al - 24% Zn alloy specimens, 1 Al and 2 Al, as shown in Figure 12 and 13 have a similarity to those of the Pb - 14% Sn specimen with exceptions. One of these differences is the dip in the left side of the curve, that is, the relative lowering of the zinc content in the one-phase region, thought to be the separation due to the pure Soret effect, is as great as, or greater than the dip in the right side of the curve thought to be the separation due to the effect of different solubilities in different phase regions. The reason for this is not known exactly, but it is surmised

that even though other things are similar, having either a different major element, a different minor element or both is sufficient cause for the difference.

When an interpretation of the graphical presentation of the results from the Cu - 5% Ag specimen is sought, finer details of the curve (such as small dips or rises) may not be seen, due to the roughness of some of the analyses. A very general trend can be recognized in which the percentage of copper is smaller, and thus the percentage of silver or solute is greater, in the higher temperature half of the specimen, as is predicted for both the pure Soret effect and for the effect of different solubilities in different phase regions. There is seen no significance for the line of demarcation between the one-phase and the two-phase regions being exactly where it is, but in general it does divide the higher solute portion of the final specimen from the lower solute portion.

It is believed that because of the large number of analyses and the relatively small amount of gross scattering of points in the plot, the graphical representation of the results for specimen 2 Cu, shown in Figure 15, shows a significant chemical composition change. In this specimen, as was previously explained, there is an apparent material imbalance because of the nonuniform shape of the specimen combined with the fact that a linear temperature scale was used. Thus with no contradictions, there is seen in Figure 15 a greater area representing material with a high chromium content than with a low chromium content, the chromium content of the original alloy being the reference point. The portion of the specimen nearest the cold end, although represented by many points,

has a median composition almost exactly that of the original alloy while the composition of all other points of the alloy have changed. This is reasonable since there should be the least diffusion of any kind, and therefore the least composition change, at the cold end of the specimen, and is further evidence that the experimental work on specimen 2 Cu is accurate. A possible qualitative interpretation of the curve utilizes the same two effects as in previous specimens. The effect of different solubilities in different phase regions causes large quantities of solute to flow toward and over the line of demarcation separating the two phase regions, drawing all of it from the region on the cold end side of the line. There is then set up by this drift of material, a deficiency of solute in the region at the very far right side of the line, as seen in the curve. Everywhere toward the hot end side of this deficient region there is a larger concentration of solute than in the original alloy. The principal factor in a proposed explanation of the dip in the solute-enriched region is again the pure Soret effect. This Soret effect is so much at work here in the very high temperature region that the indications of composition of solute is approximately twice that of the original alloy. The source of this material must have been the adjoining cooler region according to the general rule for the direction of the Soret effect in single phase solid solution alloys as found by Darken and Oriani (9).

## CHAPTER V

## CONCLUSIONS AND RECOMMENDATIONS

Conclusions.—The results of these experiments indicate that when certain homogeneous binary alloy specimens are subjected to a temperature gradient, there are developed within the specimens regions of different composition, the regions richer in solute being generally near the higher temperature ends of the specimens. Statements concerning the reasons for the final results that is, what effects have been brought into action and how, are all at the best only qualitative hypotheses. One especially important, in fact the chief purpose of the present study, was to determine what is the effect of having a two-phase region at a certain temperature adjacent to and in direct contact with a one-phase region of another temperature. Although there appeared to have been presented sufficient explanation under the heading "Qualitative Interpretation," using circumstantial evidence only, to make it possible to conclude that, even as theory predicts it, there is a flow of solute from the two-phase to the one-phase region, it is not possible to do this because conclusive evidence in the form of sufficient data is lacking. One reason that one is not able to state conclusively that the effects noted simultaneously with the pure Soret effect are those predicted is that metallographic data showing the one-phase regions adjacent to the two-phase regions is lacking. Therefore one is not sure that the right conditions existed for this effect. With specimen 1 Pb, metallographic examination revealed only one type

structure throughout the length of the specimen when viewed less than one hour after quenching. Specimen 1Al showed a one-phase region at the hot end portion and a two-phase region at the cold end portion of the specimen but the structure of a broad region near the hypothetical junction of the two regions was not discernable. After a few hours, the structure of this specimen also became completely two-phase. The results of metallographic examination of specimen 1 Cu are similar to those of specimen 1 Al. Again the unstability of the metastable material, constantly changing as it is, hinders an accurate appraisal. Specimens 2 Pb, 2 Al and 2 Cu were not examined metallographically. From the foregoing it can be said that the effect due to the two structures was possibly, but not conclusively, the cause for the analytical results obtained.

Recommendations.--Certain obvious limitations and short-comings concerning detail, method and scope of the experiments, as seen in this present work, are themselves readily suggestive of improvements needed in future studies of this kind. Generally, the improvements found to be needed are simply experimental refinements of the overall present plan of attack used in this work. Naturally, it is very desirable to keep all other conditions constant in any scientific study where one seeks to determine the effect which results from one particular variable condition or cause. To do this is to have, in effect, one equation with one unknown which easily lends itself to solution. As an example of this it is seen that the possibility of one being able to correlate the movement of solute in a binary alloy with both the temperature gradient and the microscopic or phase structure of the material is greatly enhanced

if one is able to eliminate all other variables from the equation, especially those variables caused by unwanted experimental imperfections.

Of prime importance in this type of endeavor is the means of determining the chemical composition of materials. Concerning this, it is recommended that better analytical determinations be obtained for certain alloy systems. It is suggested here that whenever possible purely instrumental methods such as those utilizing X-ray diffraction and radioactive isotopes be employed. In the present work, the simultaneous making of all the different observations upon the specimens during the time it was at the conditions of the experiment was not possible with the apparatus used, and also was not suitable here. Such a procedure was not needed to obtain results of the accuracy which was satisfactory for the present experimental studies. For future work, it seems desirable to seek to find the actual, indisputable evidence concerning what the temperature, structure and composition of a specimen is during an actual experiment in the apparatus, not just the calculated or assumed conditions. To eliminate having to assume ideal type experiments when seeking to calculate the temperatures between the measured extremes, it is suggested that more actual temperature measurements be made using the many spots between the extremes. This can be done by one of at least three ways. Many tiny thermocouples could be used, each mounted so as to get the exact temperature of the specimen and also so as to prevent metal contamination of itself and of the specimen. If a specimen rod made with one side a flat polished plane was mounted in an argon filled clear fused quartz tube for protection from atmospheric oxidation and this whole assembly mounted in a tube furnace that had a

slot along its whole length, the temperatures of any and all spots on the specimen could be taken simultaneously by optical pyrometry. For moderately high temperatures such as those employed in the Pb - 14% Sn and the Al - 14% Zn alloy experiments, temperature sensitive paints could be used. It is within the realm of possibility, by using some kind of a portable microscope and clear fused quartz tube previously mentioned, to also determine the structure of all points of a moderate temperature specimen while hot, and this simultaneous with the temperature gradient experiment. The knowledge to be gained from this procedure seems very desirable. Another experimental procedure similar to the above, that is also possible but more difficult is the chemical analysis of a hot specimen through the clear fused quartz protection tube also simultaneous with the temperature gradient experiment. This could be done with either X-ray defraction or X-ray spectroscopy but there could be little if any information gained from this procedure greater than that obtained by analyzing the cold specimen.

The importance of the work of this whole investigation is such that it should be repeated by many different experimenters using different techniques, so as to see if the results are truly reproducible and to see if something previously overlooked can definitely be found. If more were known about this phenomenon, many processes and operations in industry where it would be useful or detrimental could possibly be predicted and found. Therefore industry should be willing to sponsor further research of the above type in order that there may ultimately be a final solution to the problem.

## APPENDIX A

## TEMPERATURE CONTROL DATA

Table 1. Temperatures During Treatment of Specimen 1 Pb

Setting of Variac (volts)	Thermometer Reading at Hot End (°C.)	Thermometer Reading in Water Chamber (°C.)	Date Temperature Taken	Time Temperature Taken
41	211.5	101	9-23-54	5:45 P.M.
41	210.5	101	9-23-54	10:10 P.M.
41	205.5	101	9-24-54	8:40 A.M.
41	204.5	101	9-24-54	10:30 A.M.
42	210.5	101	9-24-54	3:55 P.M.
42	207.0	101	9-26-54	8:00 P.M.
42	209.0	101	9-27-54	2:50 P.M.
42	209.0	101	9-28-54	9:35 P.M.
42	211.2	101	9-28-54	4:40 P.M.
42	208.0	101	9-30-54	2:12 P.M.
42	213.1	101	10-1-54	3:30 P.M.
42	214.0	101	10-1-54	5:15 P.M.
42	209.5	101	10-2-54	9:25 A.M.
42	210.6	101	10-5-54	12:45 P.M.
42.5	210.5	101	10-23-54	6:00 P.M.
42.5	208.0	101	10-26-54	8:30 A.M.
42.5	208.0	101	11-5-54	11:15 A.M.
42.5	207.0	101	11-6-54	1:05 P.M.
42.5	208.4	101	11-19-54	9:35 P.M.

(Temperatures observed here but not recorded again until termination on December 20, 1954).

42.5	208.0 209°C. Ave.	101 101°C. Ave.	12-20-54 Total time = 90 days	10:00 A.M.
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Table 2. Temperatures During Treatment of Specimen 2 Pb

Setting of Variac (volts)	Thermometer Reading at Hot End (°C.)	Thermometer Reading in Water Chamber (°C.)	Date Temperatures Taken	Time Temperatures Taken
41	.....just turned on.....		1-18-55	11:45 A.M.
41	228	100	1-19-55	12:45 P.M.
40.5	224.5	100	1-20-55	2:00 P.M.
40.5	227.5	100	1-22-55	2:10 P.M.
40.5	226.5	100	1-24-55	2:05 P.M.
40.5	225.0	100	1-25-55	12:15 P.M.
(Temperatures observed here but not recorded again until termination on March 26, 1955).				
40.5	225.0 226°C. Ave.	100 100°C. Ave.	3-26-55 Total time = 67 days	12:00 Noon

Table 3. Temperatures During Treatment of Specimen 1 Al

Setting of Variac (volts)	Thermal E.M.F. of Thermocouple at Hot End (millivolts)	Temp. at Hot End (°C.)	Thermo. Reading in Water Chamber (°C.)	Date Temps. Taken	Time Temps. Taken
53	.....just turned on.....			12-29-54	2:10 P.M.
53	16.563	404.1	100	12-30-54	2:45 P.M.
56	18.077	440.0	100	12-31-54	10:35 A.M.
58	19.168	465.0	100	1-1-55	12:20 P.M.
58	19.554	475.0	100	1-5-55	12:25 P.M.
(Temperatures not observed again but is assumed to stay constant to within about 2 centigrade degrees).					
58	.....terminated.....			4-25-55	1:15 P.M.
	470°C. Ave.	100°C. Ave.		Total time = 148 days	



Table 5. Temperatures During Treatment of Specimen 2 Cu

Setting of Variac (volts)	Thermal E.M.F. of Thermocouple at Hot End (millivolts)	Temp. at Hot End ( $^{\circ}$ C.)	Temp. of Outflowing Cooling Water ( $^{\circ}$ C.)	Date Temps. Taken	Time Temps. Taken
80	21.330	516.2	28.0	5-9-55	8:40 P.M.
95	28.397	682.2	28.0	5-9-55	11:20 P.M.
100	29.680	713.0	29.3	5-10-55	5:40 P.M.
105	31.104	747.5	29.3	5-10-55	10:30 P.M.
110	31.610	759.0	29.1	5-11-55	8:10 A.M.
110	30.803	739.5	Flow increased	5-11-55	1:50 P.M.
115	31.013	745.0	27.9	5-11-55	4:35 P.M.
115	31.230	750.0	27.1	5-12-55	4:25 P.M.
115	31.705	761.6	27.4	5-13-55	2:35 P.M.
115	32.570	782.2	25.9	5-16-55	4:40 P.M.
115	31.645	760.0	26.0	5-18-55	4:35 P.M.
115	31.566	758.0	26.6	5-23-55	3:45 P.M.
115	31.330	752.5	28.2	5-28-55	4:10 P.M.
115	31.150	748.2	28.2	6-3-55	6:05 P.M.

(Temperatures not observed again but is assumed to stay constant to within about 2 centigrade degrees).

115 .....terminated..... 7-6-55 9:00 A.M.

$\overline{757^{\circ}$ C. Ave.  $\overline{28.0^{\circ}$ C. Ave.

Total time = 59 days.

## APPENDIX B

## DETAILS OF METHODS OF CHEMICAL ANALYSIS OF ALLOYS

Lead-Tin.—The source of the following procedure is that by McDow, Furbee and Clardy (20), although it was not followed exactly. Weigh a sample of alloy that will give a tin content between 0.1 and 0.2 gram into a 3 ml. Erlenmeyer flask. Add 10 ml. of concentrated sulfuric acid and about 5 grams of potassium sulfate, and heat until the alloy is dissolved. Cool to room temperature. Carefully dilute with water to about 100 ml., add 75 ml. of concentrated hydrochloric acid and 10 grams of nickel shot and connect flask with a one-hole rubber stopper and a rubber tube, one end of which extends below the surface of a beaker of water. Boil gently for 30 minutes, a few minutes before the end of which time, transfer the end of the outlet tube below the surface of a beaker of 10% sodium bicarbonate solution. Keeping the end of the tube below the surface of the sodium bicarbonate solution, place the flask in a container of ice water and allow to cool. In this way carbon dioxide replaces the steam in the flask. Quickly remove the rubber stopper and introduce first a small piece of dry ice, then sufficient dry ice to keep the solution blanketed with carbon dioxide and at a temperature below  $+10^{\circ}\text{C}$ . Immediately add 5 ml. of previously boiled starch indicator solution which contains about 1% sodium bicarbonate and 0.5% soluble starch and titrate with an iodine solution whose tin equivalent is known. The percentage of tin in the sample can now be

calculated. The tin equivalent of the iodine solution is easily found by using the exact procedure given above upon a measured portion of standard tin, either weighed directly as standard solid tin or measured from a standard solution of tin and calculated as the weight of solid tin.

Aluminum-Zinc.—A short discussion of the following method is also found under "Determination of Composition" on page 21 of this thesis. This particular procedure is for alloys that contain no other base-soluble elements and little or no other elements such as the heavy metals.

Weigh a sample of aluminum-zinc alloy that contains any weighable small amount of zinc, preferably between 0.05 and 0.5 grams, into a 200 ml. tall-form type beaker. About 10 ml. of 1:1 sulfuric acid is added and the sample allowed to dissolve with warming. The solution is diluted to about 25 ml. and enough of a cooled, concentrated solution of sodium hydroxide added to neutralize the acid and an excess equal to 5 grams of sodium hydroxide is added. If much insoluble precipitate is formed, the solution is filtered through filter paper, the precipitate washed twice with small portions of sodium hydroxide solution and the filtrate and washings diluted with water to 175 ml. in a 200 ml. tall-form beaker. This solution now contains metallic ions of zinc, aluminum and sodium only and is electrolysed with no fear of deposition of any metal other than zinc. Add approximately 5 grams of sodium cyanide to each beaker of solution before electrolyzing. For the electrodeposition use a rotating platinum anode and a platinum cathode that has previously been plated with copper, dried and weighed. Electrolyse for one hour

with a current of one ampere (approximately four volts for this solution) and at a temperature of 20°C. To terminate the electrolysis without loss of zinc, since zinc will readily redissolve in strong alkali, leave current on and gradually raise the electrodes out of the beaker while at the same time rinsing the upper exposed portion of the cathode as it emerges from the solution. As soon as the cathode is thus removed from the electrolyte solution, it is quickly immersed in distilled water and then in alcohol or acetone. Dry the cathode in an oven at 105°C. for 30 minutes. Weigh the cathode when cool. The gain in weight is zinc. Second and third deposits of zinc should not be put upon the first one as the porosity of the thick coating thus formed hinders washing and drying.

## APPENDIX C

## RESULTS OF CHEMICAL ANALYSIS

Table 6. Analysis of Specimen 1 Pb

Sample Number	Weight of Sample (gm.)	Volume of Iodine Solution Used (ml.)	Tin Equivalent of Iodine Solution Used (gm.tin/ml.)	Weight of Tin Found (gm.)	Percentage of Tin Found (%)
Total weight = 55.3872 gms. 31 weights					
1 Pb-1	1.3626	35.6	.005434	.1935	14.20
1 Pb-2	.9051	23.25	.005434	.1263	13.97
1 Pb-3	.7965	20.2	.005434	.1098	13.78
1 Pb-4	1.4128	36.0	.005434	.1956	13.85
1 Pb-5	1.2379	31.5	.005434	.1712	13.83
1 Pb-6	1.6402	41.95	.005434	.2280	13.90
1 Pb-7	2.3152	58.25	.005434	.3165	13.67
1 Pb-8	2.0698	63.2	.004520	.2857	13.80
1 Pb-9	2.2809	70.1	.004520	.3169	13.89
1 Pb-10	2.3369	58.0	.005434	.3152	13.49
1 Pb-11a	1.9114	51.4	.005150	.2647	13.85
1 Pb-11b	1.2850	34.6	.005150	.1782	13.87
1 Pb-12	2.7411	84.6	.004520		Yellow precipitate formed, results no good.
1 Pb-13	2.4296	60.15	.004520		Yellow precipitate formed, results no good.
1 Pb-14a	1.9173	51.15	.005150	.2634	13.74
1 Pb-14b	1.7474	46.9	.005150	.2415	13.82
1 Pb-15a	1.5439	40.3	.005150	.2076	13.44
1 Pb-15b	1.5626	Flask broke.....			
1 Pb-16	2.5176	73.4	.004520		Yellow precipitate formed, results no good.
1 Pb-17a	1.4259	35.2	.005150	.1813	12.71
1 Pb-17b	1.3487	33.8	.005150	.1741	12.91
1 Pb-18	2.3849	70.3	.005150		Yellow precipitate formed, results no good.
1 Pb-19	2.6233	65.9	.005150	.3394	12.94
1 Pb-20a	1.2253	30.85	.005150	.1589	12.97

(Continued)

Table 6. Analysis of Specimen 1 Pb (continued)

Sample Number	Weight of Sample (gm.)	Volume of Iodine Solution Used (ml.)	Tin Equivalent of Iodine Solution Used (gm.tin/ml.)	Weight of Tin Found (gm.)	Percentage of Tin Found (%)
1 Pb-20b	1.8260	45.2	.005150	.2328	12.75
1 Pb-21	2.0435	50.7	.005150	.2611	12.78
1 Pb-22	1.2600	36.2	.004520	.1636	12.99
1 Pb-23	2.1671	61.9	.004520	.2798	12.91
1 Pb-24	1.5204	44.2	.004520	.1998	13.14
1 Pb-25	2.0116	58.55	.004520	.2646	13.16
1 Pb-26	1.5737	46.55	.004520	.2104	13.35

Table 7. Analysis of Specimen 2 Pb

Sample Number	Weight of Sample (gm.)	Volume of Iodine Solution Used (ml.)	Tin Equivalent of Iodine Solution Used (gm.tin/ml.)	Weight of Tin Found (gm.)	Percentage of Tin Found (%)
Total weight = 68.3388 gms. 38 weights					
2 Pb-38	1.4457	.....lost.....	.....lost.....	.....lost.....	.....lost.....
2 Pb-37	1.3616	34.9	.005290	.1846	13.56
2 Pb-36	1.1417	29.0	.005290	.1534	13.44
2 Pb-35	1.0280	25.9	.005290	.1370	13.33
2 Pb-34	1.2773	31.2	.005290	.1650	12.92
2 Pb-33	1.2498	30.1	.005290	.1592	12.74
2 Pb-32	1.2526	30.0	.005290	.1587	12.67
2 Pb-31	1.8148	42.75	.005290	.2261	12.46
2 Pb-30	1.9235	46.6	.005290	.2465	12.82
2 Pb-29	2.0180	49.3	.005290	.2608	12.92
2 Pb-28	1.9540	46.7	.005434	.2538	12.99
2 Pb-27	1.8505	44.15	.005434	.2399	12.96
2 Pb-26	2.2766	53.35	.005434	.2899	12.73
2 Pb-25	2.0120	47.25	.005434	.2527	12.56
2 Pb-24	1.6818	39.8	.005434	.2163	12.86
2 Pb-23	2.0447	49.05	.005434	.2665	13.04
2 Pb-22	1.9773	48.4	.005434	.2630	13.30
2 Pb-21	2.0254	50.8	.005434	.2760	13.63
2 Pb-20	2.2072	57.55	.005434	.3127	14.17
2 Pb-19	2.4958	64.2	.005434	.3489	13.98
2 Pb-18	2.1930	.....lost.....	.....lost.....	.....lost.....	.....lost.....
2 Pb-17	2.0704	52.45	.005434	.2850	13.77
2 Pb-16	2.5968	66.8	.005434	.3630	13.98
2 Pb-15	1.9402	50.25	.005434	.2731	14.07
2 Pb-14	2.1286	54.05	.005434	.2937	13.80
2 Pb-13	2.0992	53.55	.005434	.2910	13.86
2 Pb-12	1.7324	43.35	.005434	.2356	13.60
2 Pb-11	2.0967	50.8	.005434	.2760	13.17
2 Pb-10	1.6911	44.05	.005434	.2394	14.15
2 Pb-9	1.5893	40.35	.005434	.2193	13.80
2 Pb-8	1.6067	41.3	.005434	.2244	13.97
2 Pb-7	1.9310	49.4	.005434	.2684	13.90
2 Pb-6	1.8334	49.25	.005290	.2605	14.20
2 Pb-5	1.9859	52.7	.005290	.2788	14.04
2 Pb-4	1.5380	40.7	.005290	.2153	14.00
2 Pb-3	1.6769	44.8	.005290	.2370	14.13
2 Pb-2	1.3438	35.9	.005290	.1899	14.13
2 Pb-1	1.2471	33.3	.005290	.1761	14.12

Table 8. Analysis of Specimen 1 A1

Sample Number	Weight of Sample (gm.)	Weight of Cathode Alone (gm.)	Weight of Cathode Plus Zinc (gm.)	Weight of Zinc Found (gm.)	Percentage of Zinc Found (%)
Total weight = 14.8568 gms. 18 weights					
1 A1-1	.8802	13.7740	13.9924	.2148	24.81
1 A1-2	.8076	13.7705	13.9689	.1984	24.57
1 A1-3	.6955	13.7683	13.9379	.1696	24.39
1 A1-4	.7272	13.7650	13.9348	.1698	23.35
1 A1-5	.7312	13.7647	13.9336	.1689	23.10
1 A1-6	.7162	13.7600	13.9248	.1648	23.01
1 A1-7	.6919	13.7539	13.9223	.1684	24.34
1 A1-8	.7947	13.7518	13.9476	.1956	24.61
1 A1-9	.7563	13.7268	13.9114	.1846	24.41
1 A1-10	.7843	13.7290	13.9199	.1909	24.34
1 A1-11	.8302	13.7319	13.9262	.1943	23.40
1 A1-12	.7647	13.7371	13.9269	.1898	24.82
1 A1-13	.9357	13.7377	13.9665	.2288	24.45
1 A1-14	.8509	13.7407	13.9443	.2036	23.93
1 A1-15	.8144	13.7430	13.9377	.1947	23.91
1 A1-16	.9984	13.7470	13.9822	.2352	23.56
1 A1-17	.8460	13.7770	13.9833	.2063	24.38
1 A1-18	1.2314	13.7485	14.0247	.2762	22.43

Table 9. Analysis of Specimen 2 A1

Sample Number	Weight of Sample (gm.)	Weight of Cathode Alone (gm.)	Weight of Cathode Plus Zinc (gm.)	Weight of Zinc Found (gm.)	Percentage of Zinc Found (%)
Total weight = 10.8065 gms. 18 weights					
2 A1-1	0.4350	13.5377	13.6408	.1031	23.70
2 A1-2	0.5387	13.4577	13.5798	.1221	22.67
2 A1-3	0.4915	13.6408	13.7587	.1179	23.99
2 A1-4	.6365	13.5798	13.7304	.1596	25.07
2 A1-5	.7360	13.7587	13.9225	.1638	22.25
2 A1-6	.5640	13.5364	13.6695	.1331	23.60
2 A1-7	.5258	13.6695	13.7930	.1225	23.30
2 A1-8	.7637	13.7930	13.9737	.1807	23.66
2 A1-9	.6216	13.5375	13.6868	.1493	24.18
2 A1-10	.6150	13.6868	13.8357	.1489	24.21
2 A1-11	.5737	13.5812	13.7198	.1386	24.16
2 A1-12	.5403	13.8357	13.9695	.1338	24.76
2 A1-13	.6336	13.7198	13.8677	.1479	23.34
2 A1-14	.5175	13.4570	13.5812	.1242	24.00
2 A1-15	.5480	13.7197	13.8534	.1337	24.40
2 A1-16	.5525	13.5843	13.7197	.1354	24.51
2 A1-17	.5189	13.4571	13.5843	.1272	24.51
2 A1-18	.9942	13.7304	13.9500	.2196	22.09

Table 10. Analysis of Specimen 1 Cu

Sample Number	Weight of Sample (gm.)	Weight of Cathode Alone (gm.)	Weight of Cathode Plus Silver (gm.)	Weight of Silver Found (gm.)	Percentage of Silver Found (%)	Weight of Cathode Alone (gm.)	Weight of Cathode Plus Copper (gm.)	Weight of Copper Found (gm.)	Percentage of Copper Found (%)
Total weight = 35.4812 gms. 19 weights									
1 Cu-1	2.3238	13.2810	13.3870	.1060	4.56	13.6941	15.8697	2.1756	93.62
1 Cu-2	1.4543	13.3870	13.4548	.0678	4.66	14.8763	16.2502	1.3739	94.47
1 Cu-3	1.0926	13.2850	13.3367	.0517	4.73	17.0594	18.0938	1.0344	94.67
1 Cu-4	1.3030	13.4548	13.5142	.0594	4.56	16.2502	17.4537	1.2035	92.36
1 Cu-5	1.5714	13.4088	13.4850	.0762	4.85	18.0938	19.5664	1.4726	93.71
1 Cu-6	1.6641	13.5142	13.5936	.0794	4.77	17.4537	19.0157	1.5620	93.86
1 Cu-7	2.2121	13.5936	13.7010	.1074	4.86	19.5664	21.6530	2.0866	94.32
1 Cu-8	1.4804	13.3367	13.4088	.0721	4.87	13.2780	14.6475	1.3695	92.51
1 Cu-9	1.4699	13.2805	13.3467	.0662	4.50	13.2829	14.6522	1.3693	93.16
1 Cu-10	1.2775	13.2842	13.3458	.0616	4.82	14.6475	15.8479	1.2004	93.97
1 Cu-11	1.8902	13.5340	13.6200	.0860	4.55	14.6522	16.4173	1.7651	93.38
1 Cu-12	2.5630	13.4114	13.5340	.1226	4.78	15.8479	18.2693	2.4214	94.48
1 Cu-13	2.8383	13.5580	13.6941	.1361	4.80	16.4173	19.0873	2.6700	94.07
1 Cu-14	3.0658	13.4080	13.5580	.1500	4.89	19.5577	22.4697	2.9118	94.97
1 Cu-15	4.1519	13.6200	13.8208	.2008	4.84	20.3508	24.2968	3.9460	95.04
1 Cu-16	1.3784	13.3467	13.4118	.0647	4.69	18.2693	19.5577	1.2884	93.47
1 Cu-17	1.3420	13.3458	13.4080	.0622	4.63	19.0873	20.3508	1.2635	94.15
1 Cu-18	1.1204	13.4850	13.5380	.0530	4.73	13.8208	14.8763	1.0555	94.20
1 Cu-19	1.2821	13.5380	13.5970	.0590	4.60	15.8697	17.0594	1.1897	92.79

## APPENDIX D

SAMPLE CALCULATIONS FOR CORRELATING SAMPLE WEIGHTS OF  
CHEMICALLY ANALYZED SPECIMENS WITH CORRESPONDING TEMPERATURES

Temperature of Sample 1 Pb - 1:

Weight of Sample 1 Pb - 1. . . . . 1.3626 gm.  
 Total weight of all slices from the entire  
 specimen . . . . . 55.3872 gm.  
 Temperature of the end of specimen nearest to  
 sample 1 (hot end) . . . . . 209°C.  
 Temperature of end of specimen farthestest from  
 sample 1 (cold end). . . . . 101°C.  
 Temperature difference between hot and cold ends . 108°C.

Using the above we get:

$$\frac{108}{55.3872} = 1.956^{\circ}\text{C. per gram of sample}$$

Therefore multiply the weight of the sample by 1.956 to give the temperature or distance along the absicca as follows:

$1.3626 \times 1.956 = 2.665^{\circ}\text{C.}$ , temperature difference between 1 Pb - 1 and hot end of specimen.

$209^{\circ}\text{C.} - 2.665^{\circ}\text{C.} = 206.335^{\circ}\text{C.}$ , temperature of sample. Rounded off to one decimal, temperature of specimen of 1 Pb - 1. . . . . 206.3°C.

Temperature of Sample 1 Pb - 2:

Weight of Sample 1 Pb - 2. . . . . 0.9051 gm.  
 Weight of all Samples between 1 Pb - 2 and hot  
 end of specimen (only one in this case, specimen  
 1 Pb - 1). . . . . 1.3626 gm.

Weight of all Samples from 1 Pb - 2 to the hot  
end of specimen. . . . . 2.2677 gm.

Using this total weight and the same number of  
centigrade degrees per gram of sample, as calculated  
in the previous example, we get:

$$2.2677 \times 1.956 = 4.441^{\circ}\text{C.}, \text{ temperature difference} \\ \text{between 1 Pb - 2 and hot end of specimen}$$

$$209^{\circ}\text{C.} - 4.441^{\circ}\text{C.} = 204.56^{\circ}\text{C.}$$

Rounded off to one decimal, temperature. . . . . 204.6°C.

Note:

- (1) All other samples are calculated in a similar way.
- (2) The weights of the samples which were lost during analysis are converted into temperature intervals which were inserted between the plotted points.
- (3) Samples with the same numbers, except for an additional small letter, were themselves cut from the same exceptionally thick slices as shown in Figure 8, page . Weights used for this type of sample were the combined weights of the two with the same number but with different small letters. Compositions used were the simple averages of the two similarly numbered samples.

**APPENDIX E****SPECTROSCOPIC DATA AND SAMPLE CALCULATIONS  
FOR THEIR GRAPHICAL PRESENTATION**

Table 11. Spectroscopic Data and Calculated Temperatures for Specimen 2 Cu

Identity of Sparked Spots		Transmition of 2979.7Å Chromium Line (Film Negative)	Transmition of 3010.8Å Copper Line (Film Negative)	Ratio of Transmition of Cu/Cr (Film Negative)	Indications of Chromium Content or Correlated Ratio of Cu/Cr (Film Negative)	Calculated Effective or Correlated Ratio of Cu/Cr (Film Negative) (mm.)	Calculated Average Approximate Temperature Maintained (°C.)
Film No.	Spot Position No.						
1222	1	37.2	28.5	.84	.94	2.0	31
1222	2	30.0	30.0	1.00	1.12	3.0	33
1222	3	32.2	30.1	.95	1.07	45	102
1222	4	39.0	28.3	.80	.90	99	190
1222	5	28.6	32.8	1.09	1.23	165	297
1222	6	11.6	30.2	1.67	1.88	245	428
1222	7	7.5	31.3	2.10	2.36	325	558
1222	8	31.2	38.4	1.15	1.29	342	586
1222	9	33.3	38.2	1.10	1.24	348	596
1222	10	31.5	39.7	1.15	1.29	353	604
1222	Standard 1	30.2	26.0	.91			
1222	Standard 2	33.6	29.0	.91 Ave.	1.00		
1222	Standard 3	33.0	29.6	.92	.89		
1222	Standard 4	33.7	23.6	.80			

(continued)

Table 11. Spectroscopic Data and Calculated Temperatures for Specimen 2 Cu  
(Continued)

Identity of Sparked Spots		Transmission of 2979.7Å Chromium Line (Film Negative)	Transmission of 3010.8Å Copper Line (Film Negative)	Ratio of Transmission of Cu/Cr (Film Negative)	Indications of Chromium Content or Correlated Ratio of Cu/Cr (Film Negative)	Calculated Effective or Correlated Ratio of Cu/Cr (Film Negative) (mm.)	Calculated Average Approximate Temperature Maintained (°C.)
Film No.	Spot Position No.						
1223	1	42.8	32.5	.82	.86	4	35
1223	2	39.7	33.6	.89	.94	3	33
1223	3	41.8	38.1	.93	.98	58	124
1223	4	43.6	42.3	.97	1.03	125	232
1223	5	44.7	41.9	.95	1.00	192	342
1223	6	40.7	46.8	1.12	1.18	285	493
1223	7	28.7	41.1	1.28	1.35	340	583
1223	8	32.9	47.0	1.30	1.37	342	586
1223	9	34.1	50.5	1.35	1.42	341	584
1223	10	30.1	48.0	1.40	1.48	350	599
1223	11	40.3	46.2	1.11	1.17	0	28
1223	Standard 1	39.6	36.5	.94			
1223	Standard 2	39.6	34.5	.90	Ave. 1.00		
1223	Standard 3	37.6	34.1	.93	.95		
1223	Standard 4	35.9	37.4	1.03			

(continued)

Table 11. Spectroscopic Data and Calculated Temperatures for Specimen 2 Cu  
(Continued)

Identity of Sparked Spots		Transmission of 2979.7 $\text{\AA}$ Chromium Line (Film Negative)	Transmission of 3010.8 $\text{\AA}$ Copper Line (Film Negative)	Ratio of Transmission of Cu/Cr (Film Negative)	Indications of Chromium Content or Correlated Ratio of Cu/Cr (Film Negative)	Calculated Effective or Correlated Ratio of Cu/Cr (Film Negative) (mm.)	Calculated Average Approximate Temperature Maintained ( $^{\circ}\text{C}.$ )
Film No.	Position No.						
1224	12	19.3	36.5	1.50	1.20	405	690
1224	13	22.0	32.0	1.25	1.00	424	720
1224	14	13.5	38.7	1.85	1.48	470	796
1224	15	17.6	40.0	1.67	1.33	500	844
1224	1	23.4	44.0	1.54	1.23	3	33
1224	2	20.7	38.0	1.47	1.17	2	31
1224	3	34.2	40.0	1.10	.88	45	102
1224	4	35.7	42.0	1.12	.90	112	211
1224	6	37.2	48.5	1.22	.98	205	363
1224	7	25.0	49.3	1.62	1.30	312	538
1224	8	17.2	30.0	1.40	1.12	342	587
1224	9	25.9	55.5	1.78	1.42	342	587
1224	10	17.5	45.4	1.85	1.48	348	597
1224	11a	29.2	40.2	1.25	1.00	0	28
1224	11b	40.5	45.5	1.10	.88	0	28

(continued)

Table 11. Spectroscopic Data and Calculated Temperatures for Specimen 2 Cu  
(Continued)

Identity of Sparked Spots		Transmission of 2979.7Å Chromium Line (Film Negative)	Transmission of 3010.8Å Copper Line (Film Negative)	Ratio of Transmission of Cu/Cr (Film Negative)	Indications of Chromium Content or Correlated Ratio of Cu/Cr (Film Negative)	Calculated Effective or Correlated Ratio of Cu/Cr (Film Negative) (mm.)	Calculated Average Approximate Temperature Maintained (°C.)
Film No.	Spot Position No.						
1225	1	22.0	36.1	1.37	1.10	3	33
1225	2	25.3	32.0	1.15	.92	78	155
1225	3	29.6	40.1	1.23	.99	152	276
1225	4	28.4	40.1	1.27	1.01	232	407
1225	5	19.3	42.7	1.68	1.34	326	561
1225	6	14.5	39.2	1.80	1.44	347	594
1225	7	13.6	32.0	1.62	1.29	352	603
1225	8	15.4	33.0	1.55	1.24	358	613
1225	9	14.8	41.1	1.85	1.48	369	630
1225	10	14.5	36.7	1.72	1.37	377	642
1225	11	16.1	35.5	1.60	1.28	390	665
1225	12	20.0	42.5	1.63	1.27	400	682
1225	13	7.0	39.0	2.50	2.00	417	708
1225	14	11.1	36.5	1.95	1.58	429	729
1225	15	12.8	34.5	1.75	1.40	442	750

(continued)

Table 11. Spectroscopic Data and Calculated Temperatures for Specimen 2 Cu  
(Continued)

Identity of Sparked Spots		Transmission of 2979.7 $\text{\AA}$ Chromium Line (Film Negative)	Transmission of 3010.8 $\text{\AA}$ Copper Line (Film Negative)	Ratio of Transmission of Cu/Cr (Film Negative)	Indications of Chromium Content or Correlated Ratio of Cu/Cr (Film Negative)	Calculated Effective or Correlated Ratio of Cu/Cr (Film Negative) (mm.)	Calculated Average Approximate Temperature Maintained ( $^{\circ}\text{C}.$ )
Film No.	Spot Position No.						
1226	Standard 1	27.2	36.0	1.20			
1226	Standard 2	35.7	38.4	1.05	Ave.		
1226	Standard 3	35.2	35.0	1.00	1.14	1.00	
1226	Standard 4	28.9	41.7	1.30			
1226	1	27.6	46.1	1.45		1.27	401
1226	2	15.1	42.8	1.90		1.67	410
1226	3	10.2	39.2	2.10		1.84	423
1226	4	13.7	37.2	1.80		1.58	433
1226	5	4.1	27.5	2.60		2.28	444
1226	6	10.5	40.6	2.10		1.84	451
1226	7	10.0	40.0	2.20		1.93	462
1226	8	7.5	39.0	2.50		2.20	471
1226	9	12.7	45.5	2.10		1.84	477
1226	10	13.0	38.5	1.90		1.67	490
1226	11	11.4	38.0	2.00		1.75	509

Method of calculating and sample calculation for indications of chromium concentration.—The data in columns 3, 4 and 5 of Table 11 were obtained directly from the densitometer. The negative film ratios of Cu/Cr for the standards (0.1% Cr) for each set with standards as shown in column 5, were averaged arithmetically. For any set with standards, these averages were used to convert negative film ratios of Cu/Cr for the other sparked locations of the specimens into values that are completely correlated to, and may be directly compared to, the similarly converted values of the other sets. This is done by simply dividing the negative film ratios of Cu/Cr of the specimens by the average of those of the standards. By this method, with the following data we get for Film 1222:

Position No. 1, uncorrelated ratio of transmission of Cu/Cr film negative . . . . .	.0.84
Standard, average, ratio of transmission of Cu/Cr film negative . . . . .	.0.89

Dividing we get:

$0.84/0.89 = 0.94$ , the correlated ratio of Cu/Cr  
film negative for Film 1222 position No. 1 or the  
indication of chromium content shown in column 6,  
Table 11.

Next, to get the correlation between these above correlated sets and those sets without standards, at least two spark excitation locations on each set without a standard were found that were identical in location with at least two excitation location on a set without a standard. The true composition of identical locations from different sets is assumed to be the same. That data from the set with the standard is

considered to be correct and is substituted in the unstandardized. The instrument factor or the factor between two identical positions on different sets is found by dividing the data of the correct or standardized set by the data of the unknown, unstandardized set. By a simple multiplying operation, this factor is in turn used to correct all the composition indication data of all the other excitation locations in the unstandardized set so that they too will be correlated with all other composition indications in all the five sets. As examples of these last two steps it is found, using Figure 9, page 35, that position 1 of Film 1226, previously correlated by standards, and with an indication of chromium content of 1.27, is equivalent to position 12 of Film 1225 which has a negative film ratio of Cu/Cr of 1.63. Therefore position 12 of Film 1225 is assigned an indication of chromium content of 1.27 also. Now the factor between these two identical locations is found by dividing as follows:

$$1.27/1.63 = 0.78, \text{ the correlating factor between Film 1225} \\ \text{and Film 1226.}$$

This above factor is also the factor needed to correct or correlate all the remainder of the composition data of this unstandardized set, that is, Film 1225. Other identical pairs of spark excitation locations were treated in a similar way, that is, the previously standardized and considered correct indication of composition is substituted for the uncorrected one and the factors found. These factors should, between any two sets, all be the same in value, and were found to be, except for small errors. These factors are averaged to get as nearly correct a value as possible and the remaining uncorrelated composition indications from the unstandardized set are now multiplied by this average factor.

As an example:

Position 15 of Film 1225, uncorrelated ratio of transmission  
of Cu/Cr film negative. . . . . 1.75  
Average correlating factor between Film 1225 and  
Film 1226 . . . . . 0.80

Multiplying we get:

$1.75 \times 0.80 = 1.40$ , the correlated ratio of Cu/Cr film  
negative, for position 15, Film 1225 or the indication  
of chromium content.

Method of calculating and sample calculations for temperatures of spark excitation locations.—The method employed for arriving at a temperature for each excitation location for each of the sets is based entirely upon the application of three simple assumptions pertaining to conductivity of heat. One assumption is that in any cylindrical specimen of uniform diameter, which has different temperatures for two different points along its length, the temperature of all other points between these two points lie between these two extremes of temperature and are directly proportional to their distances from the lowest of these extreme temperatures, the relationship being linear. A second assumption is that in any cylindrical specimen of certain length conducting heat between two points along the direction of its axis, the thermal conduction is directly proportional to, and the temperature drop inversely proportional to, the cross-sectional area of the cylinder, the relationship being linear. A third assumption is that in any cylindrical specimen of a certain diameter conducting heat between two points along the direction of its axis, the

thermal conduction is inversely proportional to, and the temperature drop is directly proportional to the distance between the two points, the relationship being linear.

A necessary first procedure was to analytically divide the Cu - 0.1% Cr specimen shown in Figure 9, into several simple cylinders of known size, all thermally in contact and all conducting heat in series between the two measured extremes of temperature. The ends of the several cylinders are identified in Figure 9 by the small letters, (a), (b), (c), (d), and (e). The two measured extremes of temperature are those at position (a), the outward flowing cooling water at 28°C. and at position (d), the hot junction of the thermocouple at the inner end of the thermocouple tube at 757°C. These cylinders are as follows:

Between (a) and (b), actual length = 5.0 mm., actual cross-sectional area = 416 square mm.

Between (b) and (c), actual length = 25.0 mm., actual cross-sectional area = 31.2 square mm.

Between (c) and (d), actual length = 107.0 mm., actual cross-sectional area = 416 square mm.

Between (d) and (e), actual length = 57.0 mm., actual cross-sectional area = 385 square mm.

Since the cylindrical cross-sectional areas vary, in order to deal with the cylinder lengths all on the same basis, it was needed to reduce each of the lengths to a correlated length. This length is the length the cylinder must have if it were of the same cross-sectional area as the first cylinder listed (416 square mm.) and still had the same thermal conductivity and temperature drop as with its actual dimensions. This was done by multiplying the lengths of the cylinders each by a factor, which factors are the cross-sectional areas of the first cylinder (416 square mm.) divided

by the cross-sectional areas of the cylinder in question. The conductivities of the cylinders with the new correlated lengths are still the same as the conductivities using the actual lengths. These correlated lengths are:

Between (a) and (b), correlated length = 5.0 mm.  
 Between (b) and (c), correlated length = 334.0 mm.  
 Between (c) and (d), correlated length = 107.0 mm.  
 Between (d) and (e), correlated length = 61.6 mm.

Total correlated length between measured temperature extremes, between (a) and (d) = 446.0 mm.

The above result is the length of a cylinder of 446 square mm. cross-sectional area that would have the same heat conductivity between (a) and (d) as the actual specimen used.

To get the relationship between the temperature change of the locations and their correlated distances from the reference point which is the cooling water temperature at 28°C., the total temperature difference between (a) and (d) is divided by the total correlated distance between (a) and (d) as follows:

$$\frac{757^{\circ}\text{C.} - 28^{\circ}\text{C.}}{446 \text{ mm. (correlated)}} = 1.633 \text{ centigrade degrees temperature change per mm. (correlated)}$$

The above temperature change (1.633°C.) is the actual temperature change, that is, increase above 28°C., that takes place for each actual mm. distance moved away from (a) on a cylinder of cross-sectional area of 446 square mm. To get the actual temperature or increase for each actual mm. moved away from the cold end along the specimen on a cylinder of cross-sectional area other than the 446 square mm., 446 is divided by the cross-sectional area of the cylinder in question and this result is

multiplied by the 1.633. These over-all factors are shown as follows:

Between (a) and (b),  $\frac{416}{416} \times 1.633 = 1.633$  centigrade degrees  
temperature change per actual mm.

Between (b) and (c),  $\frac{416}{31.2} \times 1.633 = 21.80$  centigrade degrees  
temperature change per actual mm.

Between (c) and (d),  $\frac{416}{416} \times 1.633 = 1.633$  centigrade degrees  
temperature change per actual mm.

Between (d) and (e),  $\frac{416}{385} \times 1.633 = 1.745$  centigrade degrees  
temperature change per actual mm.

Examples of how these last factors are used are as follows:

- (1.) Position 1, Film 1222 is between (a) and (b) on the specimen and by actual measurement is 2.0 mm. from the cooling water. Multiplying the distance by the appropriate factor and adding in the temperature of the cooling water (28°C.) gets the following after reducing to two significant figures:

$$(2.0 \times 1.633) + 28 = 31^\circ\text{C.}, \text{ the temperature shown in column 8 of Table 11 and used to plot Figure 15.}$$

- (2.) Position 6, Film 1222 is between (b) and (c) on the specimen and by actual measurement is 22.5 mm. from the cooling water, 5.0 mm. being along the whole distance between (a) and (b) by actual measurement and 18.0 mm. being along the small diameter section between (b) and (c) by actual measurement. Each of these distances is multiplied by the appropriate factor and the products added to the temperature of the low temperature end (28°C.) gets:

$$(5.0 \times 1.633) + (18.0 \times 21.80) + 28 = 428^\circ\text{C. the temperature shown in column 8, Table 11 and used to plot Figure 15.}$$

The temperatures of all other positions on the specimen may be found in a similar manner by calculating the total temperature change, in this case rise, between the position in question and the low temperature end and adding this change to the temperature of the low temperature end. Column 7, Table 11 shows the total effective or correlated distances from the low temperature end of the specimen for all positions.

## APPENDIX F

## PHASE DIAGRAMS

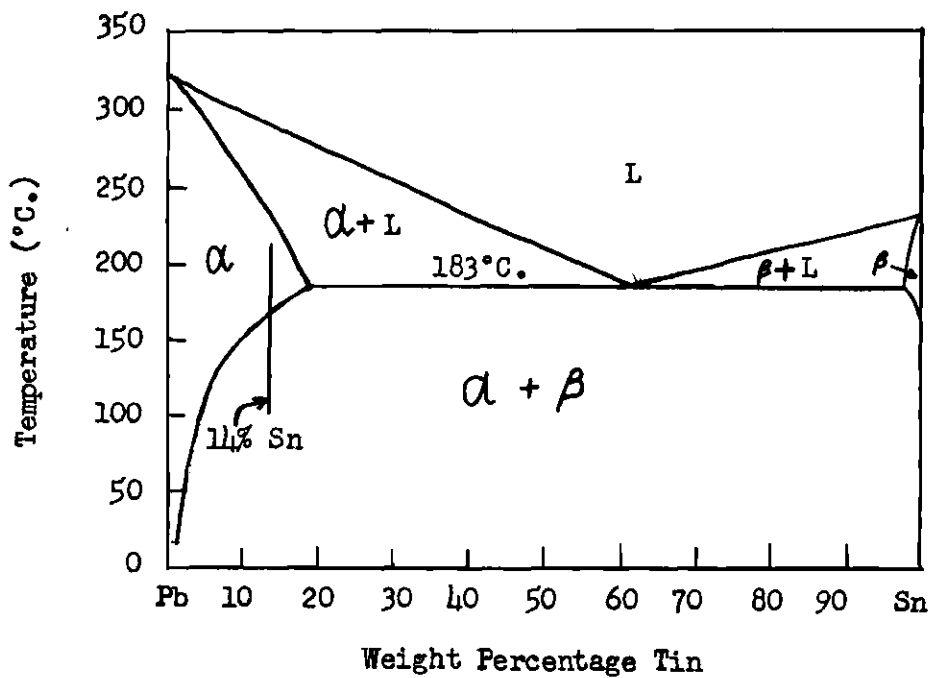


Figure 16. The Lead-Tin Phase Diagram

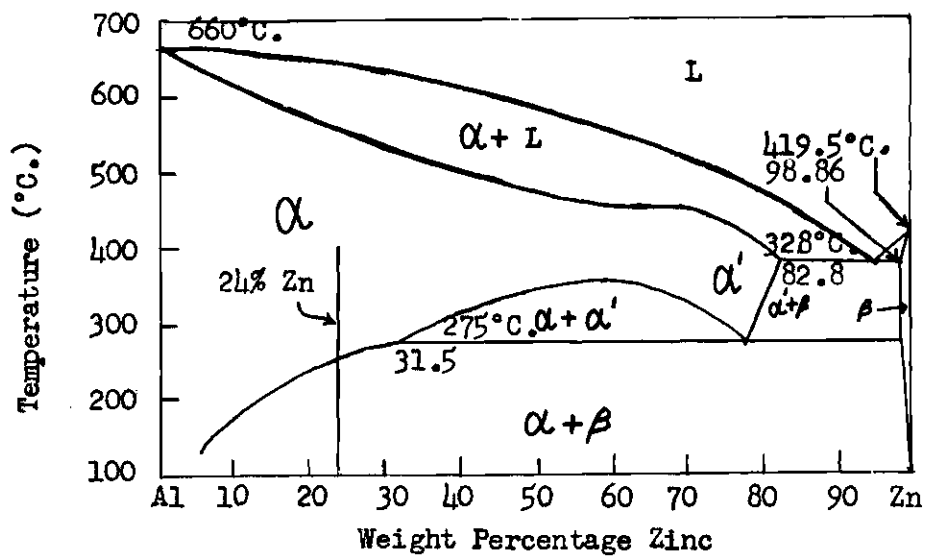


Figure 17. The Aluminum-Zinc Phase Diagram

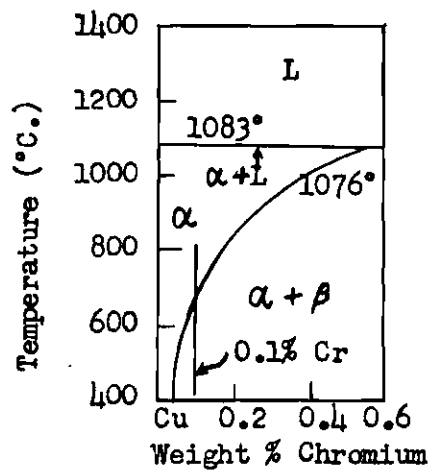
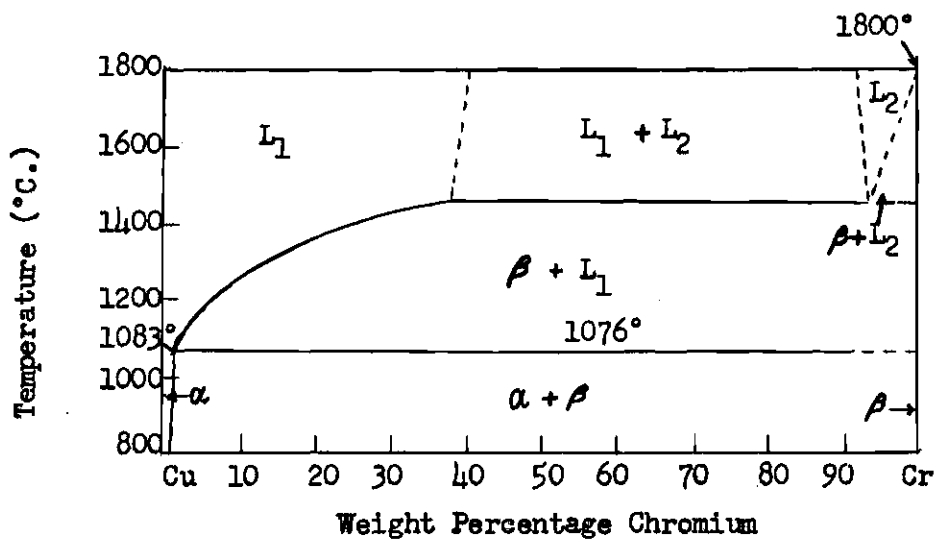


Figure 18. The Copper-Chromium Phase Diagram

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PART II

THE EFFECT OF A PRESSURE GRADIENT  
UPON CONCENTRATION IN BINARY ALLOYS

## CHAPTER I

## INTRODUCTION

Proposal.—The purpose of this second part is to determine theoretically and experimentally the answer to the following question: If a portion of an alloy of uniform composition is maintained at a pressure different from that of the remainder of the alloy, will the composition gradually change as a result of this difference in pressure?

Theoretical foundations.—Consider a piece of a homogeneous alloy at some temperature and pressure as divided into two portions. A condition of equilibrium is that the fugacity of the  $i^{\text{th}}$  component is the same in the two portions, i.e.,

$$f_i = f_i' \quad (1)$$

where one portion is referred to as the prime portion. From Equation 1,

$$\ln f_i = \ln f_i' \quad (2)$$

Now, if conditions are changed, but the equilibrium maintained,

$$d \ln f_i = d \ln f_i' \quad (3)$$

Suppose the change in conditions consists of increasing the pressure on the primed portion, while maintaining constant temperature. As the pressure changes, the concentrations of the components of the alloy will change and Equation 3 becomes

$$\left(\frac{\partial \ln f_i}{\partial N_i}\right)_{P,T} dN_i = \left(\frac{\partial \ln f_i'}{\partial N_i'}\right)_{P,T} dN_i' + \left(\frac{\partial \ln f_i'}{\partial P}\right)_{T,N_i'} dP \quad (4)$$

where  $N$  is the mole fraction.

Equation 4 applies, of course, to each component of the alloy. For a binary alloy, for example,

$$\left(\frac{\partial \ln f_1}{\partial N_1}\right)_{P,T} dN_1 = \left(\frac{\partial \ln f_1'}{\partial N_1'}\right)_{P,T} dN_1' + \left(\frac{\partial \ln f_1'}{\partial P}\right)_{T,N_1'} dP \quad (5)$$

$$\left(\frac{\partial \ln f_2}{\partial N_2}\right)_{P,T} dN_2 = \left(\frac{\partial \ln f_2'}{\partial N_2'}\right)_{P,T} dN_2' + \left(\frac{\partial \ln f_2'}{\partial P}\right)_{T,N_2'} dP \quad (6)$$

In general,  $\left(\frac{\partial \ln f_i}{\partial P}\right)_{T,N_i} = \frac{\bar{V}_i}{RT}$ , where  $\bar{V}_i$  is the partial molal volume of the  $i^{\text{th}}$  component in the solution. However, the derivative  $\left(\frac{\partial \ln f}{\partial N}\right)_{P,T}$  cannot be further reduced without additional knowledge about the particular solid solution under consideration. If it is assumed, as a first approximation, that  $f$  is proportional to  $N$ , then

$$\left(\frac{\partial \ln f}{\partial N}\right)_{P,T} = \frac{1}{N}$$

and

$$\left(\frac{\partial \ln f}{\partial N}\right)_{P,T} dN = \frac{dN}{N} = d \ln N.$$

Equations 5 and 6 now reduce to

$$d \ln N_1 = d \ln N_1' + \frac{\bar{V}_1}{RT} dP \quad (7)$$

or

$$\left( \frac{\partial \ln \frac{N_1}{N_1'}}{\partial P} \right)_T = \frac{\bar{V}_1}{RT} \quad (7)$$

and

$$d \ln N_2 = d \ln N_2' + \frac{\bar{V}_2}{RT} dP$$

or

$$\left( \frac{\partial \ln \frac{N_2}{N_2'}}{\partial P} \right)_T = \frac{\bar{V}_2}{RT} \quad (8)$$

Subtracting Equation 8 from Equation 7, we get

$$\left( \frac{\partial \ln \frac{N_1}{N_1'} \frac{N_2'}{N_2}}{\partial P} \right)_T = \frac{\bar{V}_1 - \bar{V}_2}{RT} \quad (9)$$

Little is known about the partial molal volumes of metals in solid solutions. However, again as a first approximation, it might be assumed that the difference in the partial molal volumes is equal to the difference in the molal volumes of the pure components. For example, tin with an atomic weight of 118.7 has a density of 7.3 and an atomic volume of approximately 16 cc. The corresponding figures for copper are 63.6, 8.9, and 7 cc. Thus, at say 1,000°K., the right-hand side of Equation 9 is approximately

$$\frac{7 - 16}{82.05 \times 1000} \approx -1 \times 10^{-4} \text{ atm.}^{-1},$$

and Equation 9 becomes

$$\left( \frac{\partial \ln \frac{N_{\text{Cu}}}{N_{\text{Sn}}} \frac{N'_{\text{Sn}}}{N'_{\text{Cu}}}}{\partial P} \right)_T = -1 \times 10^{-4} \text{ atm.}^{-1}. \quad (10)$$

If it is assumed that this derivative is constant, it can be investigated to obtain

$$\ln \left( \frac{N_{\text{Cu}}}{N_{\text{Sn}}} \frac{N'_{\text{Sn}}}{N'_{\text{Cu}_2}} \right) - \ln \left( \frac{N_{\text{Cu}}}{N_{\text{Sn}}} \frac{N'_{\text{Sn}}}{N'_{\text{Cu}_1}} \right) = -1 \times 10^{-4} \times \Delta P. \quad (11)$$

Suppose that in the original alloy  $N_{\text{Cu}} = N_{\text{Sn}} = 0.5$ , then

$$\ln \frac{N_{\text{Cu}}}{N_{\text{Sn}}} \frac{N'_{\text{Sn}}}{N'_{\text{Cu}_1}} = \ln 1 = 0.$$

If, for example,  $\Delta P$  is taken as 10,000 atm., Equation 11 reduces to

$$\ln \left( \frac{N_{\text{Cu}}}{N_{\text{Sn}}} \frac{N'_{\text{Sn}}}{N'_{\text{Cu}_2}} \right) = -1. \quad (12)$$

Suppose now that the portion of the alloy which was not compressed is so large relative to the compressed portion that its composition does not change, i.e.,

$$\frac{N_{\text{Cu}}}{N_{\text{Sn}}} = 1, \text{ then } \ln \frac{N'_{\text{Sn}}}{N'_{\text{Cu}}} = -1$$

and

$$\log \frac{N'_{\text{Sn}}}{N'_{\text{Cu}}} = -0.429 = 1.572,$$

therefore,

$$\frac{N'_{\text{Sn}}}{N'_{\text{Cu}}} = 0.37.$$

Thus the tin, since it occupies the larger volume, will escape from the compressed portion and the  $\frac{N'_{\text{Sn}}}{N'_{\text{Cu}}}$  will decrease from its original value of unity to an equilibrium value of only 0.37.

The Effect of Pressure on Rate of Diffusion.—High pressures might be expected to decrease diffusion rates, since, when a material is compressed, the atoms are forced closer together, and their freedom of motion decreased. Little experimental work has been done in this field (1). According to Cohen and Bruins (2), an increase of 1,500 atmospheres decreases the diffusion rate of cadmium in mercury by 5 per cent at 20°C. Radavich and Smoluchowski (3) reported that for the aluminum-copper system at 500°C., a pressure of 7,000  $\frac{\text{kg}}{\text{cm}^2}$  decreases the diffusion by 30 per cent. However, Johnson and Adams (4) found some evidence that pressure increases the rate of diffusion.

## CHAPTER II

## EXPERIMENTAL

Screw-Type Pressure Apparatus.—The following equipment was constructed to exert the necessary high pressure on the sample under study. A steel cylinder 2 inches long and 1 inch in diameter was made. Both sides were flattened at the bottom in order to hold it in a vice. A slot 1/2-inch wide and 1/4-inch high was cut through the cylinder halfway up its side. In the center of the upper half of the cylinder, a 9/16-inch diameter screw was fitted. The sample was placed in the slot under the screw. By tightening the screw, pressure was exerted on that part of the sample under it. It was estimated that the force on the sample under the screw was  $15T$ , where  $T$  is the torque in inch-pounds. Thus, if a pull of 100 pounds were used with a 10-inch wrench, the force would be 15,000 pounds. The bottom of the screw was only 7/32-inch in diameter. Its area, from which the threads had been cut, was, therefore, approximately 0.04 sq. in. and the pressure on the sample was  $\frac{15,000}{0.04} = 375,000$  psi. =  $\frac{375,000}{15} = 25,000$  atm. (Since the interest at first is in merely detecting the pressure effect, there is no attempt at an accurate calculation of the pressure).

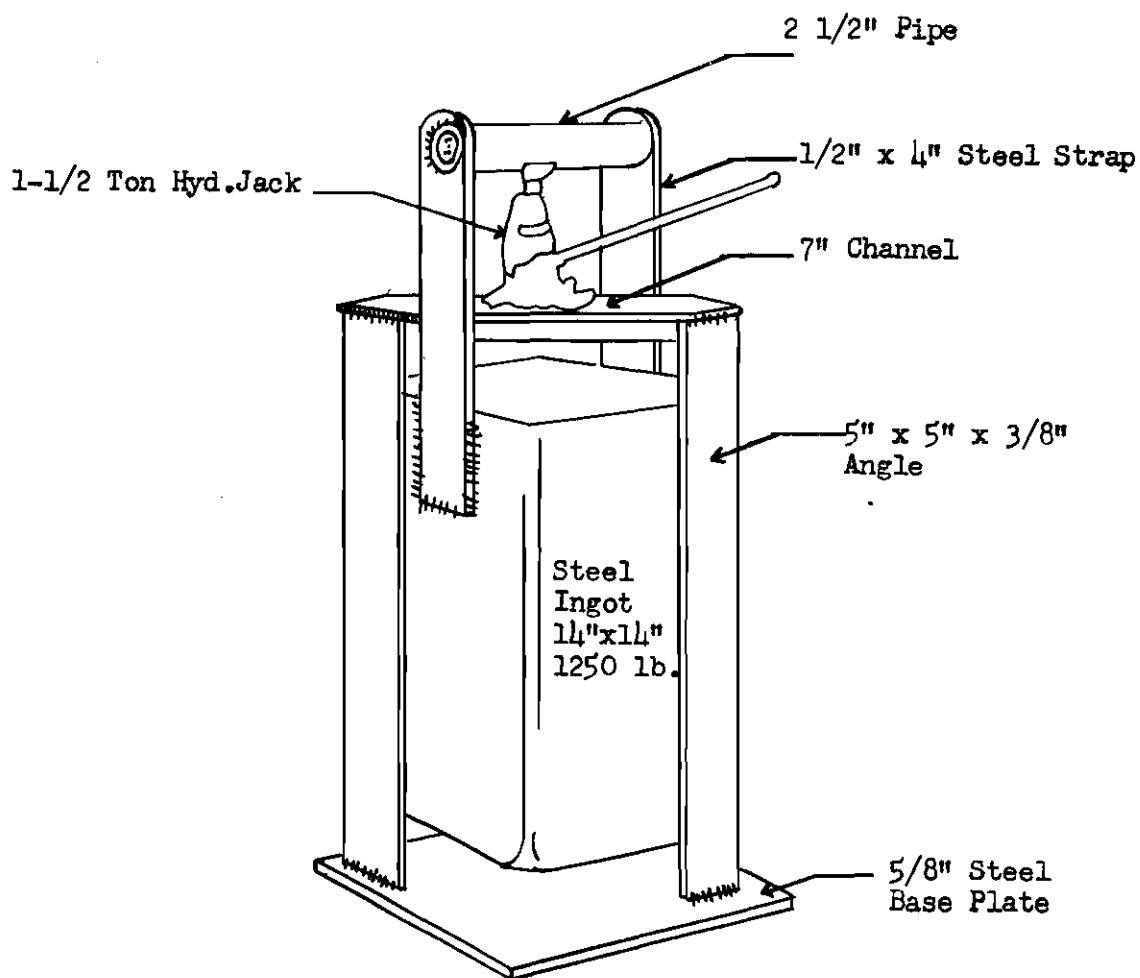
In order to maintain the sample under pressure at the chosen high constant temperature, a 550-watt electric tube furnace was used. The temperature of the furnace was controlled by means of a variac connected to a constant-voltage transformer. The cylinder holding the sample was

placed in a 1 1/4-inch Pyrex tube which fitted snugly into the furnace. One end of the Pyrex tube, which protruded about a foot out of the furnace, was closed with a ground-glass joint and fitted with a three-way stopcock. Through this stopcock the furnace could be evacuated and argon introduced.

Before introducing the sample into the furnace, tests were made to determine both the constant temperature zone of the furnace and the Variac settings which produced certain chosen temperatures. In order to do this, there was used a probe consisting of a steel cylinder, approximately the same size as the pressure cylinder, in which was placed the junction of a chromel-alumel thermocouple.

The main criticism of this method for subjecting the alloys to pressure (i.e., by means of a bolt) is that the pressure is relieved by some of the alloy creeping from under the bolt. In view of this, the bolt was always tightened several times during a given run.

Weight Type Pressure Apparatus.---In order to avoid the above difficulty another apparatus was constructed which would exert a continuous, constant force on the alloy even if the alloy does creep. The force is exerted by a large steel ingot weighing 1,255 pounds. By using a small rod between the ingot and the alloy, a high pressure can be exerted on a portion of the alloy. Figure 1, page 91 depicts the pressure-exerting apparatus which utilizes a weight.



(Sample, Heat Insulated from Base, is Located Directly Below Ingot)

Figure 1. Pressure-Exerting Apparatus

## CHAPTER III

## PROCEDURES, RESULTS AND CONCLUSIONS

Alloys Treated in Screw-Type Pressure Apparatus.--Using the apparatus in which the pressure is exerted on the sample by means of a screw, the following alloys, which at the temperatures of the experiments are all homogeneous, solid solutions, were studied: Cu-10% Sn, Cu-5% Sn, Cu-2% Sn, Cu-15% In, Pb-15% Sn, Al-10% Mg, and Al-24% Zn.

The source of these alloys was as follows: the Cu-Sn alloys were made by the Southern Research Institute; the Cu-In alloy was made in this laboratory; the Al-Mg alloy was contributed by the Dow Chemical Company; the Al-Zn alloy was contributed by the Aluminum Company of America; and, the Pb-Sn alloy was obtained commercially. (These alloys were chosen because of the considerable difference in the atomic diameters of their components. The atomic diameters are Cu-2.56 Å, In-3.24 Å, Sn-2.8 Å, Pb-3.50 Å, Al-2.86 Å, Mg-3.20 Å, and Zn-2.66 Å).

Approximately every ten days during the runs the furnace was turned off, and, as soon as the samples had cooled, the screws were retightened in order to continue to maintain the pressure on the sample. Each time this was done, it was found that the same force that was used on the screw at the beginning of the run moved the screw from approximately 1/8 to 1/4 of the turn. It was realized, of course, that this continuous decrease in pressure was due mainly to the plastic flow of the alloy from the high pressure region. This plastic flow no doubt tended to obscure the effect which was sought.

In general, these experiments failed. The most encouraging results were obtained with the Cu-5% Sn alloy which had been subjected to pressure for two months at 590°C. and are found in the upper half of Table 1, Appendix A. (The copper was determined by electrolysis and the percentage of tin was obtained by difference).

These results appear quite convincing; they seem to indicate that the tin, the element with the larger atomic volume, migrated as theory predicted, from the region of high pressure. However, it is possible that these results were merely fortuitous since those obtained with the other systems, even the Cu-Sn ones, gave no such convincing picture. The results on the other two Cu-Sn alloys, which had had essentially the same treatment as the above one, and found in the lower half of Table 1, Appendix A, are an example.

Using the dead-weight method of exerting pressure, the following systems were studied: phosphor-copper alloy containing 0.014% P, Cu-1% Pb (an eutectic mixture rather than a solid solution), and Cu-2% Sn, a solid solution.

Phosphor-Copper Alloy.—The details of the method will be illustrated by describing the run on the Cu-P system. The specimen consisted of the two halves of a disc  $5/8$ -inch in diameter and approximately  $1/8$ -inch thick. The pressure was exerted on  $1/8$ -inch portions along the straight edge of the two halves by the 1,255 pound weight. The area of the specimen supporting the weight was approximately  $5/8 \times 1/8 \times 2 = 10.64$  sq. inches. The pressure was, therefore,  $1255 \times 64/10 \sim 8000$  pounds per sq. inch  $\sim 550$  atmospheres. When this pressure, instead of 10,000 atmospheres is

substituted into Equation 11 (p.87), one finds that the  $\frac{N_{\text{Sn}}^t}{N_{\text{Cu}}^t}$  should decrease from its original value of 1 to an equilibrium value of 0.945. The temperature used was 300°C., and the time was 59 days. The sample was analyzed spectrographically using the 2553.25 Å phosphorus line and the 2614.3 Å copper line. No significant difference in the relative intensities of these lines was observed when that portion of the alloy that had been subjected to pressure was compared with a portion of the original alloy.

Copper-Lead Alloy.—Copper and lead form an eutectic mixture (melting point, 326°C.) and there is a large difference in their atomic volumes, that of lead being 18 cc. per gram-atom and that of copper being only 7 cc. per gram-atom. The large difference in atomic volume is important since the magnitude of the effect should be proportional to this difference and the eutectic type important since it would be expected that migration would take place more rapidly in this type than in solid solution, since it could take place along grain boundaries.

A run was made on this system for 64 days at 240°C. The sample was then analyzed spectrographically using the 2663.2 Å lead line and the 2997.4 Å copper line with spark excitation. A portion of the original alloy was analyzed similarly at the same time. The results are given in Table 2, Appendix A. The first two columns are the transmission readings on the lead and copper lines, respectively, and the third column is the ratio of lead line intensity to that of the copper line.

It will be noted that although the results on the blank show considerable variation they indicate that the percentage of lead in the blank

is much higher than in that portion of the sample which had been subjected to pressure. These results were encouraging.

Proof that lead had actually moved from the high-pressure zone to the low-pressure zone of the sample would require a similar analysis on the portion of the sample that was not subjected to the high pressure to show that lead had increased in concentration in this region. The small size of the specimen and its semi-circular shape prevented such an analysis. A new run, therefore, was made on a rectangular, rather than a semi-circular, specimen. This run was continued for 38 days. The results are given in Table 3, Appendix A.

The results on the blank and on that portion of the specimen which had been subjected to pressure agreed fairly well with those on the first specimen; however, those on the uncompressed portion of the specimen were lower, rather than higher, than those of the blank. In fact, they were as low as those on the compressed portion. Thus, we conclude that, although lead left the region of compression, it did not enter the region not under compression. On the contrary, lead also left this uncompressed region. This means that lead either evaporated or was removed by the molybdenum sheets that were in contact with the specimens while they were being subjected to pressure. That this latter was the case was proven by qualitative spectrographic analysis of one of these sheets which showed appreciable quantities of lead in the sheet. As mentioned previously, the Pb-Cu alloy is of the eutectic type, i.e., the lead is present as a separate phase. If it had been in solid solution, it likely would not have been removed by the molybdenum.

Copper-Tin Alloy.—A run was made on this alloy for 197 days at 300°C. The sample was then analyzed spectrographically using the 3009.15 Å tin line and the 3010.8 Å copper line with spark excitation. A portion of the original alloy was analyzed similarly at the same time. The results are given in Table 4, Appendix A. The first two columns are the transmission readings on the tin and copper lines respectively and the third column is the ratio of the tin line intensity to that of the copper line.

These results would indicate that, opposite to expectation, the element with the larger atomic volume (tin) had concentrated in the high pressure zone. This is not believed to be the case. It is quite possible that the high ratio of the tin to the copper line intensity in this region is due, not to the higher concentration of tin, but to the different physical conditions of that portion of the specimen that has been subjected to compression.

Conclusions.—Although the pressure effect was not demonstrated, the theory is believed to be sound.

The difficulties facing a successful demonstration are:

1. The selective migration of one of the components of the alloy from the high pressure region is obscured by the relatively larger plastic flow of the alloys as a whole from this region.

2. The problem of attaining and maintaining a high pressure on a portion of the alloy is difficult to solve. A high pressure can be attained, but not maintained, by the screw-type apparatus. The dead-weight type, on the other hand, maintained the pressure but, at least in this case, it

was not very high. Theoretically, of course, there is almost no limit to the pressure that could be attained in this way by using a large enough weight. The upper pressure limit is the lowest pressure at which either the piston or the specimen would collapse.

## APPENDIX A

## TABLES

Table 1. Results from Alloys Tested  
in Screw-Type Pressure Apparatus

Location of the Sample Analyzed	Per Cent Cu		Per Cent Sn	
Completely inside pressure zone	95.33		4.67	
Just inside pressure zone	95.61		4.39	
Just outside pressure zone	94.62		5.38	
Completely outside pressure zone	94.60		5.40	
Far outside pressure zone	94.41		5.59	
	2% Sn Alloy		10% Sn Alloy	
	<u>% Cu</u>	<u>% Sn</u>	<u>% Cu</u>	<u>% Sn</u>
Completely inside pressure zone	97.46	2.54	87.71	14.29
Just inside pressure zone	98.09	1.91	90.16	9.84
Just outside pressure zone	-----	-----	85.58	14.42
Completely outside pressure zone	97.43	2.57	85.58	14.42
Far outside pressure zone	97.74	2.26	86.49	13.51

Table 2. Results from Copper-Lead Alloy, First Run

<u>Transmissions</u>		Ratio $\frac{\text{Pb-2663.2}}{\text{Cu-2997.4}}$
Pb-2663.2 $\text{\AA}$	Cu-2997.4 $\text{\AA}$	
<u>On Sample (Subjected to Pressure)</u>		
66.0	17.9	0.38
47.0	12.7	0.45
39.4	10.4	0.46
57.2	20.7	0.48
<u>On Blank (Unpressed Specimen)</u>		
35.7	45.2	1.2
50.5	46.5	0.93
50.5	37.7	0.79
52.4	38.0	0.76

Table 3. Results from Copper-Lead Alloy, Second Run

<u>Transmissions</u>		Ratio	$\frac{\text{Pb-2663.2}}{\text{Cu-2997.4}}$
Pb-2663.2 Å	Cu-2997.4 Å		
<u>On Sample (Subjected to Pressure)</u>			
51.0	23.9		0.58
51.0	19.5		0.52
67.8	29.1		0.48
61.7	28.0		0.53
<u>On Blank</u>			
48.5	34.2		0.76
40.6	30.0		0.80
50.5	37.4		0.78
38.0	31.4		0.88
<u>On Sample (Not Subjected to Pressure)</u>			
62.5	23.5		0.47
60.0	25.4		0.51
70.0	32.1		0.50
77.0	36.6		0.48

Table 4. Results from Copper-Tin Alloy

<u>Transmissions</u>		Ratio	$\frac{\text{Sn-3009.15}}{\text{Cu-3010.8}}$
Sn-3009.15 Å	Cu-3010.8 Å		
<u>On Portion of Sample Subjected to Pressure</u>			
19.7	15.9		0.89
17.8	11.9		0.82
23.2	14.5		0.78
32.9	25.1		0.84
21.8	15.7		0.84
22.7	20.5		0.94
28.8	23.1		0.97
21.5	18.4		<u>0.92</u>
		Average	0.865
<u>On Untreated Sample-Standard</u>			
16.0	8.7		0.75
20.6	11.2		0.73
23.4	12.7		0.72
22.0	12.2		0.74
17.0	9.5		<u>0.76</u>
		Average	0.74
<u>On Uncompressed Portion of Sample</u>			
24.4	21.5		0.92
32.0	21.0		0.77
19.7	15.9		<u>0.89</u>
		Average	0.86

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