

THERMODYNAMIC PROPERTIES OF LIQUID

GOLD-TIN ALLOYS

A Thesis Presented
for the degree of Ph.D.
in the
University of London

by

AKSHAYA KUMAR JENA

January 1965

ABSTRACT

Review of literature shows that all the physico-chemical properties of liquid gold-tin system point to a number of anomalies. The heats of solution of gold and tin in liquid gold-tin alloys at temperatures 275, 300, 350, 400 and 450°C are measured in a liquid tin solution calorimeter which has been developed to give results with an accuracy better than $\pm 0.2\%$. The partial and integral enthalpies and the heat capacities of the alloys are computed from the experimental data. The scatter in the enthalpies does not exceed ± 20 Cal/mole for most of the alloys. There are anomalies in the system at 10 and 75 At% Au. These are discussed in terms of the nature and energies of the bonds.

CONTENTS

Title Page	1
Abstract	2
Contents	3
CHAPTER I. INTRODUCTION	6
CHAPTER II. PREVIOUS WORK	9
2.1. Introduction	10
2.2. Theories of Metallic Solutions	11
2.3. Equilibrium Diagram of Au-Sn	
Alloys	19
2.4. Physical Properties of Liquid	
Gold-Tin Alloys	20
2.5. X-ray Study	25
2.6. Thermodynamic Properties	29
2.7. Experimental Techniques	34
2.8. Conclusion	38
CHAPTER III. EXPERIMENTAL EQUIPMENT	40
(Calorimetry)	
3.1. Introduction	41
3.2. The Thermostat	42
3.3. Temperature Control System	44
3.4. The Vacuum System	47
3.5. The Crucible Assembly	48

3.6.	Temperature Measuring Unit . . .	54
3.7.	Theoretical Considerations . . .	57
3.8.	Preparation of Material . . .	62
3.9.	Experimental Procedure . . .	63
CHAPTER IV.	RESULTS	71
4.1.	Introduction	72
4.2.	Calorimetric Results	72
4.3.	Derived Results	78
CHAPTER V.	DISCUSSION	88
5.1.	Discussion of Errors	89
5.2.	Comparison of Results with those of other workers	95
5.3.	Applicability of Statistical Theories to the Liquid Gold-Tin System	98
5.4.	Discussion of the Anomalies	103
SUMMARY AND CONCLUSION		117
REFERENCES		119
ACKNOWLEDGEMENTS		128
APPENDIX I.	Heats of Solution of Solid Copper and Solid Nickel in Liquid Tin and Heats of Formation of Some Solid Copper-Nickel Alloys	129
APPENDIX II.	Details of Two Additions	139

APPENDIX III. Summary of Experimental Data	
and Results	146
APPENDIX IV. Expressions for Fitting Curves	
Through Given Sets of Points	
with Minimum Standard Deviation	156
DEFINITION OF SYMBOLS	158
LIST OF DIAGRAMS	162
DIAGRAMS	164-189

CHAPTER ONE

INTRODUCTION

INTRODUCTION

The nature of the liquid metals and particularly their alloys is not well understood⁽¹⁾. The scarcity of accurate physico-chemical data does not help to further our knowledge of metallic solutions. The experimental difficulties associated with high temperature liquid metal research and the complexity of liquid alloy structure have discouraged research in this field. However, the increasing use of liquid alloys in reactors and rockets⁽²⁾⁽³⁾ as heat transfer agents has created the demand for scientific knowledge. This has stimulated renewed interest in liquid metal research, which, in fact, has grown many fold during the past few years⁽³⁾.

In addition to the interest associated with these applications of liquid metals a theoretical interest arises from the basic desire to discover the factors which govern the alloying behaviour of the metals. The absence of long range order in liquids makes the interpretation of some physical properties much simpler. This is the first step towards the understanding of the directional properties of the solid state. Moreover, the data obtained in course of such research will find direct use in many other branches of research and industry.

The gold-tin system is of particular interest in the liquid state. The equilibrium diagram shows the existence of a number of eutectic and peritectic reactions and four compounds⁽⁴⁾. All the X-ray investigations indicate the presence of structure in the liquid state. Hendus⁽⁵⁾ concludes that some of the structure of solid AuSn is retained in the liquid alloy. The thermodynamic data of Kleppa⁽⁶⁾ show unusually high positive values for partial excess entropy of tin. The resistivity values of Roll and Uhl⁽⁷⁾ show a peak at about 25 atomic per cent tin, all of which point to the anomalous nature of the liquid gold-tin alloys. From a practical stand point this system is particularly suitable for investigation as most of the alloys are low melting and the components are readily available in a highly pure state.

During the course of this investigation some results have been obtained on the heat of formation of solid Cu-Ni alloys. These are presented in Appendix I.

CHAPTER TWO

PREVIOUS WORK

PREVIOUS WORK

2.1. Introduction

The physico-chemical properties give indirect evidence of structure. Capacity of liquids to have a volume and low heat of melting⁽⁸⁾ indicate strong bonding in the liquid state. Low compressibility⁽⁹⁾ of liquids and small changes on melting in such properties as volume, electrical resistance, thermal conductivity, specific heat, optical reflectivity and Hall coefficient, all⁽¹⁰⁾⁽¹¹⁾ indicate that the atomic arrangements, thermal vibrations and electronic nature of liquid metals are very similar to those of the solids. However, high fluidity suggests the absence of long range regularity of atomic arrangements. X-ray investigations give a similar picture of the liquid state⁽¹²⁾.

There are, however, a number of apparently contradicting evidences of structure in the metallic liquids. The theory of nucleation⁽¹³⁾ predicts the existence of embryos i.e. clusters of atoms in the liquids and yet the phenomena of supercooling suggests the absence of large groupings of molecules. All the galvanomagnetic properties⁽¹¹⁾ show that the free electron theory is satisfactory for the liquid metals. On the other hand soft X-ray spectra⁽¹⁴⁾ Knight

shifts⁽¹⁵⁾ and some thermodynamic properties⁽¹⁶⁾ suggest that the electronic structure undergoes little modification on melting.

The available physico-chemical data on the gold-tin system and their implications are discussed in the following sections. The theories of solutions correlating structure with the thermodynamic properties are summarised, and a critical review of the available experimental techniques is presented.

2.2. Theories of Metallic Solutions

The thermodynamic property which limits the stability of a phase at constant temperature and pressure is called the Gibb's free energy (G)⁽¹⁷⁾. It is related to two other functions; enthalpy (H) and entropy (S).

$$G = H - TS \quad 2.2.1.$$

H is a function of the internal energy (U), pressure (P) and volume (V).

$$H = U + PV$$

During an alloying experiment the pressure is usually kept constant. Hence the change in 'H' is given by:

$$\Delta H = \Delta U + P\Delta V$$

P and ΔV being small quantities ($P\Delta V < 0.002$ cal/mole)

ΔH is essentially equal to the change in the internal energy.

Entropy is a measure of the disorder in the system⁽¹⁸⁾. This disorder can arise due to atomic arrangement, occupation of available quantum levels for vibration, excitation of electrons to higher energy states and arrangement of the spins of the electrons. These have their corresponding contributions to the entropy. The first term could be calculated from the relative position of the atoms. The last three terms are included in the specific heat of the phase. The relationship between the specific heat and entropy is given by:

$$S_T = \int_0^T C_p d \ln T \quad 2.2.2.$$

$$\text{where, } C_p = (C_{dil} + C_v) = C_{dil} + C_{vib}(T) + C_e(T) + C_m(T) \quad .2.2.3.$$

In the above expression, the terms $C_{vib}(T)$, $C_e(T)$ and $C_m(T)$ represent the vibrational, electronic and magnetic contributions respectively.

C_{dil} is the difference between the specific heat at constant pressure and that at constant volume. It can be shown thermodynamically that the following relationship between C_p and C_v is valid⁽¹⁷⁾.

$$C_{\text{dil}} = C_p - C_v = \frac{TV\alpha^2}{\beta} \quad 2.2.4.$$

Where α = volume coefficient of expansion = $\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$,

and β = compressibility = $-\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$.

The contribution due to atomic vibrations in solids is calculated with the help of the Debye theory of specific heat⁽¹⁹⁾. A Debye solid is a harmonic oscillator. At higher temperatures the real solids become more anharmonic. Therefore, there is a contribution from the anharmonic terms in the lattice vibrations (Canh). This term is likely to be large in the liquids. The electronic specific heat is given by the following equation⁽¹⁹⁾.

$$C_e(T) = \gamma_e T \quad 2.2.5.$$

Where γ_e = a constant = $\frac{1}{2} \frac{\pi^2 n_o R}{T_o}$,

n_o = number of free electrons per atom, T_o = a constant and R = gas constant.

The magnetic term in the specific heat is usually inappreciable for all materials except those showing ferromagnetism or antiferromagnetism.

The free energy, enthalpy and entropy all undergo changes on alloying. Various attempts have been made to explain these changes with the help of statistical

models.

i) Ideal Solution Model

An ideal solution⁽²⁰⁾ is defined as one in which the activity (a) is equal to the mole fraction (x) at all concentrations and all temperatures.

$$a_1 = x_1 \quad 2.2.6.$$

It follows from equation 2.2.6. that

$$\Delta G = \sum x_i RT \ln x_i, \quad \Delta S = -R \sum x_i \ln x_i, \quad \Delta H = 0 \text{ and } \Delta V = 0.$$

These deductions imply that the solution is perfectly random, and the bond strength of unlike atom pairs is the average of the bond strengths of like atom pairs. Such a solution is possible between substances having similar atomic sizes, electrochemical properties and co-ordination numbers. In practice very few solutions approach ideality. This concept is useful in providing a limiting law. The Bi-Sn system is closest to an ideal system of all the intermetallic systems so far investigated⁽²¹⁾. Here $\Delta H = 25 \text{ cal/mole}$.

ii) Regular Solution Model

The concept of a regular solution was first proposed by Hildebrand⁽²²⁾. Guggenheim⁽²³⁾ introduced a modified version of this, known as the strictly regular solution. The assumptions involved are as

follows. a) The co-ordination number (z) is independent of composition. b) The interaction energies e_{ii} , e_{jj} and e_{ij} are independent of composition. c) The mixing is perfectly random. d) The temperature coefficient of w is zero, where

$$w = (e_{ij} - \frac{1}{2}e_{ii} - \frac{1}{2}e_{jj}) \quad 2.2.7.$$

It follows that:

$$\Delta S^e = 0 \quad 2.2.8a.$$

$$\Delta H = (Nzw)x_i x_j \quad 2.2.8b.$$

$$\Delta G^e = (Nzw)x_i x_j \quad 2.2.8c.$$

Where N = Avogadro's number.

For such a solution, the volume change on mixing is zero, the Kopp-Neumann rule is valid and the contribution due to non-configurational factors is zero.

Strictly speaking the regular solution model is not internally consistent, since a non-zero value of enthalpy implies a deviation of entropy from its ideal value. However it may be shown that the excess entropy of solutions arising from the usual magnitude of 'w' is often negligible⁽²⁴⁾. A number of metallic systems like Cd-Zn, Pb-Sn, Ga-In^(24,25) etc. display regular solution behaviour.

The scope of this model has been further increased

by allowing the constant (N_{zw}) in equation (2.2.8.) to vary linearly with composition. This is known as the sub-regular solution model⁽²⁶⁾.

iii) Quasi-chemical Model

This model has all the characteristics of a strictly regular solution except that the mixing is non-random. According to the Quasi-chemical theory the number of unlike atom pairs (ij) in a solution is given by the following expression.

$$\frac{\bar{x}^2}{(N_i - \bar{x})(N_j - \bar{x})} = e^{-\frac{2w}{kT}} \quad 2.2.9.$$

Where $z\bar{x}$ = number of 'ij' pairs,

N_i = number of 'i' atoms,

N_j = number of 'j' atoms.

It can be shown that⁽²³⁾,

$$\Delta G^e = \frac{1}{2} zRT \left\{ (1-x) \ln \frac{\beta+1-2x}{(1-x)(\beta+1)} + x \ln \frac{(\beta-1)+2x}{x(\beta+1)} \right\} \quad 2.2.10$$

$$\text{and } \Delta H = x(1-x) \left(\frac{2N_{zw}}{\beta+1} \right) \quad 2.2.11$$

$$\text{where } \beta = \left\{ 1 + 4x(1-x) \left(e^{\frac{2w}{kT}} - 1 \right) \right\}^{\frac{1}{2}} \quad 2.2.12$$

This model removes the internal inconsistency of the previous model, but like the others it ignores the contributions due to the non-configurational factors.

Predictions of short-range order in solid gold-copper alloys by this theory are in good agreement

with the results obtained by the X-ray diffraction experiments⁽²⁷⁾. The experimental enthalpies of formation of some alloys are also in satisfactory agreement with theoretical values, obtained with the help of this model and the experimental free energy of formation of those alloys⁽²⁸⁾. However for many other alloys this theory is not satisfactory^(29, 30, 31). In one case it has been demonstrated that the non-configurational factors of alloy formation are responsible for disagreement between experiment and theory^(32,33). This theory can be improved by introducing temperature and composition dependent factors into e_{ii} , e_{ij} and e_{jj} . A successful attempt in this direction has been made by Oriani and Murphy⁽³⁴⁾ in describing the behaviour of the dilute solutions of Group Ib metals in liquid tin.

iv) Average Potential Model

The basic premise of the average potential model is that the theorem of corresponding states is obeyed by both the components of the mixture. It is assumed that

a) the total energy can be expressed as a sum of the interactions $e(r_{ij})$ between all possible pairs of molecules i and j , where r_{ij} is the distance between them,

b) the potential energy of a pair of molecules is given by the following universal function.

$$e(r) = e^* \phi\left(\frac{r}{r^*}\right) \quad 2.2.13$$

where r^* and e^* are constants characteristic of the molecular species. The next step in the theory is to determine the average values of e^*_{ii} , e^*_{jj} , r^*_{ii} and r^*_{jj} in the solution. In determining the relevant average values certain assumptions are made.

c) Lennard-Jones law is operative in all the phases. This means; e^* and r^* are the co-ordinates of the minimum of $e(r)$.

d) The solution is random.

$$e) r^*_{ij} = \frac{1}{2}(r^*_{ii} + r^*_{jj})$$

f) e^* and r^* are independent of environment.

The excess free energy and enthalpy are then given by the following expressions⁽³⁵⁾.

$$\begin{aligned} \frac{\Delta G^e}{x_i x_j} = & H_i(2\theta - 9\rho^2) + \frac{1}{2}TCp_i (\delta^2 - 4\theta\delta x_j - 4\theta^2 x_i x_j) - \frac{1}{2}TCv_i [\\ & \theta(x_i - x_j) + \frac{1}{2}\delta]^2 - \frac{3}{2} RT \rho [\theta(x_i - x_j) + \frac{1}{2}\delta + 5\rho] \quad 2.2.15 \end{aligned}$$

and
at

$$\begin{aligned} \frac{\Delta H}{x_i x_j} = & (H_i - TCp_i)(2\theta - 9\rho^2) - \frac{1}{2}T \frac{2dCp_i}{dT} (\delta^2 - 4\theta\delta x_j - 4\theta^2 x_i x_j) \\ & + \frac{1}{2}T \frac{2dCv_i}{dT} [\theta(x_i - x_j) + \frac{1}{2}\delta]^2 \quad 2.2.16 \end{aligned}$$

Where

$$\delta = \left(\frac{e^*_{jj}}{e^*_{ii}} - 1 \right) \quad 2.2.17a$$

$$\rho = \left(\frac{r^*_{jj}}{r^*_{ii}} - 1 \right) \quad 2.2.17b$$

$$\theta = \left(\frac{e^*_{ij} - \frac{1}{2}e^*_{ii} - \frac{1}{2}e^*_{jj}}{e^*_{ii}} \right) \quad 2.2.17c$$

Oriani⁽³¹⁾ has demonstrated that the agreement between the experimentally determined ΔH and that obtained from theory and experimental ΔG is good in both the solid and liquid $Au_{1/2}Cu_{1/2}$ alloys. However, the theoretical values of excess entropy and enthalpy for some other systems are found to be unsatisfactory (29). The inapplicability of Average Potential Model to some of the alloy systems may be due to several reasons. The assumptions (d), (e) and (f) are applicable only in case of atoms having similar size and similar chemical properties. Further, there is enough evidence to doubt the central-force character of the pair interactions in metals and alloys (22, 31, 36, 37).

2.3. Equilibrium Diagram of Au-Sn System

The equilibrium diagram of gold-tin system is drawn in Fig. 2.3.1. There are four intermediate phases⁽⁴⁾. Three of these $AuSn$, $AuSn_2$ and $AuSn_4$ have

very little solid solubility for their components. AuSn crystallises in a NiAs type structure. The other two compounds AuSn_2 and AuSn_4 have orthorhombic unit cells. These are the three intermetallic compounds.

The other intermediate phase is an electron compound⁽³⁸⁾. It is homogeneous between 12 to 16 At%Sn. It has a simple h.c.p. structure. The bond in it is essentially metallic in nature. The crystal structure of gold rich solid solution is simple face-centred cubic and that of tin rich solid solution is tetragonal.

The compound AuSn melts congruently at a relatively high temperature of 418°C and all the others melt through peritectic reactions. There are two eutectic reactions at 280°C and 214°C and corresponding eutectics occur at 29.7 and 94.1 At%Sn respectively.

2.4. Physical Properties of Liquid Gold-Tin Alloys

i) Viscosity

Viscosity is a function of the interatomic forces existing between the constituent metallic species in the alloy. This aspect has been discussed by Yao⁽³⁹⁾. In a nearly ideal solution the atomic shapes and sizes are similar and the interaction between dissimilar atoms is the same as that between similar atoms.

The viscosity in such systems changes linearly with composition. Systems which have an equilibrium diagram in the form of a simple eutectic generally show an expansion of volume and have a positive heat of mixing. The repulsive forces between unlike atoms and the increased mobility of atoms due to volume expansion are reported as being responsible for lower viscosity of eutectic alloys^(40, 41, 42, 43). The presence of compound molecules in the liquid tends to increase the viscosity^(42, 44, 45). This is due to the mechanical effects of the larger size of the molecules. In addition to this, the decreased mobility due to contraction of volume on alloying, increased co-ordination number and increased activation energy would tend to increase the viscosity.

Considerable work has been carried out on the viscosity of liquid tin^(40, 42, 44, 46, 47), with conflicting results. In two cases^(40, 46) the viscosity near the melting point i.e. below 280°C has been reported to be higher than the values predicted by the exponential law⁽⁴⁸⁾. This abnormality has been interpreted in terms of clusters of tin containing about 20 atoms each⁽⁴⁹⁾.

Viscosities of gold and gold-tin alloys have been

reported by Gebhardt et al⁽⁵⁰⁾ over a wide range of temperature. The changes of viscosity and activation energy have been shown in Fig. 2.4.1. The viscosity-composition curve does not show any remarkable change of shape at any composition. Viscosity drops rapidly with increasing tin content and its maximum deviation from linearity occurs at about 30 At%Sn corresponding to an eutectic composition. There are small positive deviations from a smooth curve at 50 and 66 At%Sn. The activation energy at these compositions decreases with temperature. This, probably, is an indication of dissociation at higher temperatures. The maximum deviation of viscosity from linearity at 30 At%Sn could be due to the existence of an eutectic at that composition. The probable existence of any compound molecules around this composition seems to be very unlikely, although it is impossible to be certain, because of the lack of data at higher concentrations of gold.

ii) Resistivity

The resistivity is a function of atomic structure and electronic nature of the metals and alloys⁽¹⁹⁾. A simple liquid metal has a positive temperature coefficient. The resistivity of an alloy arises from

the thermal vibration of the atoms and the lack of periodicity in the lattice. Nordheim⁽⁵¹⁾ has shown that the change of resistivity due to the latter is parabolically related to composition, if the atomic volume, crystal structure and the number of free electrons are the same for both of the components of the solid alloy system. That fraction of resistivity which arises from the thermal vibration is usually linear with respect to composition. The parabolic deviation of resistivity from linearity is also found in the liquid alloy systems having similar components⁽⁵²⁾. Simple eutectic systems show linear variation of resistivity with composition⁽⁵³⁾. The presence of a compound in the liquid alloy is indicated by higher resistivity and lower temperature coefficient.

The electrical conductivities of liquid tin^(10, 54, 55) and liquid gold^(10, 55) are normal in every respect. The resistivity measurements on the liquid gold-tin alloys were made by Roll and Uhl⁽⁷⁾. The deviation of resistivity from linearity and the temperature coefficient of resistivity have been presented in Fig. 2.4.2. There is a prominent peak in the curve at about 22 At%Sn. The curve is nearly linear on both the sides of the peak. Small and relatively

insignificant humps appear at compositions corresponding to the compounds AuSn_4 , AuSn_2 and AuSn . The temperature coefficient is zero at the eutectic composition and it rises slowly on both the sides, showing additional depressions at 38 and 60 At%Sn. The coefficient is small but positive at the peak value of the resistivity.

The peculiar behaviour of resistivity has been interpreted as indicating the presence of a complex at about 25 At%Sn. At higher temperatures, the proposed complex dissociates and releases electrons which tend to keep the temperature coefficient of resistivity at a low value. It has been suggested that the liquid alloy could be regarded as a mixture of the complex and a solution rich in one of the components. The concept of molecules in a liquid metal is somewhat unsatisfactory and an alternative interpretation is considered in the discussion.

iii) Other Properties

Considerable amount of work has been done on the rest of the physical properties of liquid tin, with conflicting results. The surface tension⁽⁵⁶⁾, density^(42, 57, 58, 59) and velocity of sound⁽⁶⁰⁾, all show no deviation from a linear plot with temperature.

On the other hand the ~~thermal~~ conductivity^(10, 61) and self-diffusion coefficient measurements show a non-linear dependence on temperature which can be attributed to the presence of molecular complexes. The optical properties⁽⁶²⁾ and Hall coefficients⁽¹¹⁾ of liquid tin yield values for the conduction electrons, the effective number of which appears to be equal to the actual number of valency electrons.

The density of liquid gold^(10, 63) is linear with respect to temperature. Williams and co-workers⁽⁶⁴⁾ have determined the densities of liquid gold-tin alloys at 800°C, but they point out that the results are not accurate enough to bring out any anomaly.

Liquid gold and liquid tin both have been reported to be diamagnetic⁽⁶⁵⁾. Jan and co-workers⁽⁶⁶⁾ measured the susceptibility of AuSn between 75 and 725°K. Liquid AuSn is diamagnetic.

2.5. X-ray Study

The X-ray diffraction patterns of the liquid metals and their alloys tell us about the atomic arrangements in the liquid state. The monatomic liquid metals give rise to simple diffraction patterns consisting of a high intensity peak at a low value of $\left(\frac{\sin \theta}{\lambda}\right)$ and a number of other peaks of decreasing

intensity at higher angles⁽¹²⁾. In the liquid state, the diffraction pattern of a substitutional alloy resembles that of its solvent, whereas that of a simple eutectic is similar to the superimposed intensity patterns of its components⁽⁶⁷⁾.

The diffraction pattern of pure liquid gold resembles that of a simple liquid⁽⁵⁾. Liquid tin, on the other hand, shows a subsidiary maximum superimposed on the high angle side of the main peak^(5, 67, 68, 69, 70, 71, 72). This hump becomes less prominent at higher temperatures. Williams⁽⁶⁹⁾ summarised all the X-ray data on pure liquid tin along with the more recent ones of his own group. He concludes that there are two types of molecules in the liquid tin. Most of them are molecules of white tin and they give rise to the main peak. The subsidiary maximum is caused by the clusters of grey tin molecules present in the liquid tin. These constitute about 5-25% of the total number of atoms. It is proposed that there is a continuous interchange of atoms between the two groups. This hypothesis is supported by Pauling's theory⁽⁷³⁾ that white tin contains about 25% covalent linkage and by the magnetic susceptibility⁽¹⁵⁾ measurements which lead to the conclusion that there

is no change in electronic structure on melting and that the liquid is a direct extension of the solid.

Hendus⁽⁵⁾ was the first experimenter to examine the liquid gold-tin alloys by the X-ray diffraction technique. He studied alloys containing 50, 29.4 and 16.3 At%Sn. The intensity pattern of liquid AuSn showed double maxima. The maximum at the lower angle occurred at the average $(\frac{\sin \theta}{\lambda})$ value of the components. The position of the high angle maximum coincided with the (012) position of solid AuSn. The patterns produced by the other two alloys were similar to those of pure liquid gold. Hendus concluded that liquid AuSn contained a random liquid and another liquid having a structure similar to that of solid AuSn and that the liquids at other compositions were random. Sauerwald⁽⁷⁴⁾ compared these results with the average values of $(\frac{\sin \theta}{\lambda})$ and observed that the experimental values at 16.3 and 29.4 At%Sn are in agreement with the average values within experimental errors.

Skryshevskii⁽⁶⁷⁾ obtained the intensity patterns of liquid AuSn, AuSn₂ and AuSn₄. He confirmed the existence of double maxima at 50 At%Sn. With increasing tin content the high angle maximum decreased in intensity, whereas the low angle maximum increased

in intensity. He concluded that the double peak at 50 At%Sn is due to order in the liquid. He did not believe that liquid AuSn is a mixture of two types of molecules.

More recently Williams et al^(75,76) determined the diffraction patterns of liquid AuSn, Au_3Sn_2 , $\text{Au}_{70.6}\text{Sn}_{29.4}$, Au_3Sn and $\text{Au}_{82}\text{Sn}_{18}$. These results are essentially **the** same as those obtained by others. All these results have been presented in Table 2.5.1. Williams and co-workers observed that the high angle peak at 50 At%Sn occurred at an angle higher than those of its components, and it increased in intensity at the expense of the low angle peak with increasing gold content and decreased in intensity with increasing tin content. At about 25 At%Sn the low angle peak completely disappeared and the single peak which remained, appeared at an angle higher than the peaks of both the components of the alloy.

It is proposed that there is a compound in the liquid alloy at 25 At%Sn and liquid AuSn is composed of a liquid containing 75At%Au and a random liquid. As the gold content is increased the random liquid is decreased and the other is increased. The random liquid in AuSn has a complementary composition and the

atoms keep on interchanging between the two groups. This concept is supported by the findings of the resistivity measurements on these alloys.⁽⁷⁾

A plot of the value of $(\frac{\sin \theta}{\lambda})$ for the maximum in the X-ray diffraction pattern against composition is shown in Fig. 2.5.1. The value of $(\frac{\sin \theta}{\lambda})$ for the high angle peak is always higher than the average value and it decreases gradually with decreasing tin content of the alloy. This suggests that the compound in solution becomes more loose with increasing gold content. It is possible to extend this argument to support the views of Hendus. Thus the data from the X-ray technique has been interpreted as showing the presence of a compound in the liquid, but the exact nature of the compound is not well established.

2.6. Thermodynamic Properties

It is necessary to understand the nature of the solid alloys in order to evaluate correctly the structural peculiarities of the liquid state. Therefore the thermodynamic properties of solid alloys are reviewed along with those of liquid alloys.

It has been pointed out in one of the previous sections that there are four compounds and one gold-rich terminal solid solution in the solid state.

TABLE 2.5.1.X-ray Diffraction Data on Liquid Au-Sn System

Composition Formula	At%Sn	Temp °C	$(\frac{\sin \theta}{\lambda})$ Value of the peaks.		Investigator
			LHS	RHS	
Sn	100	232	0.178		Williams
		240	0.176	0.240	Skryshevskii
		280	0.176		Hendus
		480	0.175		Hendus
		495	0.177		Williams
AuSn ₄	80	300	0.180	0.235	Skryshevskii
AuSn ₂	66.7	360	0.180	0.227	Skryshevskii
AuSn	50	425	0.190	0.225	Williams
		430	0.185	0.225	Skryshevskii
		440	0.191	0.222	Hendus
Au ₃ Sn ₂	40	412	0.195	0.222	Williams
Au _{2.4} Sn	29.4	295	0.195	0.222	Williams
		340	0.217		Hendus
Au ₃ Sn	25	655	0.220		Williams
Au ₈₂ Sn ₁₈	18	659	0.214		Williams
Au _{5.13} Sn	16.3	750	0.210		Hendus
Au	00	1100	0.210		Hendus

Calorimetric heats of formation data at 0°C , $x_{\text{Sn}} = 0.125, 0.14, 0.155, 0.5, 0.667$ and 0.80 were obtained by Howlett, Mishra and Bever⁽⁷⁷⁾ and those at 242°C $x_{\text{Sn}} = 0.8$ and 0.667 , 350°C , $x_{\text{Sn}} = 0.5$ and 450°C , $x_{\text{Sn}} = 0.13$ and 0.06 were obtained by Kleppa⁽⁷⁸⁾. Biltz et al⁽⁷⁹⁾ determined the heats of formation of AuSn and AuSn_2 at 90°C by aqueous solution calorimetry. Bottema and Jaeger⁽⁸⁰⁾ and Kubaschewski⁽⁸¹⁾ measured the heat content of AuSn between 125°C and 308°C and 222°C and 418°C (M.P.) respectively. These results are consistent with the calorimetric results of Bever and colleagues and the recalculated results (+6.4%) of Kleppa. The data of Biltz and co-workers are however 500 to 1200 cal/gram atoms different.

The heat content of liquid AuSn was determined by Kubaschewski⁽⁸¹⁾. The specific heats derived from these results are about 8% more than those predicted by the Kopp-Neumann rule. This is an indication of the non ideal nature of the liquid alloy.

The relative partial molar heat content of solid gold in liquid tin has been reported over a wide range of temperature^(34, 82, 83, 84, 85, 86, 87, 88, 89, 90).

These measurements show that the heat-capacity of gold in solution is nearly twice the heat-capacity of pure gold. Oriani⁽²⁹⁾ has further shown that the composition dependence of $\Delta \bar{H}_{\text{Au(s)}}$ in dilute solutions of gold in tin (less than 2 At% Au) is almost zero. All these observations lead to the conclusion that gold in solution is in a complex state of association.

The Calorimetric results of Kleppa⁽⁸³⁾ on the heats of formation of liquid gold-tin alloys at 350°C from 0 to 23.4 At% Au and at 450°C from 0 to 30.8 At% Au are the only reliable ones available. The values of ΔH derived from the e.m.f. results of Kleppa⁽⁶⁾ are not very reliable and also not in agreement with the calorimetric results. However reliable data for the activity of the components at 600°C have been obtained from the e.m.f. results. These are in good agreement with those of Yanko et al⁽⁹¹⁾ measured at 269, 320 and 370°C and between 94.5 and 99.8 At% Sn. Both the components show rather strong negative deviation from ideal solution behaviour. A plot of partial entropies against composition obtained from the temperature coefficients of e.m.f. at 600°C, is shown in Fig. 2.6.1. Gold shows strong negative

deviation.* This could not be due to loss of randomness caused by the existence of clusters in the liquid alloy. On the other hand tin shows rather less pronounced negative deviation and indeed positive deviation at about 50 At% Au. Association in the liquid would only decrease the entropy. Therefore there must be other factors, like thermal, electronic and magnetic specific heats, size effects, changes of co-ordination number etc, influencing the partial entropies of the components. It has already been pointed out that the specific heats of components in solution are much different from those in the pure state. It is likely that the specific heat is making a definite contribution to the entropies.

It is not possible to generalise any more, because of the various limitations of the available data. Nevertheless it is quite clear that the liquid gold-tin alloys are anomalous. The available thermodynamic data are few and more thermodynamic data, over a wider range of temperature and composition are necessary before any further attempt is made to understand these alloys.

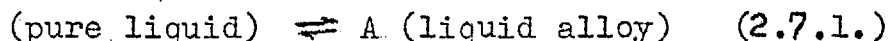
* Negative deviation in Fig. 2.6.1. corresponds to positive ΔS^e .

2.7. Experimental Techniques

The changes of free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying the formation of an alloy are the thermodynamic properties of importance. In principle, these parameters can be determined by any one of the following techniques⁽⁸⁾:

- i) E.m.f. Technique.
- ii) Equilibrium Measurements.
- iii) Calorimetric Methods.

In the methods of the first group a reaction of the form



is harnessed in an electrolytic cell and the reversible electro-motive force is measured. The free energy difference is then linearly related to the e.m.f. The enthalpy is obtained from the e.m.f. and its temperature coefficient and the entropy is calculated from the temperature coefficient. However the e.m.f. measurements are sometimes associated with errors of undetectable source. This leads to a factor of uncertainty in the results. Chipman, Elliot and Averbach⁽⁹²⁾ have described the difficulties associated with this technique and have suggested measures to counter these difficulties. If the experiment is

carried out with sufficient care and self criticism, it yields good values for the free energy change. The temperature coefficients, however, cannot be determined with much accuracy, and small scatters in e.m.f. value will introduce large errors in the temperature coefficient. Thus, it is not easy to obtain reliable values for ΔH and ΔS from such measurements.

The equilibrium techniques involve the measurement of either the vapour pressure of one of the components or the activity of one of the components present in another phase in equilibrium with the alloy. This method is again involved with all the difficulties associated with the e.m.f. method. In any case, this method is not suitable for the present purpose. The vapour pressure technique is applicable only when one of the components has high vapour pressure, whereas gold and tin, both have low vapour pressures. The technique which involves equilibrating a second phase is applicable to special cases at higher temperatures. Moreover this method is associated with difficulties due to thermal diffusion.

Calorimetry consists of directly measuring the enthalpy changes (ΔH) in a calorimeter. This

technique involves fewest corrections and less uncertainty. The results can therefore be quoted with an estimated error which can be relied upon. In order to obtain values for ΔG and ΔS the calorimetric values for ΔH must be supplemented by low temperature heat capacity values down to the absolute zero, and the techniques used in obtaining such data are very much specialised.

The foregoing discussion shows that the e.m.f. measurements can give good values for ΔG and not very reliable values for ΔH and ΔS , and that the calorimetric technique can give good values for ΔH and the supplementary data required to obtain values for ΔG and ΔS will necessitate the use of special experimental technique and equipment. It is therefore better to measure free energy changes by the e.m.f. technique, the enthalpy changes by calorimetry and to obtain the values for ΔS from the thermodynamic relationship between the three parameters.

There are a number of calorimetric methods available for the determination of enthalpy of formation. These could be classed under the following heads⁽⁹³⁾.

i) Acid solution calorimetry.

- ii) Combustion calorimetry.
- iii) Direct mixing calorimetry.
- iv) Metal solution calorimetry.

Acid solution calorimetry was once very popular, but at present it is hardly used, because of its following drawbacks.

- a) The heats of solution are large compared with the heats of formation in metal systems.
- b) It is limited to low temperature measurements.
- c) The rate of solution is sometimes too slow.
- d) Final reaction product is often uncertain.

The problems of combustion calorimetry are very much similar to those of acid solution calorimetry. The heat effects on reaction are large and the reaction products are usually in undefined states of oxidation.

The direct mixing calorimetry consists of mixing two liquid metals in a calorimeter and measuring the heats of mixing. This method requires large quantities of pure metals, which are in some cases uneconomical. The imperfect and slow mixing of the constituents, oxidation of the components and inexact knowledge of the temperature of the added melts give rise to most of the other difficulties.

The principles of metal solution calorimeter are the same as those of acid solution calorimeter.

But it uses a liquid metal or alloy as the solvent.

It possesses the following advantages over others:

- i) The heats of solution are generally of the same order of magnitude as the heats of formation. Hence multiplication of experimental errors inherent in such processes are reduced.
- ii) The final state of the solute is well defined.
- iii) The side reactions are absent.
- iv) The rate of the solution process can be enhanced by working at reasonably high temperatures.
- v) Widely different heat effects can be measured.

These aspects of calorimetry have been discussed by Kubaschewski and Hultgren⁽⁹⁴⁾. Out of the various techniques available the metal solution calorimetry is well suited for the present purpose.

2.8. Conclusion

The structures of liquid metals are similar in many respects to those of solids. However the properties of liquid gold-tin system show several anomalies. The X-ray data show intensity peaks with subsidiary maxima and suggest the existence of a complex in the liquid state at about 25 At%Sn. A similar picture is

given by the resistivity which shows a maximum at 22 At%Sn. On the other hand the viscosity and density appear not to support the above hypothesis.

In addition to these structural and physical peculiarities the thermodynamic properties vary widely from any simple model of a liquid alloy. The activities show strong negative deviation. The heat of formation is large and negative. The excess partial entropy of tin is positive. The relative partial heat content of gold shows strong temperature dependence, but zero composition dependence.

From this survey it appears profitable to examine the thermodynamic parameters in this system and liquid tin solution calorimetry is apparently the most appropriate experimental technique..

CHAPTER THREE

EXPERIMENTAL EQUIPMENT

(CALORIMETRY)

EXPERIMENTAL EQUIPMENT (CALORIMETRY)

3.1. Introduction

The heats of formation of liquid gold-tin alloys have been determined with the help of a liquid tin solution calorimeter. This metal solution calorimeter is essentially an isothermal calorimeter. It has a constant temperature environment. The space between the environment and the crucible containing the solvent metal, is kept under vacuum in order to reduce the heat transfer and the oxidation of the solvent metal. The heat transfer coefficient is derived from the rate of approach to equilibrium of the crucible and contents. The heat capacity of the calorimeter is determined by altering the heat content of the system by a known small amount. Any unknown heat effect is calculated in terms of the known temperature change of the solvent metal, the heat exchanged with the constant temperature environment and the heat capacity of the calorimeter.

The primary aim in designing this calorimeter has been to achieve a constant temperature environment and a minimum and rational heat transfer coefficient. The theoretical aspects of the design have been discussed by Kravitz and Leach⁽⁹⁵⁾.

3.2. The Thermostat

The environment is designed so that its temperature is stable to at least $\pm 0.001^{\circ}\text{C}$. It consists of a large molten salt bath in which is immersed an evacuated steel container. Out of the various available techniques (88, 93, 96, 97, 98, 99) a salt bath, in addition to being cheap is easily maintained at an uniform temperature with the help of forced convection⁽¹⁰⁰⁾. The salt is a 50% mixture of sodium nitrate and potassium nitrate and is completely fluid at 228°C . It is contained in a steel vessel 26" in diameter, 33" deep with a wall thickness of $\frac{1}{4}$ ". The thermal insulation is provided by an 8" thick layer of "Selfrac" lightweight firebricks. The thermal conductivity of these bricks is approximately 5×10^{-4} cal/sec/cm²/cm/ $^{\circ}\text{C}$ at 300°C . The outer container is a $\frac{1}{8}$ " thick galvanised mild steel vessel 42" in diameter and 41" in depth.

The evacuated container is supported by a mild steel frame which is kept partially immersed in the salt bath. The top plate of the frame supports the insulating material for the cover of the bath. It consists of a layer of "Sindanyo" and a 4" thick layer of glass wool followed by a final layer of "Sindanyo".

This arrangement prevents the salt from saturating the glass wool and reducing its insulating properties.

The salt bath is heated by seven coaxial MgO insulated heaters clamped to the outside of the container. These are 84" long, $\frac{5}{16}$ " diameter, 680-watts, 250 volts, inconel sheathed industrial heating elements supplied by A.E.I. Six of these heaters are vertical and are equispaced in groups of two. The seventh is placed along the circumference of the salt container at the salt level. The terminals of the heaters are taken out through holes in the outer container and are connected at room temperature in parallel to a 20 Amp. Variac. This arrangement was necessary to prevent the salt from creeping into the insulation of the heaters and causing electrical breakdown. The power to the variac is supplied by a 3 KW constant voltage ($\pm 1\%$) transformer. Three 1KW heaters are placed in-between the other heaters in order to serve as boosters. These are connected in parallel directly to the mains.

The temperature of the salt bath is kept uniform by continuous stirring. The stirrer system consists of a 12-bladed turbine, mounted on a pinion and driven by a spur gear, both being situated at the base

of the salt bath. The speed ratio of this combination is 3/17. The pinion and the spur gear are mounted on corrosion resistant alloy steel bearings, supplied by Hoffmann Manufacturing Co. A ½" diameter mild steel shaft passes through a self aligning bearing mounted on the top of the salt bath and connects the pinion to a ½ h.p. synchronous motor. The motor drives the pinion at 280 r.p.m. giving a net speed of 50 r.p.m. to the turbine. This speed has been found to be suitable⁽¹⁰¹⁾.

The salt bath is effectively divided into two chambers by a 21" diameter, 20" deep stainless steel cylinder mounted on the frame which carries the vacuum container. This arrangement which directs the flow of salt caused by the turbine forces the salt to move upwards in the outer chamber and downwards in the inner chamber. Thus fresh salt always comes in contact with the outside wall of the bottle and the inside wall of the salt container (Fig. 3.2.1.).

3.3. Temperature Control System

The required control of temperature is achieved by varying the voltage applied to the control heater which is wound round the stainless steel cylinder.

The heater is a 42 feet long, 0.1" diameter, 500-watts, stainless steel sheathed industrial heating element. It is powered by the stabilised source through a variac and a saturable reactor.

A platinum resistance thermometer, with a temperature coefficient of about $0.36 \Omega/^{\circ}\text{C}$ ($T \approx 350^{\circ}\text{C}$) is used to sense the temperature fluctuations of the salt bath. The resistance bulb of the thermometer is connected to three lead wires of platinum which make electrical contact with three copper wires through pools of mercury. These pools of mercury are kept immersed in an ice-water bath. This arrangement eliminates thermal and electro-chemical e.m.f.s, which have caused a lot of trouble in the past. The copper lead wires are connected to a Wheatstone bridge so that the thermometer forms one arm of the bridge. The bridge is powered from a 6V battery and a Tinsley moving coil reflecting galvanometer (Type 4500A) detects out of balance currents. A beam of light from a 24-watt bulb is reflected by the galvanometer mirror and falls on a specially mounted cadmium sulphide photoconductive cell (Mullard ORP 90). It has an internal resistance of about 4000Ω when the cell is fully lighted and virtually infinite resistance

in the absence of light. The varying resistance of the photocell due to changes in light intensity varies the current drawn from a 12V battery. A magnetic amplifier is used to amplify the current which is then passed through the control winding of a saturable reactor, which is connected in series with the control heater. The voltage (A.C.) applied to the control heater is changed with change of current (D.C.) in the control winding.

The Circuit diagram is shown in Fig. 3.3.1.

A calculation shows that a change of 0.001°C in the salt temperature is represented by a change of 10^{-9} amps in the galvanometer, whose sensitivity is 1600 mm/ μA at one meter. The photocell is placed at a distance of 1.3 meters, so that the rectangular image of the light spot moves about 2 mm/ 0.001°C . When the spot is fully on the cell the current in the control heater is very small. On the other hand, when the spot is away from the photocell, the current is 1.2 to 1.5 amps corresponding to about 10% of the power input to the salt bath. Since the width of the spot is 12 mm. and the fluctuations in the control heater current is ± 0.1 amps, the salt bath temperature as measured by the resistance thermometer is well

within the required limits.

3.4. The Vacuum System

It has been pointed out that the vacuum container is in essence the constant temperature environment. It is a flanged mild steel vessel, 10" in diameter, 12" deep and $\frac{3}{4}$ " thick. The access is through a 5" diameter, 20" long and $\frac{1}{2}$ " thick flanged cylindrical neck, giving it the general shape of a long necked bottle. The inner surface of the bottle is plated with chromium in order to reduce oxidation and prevent it from being attacked by molten tin. The bottom half of the neck is kept immersed in the salt bath, so as to decrease the heat losses from the bottle. The top quarter of the neck, containing the vacuum seals is water cooled. The neck supports a 5" diameter, 4" long flanged brass cylinder which carries the vacuum gauge heads and the connections to the vacuum pumps (Fig. 3.2.1.).

A vacuum, better than 10^{-5} mm Hg. is maintained with the help of an Edwards backing pump (Model ISC 50B) and a 2" water cooled oil diffusion pump. This combination initially takes about 5 minutes to reduce the pressure to 5×10^{-4} mm Hg. and a further hour to reduce the pressure to a value lower than

10^{-5} mm Hg., as measured by a Penning type vacuum gauge. However, any increase in pressure due to additions of samples is reduced to 10^{-5} mm Hg., in about 10 to 15 seconds.

All the vacuum seals at the room temperature are made with neoprene rubber O-rings. The seal in the salt bath between the bottle and the neck is made with a 22 gauge annealed copper wire. The wire is welded to form a closed loop, annealed, cleaned and bolted tight between the flanges.

A high vacuum in the bottle reduces the errors due to oxidation of metals, brings the thermal disturbances to a minimum and decreases the heat transfer coefficient by virtually eliminating conduction and convection due to gases. According to Smoluschowski⁽¹⁰²⁾ the heat transfer coefficient (k') is proportional to pressure (P) and $k' = 0$ when $P = 0$, at pressures below 0.05 mm Hg. Thus at low pressures the heat transfer due to gas conduction and convection between different parts of the calorimeter will be greatly reduced.

3.5. The Crucible Assembly

The calorimeter proper consists of a crucible to contain the molten metal and its supports, a mechanism

to stir the metal and an arrangement for introducing specimens.

The molten metal is contained in a spun molybdenum crucible 2" in diameter and 3" deep with a wall thickness of 0.04". It weighs approximately 147 gms. The depth of liquid inside the crucible is maintained at 1.7". The crucible is supported by three steel pins, each being 1 mm. in diameter. The total area of contact is less than 0.2 sq. cm. The pins are screwed into three stainless steel supports, which are suspended from a radiation shield located on three pegs situated at the bottom of the neck of the bottle. This radiation shield with four others is suspended by three stainless steel rods from the top plate (Fig. 3.5.1.).

The position of the crucible is such that the centre of the metal bath is 5" distant from the side and bottom walls and 7" distant from the top. This arrangement leaves the metal bath at the centre of a temperature uniform zone (Fig. 3.6.2.). The distribution of temperature inside the bottle has been measured and has been found to be satisfactory. That is to say the temperature reading from a bare Pt/Pt-13%Rh thermocouple was taken as a function of

its position inside the bottle. The temperature was constant to $\pm 0.01^\circ\text{C}$.

For problems of heat transfer the present system can be approximated to a case of two concentric spheres of diameter 10" and 2" respectively. It can be shown⁽¹⁰³⁾ that the net transfer of energy by radiation per second (q) between two concentric spheres is given by the following expression.

$$q_{1 \rightarrow 2} = A_1 \sigma (T_1^4 - T_2^4) \frac{1}{\frac{1}{e_1} + \frac{A_1}{A_2} \frac{1}{e_2} - \frac{A_1}{A_2}}$$

Where, A_1 = surface area of the inner sphere,

T_1 = absolute temperature of the inner sphere,

e_1 = emissivity of the inner sphere,

and σ = radiation constant.

The subscript 2 referring to the same parameters for the outer sphere.

For our present purpose,

$$\frac{A_1}{A_2} \approx \frac{1}{25}$$

The factor ($f(e)$) containing all the terms in emissivities in the equation for 'q' above is then given by;

$$f(e) = \frac{1}{e_1} + \frac{1}{25} \cdot \frac{1}{e_2} - \frac{1}{25}$$

It is easily seen that when e_1 is changed from one to 0.25, $f(e)$ is increased by 300%, whereas $f(e)$ increases by about 5% when e_2 is changed from one to 0.25. This analysis shows that the condition of the inner surface of the bottle is not very important. On the other hand, maintenance of a bright surface on the crucible is definitely desirable. For this reason the crucible is always given a very good polish before it is used for any experiment.

The metal bath is stirred in order to obtain uniformity in temperature and composition. The stirrer consists of a 36" long metal tube and a number of blades attached to the lower end. The stirrer shaft passes through a bearing situated in the bottom radiation shield, a double Wilson seal mounted on the top plate, and two other bearings. The hollow stirrer tube serves as a thermocouple well. The twisting of the couple is prevented by producing an oscillating motion. The rotating motion of a constant speed motor mounted on the top plate is converted into an oscillating motion with the help of a crank and a connecting rod. The stirrer makes 96 cycles/min. In a half cycle a blade sweeps over 90° and during the other half it swings back to its

original position.

Two types of stirrers have been used during this investigation. Initially the stirrer was made entirely of stainless steel; later the portion immersed in the liquid metal was changed to molybdenum due to its greater resistance to attack by tin containing dissolved metal. The stainless steel stirrer is made by electron beam welding a 2" sq., 0.015" thick stainless steel sheet to one end of a 0.275" diameter and 0.010" thick stainless steel tube. The sheet is cut and bent so as to give four vertical 1" high and 0.4" wide blades. It was found to be suitable for experiments with pure tin, but it is highly unsuitable for metal baths containing more than 10 At% Au. Stainless steel is badly attacked by gold-rich solutions. A special molybdenum stirrer was prepared to deal with these solutions. A blind hole was drilled along the axis of a 0.41" diameter 4.1" long molybdenum rod. It was ground to the required size giving a wall thickness of 0.020" and three blades made out of one piece of molybdenum sheet were mechanically pressed into position. Finally a 0.255" bore and 0.010" thick stainless steel tube was brazed to the open end of the stirrer with a special

silver-palladium alloy. The details of this stirrer are shown in Fig. 3.5.2.

The samples are added to the calorimeter through a 1" straight through diaphragm valve. It is soldered to the top plate of the vacuum system, which supports the crucible assembly. The valve opens to a ½" stainless steel tube which leads the sample into the crucible. A number of bends are given to this tube in order to reduce the speed of the descending specimen. The top of the valve is connected to a 12 mm. bore pyrex tube through a Wilson seal. The free end of the tube is slightly bent and then joined to a B.19 socket. Another piece of similar glass tube is closed at one end and is bent to form a 90° angle. The free end is joined to a B.19 cone. This tube, carrying the specimen, is connected to the addition system. The valve is opened and the glass tube is pushed down through the valve. The specimen is added by rotating the specimen tube on the ground glass joint (Fig. 3.5.3.).

There is provision for evacuating the specimen chamber before it is connected to the main vacuum system. A small auxiliary valve is soldered to the top of the diaphragm valve. The auxiliary valve is

connected to the backing pump for purposes of evacuation.

3.6. Temperature Measuring Unit

The temperatures are measured using thermocouples and a potentiometer unit. A Tinsley vernier potentiometer (Type 4363) is used in conjunction with a Tinsley photocell galvanometer amplifier (Type 5214) and a Tinsley indicating galvanometer (Type SS2 45E). The potentiometer is capable of reading 0.190100 V in units of $1\mu\text{V}$. It draws its power from a 2V battery and is standardised against a standard cadmium cell. The potentiometer is connected to the amplifier through a thermal compensator which includes a four place sensitivity switch. The compensator is used for backing off any unwanted e.m.f. present in the measuring circuit. There is provision for varying the amplification of the preamplifier. The indicating galvanometer has a built in 10 cm scale. With a thermocouple of 60Ω resistance, the maximum sensitivity of the measuring unit, as measured by the indicating galvanometer is about $5\text{ cm}/\mu\text{V}$. However operating sensitivity is maintained between 2 to $3\text{ cm}/\mu\text{V}$, as it is enough to permit the temperature readings to be estimated to better than $\pm 0.001^\circ\text{C}$.

In order to reduce vibrations, the galvanometer and the amplifier are mounted on a wall bracket.

36 S.W.G. chromel-alumel couples are used for measuring the temperatures. These consist of lapped and braided conductors, braided overall with glass. One end of the couple is welded in a carbon arc without any flux. This junction is attached to a clip made out of 0.004" stainless steel sheet (Fig. 3.6.1.) and is pushed down to the bottom of the hollow stirrer shaft. The clip fixes the position of the couple and also ensures good thermal contact with the tube wall. In order to minimise electrical pickup due to the movement of the thermocouple wires, that part of the couple near the penning gauge head is protected by μ -metal foils and the rest of the couple is protected from draught by a rubber tube. The free ends of thermocouple wires are soft soldered to 26 gauge copper wires. The junctions are kept immersed in small pools of oil maintained in glass tubes. These are placed in a thermos packed with wet and finely ground ice. The top of this cold junction is well insulated and protected from draught. The copper wires are connected to the potentiometer.

It has been found that the thermocouple wires,

as supplied, do not give reproducible results as they show sensitivity to temperature gradients inside the bottle. This effect is eliminated by annealing all couples before use. This is done electrically. An alternating current from a variac is passed through the couple and is gradually increased to 1.7 amps, maintained there for fifteen minutes and then slowly decreased to zero. The effects of annealing these couples are shown in Fig. 3.6.2. where the temperature profile inside the bottle is measured with an annealed and an unannealed thermocouple.

The salt temperature is measured with another chromel-alumel couple. It is also fixed to a clip and pushed down a thermocouple well. The salt temperature can also be derived from the setting of the Wheatstone bridge. The resistance of the thermometer can be measured to $\pm 0.01\Omega$ which is roughly equivalent to $\pm 0.02^{\circ}\text{C}$. The accuracy of the bridge has been confirmed using a standard Pt/Pt-13%Rh Couple.

The average thermoelectric power of a chromel-alumel couple between 250 and 450°C is about $43\mu\text{V}/^{\circ}\text{C}$. The sensitivity of the indicating galvanometer is usually $2\text{ cms}/\mu\text{V}$ and it is easily read to 0.5 mm .

Thus the temperature change can be estimated to 0.0006°C .

3.7. Theoretical Considerations

There are in effect two surfaces in the calorimeter; the inside surface of the bottle (surrounding) and the outside surface of the crucible. At a particular instant let their temperatures be T_s and T respectively, such that $T_s > T$. Then under steady state conditions the rate of heat exchange is given by the following expression (102).

$$\dot{q} = K_R (T_s^4 - T^4) + K_c (T_s - T) + h(T_s - T) \quad 3.7.1.$$

where K_R , K_c and h are constants and the three terms are due to radiation, conduction and convection respectively. Writing ΔT for $(T_s - T)$.

$$\dot{q} = K_R 4T_s^3 \left[1 - \frac{3}{2} \left(\frac{\Delta T}{T_s} \right) + \left(\frac{\Delta T}{T_s} \right)^2 - \frac{1}{4} \left(\frac{\Delta T}{T_s} \right)^3 \right] \Delta T + K_c \Delta T + h \Delta T$$

ΔT is often of the order of $\pm 0.5^{\circ}\text{K}$. Taking 600°K for T_s the term in the square bracket is reduced to 1 ± 0.001 . Since T_s is kept constant, and contributions due to conduction and convection have been shown to be small (101) one can neglect the time dependence K_c and write

$$\dot{q} = K(T_s - T) \quad 3.7.2.$$

where $K = (4T_s^3 K_R + K_c + h) = \text{a constant.}$

When a specimen is added to the calorimeter, the temperature of the metal bath is changed. It then follows that at a particular instant

$$\frac{dq_{sp}}{dt} + \frac{dq_{cal}}{dt} = K(T_s - T) \quad 3.7.3.$$

where $\frac{dq_{sp}}{dt}$ = rate at which heat is absorbed by the specimen

$\frac{dq_{cal}}{dt}$ = rate at which heat is absorbed by the
calorimeter

and $K(T_s - T)$ = rate at which heat is received from
the surrounding.

At equilibrium,

$$\frac{dq_{sp}}{dt} = 0,$$

and $T = T_e = \text{a constant.}$

$$\text{Hence, } \left(\frac{dq}{dt}\right)_e = K(T_s - T_e) \quad 3.7.4.$$

Using the results of 3.7.4., the equation 3.7.3. can be rewritten as,

$$\frac{dq_{sp}}{dt} + \left(\frac{dq}{dt}\right)_e + C_p \frac{dT}{dt} = K(T_s - T) \quad 3.7.5.$$

where C_p = Heat capacity of the calorimeter at the

particular instant.

Proper substitution and integration corresponding to the temperature 'T' and time 't' gives,

$$\int_{T_o}^T dq_{sp} + \int_{T_e}^T C_p dT = \int_{t_o}^t K(T_e - T)dt \quad 3.7.6.$$

$$\text{But } \int_{T_o}^T dq_{sp} = n_{sp} \int_{T_o}^{T_e} C_{p_{sp}} dT + n_{sp} Q_{T_e} + \int_{T_e}^T n_{sp} C_{p_{sp}(\text{sol'n})} dT$$

where Q_{T_e} = heat absorbed by a mole of specimen on solution at T_e ,

n_{sp} = number of moles of the specimen,

T_o = initial temperature of the specimen,

$$\text{and } \int_{T_o}^{T_e} C_{p_{sp}} dT = (H_{T_e} - H_{T_o})_{sp}$$

Making the necessary substitutions,

$$\begin{aligned} n_{sp}(H_{T_e} - H_{T_o})_{sp} + n_{sp} Q_{T_e} + \int_{T_e}^T [C_p + n_{sp} C_{p_{sp}(\text{sol'n})}] dT \\ = \int_{t_o}^t K(T_e - T)dt \quad 3.7.7. \end{aligned}$$

If C_{p_f} is the average value of the heat capacity of the calorimeter such that

$$\int_{T_e}^T [C_p + n_{sp} C_{p_{sp}}(\text{sol'n})] dT = C_{p_f} \int_{T_e}^T dT, \\ n_{sp} (H_{T_e} - H_{T_o})_{sp} + n_{sp} Q_{T_e} + C_{p_f} (T - T_e) = K \int_{t_o}^t (T_e - T) dt \quad 3.7.8.$$

Differentiation of equation 3.7.8. gives,

$$d \ln(T_e - T) = -k dt \quad . . . 3.7.9.$$

$$\text{where } k C_{p_f} = K \quad . . . 3.7.10.$$

It follows that,

$$\ln(T_e - T) = -kt + c \quad . . . 3.7.11.$$

Substitution of 3.7.10 in 3.7.8. gives,

$$Q_{T_e} = \frac{C_{p_f}}{n_{sp}} \left[(T_e - T) + k \int_{t_o}^t (T_e - T) dt \right] - (H_{T_e} - H_{T_o})_{sp} \quad 3.7.12.$$

$$\text{When } Q_{T_e} = 0 \quad . . . 3.7.13.$$

$$C_{p_f} = \frac{n_{sp}^e (H_{T_e} - H_{T_o})_{sp}}{\left[(T_e - T) + k \int_{t_o}^t (T_e - T) dt \right]} \quad . . . 3.7.14.$$

Equation 3.7.11. shows that 'k' can be obtained for any addition from a plot of $\log(T_e - T)$ against 't'. The heat capacity of the calorimeter ' C_{p_f} ' is obtained with the help of equation 3.7.14 by making additions for which equation 3.7.13 is valid or for which Q_{T_e} is known. Knowing C_{p_f} , the unknown heat

effect of any addition is determined using equation 3.7.12. The additions which are intended for determining C_{p_f} are known as calibrating additions.

Usually a number of additions are made to a particular load of metals in the crucible. If O , m , r represent the number of additions and $C_{p_f}^r$ is the measured value of C_{p_f} for the r th addition, $C_{p_f}^m$ can be calculated with the help of the following expression.

$$C_{p_f}^m = C_{p_f}^r + \sum_{i=1}^i \bar{C}_{p_i} (n_i^m - n_i^r) \quad 3.7.15$$

where n_i^r = number of moles of component 'i' in the crucible at the end of the addition,

$\bar{C}_{p_i}$ = partial molar heat capacity of component 'i',

$$\text{and } \bar{C}_{p_i} = C_{p_i}^o + \left(\frac{\partial \Delta H_i}{\partial T} \right)_x \quad 3.7.16$$

When a number of calibrating additions are made for a set of runs, the measured values are plotted against the theoretical values obtained from (3.7.15.). The value of $C_{p_f}^r$ obtained from the average line is then used in equation 3.7.15. to obtain values for $C_{p_f}^m$.

3.8. Preparation of Material

Tin, gold and tungsten have been used during the course of the present experiments. The source and purity of these metals are recorded in Table 3.8.1.

Tin is received in the form of 1 kg. bars. Each bar is cut into six units by a band saw. To prevent undue contamination, a blade is kept reserved for this purpose only. The oxide layer is removed by filing the surface. Tin is then degreased and loaded into the crucible. For calibrating additions, spherical pieces of tin weighing about 0.5-0.7 gms each are cut from the same source as the main load.

Gold is obtained as 3 mm. rods and 18 S.W.G. wires. The rods are cleaned with acetone, cut into suitable lengths by a clean pair of shears, and loaded into the crucible. The wires are cleaned, coiled into specimens weighing about 0.6 gms each and annealed under vacuum (10^{-5} mm. Hg.) for a few hours at 600°C . These are suitable for addition to gold-tin alloys containing less than 70 At% Au. For additions to the remaining alloys which were richer in gold and in which the samples dissolved less rapidly, specimens prepared from thin (0.25 mm) strips of rolled wire

are used.

Specimens of tungsten are prepared by cutting 4 mm. diameter rods into pieces 0.4-0.5 mm. long. These are annealed at 800°C for 8 hours under vacuum (10^{-5} mm. Hg.), before being used as calibrating additions.

3.9. Experimental Procedure

All the calorimetric experiments have been divided into a number of runs. Each run consists of all the additions made to a particular load of metal. To perform a run we proceed as follows.

The salt bath is raised to the temperature at which the experiment is going to be performed. The main heater current is adjusted to the required value determined from previous experience. The calorimetric assembly is cleaned with ether, and greased and oiled at the required points. The crucible is well polished with fine silicon carbide paper, and loaded with either tin or gold and tin. The weight is calculated so as to have about 90 cc of liquid in the crucible. The crucible is placed in position on its supports and the lengths of the rods supporting the lower radiation shield are adjusted. A chromel-alumel couple, prepared in the manner already

Table 3.8.1.

Material	Source	Purity %	Assay %
Tin	Capper Pass and Sons Ltd.	99.999 (Pass S)	Sb 0.0001
			Pb 0.0002
			Cu <0.0001
			Fe <0.0001
			Bi 0.0001
			As <0.0001
			Ag <0.0001
Gold	Johnson Matthey and Co. Ltd.	99.999	Cu 0.0001
			Cd 0.0001
			In 0.0001
			Pb 0.0001
			Mn 0.0001
			Na <0.0001
			Zn 0.0002
Tungsten	Johnson Matthey and Co. Ltd.	99.99	Fe 0.0040
			Mo 0.0030
			Cu <0.0001
			Mg <0.0001

described, is pushed down the stirrer shaft. Finally the airlock on the addition line is closed. The calorimetric assembly is now ready to go in.

The bottle which is always kept under vacuum, is cut off from the vacuum system and high purity (99.995%) argon is let in through a needle valve mounted on the vacuum line. The top cover is removed and the crucible assembly is introduced through the neck. The radiation shield is located on its pegs by bringing two marks one on the top plate and one on the bottle neck, on the outside to proper alignment. The vacuum system is now connected to the bottle and the argon supply is cut off. In about five minutes the pressure goes down to 5×10^{-4} mm. Hg. and then it decreases more slowly.

The tin stirrer is pushed down till it touches the solid metals in the crucible. As the metal starts melting the stirrer is pushed further down. When it reaches the bottom it is pulled out by about $\frac{1}{4}$ " and attached to the driving mechanism. In the mean time the temperature is measured and the couple is calibrated against the melting point of tin, if the load happens to be pure tin. Depending upon the temperature of operation, it takes about 1 to 4 hours

for the load to melt. Usually it is left overnight, so that it may approach the temperature of the salt bath.

Next morning, the stirrers are started, the bridge is set for the required temperature and the controller is put into operation. The specimen is weighed and loaded in the addition system, which is then evacuated and filled with argon. This operation is repeated three times before it is finally evacuated and connected to the main system by opening the airlock valve. The glass tube of the addition system is pushed down to the bottom of the valve. The extension of the glass tube containing the specimen is enclosed in a ice-water bath maintained in a Dewar Flask (Fig. 3.5.3.).

The mechanical and the electrical zeros of the galvanometer and preamplifier unit are adjusted by shorting the amplifier. The thermal zero is adjusted by shorting the terminals of one of the thermocouples and backing off any potential in the circuit. The cold junction is packed with finely ground wet ice. The temperature of the metal bath is noted as it approaches the equilibrium. Once the steady state is reached, the different zeros and

the sensitivity of the measuring unit are checked. Any change in the reading due to the drift in the potentiometer battery voltage is recorded. A stop **clock** is kept ready and the specimen is added by turning the specimen tube on the ground glass joint. The clock is started as soon as the light spot on the galvanometer starts moving. Readings of the potentiometer and the galvanometer are taken at fixed intervals of time, the total time over which readings are taken being 12 to 25 minutes, depending upon the rate of solution of the specimen. In case of calibrating additions readings are taken after every 15 seconds for the first three minutes and then after intervals of 30 seconds. During a gold addition, however, readings are taken after every 10 seconds for the first minute. While the experiment is being performed, the drifts of the battery voltage are noted and readjusted. The potentiometer is read to $1\mu\text{V}$. Smaller divisions of potential are obtained from galvanometer deflections.

When the required number of time-temperature readings have been taken, the measuring unit is tested for all the drifts, i.e. Galvanometer drift, potentiometer drift etc. The addition tube is withdrawn and the

airlock is closed. The vacuum is broken by introducing argon into the addition tube. The glass tubes are separated and the next specimen is loaded. The metal bath is then allowed to come to equilibrium before the next addition is made.

When the required number of additions have been made, the equipment is dismantled by a procedure opposite to the one already described, except that the crucible assembly is withdrawn while the metal bath in the crucible is still molten.

The readings obtained from the measuring unit are converted into microvolts by taking due account of the drifts. These are subtracted from the temperature of the steady state and the common logarithms of these differences are plotted against time. The constant 'k' of equation 3.7.11. is calculated from the slope of this line. A point lying on the average line is chosen for the purposes of calculation and its co-ordinates (T,t) noted. The term $\int_{t=0}^t (T_e - T)dt$ is analytically determined with the help of the following expression.

$$\int_{t=0}^t (T_e - T)dt \simeq \sum_{k=1}^k \frac{1}{2}(t_k - t_{k-1}) (\Delta T_k + \Delta T_{k-1}) \quad 3.9.1.$$

Here, subscript 'k' represents the number of readings

and the point (T,t) represents the kth reading.

The other term ($H_{T_e} - H_{T_o}$) in equations 3.7.12. and 3.7.14. is calculated from the existing data^(104, 105). Hultgren and co-workers⁽¹⁰⁵⁾ have considered some of the most recent measurements made on tin. Therefore, their data have been used in formulating the following expression for tin, where T is greater than 505°K.

$$(H_T - H_{273.15})_{\text{Sn}(1)} = 6.70T - 0.723 \times 10^5 T^{-1} + 19.9$$

cal/mole

. . . . 3.9.2.

Similar equations have also been formulated for gold and tungsten.

$$(H_T - H_{273.15})_{\text{Au}(s)} = 5.66T + 0.62 \times 10^{-3} T^2 - 1592.6$$

cal/mole

. . . . 3.9.3.

$$(H_T - H_{273.15})_{\text{W}(s)} = 5.74T + 0.38 \times 10^{-3} T^2 - 1596.1$$

cal/mole

. . . . 3.9.4.

The value of T_e for use in these equations is obtained either from the calibrated thermocouple reading or from the bridge setting. For the sake of uniformity the bridge setting has been adopted for

all the calculations. C_{p_f} of a calibrating addition is calculated using equation 3.7.14., whereas C_{p_f} for any other addition is calculated with the help of equations 3.7.15. and 3.7.16. Data for these equations are obtained by extrapolating data obtained from other sources (21, 101, 105) and from prior experimental results. Q_{T_e} , the total heat absorbed by a mole of addition at T_e is then calculated using equation 3.7.12.

These results have been analysed in terms of thermodynamic properties in a following chapter on the results. Complete details of readings obtained during two additions have been presented in Appendix II.

CHAPTER FOUR

RESULTS

RESULTS

4.1. Introduction

The experimental data obtained from the calorimeter are analysed in the following pages. The analysis yields values for the partial heat contents of gold and tin at several compositions and temperatures. These results are treated using standard thermodynamic equations so as to obtain partial and integral values of enthalpy at various compositions and temperatures. The temperature dependence of enthalpy is used to calculate the heat capacities of all the alloys investigated.

4.2. Calorimetric Results

In order to obtain information on the thermodynamic properties of the liquid gold-tin alloys, the heats of solution of solid gold in pure liquid tin and liquid gold-tin alloys are measured. Q , the heat absorbed per mole of addition, is calculated with the help of equations presented in the previous chapter.

Q and the other related quantities associated with additions to initially pure tin bath have been listed in Table AIII.1. With the help of these data it is possible to obtain values for the relative partial

molar heat contents of gold at infinite dilution.

When gold is added to the pure tin bath, a gold-tin alloy is formed and the total heat effect, when divided by the total number of moles, will give the heat of formation of that alloy. This is mathematically represented by the following equation.

$$\Delta H_{T,x_i} = \frac{\sum_{m=0}^m (n_{sp,i} Q_{T,i} + n_{sp,j} Q_{T,j})}{\sum_{m=0}^m (n_{sp,i} + n_{sp,j})} \quad 4.2.1.$$

Here,

$$x_i = \frac{\sum_{m=0}^m n_{sp,i}}{\sum_{m=0}^m (n_{sp,i} + n_{sp,j})} \quad 4.2.2.$$

m = number of additions, and 'i' and 'j' represent gold and tin additions respectively. The values of ΔH thus obtained are fitted into an equation of the form

$$y = bx \quad \dots \dots 4.2.3.$$

so as to give minimum standard deviation '5'. The expressions used in obtaining equations with minimum standard deviation are given in Appendix IV.

Knowing ΔH as a function of mole fraction, the partial properties are obtained with the help of standard equations⁽¹⁷⁾.

$$\Delta\bar{H}_{i,T,x_i} = \Delta H_{T,x_i} + (1-x_i) \left(\frac{\partial \Delta H}{\partial x} \right)_{T,x_i} \quad . \quad . \quad .4.2.4.$$

$$\text{and } \Delta\bar{H}_{i,T,x_i \rightarrow 0} = \left(\frac{\partial \Delta H}{\partial x} \right)_{T,x_i \rightarrow 0} \quad . \quad . \quad .4.2.5.$$

from equations 4.2.3., 4.2.5., and AIV.9, one obtains,

$$\Delta\bar{H}_{i,T,x_i \rightarrow 0} = b = \frac{\sum xy}{\sum x^2} \quad . \quad . \quad .4.2.6.$$

where 'x' and 'y' represent 'x_i' and 'ΔH' respectively. Thus the results of 4.2.1. are directly substituted in 4.2.6. to obtain results for $\Delta\bar{H}_{i,T,x_i \rightarrow 0}$. These results have been listed in Table AIII.2.

The observations of Oriani⁽³⁴⁾ justify the use of a linear equation of the form 4.2.3. He shows that the heat of solution of gold in tin is independent of composition up to 2 atomic %Au. Moreover an equation of the form AIV.11, although much more complicated, yields results which fall within the normal scatter.

The heat of solution of gold in pure tin at 247 and 300°C have been measured in this calorimeter in collaboration with Kravitz⁽¹⁰¹⁾. These results are recalculated using the specific heat data of Hultgren⁽¹⁰⁵⁾. These data and those of Table AIII.2 fit well on to a curve (Fig. 4.2.1.) of the following

form.

$$\Delta \bar{H}_{\text{Au(s)}, x_{\text{Au}} \rightarrow 0} = -[6479 - 3.44T + 50 \times 10^{-12} T^{-5} + 500 \times 10^{-28} T^{-12}]$$

4.2.7.

where T = temperature in $^{\circ}\text{C}$.

The values of $\Delta \bar{H}_{\text{Au(s)}, x_{\text{Au}} \rightarrow 0}$ at different temperatures are calculated from the above equation.

For many purposes values for $\Delta \bar{H}_{\text{Au(l)}}$ are needed. In order to obtain this from $\Delta \bar{H}_{\text{Au(s)}}$, the heat of melting of gold at different temperatures is required. This is calculated from the following equation formulated from the published data⁽¹⁰⁵⁾.

$$\Delta H_T = 2955 + \int_{1336}^T (7.00 - (5.66 + 1.24 \times 10^{-3} T)) dT$$

4.2.8.

All these results are tabulated in Table 4.2.1.

Considering the experiments in which specimens of pure metals are added to the alloys and proceeding according to the equation 4.2.1. the following expression is obtained.

$$\Delta H_{T, x_i} = \frac{(n_i^* + n_j^*) \Delta H^* + \sum_{m=1}^m (n_{\text{sp}, i} Q_i + n_{\text{sp}, j} Q_j)}{(n_i^* + n_j^*) + \sum_{m=1}^m (n_{\text{sp}, i} + n_{\text{sp}, j})} \quad 4.2.9.$$

Here,

$$x_i = \frac{n_i^* + \sum_{m=1}^m n_{\text{sp}, i}}{(n_i^* + n_j^*) + \sum_{m=1}^m (n_{\text{sp}, i} + n_{\text{sp}, j})} \quad 4.2.10.$$

and n_i^* , n_j^* and ΔH^* represent the alloy formed by the zeroth addition i.e. the alloy in the calorimeter at the beginning of the experiment.

Table 4.2.1.

Values of Heats of Solution of Gold in Liquid Tin at Infinite Dilution.

$\Delta \bar{H}_{Au}$ (Experimental)			$\Delta \bar{H}_{Au}$ (From Average Line)		
Temp °C	$\Delta \bar{H}_{Au(s), x_{Au} \rightarrow 0}$		Temp °C	$\Delta \bar{H}_{Au(s)}$	$\Delta \bar{H}_{Au(l)}$
				$x_{Au} \rightarrow 0$	$x_{Au} \rightarrow 0$
247.0	-5775 $\pm$ 12		250	-5754	-8557
300.4	-5476 $\pm$ 9		275	-5580	-8400
302.3	-5461 $\pm$ 6		300	-5477	-8313
351.1	-5289 $\pm$ 3.5		350	-5286	-8152
400.0	-5104 $\pm$ 2.5		400	-5108	-8001
450.0	-4938 $\pm$ 6		450	-4934	-7850

In principle ΔH could be expressed as a function of ΔH^* and x_i and a value for ΔH^* could be found using the equations of Appendix IV. But the shape of the ΔH vs. x_i curve is uncertain and the equations involved are complicated (AIV.3, 4, 6, 7). Since the number of points are small, these equations under

certain circumstances will introduce large errors in the results.

Therefore these results are treated differently. The heat evolved due to an addition of n moles could be expressed accurately by the following equation.

$$nQ = \int_0^n \Delta \bar{H} dn \quad 4.2.11.$$

Expressing $\Delta \bar{H}$ as a linear function of x over this limited composition range,

$$\Delta \bar{H}_i = a + bx_i = a + b\left(\frac{n_i^* + n_i}{n_i^* + n_j^* + n_i}\right) \quad . . .4.2.12.$$

Substituting 4.2.12. in 4.2.11., the following relationship is obtained.

$$Q_i = a + b\left(1 - \left(\frac{n_j^*}{n_i}\right) \ln\left(1 + \frac{n_i}{n_i^* + n_j^*}\right)\right) \quad . . .4.2.13.$$

Comparison between the equations 4.2.12. and 4.2.13. shows that,

$$\Delta \bar{H}_{i,x_i} = Q_i \quad 4.2.14.$$

when,

$$x_i = 1 - \left(\frac{n_j^*}{n_i}\right) \ln\left(1 + \frac{n_i}{n_i^* + n_j^*}\right) \quad 4.2.15.$$

In the equation 4.2.15., $(n_i^* + n_j^*) \approx 5$, $n_i \approx 0.005$

and $\left(\frac{n_i}{n_i^* + n_j^*}\right) \ll 1$. Expanding the exponential term

in powers of $\left(\frac{n_i}{n_i^* + n_j^*}\right)$ and neglecting the higher

order terms the following relationship is obtained.

$$x_i = \frac{n_i^*}{n_i^* + n_j^*} + \frac{1}{2} \frac{n_j^* n_i}{(n_i^* + n_j^*)(n_i^* + n_j^*)} \simeq x^{av} \quad . \quad . \quad . \quad 4.2.16.$$

Here,

$$x^{av} = \frac{1}{2} \left(\frac{n_i^*}{n_i^* + n_j^*} + \frac{n_i^* + n_i}{n_i^* + n_j^* + n_i} \right) =$$

$$\frac{n_i^*}{n_i^* + n_j^*} + \frac{1}{2} \frac{n_j^* n_i}{(n_i^* + n_j^*)(n_i^* + n_j^* + n_i)} \quad 4.2.17.$$

x_i is calculated using 4.2.16 and 4.2.17., $\Delta \bar{H}_{x_i}$ is obtained from 4.2.14 and $\Delta \bar{H}_{Au(1)}$ is computed using 4.2.14. and 4.2.8. The experimentally observed quantities are in Table AIII.3 and the rest are in Table 4.2.2.

4.3. Derived Results

The partial and integral enthalpies of a binary system are related to each other by the following equations⁽¹⁰⁶⁾.

$$\Delta \bar{H}_{j, x_i^*} - \Delta \bar{H}_{j, x_i} = - \int_{\Delta \bar{H}_{i, x_i}}^{\Delta \bar{H}_{i, x_i^*}} \frac{x_i}{x_j} \cdot d\Delta \bar{H}_i \quad . \quad . \quad . \quad 4.3.1a.$$

Table 4.2.2.

Experimental Values of $\Delta\bar{H}_{\text{Au(s)}}$, $\Delta\bar{H}_{\text{Sn(l)}}$ and $\Delta\bar{H}_{\text{Au(l)}}$
at Different Temperatures and Compositions.

Temp °C	Run No.	Composition At% Au	$\Delta\bar{H}_{\text{Au(s)}}$	$\Delta\bar{H}_{\text{Au(l)}}$	$\Delta\bar{H}_{\text{Sn(l)}}$
275	32.1	10.071	-5810	-8630	-
	32.2	10.204	-5913	-8733	-
	32.4	10.318	-5863	-8683	-
300	32.5	10.426	-5608	-8444	-
	32.6	10.537	-5597	-8433	-
	32.8	10.648	-5600	-8436	-
	35.29	69.862	+801	-2035	-
	35.26	69.930	-	-	-5164
350	32.9	10.765	-5268	-8134	-
	32.10	10.887	-5310	-8176	-
	32.12	11.009	-5328	-8194	-
	33.1	28.878	-4114	-6980	-
	33.2	29.085	-4101	-6967	-
	33.4	29.254	-4057	-6923	-
	33.13	30.511	-3895	-6761	-
	33.15	30.652	-3906	-6772	-
	35.22	70.277	+1054	-1812	-
	35.18	70.757	+1071	-1795	-
	35.14	70.997	+1108	-1758	-
	35.21	70.385	-	-	-5023
	35.19	70.645	-	-	-5055
	35.15	70.877	-	-	-5086

Table 4.2.2. Continued

Temp °C	Run No.	Composition At%Au	$\Delta H_{\text{Au(s)}}$	$\Delta H_{\text{Au(l)}}$	$\Delta H_{\text{Sn(l)}}$
400	32.13	11.134	-5012	-7905	-
	32.14	11.262	-5063	-7956	-
	32.16	11.390	-4983	-7876	-
	33.5	29.395	-3780	-6673	-
	33.6	29.544	-3760	-6653	-
	33.8	29.703	-3704	-6597	-
	35.6	71.652	+1159	-1734	-
	35.7	71.685	+1169	-1724	-
	35.9	71.718	+1167	-1726	-
	35.13	71.102	-	-	-5001
	35.11	71.361	-	-	-5031
	35.10	71.614	-	-	-5071
	36.2	73.927	+1342	-1551	-
	36.4	73.964	+1259	-1634	-
425	34.1	49.634	-677	-3582	-
	34.2	49.740	-586	-3491	-
	34.4	49.843	-546	-3451	-
450	31.1	10.064	-4816	-7732	-
	31.2	10.196	-4806	-7722	-
	31.3	10.337	-4826	-7742	-
	32.17	11.526	-4740	-7656	-
	32.18	11.663	-4799	-7715	-
	32.20	11.798	-4791	-7707	-
	33.9	29.888	-3433	-6349	-
	33.10	30.102	-3434	-6350	-
	33.12	30.324	-3386	-6302	-

Table 4.2.2. Continued

Temp °C	Run No.	Composition At%Au	$\Delta\bar{H}_{\text{Au(s)}}$	$\Delta\bar{H}_{\text{Au(l)}}$	$\Delta\bar{H}_{\text{Sn(l)}}$
450	34.5	49.945	-520	-3436	-
	34.6	50.040	-544	-3460	-
	34.8	50.137	-487	-3403	-
	34.9	50.115	-	-	-2454
	35.1	71.783	+1187	-1729	-
	35.2	71.814	+1234	-1682	-
	35.4	71.844	+1244	-1672	-
	35.5	71.747	-	-	-5007
	36.6	74.033	+1412	-1504	-
	36.9	74.067	+1420	-1496	-
	36.10	74.101	+1455	-1461	-

$$\Delta \bar{H}_{j,x_i^*} - \Delta \bar{H}_{j,x_i} = \left[-x_i(1-x_i)\beta \right]_{x_i}^{x_i^*} + \int_{x_i}^{x_i^*} \beta dx_i \quad 4.3.1b.$$

where,
$$\beta = \frac{\Delta \bar{H}_i}{(1-x_i)^2} \quad 4.3.1c.$$

$$\Delta H_{x_i} = x_i \Delta \bar{H}_{i,x_i} + (1-x_i) \Delta \bar{H}_{j,x_i} \quad 4.3.2.$$

At 450°C there are experimental values of $\Delta \bar{H}_{Au(1)}$ at seven different compositions and $\Delta \bar{H}_{Sn(1)}$ at two compositions. These are treated using equations 4.3.1b., 4.3.1c., and 4.3.2. and values of $\Delta \bar{H}_{Au(1)}$ $\Delta \bar{H}_{Sn(1)}$ and ΔH at round figure mole fractions are analytically computed for all compositions between zero and 50 At%Au. The computed and experimental values of $\Delta \bar{H}_{Sn(1)}$ at 50 At%Au agree well.

$$\Delta \bar{H}_{Sn(1),x_{Au} = 0.50115} = \begin{cases} -2454, & \text{Experimental} \\ -2451, & \text{Computed} \end{cases}$$

Beyond this range of compositions the β function is rather complex. Therefore the required thermodynamic properties are obtained by graphically integrating equation 4.3.1a. The shape of the curve to be integrated is determined by the experimental value of $\Delta \bar{H}_{Sn(1)}$ at 71.75 At%Au. The data thus obtained are recorded in Table 4.3.1. and plotted in Fig. 4.3.1.

Table 4.3.1.

Enthalpies of Liquid Gold-Tin Alloys at Round Figure Mole Fraction

Cal/Mole Properties	Temp ^o C	x _{Au} =0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.75
ΔH	275	0.0	-863	-	-	-	-	-	-	-
	300	0.0	-843	-	-	-	-	-	-2970	-
	350	0.0	-818	-1621	-2339	-	-	-	-2772	-
	400	0.0	-798	-1574	-2264	-2780	-3029	-2971	-2732	-2555
	450	0.0	-781	-1532	-2195	-2691	-2940	-2899	-2690	-2512
$\Delta \bar{H}_{Au(l)}$	275	-8400	-8698	-	-	-	-	-	-	-
	300	-8313	-8446	-	-	-	-	-	-2030	-
	350	-8152	-8182	-7823	-6845	-	-	-	-1830	-
	400	-8001	-7944	-7545	-6595	-5160	-3481	-2285	-1815	-1530
	425	-	-	-	-	-	-3464	-	-	-
	450	-7850	-7740	-7287	-6349	-5000	-3447	-2310	-1840	-1400
$\Delta \bar{H}_{Sn(l)}$	275	0.0	+8.0	-	-	-	-	-	-	-
	300	0.0	+2.0	-	-	-	-	-	-5165	-
	350	0.0	+0.5	-70	-407	-	-	-	-4970	-
	400	0.0	-4.0	-81	-408	-1193	-2577	-4000	-4872	-5632
	450	0.0	-8.0	-93	-415	-1152	-2433	-3783	-4675	-5850

Table 4.3.2.

Heat Capacities of Liquid Gold-Tin Alloys at 425°C.

Property Cal/mole/°C	$x_{\text{Au}} = 0.0$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.75
ΔC_p	0.0	+0.34	+0.83	+1.37	+1.77	+1.78	+1.44	+0.91	+0.86
$\Delta \bar{C}_{p\text{Au}(l)}$	3.0	+4.08	+5.10	+4.92	+3.20	+0.68	-0.50	-0.50	+2.60
$\Delta \bar{C}_{p\text{Sn}(l)}$	0.0	-0.08	-0.24	-0.15	+0.82	+2.88	+4.34	+4.20	-4.36

The values of $\Delta\bar{H}_{\text{Au}(1)}$ at 400°C are treated in the same manner except that $\Delta\bar{H}_{\text{Au}(1)}$ at $x_{\text{Au}} = 0.5$ is obtained by extrapolating experimental values at 450°C and 425°C . $\Delta\bar{H}_{\text{Au}(1)}$ at 425°C is taken from the best line parallel to the curve ($\Delta\bar{H}_{\text{Au}(1)}$ vs. x_{Au}) at 450°C and drawn through the experimental points at 425°C . All these results are included in Table 4.3.1. and Fig. 4.3.1.

The plot in Fig. 4.3.1. shows that there are humps in the curves for $\Delta\bar{H}_{\text{Au}(1)}$ at about 70 At%Au. If smooth curves are drawn through the experimental points, the computed values of $\Delta\bar{H}_{\text{Sn}(1)}$ around 71 At%Au will be about 200 Cal/mole different from the experimentally obtained values. This is more than ten times greater than the experimental error. It has been shown that the agreement between the computed and experimental values of $\Delta\bar{H}_{\text{Sn}(1)}$ at 50 At%Au is very good. The experimental values of $\Delta\bar{H}_{\text{Au}(1)}$ and $\Delta\bar{H}_{\text{Sn}(1)}$ around composition 71 At%Au have been plotted along with the computed curves in Fig. 4.3.2., Fig. 4.3.3., and Fig. 4.3.4. The computed line for 350°C in Fig. 4.3.4. has been taken as parallel to that at 400°C . It is clear that the slopes of the computed lines agree well with those of the experimental

points. Smooth curves drawn to avoid the humps would have slopes much different from those shown by the computed lines. Hultgren and co-workers⁽¹⁰⁵⁾ have predicted the existence of these humps. It is therefore believed that the humps are real.

The experimental points at other temperatures are treated using equations 4.3.1b., 4.3.1c., and 4.3.2. and required properties are computed. The values of $\Delta\bar{H}_{\text{Au}(1)}$ and $\Delta\bar{H}_{\text{Sn}(1)}$ at 350°C and $x_{\text{Au}} = 0.7$ are taken from Fig. 4.3.4. The experimental values of $\Delta\bar{H}_{\text{Au}(1)}$ and $\Delta\bar{H}_{\text{Sn}(1)}$ at 300°C around $x_{\text{Au}} = 0.698$ have been adopted for $x_{\text{Au}} = 0.7$. Because of the large uncertainties in these two results the composition dependence has been neglected. These data appear in Table 4.3.1. and Fig. 4.3.1.

It has been pointed out in a previous chapter that,

$$\left(\frac{\partial \Delta\bar{H}}{\partial T}\right)_P = \Delta C_p$$

This expression shows that the integral and partial values of specific heat can be obtained from the temperature coefficients of the integral and partial enthalpies. $\Delta\bar{H}_{\text{Sn}(1)}$ and $\Delta\bar{H}_{\text{Au}(1)}$ have been plotted against temperature in Fig. 4.3.5. and Fig. 4.3.6.

respectively. They clearly show the way in which the slopes change with composition. The partial and integral values of specific heat have been calculated from the slopes at 425°C, recorded in Table 4.3.2., and plotted in Fig. 4.3.7. The integral values thus obtained are consistent with those computed from the heats of formation of the alloys.

CHAPTER FIVE

DISCUSSION

DISCUSSION

5.1. Discussion of Errors

The errors in the reported values can be separated into two categories.

1. Random Errors,
2. Systematic Errors.

Inspection of equations 3.7.12, 3.7.14, and 3.7.15 shows that random errors arise from uncertainties in the corrected value of

$$\Delta T(\Delta T_{\text{Cor}} = \Delta T_{\text{ob}} + k \int_{t_0}^{t_{\text{ob}}} \Delta T dt),$$

initial temperature of the specimen (T_0), the equilibrium temperature of the tin bath (T_e), the weight of the specimen and the estimated value of C_{p_f} for non-calibrating additions. Uncertainty in the measurement of temperature change is $0.0125 \times \frac{1}{40}^\circ\text{C}$. Errors in ΔT_{Cor} depend upon the uncertainties in ΔT and the relative magnitudes of ΔT_{ob} and $k \int_{t_0}^{t_{\text{ob}}} \Delta T dt$. In other words faster rates of solution should lead to smaller errors. Calibrating additions and additions of gold to liquid tin are associated with small reaction times. In these experiments, the uncertainties, calculated from the scatter in the plots of $\log \Delta T$

against 't' are on the average $\pm 0.12\%$ in ΔT_{ob}
 $\pm 0.3\%$ in 'k' and $\pm 0.15\%$ in $\int_{t_o}^{t_{ob}} \Delta T dt$. The last
term is normally 1/6th of ΔT_{Cor} . Hence the total
error in ΔT_{Cor} is $\pm 0.2\%$. The uncertainty in ΔT
is greater than the uncertainty introduced in it
through uncertainty in potential measurement. This
difference arises from oxidation effects, time lag
in the measuring unit, thermal and compositional
non-uniformity etc. The uncertainty in the weight
of the specimen is 0.003%. Equilibrium temperature
(T_e) is taken from the bridge reading which is read
to 0.01². This is equivalent at 350°C to an un-
certainty of less than 0.005% in the heat content.
The error in the estimated Cp_f value is approximately
0.005 Cal in 50 Cal, i.e. 0.01%. Thus the total
random error should be under 0.25%. This is reflected
in the scatter one gets in the results. The scatter
in the experimental values of Cp_f is always under
this value. The heats of solution of gold in liquid
tin have an average scatter of 5 cal/mole (Table AIII.2)
which is just under 0.2% of the total heat effect.

Uncertainties in the alloy additions as indicated
by the scatters in the experimental points are rela-
tively greater. Table 5.1.1. contains the R.M.S.

value of scatter in Cal/mole as well as in percentage of the total heat effect. In calculating the R.M.S. value the composition dependence has been taken into account.

Inspection of Table 5.1.1. shows that the percentage error is a function of total heat effect, temperature and composition. Since the magnitude of total heat effect (Q^*) has very little effect on the uncertainties in ΔT , the percentage error is less for ~~higher~~ magnitudes of Q^* . Changes of temperature bring about changes in thermal fluctuations, rate of solution and rate of mixing. The latter two are probably more serious near the melting point where the scatter is found to be greater. The rate of solution and the rate of achieving uniformity in composition and temperature are also changed by any change in the alloy composition. Relatively greater scatter in the results obtained with the alloy containing 10 At% Au is most likely due to the fact that the experiments with this alloy were carried out with a stainless steel stirrer, which is susceptible to attack by alloys containing high percentage of gold.

Random errors in the measured heats of solution

Table 5.1.1.

Random Errors in the Experimental Values of the Heats of Solution of Gold in Liquid Gold-Tin Alloys.

Approximate composition x_{Au}	R.M.S. Scatter											
	275°C		300°C		350°C		400°C		425°C		450°C	
	Cal/ mole	%of Q^*	Cal/ mole	%of Q^*	Cal/ mole	%of Q^*	Cal/ mole	%of Q^*	Cal/ mole	%of Q^*	Cal/ mole	%of Q^*
0.00	-	-	± 6	0.15%	± 3.5	0.1%	± 2.5	0.1%	-	-	± 6	0.3%
0.10	± 39	0.9%	± 5	0.15%	± 25	0.8%	± 20	0.7%	-	-	± 18	0.9%
0.30	-	-	-	-	± 11	0.6%	± 7	0.6%	-	-	± 12	2.0%
0.50	-	-	-	-	-	-	-	-	± 37	1.8%	± 20	0.9%
0.71	-	-	-	-	± 7	0.2%	± 3	0.1%	-	-	± 23	0.6%
0.74	-	-	-	-	-	-	± 42	1.1%	-	-	± 13	0.3%

$\pm Q^*$ = Total Heat Effect

of tin in liquid gold-tin alloys are ± 3 Cal/mole (0.3%). The error introduced into the computed values for tin by the experimental scatter in the heats of solution of gold is 20 Cal/mole at 450°C. for the alloy containing 50 At%Au. Hence the maximum error in the reported value of the heats of formation is 20 Cal/mole.

Systematic errors arise from the errors in the reported heat capacities. For tin, gold and tungsten the values of C_p used in the calculations have quoted errors of ± 0.05 , 0.3 and 0.4% respectively. Hence the systematic errors in $\Delta \bar{H}_{\text{Au(s)}, x_{\text{Au}} \rightarrow 0}$ and $\Delta \bar{H}_{\text{Au(s)}, x_{\text{Au}}}$ are 10 Cal/mole and 20 Cal/mole respectively. $\Delta \bar{H}_{\text{Au(l)}}$ incorporates the heat of fusion of gold which has an uncertainty of 30 Cal/mole. Systematic error in $\Delta \bar{H}_{\text{Au(l)}}$ is probably greater than 50 Cal/mole because of the unknown contribution made by the assumption that the heat capacity of supercooled liquid gold is obtained by extrapolating the high temperature data.

There is a small systematic error introduced by the assumption that the salt temperature is the same as the equilibrium temperature of the calorimeter. However, it has been observed from pure tin runs that

the temperature difference is less than 0.2°C at 350°C . The error due to this, introduced through the heat content is less than 1 Cal/mole.

The following table summarizes the errors contributed by different variables in the case of solution of gold in pure tin at 450°C .

Table 5.1.2.

Analysis of Errors in $\Delta\bar{H}_{\text{Au}(1),x_{\text{Au}} \rightarrow 0}$ at 450°C .

Random Errors		Systematic Errors	
	Cal/mole		Cal/mole
$\Delta T_{\text{Cor}}, \Delta T_{\text{ob}}$	(0.133%)* 2.81	Heat Content of Tin	1.0
$k \int \Delta T dt$	(0.0916%) 1.94	Heat Content of Gold	8.5
Weight of Specimen		$\Delta H_{\text{fusion, Gold}}$	30.0
	(0.0035%) 0.07	Temperature Difference	
Equilibrium Temperature		between T_e and salt	
of Tin	(0.009%) 0.19	Temperature	0.5
Computed Heat		Unknown contribution from	
Capacity	(0.011%) 0.24	Super Cooled Liquid Gold x	
Difference	(0.355%) 0.75		
TOTAL	(0.284%) ± 6.00	TOTAL	$\pm (40+x)$

* % of the total heat effect.

5.2. Comparison of Results with those of Other Workers

The heats of solution of solid gold in liquid tin is plotted against temperature in Fig. 4.2.1. along with all the other available data. Results obtained during this investigation appear to be less exothermic because of the use of the recent heat content data reported by Hultgren and co-workers⁽¹⁰⁵⁾ for tin. When these results are calculated using the heat content data of Kelley⁽¹⁰⁴⁾ the agreement is better. Results of Kleppa⁽⁸³⁾ (increased by 6.4% to correct for a calibration error) at 242, 270, 350 and 450°C; Ticknor and Bever⁽⁸²⁾ at 240°C; Leach and Bever⁽⁹⁰⁾ at 240, 300 and 350°C and Orr, Goldberg and Hultgren⁽⁸⁸⁾ at 243°C compare well with those reported here. Other values of Bever and co-workers^(82, 90) at 300 and 350°C are on the average 75 Cals more exothermic. This falls within the scatter of their experimental values. Each of Oriani's^(34, 86) results at 418 and 425°C are 90 Cals more negative. He used a calorimeter which is electrically calibrated. It is known from Kleppa's results that electrical calibration at times introduces systematic errors. The data of Hultgren and

co-workers^(84, 89) for $\Delta\bar{H}_{\text{Au(s)}}$ at 328 and 427°C are 75 and 90 Cals more negative respectively. This is greater than their reported scatter and it is difficult to account for this discrepancy. However their value at 328°C is about 40 Cals higher than the average of all the other values.

Recently some new results on the heats of solution of gold and tin in liquid gold-tin alloys near the composition AuSn at the temperature 423°C have been announced by Masse⁽¹⁰⁷⁾. In calculating $\Delta\bar{H}_{\text{Au(l)}}$ from $\Delta\bar{H}_{\text{Au(s)}}$ he ignored the temperature dependence of the heat of fusion of gold. Taking this into account his results at $x_{\text{Au}} = 0.5$ and $T = 423^\circ\text{C}$ are -3520 Cal/mole for $\Delta\bar{H}_{\text{Au(l)}}$, -2435 Cal/mole for $\Delta\bar{H}_{\text{Sn(l)}}$ and -2978 Cal/mole for $\Delta\bar{H}$ compared with -3464 Cal/mole, -2505 Cal/mole and -2984 Cal/mole respectively obtained during the present investigation. The heat of solution of gold is more negative than the present results. This is consistent with the behaviour of other results of Hultgren and co-workers. If in this case the discrepancy is attributed to a systematic error for example in calibration it is difficult to explain why the value for $\Delta\bar{H}_{\text{Au(l)}}$ is larger, $\Delta\bar{H}_{\text{Sn(l)}}$ is smaller than the present results

but ΔH shows excellent agreement. However if the composition is assumed to be in error by 0.4% the agreement is exact. The compositions of the alloys in the present work have been calculated from the weights of gold, tin and any gold-tin alloy used in the preparation of the load and it is thought that any error will not exceed 0.1%. Masse has also computed the composition in a similar manner. In spite of this it seems likely that a part of the difference arises from an error in the determination of the composition. The good agreement between the two values for the heat of formation is to be expected as the composition dependence is small near 50 At%Au. Kleppa⁽⁸³⁾ has calorimetrically measured the heats of formation of some liquid gold-tin alloys at 350 and 450°C. His results have been plotted along with the present ones in Fig. 4.3.1. The agreement between the two sets of results is within 10 Cals. Hultgren and co-workers⁽¹⁰⁵⁾ have combined the heat content measurements of Kubaschewski⁽⁸¹⁾ with the heat of formation measurements of Bever and co-workers⁽⁷⁷⁾ and obtained values for the heat of formation of liquid AuSn. These are about 300 Cals less exothermic than the results reported here and the results

of Masse.

The value of ΔC_p at 423°C obtained from the computed results of Hultgren et al⁽¹⁰⁵⁾ is 1.1 Cal/mole/ $^\circ\text{C}$. Present results give 1.78 Cal/mole/ $^\circ\text{C}$ at 425°C . Considering the fact that this particular value of ΔC_p is based on one value of $\Delta \bar{H}_{\text{Au}}$ (425°C) showing relatively high scatter, the agreement is considered to be satisfactory. However the ΔC_p values obtained for the other compositions should be more reliable.

5.3. Applicability of Statistical Theories to the Liquid Gold-Tin System

In reviewing the statistical theories of metallic solutions in the Section 2.2., it was pointed out that a number of structural characteristics of the solutions are brought out by the various theories. It is therefore profitable to see how far these theories are applicable to the liquid gold-tin system and how much they tell about the structure.

It is convenient to compare the experimental values of the function $\frac{\Delta H}{x_i x_j}$ with those predicted by the theories. The experimental values obtained at 450°C are plotted against x in Fig. 5.3.1. For an ideal solution this function is zero. The regular

solution theory predicts the relationship given by the equation 2.2.8b., where the term (Nzw) is independent of composition. This is represented by a straight horizontal line drawn through $\frac{\Delta H}{x_i x_j}$ at $x_i = 0$. In a subregular solution the term (Nzw) is a linear function of x . The tangent to the experimental curve at $x_i = 0$ suitably represents the subregular behaviour. The quasi-chemical theory gives a relationship which contains an exponential term. When this is expanded and the higher order terms are omitted the equation takes the following form.

$$\frac{\Delta H}{x_i x_j} = (Nzw) - \frac{2(Nzw)^2}{2RT} \cdot x_i x_j$$

The term (Nzw) is equal to the value of $\frac{\Delta H}{x_i x_j}$ at $x_i = 0$. The second term is calculated from the first. The final relationship is then,

$$\frac{\Delta H}{x_i x_j} = -7700 - 8258x_i x_j$$

This parabolic function is plotted in Fig. 5.3.1.

Relationship between $\frac{\Delta H}{x_i x_j}$ and x_i as predicted by the average potential model is given by the equation 2.2.16. In order to evaluate this equation H , C_p and S are computed from the heats of sublimation and

the specific heats of tin⁽¹⁰⁵⁾. At 450°C,
 $H_{\text{Sn}} = -70.200 \text{ K.Cal/mole}$, $C_{p\text{Sn}} = 6.85 \text{ Cal/mole/}^\circ\text{C}$;
 $\frac{dC_{p\text{Sn}}}{dT} = 0$ and $\delta = 0.191$. ρ is calculated from the
 X-ray data⁽⁶⁷⁾ and its value is -0.120. The tem-
 perature coefficient of C_v is calculated with the
 help of equation 2.2.4. Values of 'V' and Volume
 Coefficient of expansion (α) are taken from the
 Metals Handbook⁽¹⁰⁸⁾ and Compressibility (β) is
 computed from the results of Gordon⁽⁶⁰⁾. Using
 these data $\frac{\Delta H}{x_{\text{Au}}x_{\text{Sn}}}$ is expressed as a function of Θ
 and x_{Sn} . Θ is calculated from the experimental
 value of $\frac{\Delta H}{x_i x_j}$ at $x_{\text{Sn}} = 1$. The numerical value is
 0.116. The final relationship is given by the
 following expression.

$$\frac{\Delta H}{x_{\text{Au}}x_{\text{Sn}}} = -7674 + 6x_{\text{Sn}} - 32x_{\text{Sn}}^2$$

This is plotted in Fig. 5.3.1.

The diagram shows that the regular solution
 model and the average potential model are far from
 approaching the experimental data at all compositions.
 On the other hand the sub-regular and the quasi-
 chemical theories approach the experimental data in
 very dilute solutions and deviate strongly at higher

concentrations.

The disagreement with the regular solution model may be partly due to the non-randomness of the solution. This is indicated by the relatively better agreement obtained between the experimental points and the quasi-chemical theory which takes into account the order in a solution. But this theory like the regular solution theory shows serious lack of agreement with the experimental data at higher compositions. Both of these models assume that "zw" is independent of composition. In the present case this is not valid as indicated by the fact that the sub-regular solution model fits the experimental curve better than any other. However this theory also fails at higher concentrations of gold. The disagreement with the theories at lower temperatures is expected to be more serious because of the increasingly unusual behaviour of the alloy at the tin rich end (Fig. 4.3.1.). The common assumption of these theories, that the contribution due to non-configurational factors is zero, must be inapplicable to these systems. This conclusion is strongly supported by the experimental heat capacities of the alloys (Fig. 4.3.7.).

The average potential model takes into account the non-configurational factors which the others neglected. In spite of this the agreement with the experiment is extremely poor. In this theory although the non-configurational factors have been considered, some configurational factors have been omitted and it is assumed that the theorem of corresponding states is obeyed and the Lennard-Jones law is operative. There is enough evidence to cause serious doubt about the applicability of these assumptions to metal solutions^(22, 31, 36, 37).

It is also unlikely that the assumption that e^* and r^* (Section 2.2.) are independent of environment, is valid for metals showing strong attraction for each other like gold and tin.

None of these theories take enough variables into consideration so as to account for the behaviour of the gold-tin system. However they strongly suggest that the co-ordination number and the interaction parameter are composition dependent, that there is association in the liquid state and that there is most likely a large contribution from the non-configurational factors.

5.4. Discussion of the Anomalies

Comparison of the present work with various theories shows that there is the probability of a large contribution from the non-configurational factors. This should be strongly reflected in the entropies of the system. Entropies can be determined by combining the present results with the free energies of these alloys.

Kleppa⁽⁶⁾ reported the electromotive forces of a galvanic cell of the form $\text{Sn}(l)/\text{Sn}^{++}/(\text{Sn}+\text{Au})(l)$ at 600 and 500°C. He stated that the e.m.f. vs. temperature relationship of all the alloys except four were linear and presented the e.m.f. vs. temperature plots for those four alloys. The electromotive forces taken from Kleppa's data are presented in Table 5.4.1.

The partial molar free energies of tin can be calculated using the relationship

$$\Delta \bar{G}_{\text{Sn}(l)} = -nFE,$$

where n = Valency of the tin ion,

F = Faraday constant,

and E = Electromotive force.

Values of the function

$$\phi_{\text{Sn}} = \frac{\Delta \bar{G}_{\text{Sn}(l)}}{(1-x_{\text{Sn}})^2}$$

Table 5.4.1.

Electromotive forces of the cell $\text{Sn}(1)/\text{Sn}^{++}/(\text{Sn}+\text{Au})(1)$ at 450°C . Extrapolated from data obtained by Kleppa.

Compo- sition x_{Sn}	E.m.f. m.v.	Compo- sition x_{Sn}	E.m.f. m.v.	Compo- sition x_{Sn}	E.m.f. m.v.
0.9026	3.785	0.5480	52.58	0.4426	89.02
0.8125	9.270	0.5302	59.57	0.3596	122.7
0.6815	24.62	0.5091	65.36	0.2941	154.6
0.6085	38.35	0.4982	68.27	0.2589	175.9
				0.2223	198.0

are obtained from the free energy data and are plotted against x_{Sn} . A smooth curve is drawn through these points and values of $\Delta\bar{G}_{\text{Sn}(1)}$ at round figure mole fractions are taken from this plot between $x_{\text{Sn}}=1$ and $x_{\text{Sn}}=0.25$. The shape of this curve is such that it is difficult to extrapolate it to pure gold. A value of $\Delta\bar{G}_{\text{Au}(1)}$ at one composition is needed in order to obtain the partial molar free energies of gold. $\Delta\bar{G}_{\text{Au}(1)}$ at 450°C could not be obtained from the equilibrium diagram because of the presence of an intermediate phase whose thermodynamic properties

are not known. Therefore $\Delta\bar{G}_{\text{Au}(1)}$, at 500°C , $x_{\text{Sn}}=0.2$ is obtained from the equilibrium diagram

($\Delta\bar{G}_{\text{Au}(1)}$, $x_{\text{Sn}}=0.2 = -1363$ Cal/mole at 500°C). This is combined with the function ' $\mathcal{L}_{\text{Sn}}$ ' calculated from Kleppa's ⁽⁶⁾ results at 500°C and a value of -2375 Cal/mole is obtained for $\Delta\bar{G}_{\text{Au}(1)}$, at 500°C , $x_{\text{Sn}}=0.3$.

Application of the following equation to the computed free energy and the experimental enthalpies (Fig. 4.3.6.) yields -2340 Cals/mole for $\Delta\bar{G}_{\text{Au}(1)}$ at 450°C , $x_{\text{Sn}}=0.3$.

$$\int_{T_1}^{T_2} d\left(\frac{\Delta\bar{G}_i}{T}\right) = \int_{T_1}^{T_2} \Delta\bar{H}_i d\left(\frac{1}{T}\right)$$

The curve for $\mathcal{L}_{\text{Sn}}$ at 450°C is extrapolated so as to be consistent with the computed value of $\Delta\bar{G}_{\text{Au}(1)}$.

Partial free energies for gold at other compositions are calculated by proper integration ⁽¹⁰⁹⁾. Excess

free energies are obtained by subtracting the ideal partial free energies ($TR\ln x$) from the observed

values. These are combined with the present enthalpy results and values for partial excess entropies are

obtained. Enthalpies for alloys containing more

than 75 At% Au are obtained by extrapolating the

function $\frac{\Delta\bar{H}_{\text{Au}(1)}}{(1-x_{\text{Au}})^2}$. The partial and integral values

of free energy, excess free energy, enthalpy and excess entropy are presented in Table 5.4.2., and the excess entropies are plotted in Fig. 5.4.1.

Table 5.4.2.

Thermodynamic Properties of Liquid Au-Sn Alloys at
450°C.

A. Component, Au

x_{Au}	$\Delta G_{\text{Au}(1)}$ Cal/mole	$\Delta \bar{G}_{\text{Au}(1)}^e$ Cal/mole	$\Delta \bar{H}_{\text{Au}(1)}$ Cal/mole	$\Delta \bar{S}_{\text{Au}(1)}^e$ Cal/mole/°C
0.0	-∞	-8800	-7850	1.31
0.1	-11375	-8065	-7740	0.45
0.2	-9545	-7230	-7287	-0.08
0.3	-8020	-6290	-6349	-0.08
0.4	-6450	-5135	-5000	0.19
0.5	-4910	-3915	-3447	0.65
0.6	-3465	-2730	-2310	0.58
0.7	-2340	-1825	-1840	-0.02
0.75	-1825	-1410	-1400	0.01
0.8	(-1400)*	(-1080)	(-960)	(0.16)
0.9	(-660)	(-510)	(-275)	(0.32)
1.0	0	0	0	0.00

*Extrapolated Values

Table 5.4.2. Continued.

B. Component Sn.

x_{Sn}	$\Delta \bar{G}_{\text{Sn}(1)}$ Cal/mole	$\Delta \bar{G}_{\text{Sn}(1)}^e$ Cal/mole	$\Delta \bar{H}_{\text{Sn}(1)}$ Cal/mole	$\Delta \bar{S}_{\text{Sn}(1)}^e$ Cal/mole/ $^{\circ}\text{C}$
1.0	0	0	0	0.00
0.9	-180	-30	-8	0.03
0.8	-490	-170	-93	0.11
0.7	-1000	-490	-415	0.10
0.6	-1860	-1125	-1152	-0.04
0.5	-3125	-2130	-2433	-0.42
0.4	-4900	-3585	-3783	-0.27
0.3	-7000	-5270	-4675	0.82
0.25	-8360	-6370	-5850	0.72
0.2	(-9830)	(-7520)	(-7380)	(0.19)
0.1	(-14110)	(-10800)	(-11310)	(-0.70)
0.0	-∞	(-15700)	(-16400)	(-0.97)

Table 5.4.2. Continued.

<u>C. Integral Properties</u>				
x_{Au}	ΔG	ΔG^e	ΔH	ΔS^e
	Cal/mole	Cal/mole	Cal/mole	Cal/mole/ $^{\circ}\text{C}$
0.0	0	0	0	0.00
0.1	-1300	-835	-781	0.07
0.2	-2300	-1580	-1532	0.07
0.3	-3105	-2230	-2195	0.05
0.4	-3695	-2730	-2691	0.05
0.5	-4020	-3025	-2940	0.12
0.6	-4040	-3070	-2899	0.24
0.7	-3740	-2860	-2690	0.24
0.75	-3460	-2650	-2512	0.19
0.8	(-3085)	(-2370)	(-2245)	(0.17)
0.9	(-2005)	(-1540)	(-1388)	(0.22)
1.0	0	0	0	0.00

Entropies of formation of liquid alloys arise from sources like the change of configuration, i.e. mixing, creation of vacancies or holes, changes in the vibrational spectrum, changes in the magnetic properties and excitation of conduction electrons. Ideally the excess entropy is zero. Any departure of the configurational factor from ideality should produce ~~negative~~ excess entropy. But in fact the plot shows positive values at all compositions. This implies that there is a positive contribution to the entropy of formation of these alloys from all other sources, and the magnitude of the contribution is larger than that of the configurational factor. In order to obtain information on the atomic arrangement in the liquid alloy the configurational contribution to the entropy should be known. This is separated by estimating the contribution due to the other changes.

Gordon⁽⁶⁰⁾ has successfully accounted for the increase in specific heat of liquid Sn, Pb, Na and Hg in terms of creation of holes. Any change in the concentration of holes produces changes in the entropy of formation, which can be calculated from the

following relationship⁽²⁰⁾.

$$\Delta S = \int_V^{V + \Delta V} \left(\frac{\partial S}{\partial V} \right)_T dV \approx \frac{1}{\beta} \Delta V$$

where V = the average molar volume.

This expression also takes into account a part of the vibrational contribution. Lack of satisfactory data on the volume of mixing prevents one from making an estimation. But the relationship shows that the sign of ΔV determines the sign of the ΔS . High negative value of the enthalpies of gold-tin alloys suggest that the ΔV is most likely negative.

There is no established theory of the specific heat of liquids so as to enable one to calculate the vibrational contribution to entropy. Any attempt to make an approximate estimation from the Debye theory⁽¹⁹⁾ also fails because of lack of data on compressibility. In general it could be said that the creation of polar bonds decreases the entropy and vice versa. This concept is discussed by Kubaschewski⁽⁸⁾ and supported by the properties of Mg_3Sb_2 and Mg_3Bi_2 ⁽⁸⁾.

Liquid gold and liquid tin are diamagnetic⁽⁶⁵⁾ and from the work of Jan et al⁽⁶⁶⁾ it appears that the liquid alloys are also diamagnetic. Therefore

the magnetic contribution to the entropy is negligible.

The electronic contribution is given by $\Delta \epsilon T$ (Equation 2.2.5.)⁽¹⁹⁾. Values of γ_e for solid gold and white tin are 1.8×10^{-4} and 4.2×10^{-4} Cal/mole deg⁻² respectively. The optical properties⁽⁶²⁾ and Hall coefficients⁽¹¹⁾ show that electronically liquid tin is similar to solid tin. The properties of gold being normal in all respects liquid gold must be similar to solid gold in this respect. If the value of γ_e of the alloy containing 50 At% Au becomes close to zero at 450°C an entropy change of -0.22 e.u. would be obtained. This shows that the appearance of covalent linkage in the alloy would make a negative contribution to the entropy and the magnitude of the contribution would be of the order of 0.2 e.u.

The total effect of all the non-configurational factors can be estimated from the relationship

$$\Delta S = \int \frac{\Delta C_p}{T} dT$$

Assuming ΔC_p to be linear with respect to temperature the experimental ΔC_p values (Table 4.3.2.) become numerically equal to the contributions made by the non-configurational factors to ΔS (Fig. 4.3.7.).

When the non-configurational contribution is subtracted

from ΔS^e the excess entropy due to configurational factor becomes negative, the maximum negative value being 1.75 e.u., (Fig. 5.4.1.). This value should not exceed 1.38 e.u. This shows that the computed non-configurational contribution is only approximate.

The above discussion points to the fact that the contributions due to all the factors (both configurational and non-configurational) are negative in case of any change in the bond type from metallic to polar. It is observed from Fig. 5.4.1. that at 450°C there is less pronounced positive deviation at about 45 and 75 At%Au. The contribution due to the non-configurational factors is again less positive at 75 At%Au but it is not any different from the general behaviour at 45 At%Au (Fig. 4.3.7.). When the excess entropy curve is extrapolated to 600°C using the ΔC_p values there still exists a depression (Fig. 5.4.1.) at 75 At%Au but the anomaly at the other composition disappears. A similar pattern is presented by the heats of formation tabulated overleaf. The table shows that the peak value of ΔH moves towards the gold rich end as the temperature is increased. From these observations

TABLE 5.4.2.

Heats of Formation of Au-Sn Alloys at 400, 450 and 600°C.

Temp	$x_{\text{Au}} =$							
°C	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.75
400	-798	-1574	-2264	-2780	-3029	-2971	-2732	-2555
450	-781	-1532	-2195	-2691	-2940	-2899	-2690	-2512
600	-730	-1408	-1990	-2426	-2673	-2683	-2555	-

it is tempting to suggest the existence of clusters of molecules in the alloy, but the high positive value of excess entropy does not support this idea. Therefore it is thought that at 75 At%Au there is a different type of bond between the atoms and these are continuously changing position relatively rapidly. Support for this concept is found in the viscosity data (Fig. 2.4.1.) and also in the X-ray (Fig. 2.5.1.) and the resistivity data (Fig. 2.4.2.).

The above observations also suggest that there is a certain amount of structure in the alloy at about 45 At%Au, and 450°C. Around this composition the alloy is nearest to the liquidus. It is therefore probable that the liquid retains a part of the

structure of the solid which disappears rapidly with increasing temperature (i.e. below 600°C).

There are other anomalies in the liquid gold-tin system at the tin rich end. The heats of solution of gold in tin rich alloys become more exothermic with increasing concentration of gold. This phenomenon is more pronounced at lower temperatures, (Fig. 4.3.1.). Assuming random mixing ΔH can be given by the following expression

$$\Delta H = Nz x_{\text{Au}} x_{\text{Sn}} (e_{\text{AuSn}} - \frac{1}{2} e_{\text{SnSn}}^{\circ} - \frac{1}{2} e_{\text{AuAu}}^{\circ}) + \frac{1}{2} Nz x_{\text{Au}}^2 (e_{\text{AuAu}} - e_{\text{AuAu}}^{\circ}) \\ + \frac{1}{2} Nz x_{\text{Sn}}^2 (e_{\text{SnSn}} - e_{\text{SnSn}}^{\circ}) \quad . \quad . \quad . \quad .5.4.1.$$

The equation shows that ΔH is a function of z and the energies of Sn-Sn, Au-Au and Au-Sn bonds. Since this phenomenon occurs in the alloy containing less than 10At% Au z and the energies of Au-Sn bond are unlikely to change appreciably. The strength of the Sn-Sn bond is also not going to be much different from that in pure tin. The same assumption cannot be made for the Au-Au bond in solution, as it is in an environment completely different from pure gold. This concept has been successfully used by Oriani and Murphy⁽³⁴⁾ and Bever and co-workers⁽¹¹⁰⁾ in interpreting the heat effects in dilute solutions. The

unusual behaviour of gold in solution is indicated by its high excess partial entropy (Fig. 5.4.1.).

Zener⁽¹¹¹⁾ has pointed out that most solutes in dilute solutions undergo vibrational changes. It is therefore assumed that Δe_{AuAu} has a definite value and it is a linear function of x_{Sn} .

$$\Delta e_{\text{AuAu}} = ax_{\text{Sn}} \quad 5.4.2.$$

Incorporating all these assumptions in equation 5.4.1. the following expression is obtained.

$$\Delta \bar{H}_{\text{Au}} = (Nzw)x_{\text{Sn}}^2 + (Nza)x_{\text{Sn}}^2 x_{\text{Au}}$$

$$\text{Here, } w = (e_{\text{AuSn}} - \frac{1}{2}e_{\text{AuAu}}^0 - \frac{1}{2}e_{\text{SnSn}}^0)$$

$$\text{and } (Nzw) = \Delta \bar{H}_{\text{Au}, x_{\text{Au}} \rightarrow 0}$$

This expression describes the experimental results well, when -21, -20, -18 and -17 K.Cals are substituted for (Nza) for temperatures 300, 350, 400 and 450°C respectively. The decreasing value of the constant indicates that with increasing temperature the solution approaches the ideal condition.

The values assigned to the constant appear to be high. But these should be considered in relation to the strength of the Au-Au bond which is given by the heat of sublimation of gold (85 K.Cal/mol ϕ).

Moreover the magnitude of (N_{za}) can be changed by making Δe_{AuAu} a non-linear function of x_{Sn} and removing the assumption that the solution is random. Application of quasi-chemical theory gives a value of -1 K.Cal for (N_{za}) , but the theoretical values of $\Delta \bar{H}_{Au}$ do not agree well with the experimental curve.

SUMMARY AND CONCLUSIONS

A liquid tin solution calorimeter previously reported by Kravitz has been further developed so that under good experimental conditions it yields results with an accuracy better than $\pm 0.2\%$. The heats of solution of gold in liquid tin and gold and tin in liquid gold-tin alloys have been measured at 275, 300, 350, 400 and 450°C . The relative partial and integral heat contents of the alloys calculated from the experimental data show maximum scatter of ± 20 Cals/mole. The results for the enthalpies give values of the heat capacity of the alloy. Values for the free energies and entropies of the liquid gold-tin system at 450°C have been derived from the present results and the extrapolated high temperature data of Kleppa.

Both the enthalpies and the entropies show anomalies at 10 and 75 At% Au. The behaviour at the gold rich end is consistent with the observations of X-ray and resistivity studies. The peculiarities of the partial heat contents of gold at the tin rich end have been explained on the basis of the relative strength of the Au-Au bond in solution.

At all compositions the properties become more

anomalous at lower temperatures. Therefore accurate free energy data at these temperatures will be needed to reveal greater details of the structural peculiarities.

Data on the volume changes on alloying and the compressibilities of the alloys would be helpful to have in order to be able to determine the contributions to the excess entropy arising from volume changes.

REFERENCES

1. Frost B. R. T., Progr. Metal Physics, 1954, 5, p.36.
2. Rosenblum L., J.Metals, 1963, Sept., p.637.
3. Frost B. R. T., J.Nuclear Matls., 1962, 2 (2), p.109.
4. Hansen P. M., "Constitution of Binary Alloys", McGraw-Hill Book Co., 1958.
5. Hendus H., Z.Naturforschung, 1947, 2 (a), p.505.
6. Kleppa O. J., J.Amer.Chem.Soc., 1950, 72, p.3346.
7. Roll V. A. and E. Uhl, Z.Metallkunde, 1959, 50, p.159.
8. Kubaschewski, O. and E. L. Evans, "Metallurgical Thermochemistry", Pergamon Press, 1958.
9. Handbook of Physical Constants, Geological Society of America, 1942.
10. Miller R. R., Liquid Metals Handbook, Chapter 1, Dept. of Navy, Washington, 1952.
11. Cusack N. E., Report Progr.Phys., 1963, 26, p.361.
12. Radchenko I. V., Uspakhi Fizicheskikh Nauk, 1957, 61 (2), p.249.
13. Hollomon J. H. and D. Turnbull, Progr. Metal Physics, 1953, 4, p.333.
14. Catterall J. A. and J. Trotter, Phil.Mag., 1963, 8, p.897.

15. Knight W. D., A. G. Berger and V. Heine, Ann. of Phys., 1959, 8, p.173.
16. Laurie G. H. and J. N. Pratt, Trans. Faraday Soc. 1964, 60, p.1391.
17. Lewis G. N. and M. Randal, "Thermodynamics and the Free Energy of Chemical Substances", McGraw-Hill Book Co., 1923.
18. Fowler R. H. and E. A. Guggenheim, "Statistical Thermodynamics", Cambridge University Press, 1960.
19. Mott N. F. and H. Jones, "The Theory of the Properties of Metals and Alloys", Oxford University Press, 1936.
20. Guggenheim E. A., "Thermodynamics", North-Holland Publishing Co., 1959.
21. Kubaschewski O. and J. A. Catterall, "Thermochemical Data of Alloys", Pergamon Press, 1956.
22. Hildebrand J. H. and R. L. Scott, "Regular Solutions", Prentice-Hall Inc., 1962.
23. Guggenheim E. A., Mixtures, Oxford University Press, 1952.
24. Oriani R. A. and C. B. Alcock, Trans.A.I.M.E., 1962, 224, p.1104.

25. Kichizo Niwa and M. Shimoji, "The Physical Chemistry of Metallic Solutions and Intermetallic Compounds", NPL Symposium No. 9, H.M.S.O., London, 1959.
26. Hardy H. K., *Acta.Met.*, 1953, 1, p.202.
27. Oriani R. A., *J.Appl.Physics*, 1950, 21, p.1068.
28. Oriani R. A., *Acta.Met.*, 1954, 2, p.608.
29. Oriani R. A., *The Physical Chemistry of Metallic Solutions and Intermetallic Compounds*, NPL Symposium No. 9, H.M.S.O., London, 1959.
30. Alcock C. B., *ibid.*
31. Oriani R. A., *J.Phys.Chem.Solids* 1957, 2, p.327.
32. De Sorbo W., *Acta.Met.*, 1955, 3, p.227.
33. Oriani R. A., *Acta.Met.*, 1955, 3, p.232.
34. Oriani R. A., and W. K. Murphy, *The Physical Chemistry of Metallic Solutions and Intermetallic Compounds*, NPL Symposium No. 9, H.M.S.O., London, 1959.
35. Prigogine I., A. Bellemans and V. Mathot, "The Molecular Theory of Solutions", North-Holland Publishing Co., Amsterdam, 1957.
36. Jones H., *Physica*, 1949, 15, p.13.
37. Seitz F., "Modern Theory of Solids", McGraw-Hill Co., N.Y., 1940.

38. Hume-Rothery W. and G. V. Raynor, "The Structure of Metals and Alloys", Institute of Metals, 1954.
39. Yao Tung-Ping, Giesserei Techn-Wessensch Beihefte, 1957, 17, p.897.
40. Jones W. R. D. and J. B. Davies, J.Inst.Metals, 1957-58, 86, p.164.
41. Jones W. R. D. and W. L. Bartlett, J.Inst.Metals, 1952-53, 81, p.145.
42. Fisher H. J. and A. Phillip, Trans.A.I.M.E., 1954, 200, p.1060.
43. Belashchenko D. K., DAN., 1957, 117, p.98.
44. Gebhardt E., M. Becker and S. Schafer, Z.Metallkunde, 1952, 43, p.292.
45. Samarin A. M., JISI, 1962, 200, p.95.
46. Yao T. P. and V. Kondic, J.Inst.Metals, 1952-53, 81, p.17.
47. Stott V. H., Proc.Phys.Soc., 1933, 45, p.530.
48. Frenkel J., "Kinetic Theory of Liquids", Dover Publications, 1955.
49. McLaughlin E. and A. R. Ubbelohde, Trans. Faraday Soc. 1960, 56, p.988.
50. Gebhardt E., M. Becker and K. Kostlin, Z.Metallkunde, 1956, 47, p.684.
51. Nordheim L., Ann.D.Physik, 1931, 2, p.641.

52. Roll V. A. and N. K. A. Swami, Z.Metallkunde, 1961, 52, p.111.
53. Roll V. A. and P. Basu, Z.Metallkunde, 1963, 54, p.511.
54. Adams P., Ph.D. Thesis, University of London, 1964.
55. Roll V. A. and H. Motz, Z.Metallkunde, 1957, 48, p.272.
56. Melford D. A. and T. P. Hoar, J.Inst.Metals, 1956-57, 85, p.197.
57. Bornemann K. and P. Siebe, Z.Metallkunde, 1922, 14, p.329.
58. Kirshenbaum A. D. and J. A. Cahill, Trans.ASM, 1962, 55, p.844.
59. Lucas L. D., Les Memoires Scientifiques, 1964, January, p.1.
60. Gordon R. B., Acta.Met., 1959, 7, p.1.
61. Pashaev B. P., Soviet Phys. Solid State, 1961, 3, p.306.
62. Hodgson J. N., Phil.Mag., 1961, 6, p.509.
63. Gebhardt E. and S. Dorner, Z.Metallkunde, 1951, 42, p.353.
64. Orton B. R. and G. I. Williams, Fulmer Research Institute , Research Report R.129/6/August, 1961.

65. Shimizu Y., Sci.Rep. Tohoku Imp. Univ. 1937, 25, p.921.
66. Jan J. P., W. B. Pearson, A. Kjekshus and S. B. Woods, Canadian J. of Physics, 1963, 41, p.2252.
67. Skryshevskii A. F., Ukrainsk.Fiz.Zhur., 1957, 11 (4), p.363.
68. Gammertsfelder C., J.Chem.Phys., 1941, 9, p.450.
69. Williams G. I., Phil.Mag., 1963, 8 (85), p.141.
70. Danilov A. I., Dokl.Akad.Nauk.SSSR, 1952, 82, p.561.
71. Bublik A. I., Soviet Physics Crystallography, 1957, 2, p.240.
72. Richter H. and S. Steeb, Naturwissenschaften, 1958, 24, p.512.
73. Pauling L., "The Nature of the Chemical Bond", Cornell University Press, 1960.
74. Sauerwald F, Z.Metallkunde, 1950, 41, p.214.
75. Orton B. R. and G. I. Williams, Fulmer Research Institute, Research Report R. 129/3/May, 1959.
76. Orton B. R. and G. I. Williams, Fulmer Research Institute, Research Report R. 129/4/March, 1960.
77. Howlett B. W., Private Communication.
78. Kleppa O. J., J.Phys.Chem., 1956 (b), 60, p.858.
79. Biltz W., G. Rohlfes and H. V. Vogel, Z.Anorg.

- U. Allgem.Chem., 1934, 220, p.113.
80. Bottema J. A. and F. M. Jaeger, Proc.Akad,Amsterdam, 1932, 35, p.916.
81. Kubaschewski O., Z.Physik.Chem., 1943, 192, p.292.
82. Ticknor L. B. and M. B. Bever, Trans.A.I.M.E., 1952, 194, p.94.
83. Kleppa O. J., J.Phys.Chem., 1956 (a), 60, p.842.
84. Orr R. L., A. Goldberg and R. Hultgren, Rev.Sci. Instr., 1957, 28, p.767.
85. Day G. F. and R. Hultgren, J.Phys.Chem., 1962, 66, p.1532.
86. Oriani R. A. and W. K. Murphy, J.Phys.Chem., 1958, 62, p.327.
87. Orr R. L., A. Goldberg and R. Hultgren, J.Phys. Chem., 1958, 62, p.325.
88. Orr R. L., A. Goldberg and R. Hultgren, First Technical Report, Contract No. DA-04-200-ORD-171, T.O.8, Mineral Research Laboratory, University of California, 1955.
89. Carpenter R. W., R. L. Orr and R. Hultgren, Third Technical Report, Contract No. DA-04-200-ORD-171, T.O. 15, Mineral Research Laboratory, University of California, 1959.
90. Leach J. S. Ll., Unpublished work.

91. Yanko J. A., A. E. Drake and F. Hovorka, Trans. Electrochem.Soc., 1946, 89, p.357.
92. Chipman J., J. F. Elliot and B. L. Averbach, The Physical Chemistry of Metallic Solutions and Intermetallic Compounds, NPL Symposium No. 9, H.M.S.O., London, 1959.
93. Bever M. B. and B. W. Howlett, Seminar on "Calorimetric Methods Used in Solid State Metallurgical Investigations", Dept. of Metallurgy, M.I.T., U.S.A., 1960.
94. Kubaschewski O. and R. Hultgren, "Experimental Thermochemistry", V.2, Chapter 16, Interscience Publishers, New York, 1962.
95. Kravitz S. and J. S. Ll. Leach, To be Published in J.Sci.Inst.
96. Kleppa O. J., J.Phys.Chem., 1955, 59, p.175.
97. Gordon P., Trans.A.I.M.E., 1955, September, p.1043.
98. Kubaschewski O and W. A. Dench, "Physical Measurements at High Temperatures", Butterworth 1959.
99. Howlett B. W., J. S. Ll. Leach, L. B. Ticknor and M. B. Bever, Rev.Sci.Inst., 1962, 33, p.6.
100. Beattie J. A., Rev.Sci.Inst., 1931, 2, p.458.

101. Kravitz S., Ph.D. Thesis, University of London, 1963.
102. Jakob M. and G. A. Hawkins, "Elements of Heat Transfer", Chapman and Hall, 1957.
103. Cremer H. W. and S. B. Watkins, "Chemical Engineering Practice", V.7, Heat Transfer, Butterworths, 1963.
104. Kelley K. K., "Contribution to Data on Theoretical Metallurgy XIII", Bureau of Mines Bulletin 584, U.S.Govt. Printing Office, Washington, 1960.
105. Hultgren R., R. L. Orr, P. D. Anderson and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys", John Wiley and Sons Inc., 1963.
106. Wagner C., "Thermodynamics of Alloys", Addison-Wesley, 1952.
107. Masse J. D. G., Master's Thesis, University of California, 1964.
108. Metals Hand Book, 8th Edition, VI, ASM, 1961.
109. Darken L. S. and R. W. Gurry, "Physical Chemistry of Metals", McGraw Book Co., 1953.
110. Cohen J. B., B. W. Howlett and M. B. Bever, Trans. A.I.M.E., 1961, 221, p.683.
111. Zener C., "Thermodynamics in Physical Metallurgy", ASM, 1950.

Acknowledgements

The author is indebted to Dr. J. S. Llewelyn Leach for his continued interest and guidance throughout the course of this work.

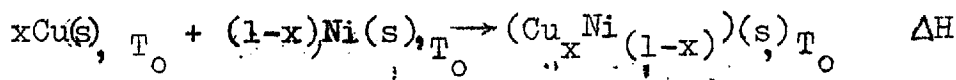
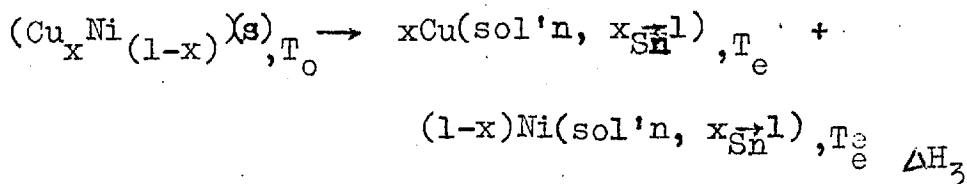
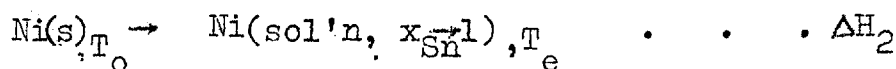
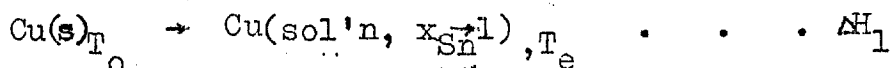
He gratefully acknowledges his appreciation to Professor J. G. Ball for providing the laboratory facilities.

Thanks are due to the C.S.I.R., Government of India for awarding him the A.O.C. Scholarship and the U.K.A.E.A. for providing financial support for the project.

Finally the author would like to thank Mr. V. Ramaswamy and Mr. J. D. Shotton for their valuable assistance.

APPENDIX I.Heats of Solution of Solid Copper and Solid Nickel
in Liquid Tin and Heats of Formation of some Solid
Copper-Nickel Alloys.

The heats of formation of some copper-nickel alloys have been determined in the liquid tin solution calorimeter. The method of calculating the heat of formation from the experimental data is illustrated below.



$$\therefore \Delta H = x \Delta H_1 + (1-x) \Delta H_2 - \Delta H_3$$

ΔH_1 , ΔH_2 and ΔH_3 are determined experimentally and are described as total heat effects on solution.

The alloys and their components used in this investigation were presented by The International Nickel Company (Mond) Limited. The specimens had been taken from hot rolled and machined plates produced

from alloys prepared by vacuum melting electrolytic copper and carbonyl nickel (99.95%) in fused alumina crucibles. The approximate content of impurities in these samples are stated to be:

Carbon 0.002 - 0.01%

Aluminium <0.01 - 0.02%

Silicon <0.005 - 0.01%

Iron 0.01 - 0.02%

In order to have specimens suitable for addition to the calorimeter small pieces are cut from the samples and rolled into strips (1 mm. x 0.1 mm.). These are cut into suitable lengths (7 mm.), pickled in dilute nitric acid to clean the surface, sealed in evacuated tubes and annealed for 5 to 6 hours at 700-800°C.

The results of the experiments with copper are presented in Table AI.1. It contains the total heat effects and the relative partial molar heat contents of copper. The latter is calculated using equations 4.2.14., 4.2.16. and 4.2.17. and the heat contents tabulated by Hultgren and co-workers⁽¹⁾. The values of $\Delta \bar{H}_{\text{Cu(s)}}$ are plotted against mole fractions of copper in Fig. AI.1. and the following equation is obtained for the best line.

Table AI.1.

Heat of Solution of Copper in Liquid Tin at 350°C.

T _e Temperature °C.	Run No.	Σn_{Cu} x10 ³ moles	Σn_{Sn} moles	Σn_{Ni} x10 ³ moles	Total Heat Effect Cal/mole	H _{T_e} - H _{T_o} Cal/mole	$\Delta \bar{H}_{Cu(s)}$ at 350°C cal/mole	x _{Cu} x10 ²	Remarks
348.7	15.3	9.8599	5.1088	-	4603.7	2129.6	2477	0.096	
348.5	15.4	19.8647	5.1088	-	4541.4	2128.3	2417	0.290	
348.1	15.6	29.7576	5.1188	-	4489.3	2125.3	2369	0.482	$\Delta \bar{H}_{Cu(s)} = 2.4$ Cal/mole/°C
347.9	15.8	39.9575	5.1298	-	4533.8	2124.3	2414	0.675	
347.9	15.9	49.8615	5.1298	-	4495.8	2123.7	2376	0.868	
350	21.2	7.8785	5.1269	-	4628.9	2137.6	2491	0.077	
350	21.3	15.7287	5.1269	-	4583.8	2137.6	2446	0.230	
350	21.4	23.5757	5.1269	-	4572.8	2137.6	2435	0.382	
350	21.7	40.3596	5.1359	-	4574.8	2137.6	2437	0.697	
350	21.8	48.5049	5.1359	-	4509.2	2137.6	2372	0.858	
350	23.2	7.0538	5.1261	-	4624.4	2137.6	2487	0.069	
350	23.4	14.0101	5.1361	-	4593.4	2137.6	2456	0.205	
350	23.5	21.0812	5.1361	-	4544.4	2137.6	2407	0.340	
350	23.7	28.0264	5.1446	-	4496.2	2137.6	2359	0.475	
350	22.9	9.7372	5.1456	22.7525	3609.5	2137.6	21472	0.142	x _{Ni} x10 ² = 0.439

$$\Delta \bar{H}_{\text{Cu(s)}}, 350^{\circ}\text{C} = 2510 - 29000x_{\text{Cu}}, (\pm 8 \text{ Cal}, x_{\text{Cu}} < 0.004)$$

Hence at 350°C ,

$$\Delta \bar{H}_{\text{Cu(s)}}, x_{\text{Sn}} \rightarrow 1 = 2510 \pm 8 \text{ Cal/mole}$$

and the total heat effect,

$$\Delta H_1 = 4648 \pm 8 \text{ Cal/mole.}$$

The Table AI.1. also contains one result for the heat of solution of copper in liquid tin containing nickel. This is however, not very accurate because of the slow solution rate.

The results of experiments with solid nickel are treated in the same manner and the details are presented in Table AI.2. The heats of solution of nickel are plotted against composition in Fig. AI.1. and the following relationship is computed from the average line.

$$\Delta \bar{H}_{\text{Ni(s)}}, 350^{\circ}\text{C} = -11625 + 21000x_{\text{Ni}}, (\pm 23 \text{ Cal}, x_{\text{Ni}} < 0.005)$$

Hence at 350°C ,

$$\Delta \bar{H}_{\text{Ni(s)}}, x_{\text{Sn}} \rightarrow 1 = -11625 \pm 23 \text{ Cal/mole}$$

and the total heat effect, $\Delta H_2 = -9115 \pm 23 \text{ Cal/mole}$

The other results presented in Table AI.2. are not very accurate because of long solution time and uncertain 'k' line. However the dependence of

Table AI.2.
Heat of Solution of Nickel in Liquid Tin at 350°C.

Run	Temp- ture- C.	Zn Ni_3 moles $\times 10^3$	Zn Sn moles	Zn Cu_2 moles $\times 10^3$	Total Heat Effect Cal/mole	H T_e - H T_o Cal/mole	ΔH_{Ni} at 350°C Cal/mole	X_{Ni_2} $\times 10^2$	Remarks
350	24.2	5.5800	5.1258	-	-9108.3	2509.8	-11618	0.054	
350	24.4	11.0135	5.1348	-	-9073.9	2509.8	-11584	0.161	
350	24.5	16.6752	5.1348	-	-9017.2	2509.8	-11527	0.269	
350	24.7	21.8924	5.1447	-	-9078.1	2509.8	-11588	0.373	
350	23.9	5.2495	5.1532	28.0264	-8855.6	2509.8	-11365	0.051	$X_{Cu} = 0.540$ $X_{av} = 0.932$
350	21.11	13.6076	5.1448	48.5049	-8454.6	2509.8	-10964	0.197	
350	21.12	20.8857	5.1448	48.5049	-8331.2	2509.8	-10841	0.331	

$\Delta\bar{H}_{\text{Ni(s)}, x_{\text{Sn}} \rightarrow 1}$ on x_{Cu} is approximately 62 K Cal/mole.

The total heat effects on solution of alloys are recorded in Table AI.3. The average values of the heat effects are adopted for ΔH_3 . The heats of formation of the alloys determined from the values of ΔH_1 , ΔH_2 and ΔH_3 are also included in the table. and copper

The heats of solution of solid nickel/in liquid tin at infinite dilution, when recalculated using the data of Kelley⁽²⁾ on the heat content of tin ($\Delta\bar{H}_{\text{Cu(s)}} = 2620$ Cal/mole and $\Delta\bar{H}_{\text{Ni(s)}} = -11840$ Cal/mole), are consistent with all the other experimental data^(3, 4, 5, 6, 7, 8, 9, 10, 11, 12). Present work suggests that the composition dependence of the heat of solution of copper tends to change from -29 K Cal/mole at compositions less than $x_{\text{Cu}} = 0.004$ to -5 K Cal/mole at higher concentrations of copper. Whereas the composition dependence reported by Oriani and Murphy^(7,9) is -5.2 K Cal/mole at 425°C over the composition range $x_{\text{Cu}} = 0.00-0.02$. Composition dependence of $\Delta\bar{H}_{\text{Ni(s)}}$ found during this investigation (21 K Cal/mole at 350°C) agrees well with those reported by Oriani and Murphy⁽⁹⁾ (23.77 K Cal/mole at 640°C) and Day and Hultgren⁽¹¹⁾ (20.5 K Cal/mole at 637°C). Influence of x_{Cu} on

Table AI.3.

Total Heat Effects on Solution of Cu-Ni Alloys in Liquid Tin.

Compo- sition of the alloy. At%Ni	Run No.	T _e Tin Tempe- rature °C	T _o Initial Temp. of the alloy °C	Σn_{Sn} moles	Σn_{alloy} $\times 10^3$ moles	x_{alloy} $\times 10^2$	Total Heat Effect Cal/ mole	Total Heat Effect at x_{alloy}^0 Cal/ mole	ΔH_{alloy} Cal/mole
27.24	26.2	350	0	5.1351	6.4991	0.063	729		
	26.3	350	0	5.1351	13.8081	0.197	547	+662 [±] 76	237 [±] 88
	26.5	350	0	5.1463	20.8568	0.336	709		
52.47	25.2	350	0	5.1203	5.7519	0.056	-2995		
	25.3	350	0	5.1203	12.4824	0.178	-3007	-3000 [±] 6	428 [±] 22
	25.4	350	0	5.1203	17.9032	0.296	-2816	-	-
69.40	28.2	350	0	5.1014	5.6938	0.056	-5836		
	28.3	350	0	5.1014	11.1634	0.165	-5982	-5824 [±] 113	920 [±] 130
	28.4	350	0	5.1014	16.8390	0.274	-5654		

$\Delta\bar{H}_{\text{Ni(s)}, x_{\text{Sn}} \rightarrow 1}$ is 62 K Cal/mole compared with 16 K Cal/mole calculated using the equations presented by Alcock and Richardson⁽¹³⁾. These equations are based on the assumption that the solution is perfectly random. High negative value of the heat of solution of nickel suggests the presence of a certain degree of order in the solution. This is most likely the major factor contributing to the difference between theory and experiment.

The heats of formation of the alloys are plotted against composition in Fig. AI.2. It also contains other experimental values^(8, 9, 14, 15, 16). Present results at 25 and 50 At%Ni agree well with other results except those of Leach and Bever⁽⁸⁾. All the existing data suggest that their values for $\Delta\bar{H}_{\text{Cu(s)}}$ and $\Delta\bar{H}_{\text{Ni(s)}}$ are in error. When their results are recalculated using the heats of solution data reported here, the recalculated values fall within 50 calories of other results. The heat of formation of the alloy containing 70 At%Ni is relatively much higher and probably anomalous.

Quoted errors in all the results represent average deviations from the mean.

References

1. Hultgren R., R. L. Orr, P. D. Anderson and K. K. Kelley. "Selected Values of the Thermodynamic Properties of Metals and Alloys". John Wiley and Sons, 1963.
2. Kelley K. K., Contributions to the Data on Theoretical Metallurgy XIII, Bureau of Mines Bulletin 584, U.S. Govt. Printing Office, Washington, 1960.
3. Tichnor L. B. and M. B. Bever, Trans, AIME, 1952, 196, p.941.
4. Kleppa O. J., J.Phys.Chem., 1956, 60, p.842.
5. Orr R. L., R. Hultgren, Inst. of Engineering Research Report, Univ. of California, Berkely, series no.76, Issue No. 2, 1956.
6. Oriani R. A. and W. K. Murphy, J.Phys.Chem., 1958, 62, p.327.
7. Oriani R. A. and W. K. Murphy, "The Physical Chemistry of Metallic Solutions and Intermetallic Compounds". N.P.L. Symposium No. 9, HMSO, London 1959.
8. Leach J. S. Ll. and M. B. Bever, Trans AIME, 1959, 215, p.728.
9. Oriani R. A. and W. K. Murphy, Acta.Met. 1960, 8, p.23.

10. Kravitz S., Ph.D. Thesis, University of London, 1963.
11. Day G. F. and R. Hultgren, J.Phys.Chem., 1962, 66, p.1532.
12. King C. R. and O. J. Kleppa, Acta.Met., 1964, 12, p.87.
13. Alcock C. B. and F. D. Richardson, Acta.Met., 1958, 6, p.385.
14. Kubaschewski O., W. A. Dench and V. Genta, "The Physical Chemistry of Metallic Solutions and Intermetallic Compounds", N.P.L. Symposium No. 9, HMSO, London 1959.
15. Pratt J. N., *ibid*, Paper IK.
16. Rapp R. A., and F. Maak, Acta.Met. 1962, 10, p.63.

APPENDIX IIDetails of Two Additions.Run. - 13.2

Date. 30.1.63.

Time. 12.35.

- | | |
|---|--|
| 1. Weight of load | 601.6706 gms. |
| 2. Weight of specimen | 1.7032 gms. |
| 3. Type of specimen | 3 pieces of tin at 0°C. |
| 4. Bridge resistance | 213.49 Ω |
| 5. Main heater current | 12.5 amps. |
| 6. Stirrer (Tin) speed | 96 rpm. |
| 7. Vacuum | 2×10^{-5} mm.Hg. |
| 8. Galvanometer zero | a) Before Experiment 0 |
| | b) After Experiment 0 |
| 9. Galvanometer Reading, when
connected to the standard cell | a) Before Experiment -1.8cm. |
| | b) After Experiment -1.4cm. |
| 10. Salt couple (Cr/Al) Reading | a) Before Experiment 12728 μ V.,
-0.4 cm. |
| | b) After Experiment 12728 μ V.,
-0.4 cm. |
| 11. Tin couple (Cr/Al) Reading | Before Experiment 12804 μ V.,
-0.55 cm. |
| 12. Sensitivity | 2.5 cms. $\equiv$ 1 μ V. (1 mm. $\equiv$ 0.04 μ V) |

13. Drift in the battery voltage

± 4 mm. drift in the standard cell setting $\approx$

± 1 mm. drift in the couple (TIN) reading.

For this addition, equation 3.7.13. is valid.

Therefore 'Cp_f' is calculated using equation 3.7.14.

From Fig. AII.1.

$$k = -(\text{slope}) 2.3026 = 0.000499 \text{ sec.}^{-1}$$

Taking, $t = 135$ sec. and $T = 12757.57 \mu\text{V.}$,

$$(T_e - T) = 46.21 \mu\text{V.}$$

Using equation 3.9.1.,

$$k \int_0^{135} (T_e - T) dt = k \times 6134.775 \mu\text{V. sec.} = 3.061 \mu\text{V.}$$

$$\therefore \left[(T_e - T) + k \int_0^t (T_e - T) dt \right] = (46.21 + 3.061) \mu\text{V.} = 49.271 \mu\text{V.}$$

$$n_{\text{Sn}} = \frac{1.7032}{118.7} \text{ moles} = 14.3488 \times 10^{-3} \text{ moles.}$$

From the bridge reading,

$$T_e = 303.96^\circ\text{C} \approx 577.1^\circ\text{K.}$$

From equation 3.9.2., $(H_{577.1} - H_{273.15})_{\text{Sn}} = 3761.6 \text{ Cal/mole}$

$$Cp_f = \frac{n(H_{T_e} - H_{T_0})_{\text{sp}}}{(T_e - T) + k \int_0^t (T_e - T) dt} = \frac{14.3488 \times 10^{-3} \times 3761.6}{49.271} \text{ Cal}/\mu\text{V.}$$

Taking the thermoelectric power (θ) of the couple as

$$42.5 \mu\text{V}/^\circ\text{C}, \quad Cp_f = 1.09545 \text{ Cal}/\mu\text{V} \approx 46.557 \text{ Cal}/^\circ\text{C.}$$

Table AII.1.

R.13.2.

Correc-	Time	Potent-	Galvan-	meter	Reading	cm.	Due to	drift in	the bat-	tery	voltage	μV.
tion	sec.	meter	meter	μV.	μV.	(μV.)	10 ⁸	(μV.)	(μV.)	(μV.)	(μV.)	(μV.)

0.00	0	12804	-0.55	12803.78	00.00	-	1.7084	1.6948	1.6871	1.6823	1.6785	1.6751	1.6713	1.6680	1.6647	1.6602	1.6551	1.6481	1.6416	1.6348	1.6282	1.6218	1.6155	1.6089	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376
0.00	15	12752	+1.70	12752.68	51.10	1.7084	1.6948	1.6871	1.6823	1.6785	1.6751	1.6713	1.6680	1.6647	1.6602	1.6551	1.6481	1.6416	1.6348	1.6282	1.6218	1.6155	1.6089	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376	
0.00	30	12754	+0.65	12754.26	49.52	1.6948	1.6871	1.6823	1.6785	1.6751	1.6713	1.6680	1.6647	1.6602	1.6551	1.6481	1.6416	1.6348	1.6282	1.6218	1.6155	1.6089	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376		
0.00	45	12755	+0.30	12755.12	48.66	1.6871	1.6823	1.6785	1.6751	1.6713	1.6680	1.6647	1.6602	1.6551	1.6481	1.6416	1.6348	1.6282	1.6218	1.6155	1.6089	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376			
0.00	60	12756	-0.85	12755.66	48.12	1.6823	1.6785	1.6751	1.6713	1.6680	1.6647	1.6602	1.6551	1.6481	1.6416	1.6348	1.6282	1.6218	1.6155	1.6089	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376				
0.00	75	12756	+0.20	12756.08	47.70	1.6785	1.6751	1.6713	1.6680	1.6647	1.6602	1.6551	1.6481	1.6416	1.6348	1.6282	1.6218	1.6155	1.6089	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376					
0.00	90	12756	+1.15	12756.46	47.32	1.6751	1.6713	1.6680	1.6647	1.6602	1.6551	1.6481	1.6416	1.6348	1.6282	1.6218	1.6155	1.6089	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376						
-0.01	105	12757	-0.30	12756.87	46.91	1.6713	1.6680	1.6647	1.6602	1.6551	1.6481	1.6416	1.6348	1.6282	1.6218	1.6155	1.6089	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376							
-0.01	120	12757	+0.60	12757.23	46.55	1.6680	1.6647	1.6602	1.6551	1.6481	1.6416	1.6348	1.6282	1.6218	1.6155	1.6089	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376								
-0.01	135	12758	-1.05	12757.57	46.21	1.6647	1.6602	1.6551	1.6481	1.6416	1.6348	1.6282	1.6218	1.6155	1.6089	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376									
-0.01	150	12758	+0.15	12758.05	45.73	1.6602	1.6551	1.6481	1.6416	1.6348	1.6282	1.6218	1.6155	1.6089	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376										
-0.01	180	12758	+1.50	12758.59	45.19	1.6551	1.6481	1.6416	1.6348	1.6282	1.6218	1.6155	1.6089	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376											
-0.01	210	12759	+0.80	12759.31	44.47	1.6481	1.6416	1.6348	1.6282	1.6218	1.6155	1.6089	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376												
-0.01	240	12760	-0.05	12759.97	43.81	1.6416	1.6348	1.6282	1.6218	1.6155	1.6089	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376													
-0.01	270	12761	-0.80	12760.65	43.13	1.6348	1.6282	1.6218	1.6155	1.6089	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376														
-0.02	300	12761	+0.80	12761.30	42.48	1.6282	1.6218	1.6155	1.6089	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376															
-0.02	330	12762	-0.15	12761.92	41.86	1.6218	1.6155	1.6089	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376																
-0.02	360	12762	+1.35	12762.52	41.26	1.6155	1.6089	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376																	
-0.02	390	12763	+0.40	12763.14	40.64	1.6089	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376																		
-0.02	420	12764	-0.55	12763.76	40.02	1.6023	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376																			
-0.02	450	12764	+0.85	12764.32	39.46	1.5962	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376																				
-0.03	480	12765	-0.15	12764.91	38.87	1.5896	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376																					
-0.03	510	12765	+1.20	12765.45	38.33	1.5835	1.5771	1.5706	1.5646	1.5502	1.5376																						
-0.03	540	12766	+0.10	12766.01	37.77	1.5771	1.5706	1.5646	1.5502	1.5376																							
-0.03	570	12767	-1.00	12766.57	37.21	1.5706	1.5646	1.5502	1.5376																								
-0.03	600	12767	+0.30	12767.09	36.69	1.5646	1.5502	1.5376																									
-0.04	660	12768	+0.80	12768.28	35.50	1.5502																											
-0.04	720	12769	+0.85	12769.30	34.48	1.5376																											

Run. - 34.4

Date 19.3.64.

1. Weight of load
 - 2.2735 gms. Tungsten
 - 327.2360 gms. Tin
 - 538.5165 gms. Gold
2. Weight of specimen 2.3584 gms.
3. Type of specimen 3 pieces of gold specimen
4. Bridge resistance 255.66 Ω
5. Main heater current 14 Amps.
6. Stirrer (Tin) speed 96 rpm.
7. Vacuum 1×10^{-5} mm.Hg.
8. Galvanometer zero
 - a) Before Experiment 0
 - b) After Experiment 0
9. Galvanometer Reading when connected to the standard cell
 - a) Before Experiment 0
 - b) After Experiment -
10. Salt couple (Cr/Al) Reading
 - a) Before Experiment 17564 μ V.,
+0.5 Cm.
 - b) After Experiment 17564 μ V.,
+1.0 Cm.
11. Tin couple (Cr/Al) Reading
 - Before Experiment 17670 μ V.,
-1.0 Cm.
12. Sensitivity 2 Cm. $\approx$ 1 μ V. (1 mm. = 0.05 μ V)

13. Drift in the Battery Voltage

± 5 mm. drift in the standard cell setting $\equiv$

± 4 mm. drift in the couple (tin) reading.

Note: The drifts are noted against appropriate time in centimetres and are bracketted.

Since equation 3.7.13. is not valid, the quantity Q_{T_e} is calculated with the help of equation 3.7.12.

From Fig. AII.2.

$$k = 0.000972 \text{ sec.}^{-1}$$

Taking $t = 180$ sec. and $T = 17653.990 \mu\text{V.}$,

$$(T_e - T) = 15.51 \mu\text{V.}$$

Using equation 3.9.1.,

$$k \int_0^{180} (T_e - T) dt = k \times 3011.4625 \mu\text{V.} = 2.927 \mu\text{V.}$$

$$\therefore \left[(T_e - T) + k \int_{t_0}^t (T_e - T) dt \right] = (15.51 + 2.927) \mu\text{V.} = 18.437 \mu\text{V.}$$

From the Bridge reading,

$$T_e = 425^\circ\text{C} \equiv 698.15^\circ\text{K}$$

From equation 3.9.3.,

$$(H_{698.15} - H_{273.15})_{\text{Au}} = 2661.1 \text{ Cal/mole}$$

$$n_{\text{Au}} = \frac{2.3584}{197} = 11.9716 \times 10^{-3} \text{ moles.}$$

Table AII.2.

R. 34.4.

Corrected Time Potent-galvan-
trometer ometer
Due to sec. Reading Reading
drift in mV. Cm.
the bat-
tery
voltage
mV.

0.000	0	17669	+1.00	17669.500	0.00	-
-0.005	10	17647	-0.50	17646.745	22.755	1.3571
-0.005	20	17649	+2.50	17650.245	19.255	1.2845
-0.010	30	17652	-1.00	17651.490	18.010	1.2555
-0.015	40	17652	-0.55	17651.710	17.790	1.2502
-0.015	50	17652	-0.10	17651.935	17.565	1.2446
-0.020	60	17652	+0.25	17652.105	17.395	1.2404
-0.025	75	17652	+0.80	17652.375	17.125	1.2336
-0.030	90	17653	-0.70	17652.620	16.880	1.2274
-0.035	105	17653	-0.20	17652.865	16.635	1.2210
-0.040	120	17653	+0.30	17653.110	16.390	1.2146
-0.045	135	17653	+0.80	17653.355	16.145	1.2080
-0.050	150	17654	-0.90	17653.500	16.000	1.2041
-0.055	165	17654	-0.40	17653.745	15.755	1.1974
-0.060	180	17654	+0.10	17653.990	15.510	1.1906
(-0.15 cm)						
-0.070	210	17654	+1.00	17654.430	15.070	1.1784
-0.080	240	17655	-0.05	17654.895	14.605	1.1645
-0.090	270	17655	+0.85	17655.335	14.165	1.1511
-0.100	300	17656	-0.45	17655.675	13.825	1.1407
-0.110	330	17656	+0.40	17656.090	13.410	1.1274
-0.120	360	17657	-0.80	17656.480	13.020	1.1146
-0.130	390	17657	0.00	17656.870	12.630	1.1014
-0.140	420	17657	+0.80	17657.260	12.240	1.0878
-0.150	450	17658	-0.65	17657.525	11.975	1.0783
-0.165	495	17658	+0.50	17658.085	11.415	1.0575
-0.170	510	17658	+0.85	17658.255	11.245	1.0509
-0.180	540	17659	-0.50	17658.570	10.930	1.0386
-0.190	570	17659	+0.20	17658.910	10.590	1.0249
-0.200	600	17659	+0.85	17659.225	10.275	1.0118
(-0.5 cm)						
0.000	630	17660	-1.10	17659.450	10.050	1.0021
-0.015	660	17660	-0.50	17659.735	9.765	0.9896
-0.025	690	17660	+0.10	17660.025	9.475	0.9765
-0.040	720	17660	+0.70	17660.310	9.190	0.9633
(-1.00 cm)						

In order to obtain $C_{p_f}^{34.4}$ we proceed as follows:

From the calibration addition,

$$C_{p_f}^{34.3} = 1.37044 \times 42.5 = 58.2437 \text{ Cal/}^\circ\text{C.}$$

Using equation 3.7.16.,

$$\bar{C}_{p_{Au}} = C_{p_{Au}}^{\circ} + \left(\frac{\partial \Delta \bar{H}_{Au}}{\partial T} \right)_{x_{Au}=0.5} = (6.526 + 3.25) = 9.776 \text{ Cal/mole/}^\circ\text{C.}$$

The quantity $\left(\frac{\partial \Delta \bar{H}_{Au}}{\partial T} \right)_{x_{Au}=0.5}$ has been obtained by extrapolating prior experimental data.

Now, using equation 3.7.15.,

$$\begin{aligned} C_{p_f}^{34.4} &= C_{p_f}^{34.3} + \sum \bar{C}_{p_i} (n_i^{34.4} - n_i^{34.3}) \\ &= (58.2437 + 9.776 \times 11.9716 \times 10^{-3}) \text{ Cal/}^\circ\text{C} = \\ &58.361 \text{ Cal/}^\circ\text{C} = 1.3732 \text{ Cal/}^\mu\text{V.} \end{aligned}$$

$$\begin{aligned} \therefore Q_{T_e} &= \frac{1.3732 \times 18.437}{11.9716 \times 10^{-3}} - 2661.1 \\ &= 2114.8 - 2661.1 = -546 \text{ Cal/mole.} \end{aligned}$$

APPENDIX III

Summary of Experimental Data and Results

Summary of Data and Results of Experiments Involving Additions of Gold and Tin to Liquid Tin.

Table AIII.1a.

Run	P_e	$n_j \times 10^3$	$n_i \times 10^3$	ΔT_{ob}	$k \times 10^3$	t_{obs}	C_p^*	Cal/mole of addition	$\theta_{TP}^e + \theta_{TP}^{av}$
13.0	-	5054.23	-	-	-	-	-	-	-
13.1	304.3	14.6091	-	-	-	-	-	-	-
13.2	304.0	14.3488	-	-	-	-	-	-	-
13.3	303.5	-	-	-	-	-	-	-	-
13.4	303.8	14.3378	-	-	-	-	-	-	-
13.5	303.4	14.0219	-	-	-	-	-	-	-
13.6	-	13.9014	-	-	-	-	-	-	-
13.7	301.4	13.7338	-	-	-	-	-	-	-
13.8	301.1	-	-	-	-	-	-	-	-
13.9	301.3	-	-	-	-	-	-	-	-
13.10	301.3	14.2536	-	-	-	-	-	-	-
14.0	-	5071.49	-	-	-	-	-	-	-
14.1	350.8	12.5257	-	-	-	-	-	-	-
14.2	350.5	-	-	-	-	-	-	-	-
14.3	350.6	-	-	-	-	-	-	-	-
14.4	350.8	11.8997	-	-	-	-	-	-	-
14.5	350.5	-	-	-	-	-	-	-	-
14.6	350.6	12.7430	-	-	-	-	-	-	-
14.7	352.1	15.5501	-	-	-	-	-	-	-
14.8	351.6	-	-	-	-	-	-	-	-
14.9	351.7	-	-	-	-	-	-	-	-
14.10	351.7	-	-	-	-	-	-	-	-
14.11	351.8	14.6891	-	-	-	-	-	-	-

* The Thermoelectric Power θ^e has been taken as $42.5 \mu V/^\circ C$.
 $\dagger P_{av}$ is $302.3^\circ C$ for Run 13 and $351.1^\circ C$ for Run 14.
 $\ddagger$ There was a gap of one day between the runs 14.6 and 14.7.

Table AIII.1b.

Run No.	T _e °C	Sn n _j × 10 ³ moles	Au n _i × 10 ³ moles	ΔT _{ob} μV	k × 10 ³ sec ⁻¹	k _t ^{ob} ΔT _{dt} t _o	Cp _f Cal/°C	Q _{T_e}
29.0	-	5127.89	-	-	-	-	-	-
29.1	400	10.5950	-	+38.000	0.877	+6.254	45.000	-
29.2	400	-	6.0660	-11.865	0.881	-3.133	44.810	-5105
29.3	400	-	6.7533	-13.200	0.881	-3.474	44.880	-5105
29.4	400	10.2873	-	+38.165	0.881	+5.124	44.668	-
29.5	400	-	6.9178	-12.175	0.925	-4.739	45.015	-5088
29.6	400	-	6.1487	-12.960	0.913	-2.262	45.075	-5124
29.7	400	-	5.9228	-12.750	0.893	-1.770	45.135	-5102
29.8	400	9.6240	-	+34.765	0.888	+5.245	45.214	-
30.0	-	5135.56	-	-	-	-	-	-
30.1	450	10.0859	-	+38.04	1.120	+7.361	44.989	-
30.2	450	-	6.5523	-10.86	1.130	-2.302	44.875	-4946
30.3	450	9.294	-	-	-	-	-	-
30.4	450	8.9284	-	+33.755	1.130	+6.609	44.796	-
30.5	450	-	7.7827	-13.265	1.143	-2.401	45.070	-4959
30.6	450	-	7.1188	-11.900	1.152	-2.168	45.135	-4923
30.7	450	-	7.7452	-12.660	1.175	-2.548	45.210	-4913
30.8	450	10.6639	-	+41.955	1.115	+5.636	45.378	-
30.9	450	-	7.1898	-12.285	1.114	-1.930	45.350	-4934

Table AIII.2.

Details of Calculations of $\Delta H_1, T, x_1 \rightarrow$.

Run	T	$T_{\text{emp.}}^{\circ}\text{C.}$	$\Sigma n_1 x_1 \times 10^3$	$\Sigma n_1 + \Sigma n_j$	$-\Sigma n_1 n_j$	cal.	$-\Delta H_1 \times 10^3$	cal/mole	$x_1 \times 10^3$	$\Delta H_1, x_1 \rightarrow$	cal/mole
13.3	302.3	7.9787	5.09162	43.6212	84.1695	16.3291	1.5672	2.9875	-5461 $\pm$ 6		
13.8	302.3	15.3995	5.154578	127.4359	24.6848	4.5227					
13.9	302.3	23.3487	5.162527								
14.2	351.1	5.9223	5.089939	31.3586	6.1609	1.1635					
14.3	351.1	11.4918	5.095509	60.8268	11.9375	2.2553					
14.5	351.1	17.0243	5.112941	90.1380	17.6294	3.3296					
14.8	351.1	22.4400	5.146650	118.7545	23.0741	4.3601					
14.9	351.1	27.8502	5.152060	147.2879	28.5882	5.4056					
14.10	351.1	33.3360	5.157546	176.2310	34.1695	6.4635					
29.2	400	6.0660	5.144549	30.9669	6.0194	1.1791					
29.3	400	12.8193	5.151302	65.4425	12.7041	2.4886					
29.5	400	19.7371	5.168507	100.6403	19.4718	3.8187					
29.6	400	25.8858	5.174656	132.1462	25.5372	5.0024					
29.7	400	31.8086	5.180579	162.3644	31.3410	6.1400					
30.2	450	6.5523	5.152197	32.4077	6.2901	1.2717					
30.5	450	14.3350	5.178203	71.0021	13.7117	2.7683					
30.6	450	21.4538	5.185321	106.0479	20.4515	4.1374					
30.7	450	29.1990	5.193067	144.1001	27.7485	5.6227					
30.9	450	36.3888	5.210920	179.5746	34.4612	6.9832					

* $\Sigma n_j, T_j$ has been taken as zero for all the runs.-4938 $\pm$ 6-5104 $\pm$ 2.5-5289 $\pm$ 3.5

Table AIII.3.

Summary of Data and Results of Experiments involving additions of Gold, Tin and Tungsten to molten Gold-Tin Alloys.

Run No.	T _e °C	Sn n _j × 10 ³ moles	Au n _i × 10 ³ moles	W n _c × 10 ³ moles	ΔT _{ob} μV.	k × 10 ³ sec ⁻¹	t _{ob} k _t sec	ΔT _{dt} μV	C _p [*] Cal/°C	Q _{T_e} Cal/mole of addition.
31.0	-	4333.56	481.534	-	-	-	-	-	-	-
31.1	450	-	6.8842	-	-10.080	1.155	-2.700	45.583	-4816	
31.2	450	-	7.2802	-	-11.000	1.130	-2.425	45.664	-4806	
31.3	450	-	7.8487	-	-12.135	1.139	-2.459	45.752	-4826	
31.4	450	-	-	12.4247	+23.640	1.117	+8.086	45.830	-	
32.0	-	4333.87	481.518	-	-	-	-	-	-	-
32.1	275	-	7.6084	-	-23.790	0.432	-3.198	49.288	-5810	
32.2	275	-	6.6700	-	-22.025	0.431	-2.174	49.404	-5913	
32.3	275	-	-	17.7466	+23.590	0.416	+1.765	49.513	-	
32.4	275	-	5.6716	-	-18.450	0.424	-1.793	49.610	-5863	
32.5	300	-	5.9959	-	-17.885	0.492	-1.633	49.002	-5608	
32.6	300	-	5.9619	-	-15.755	0.489	-3.565	49.080	-5597	
32.7	300	-	-	15.9072	+22.915	0.503	+2.086	49.178	-	
32.8	300	-	6.0518	-	-18.360	0.490	-1.196	49.257	-5600	
32.9	350	-	6.6751	-	-16.490	0.676	-1.883	47.759	-5268	
32.10	350	-	6.6558	-	-15.510	0.673	-3.026	47.836	-5310	
32.11	350	-	-	15.6140	+25.710	0.670	+3.755	47.933	-	
32.12	350	-	6.6652	-	-16.220	0.666	-2.385	48.011	-5328	

* The Thermoelectric Power 'Θ' has been taken as 42.5 μV/°C for all temperatures.

Table AIII.3. Continued.

Run No.	T _e °C	Sn n _j × 10 ³ moles	Au n _i × 10 ³ moles	W n _c × 10 ³ moles	ΔT _{ob} μV.	k × 10 ³ sec ⁻¹	$\int_{t_0}^{t_{ob}} \Delta T dt$ k μV	C _p _f Cal/°C	Q _{T_e} Cal/mole of addition
32.13	400	-	7.0431	-	-13.385	0.887	-2.667	46.877	-5012
32.14	400	-	6.9959	-	-14.670	0.883	-1.570	46.956	-5063
32.15	400	-	-	12.3376	+23.930	0.894	+3.272	47.033	-
32.16	400	-	7.1840	-	-13.877	0.889	-2.221	47.114	-4983
32.17	450	-	7.8376	-	-10.315	1.161	-3.255	47.009	-4740
32.18	450	-	7.3414	-	-11.275	1.132	-1.805	47.090	-4799
32.19	450	-	-	12.4105	+25.110	1.178	+5.680	47.168	-
32.20	450	-	7.6858	-	-11.085	1.163	-2.511	47.254	-4791
33.0	-	3595.02	1452.02	-	-	-	-	-	-
33.1	350	-	15.3736	-	-20.745	0.637	-2.056	55.553	-4114
33.2	350	-	14.1165	-	-18.782	0.650	-1.952	55.724	-4101
33.3	350	-	-	15.2953	+22.230	0.627	+2.556	55.819	-
33.4	350	-	10.0919	-	-13.070	0.652	-1.360	55.941	-4057
33.5	400	-	10.1807	-	-8.552	0.839	-1.877	53.159	-3780
33.6	400	-	11.4010	-	-10.080	0.878	-1.395	53.298	-3760
33.7	400	-	-	12.3616	+21.137	0.806	+2.879	53.376	-
33.8	400	-	11.7335	-	-9.210	0.827	-2.020	53.519	-3704
33.9	450	-	15.2766	-	-5.940	1.118	-1.547	52.774	-3433
33.10	450	-	16.1051	-	-6.493	1.093	-1.379	52.972	-3434
33.11	450	-	-	12.3316	+23.230	1.102	+3.973	53.049	-
33.12	450	-	16.7076	-	-6.170	1.116	-1.311	53.254	-3386

Table AIII.3. Continued.

Run No.	T _e °C	Sn n _j × 10 ³ moles	Au n _i × 10 ³ moles	W n _c × 10 ³ moles	ΔT _{ob} μV.	k × 10 ³ sec ⁻¹	k _{ob} t _o μV	ΔT _{dt}	Cp _f Cal/°C	Q _{T_e} Cal/mole in addition
33.13	350	-	10.9147	-	-11.760	0.666	-2.124		57.466	-3895
33.14	350	-	-	15.6184	+22.145	0.593	+2.398		57.563	-
33.15	350	-	10.2320	-	-9.355	0.642	-3.692		57.687	-3906
34.0	-	2756.83	2710.49	-	-	-	-		-	-
34.1	425	-	12.5726	-	-12.670	0.941	-5.586		58.063	-677
34.2	425	-	10.5228	-	-12.895	0.977	-3.060		58.166	-586
34.3	425	-	-	12.3654	+18.800	0.945	+4.628		58.244	-
34.4	425	-	11.9716	-	-15.510	0.972	-2.927		58.361	-546
34.5	450	-	10.5391	-	-13.465	1.100	-4.589		57.171	-520
34.6	450	-	10.2731	-	-12.925	1.111	-4.461		57.271	-544
34.7	450	-	-	11.4750	+18.145	1.094	+5.273		57.343	-
34.8	450	-	11.3269	-	-16.355	1.115	-3.228		57.454	-487
34.9	450	16.2460	-	-	-20.645	1.089	-7.072		57.560	-2454
35.0	-	1606.72	4084.35	-	-	-	-		-	-
35.1	450	-	6.2152	-	-14.550	1.064	-4.608		55.309	1187
35.2	450	-	6.1208	-	-16.287	1.058	-2.781		55.363	1234
35.3	450	-	-	11.4729	+20.405	1.072	+3.814		55.435	-
35.4	450	-	5.9949	-	-13.737	1.074	-4.944		55.488	1244
35.5	450	17.7254	-	-	-2.365	1.070	-0.919		55.599	-5007

Table AIII.3. Continued.

Run No.	T _e °C	Sn n _j × 10 ³ moles	Au n _i × 10 ³ moles	W n _c × 10 ³ moles	ΔT _{ob} μV.	k × 10 ³ sec ⁻¹	$k \int_{t_0}^{t_{ob}} \Delta T dt$ μV	C _p _f Cal/°C	Q _{T_e} Cal/mole of addition
35.6	400	-	6.6741	-	-13.312	0.831	-5.087	56.386	1159
35.7	400	-	6.5609	-	-11.185	0.816	-6.932	56.444	1169
35.8	400	-	-	11.8188	+19.710	0.837	+1.975	56.518	-
35.9	400	-	6.5756	-	-13.715	0.824	-4.390	56.576	1167
35.10	400	19.2216	-	-	-7.312	0.870	-1.991	56.906	-5071
35.11	400	21.5939	-	-	-8.395	0.870	-1.398	57.042	-5031
35.12	400	-	-	11.9368	+17.450	0.826	+4.252	57.117	-
35.13	400	20.4650	-	-	-6.930	0.859	-1.861	57.245	-5001
35.14	350	-	8.1386	-	+11.402	0.615	+7.250	60.876	+1108
35.15	350	23.1356	-	-	-12.430	0.625	-3.797	61.022	-5086
35.16	350	-	-	8.5297	-	-	-	-	-
35.17	350	-	-	11.8906	+14.385	0.621	+3.205	61.147	-
35.18	350	-	8.1386	-	+11.842	0.607	+6.508	61.197	+1071
35.19	350	21.7953	-	-	-10.380	0.617	-4.359	61.334	-5055
35.20	350	-	-	15.3353	+20.670	0.609	+1.912	61.429	-
35.21	350	21.4954	-	-	-11.205	0.612	-2.807	61.565	-5023
35.22	350	-	8.1381	-	+13.800	0.606	+4.320	61.636	+1054
35.26	300	23.2721	-	-	-11.767	0.456	-10.115	64.654	-5164
35.27	300	-	9.1629	-	-	-	-	-	-
35.28	300	-	-	16.3956	+16.425	0.451	+3.121	64.835	-
35.29	300	-	9.1015	-	+3.125	0.433	+12.700	64.914	+801

Table AIII.3. Continued.

Run No.	T _e °C	Sn n _j × 10 ³ moles	Au n _i × 10 ³ moles	W n _c × 10 ³ moles	ΔT _{ob} μV.	k × 10 ³ sec ⁻¹	k _t ^{ob} t _o	ΔT _{dt} μV	C _p _f Cal/°C	Q _{T_e} Cal/mole of addition
36.0	-	1208.67	3417.09	-	-	-	-	-	-	-
36.1	400	-	6.6193	-	-	-	-	-	-	-
36.2	400	-	6.6335	-	4.96	1.000	17.618	47.958	+1342	-
36.3	400	-	-	10.2208	18.807	1.012	3.264	48.022	-	-
36.4	400	-	6.5305	-	5.195	1.000	16.4954	48.083	+1259	-
36.5	450	-	6.1203	-	-	-	-	-	-	-
36.6	450	-	6.0954	-	10.095	1.283	13.052	47.409	1412	-
36.7	450	-	-	9.7770	-	-	-	-	-	-
36.8	450	-	-	9.6427	19.007	1.286	4.734	47.531	-	-
36.9	450	-	6.0457	-	12.575	1.276	10.344	47.587	1420	-
36.10	450	-	6.0254	-	12.192	1.277	10.811	47.643	1455	-

Table AIII.4.

Constants used in the calculation of results of tables

Constants	Temp °C	Approximate $x_{\text{Au}} =$					
		0.0	0.1	0.3	0.5	0.7	0.74
$\bar{C}_{\text{pAu(s)}}$ Cals/mole/°C	275	-	17.34	-	-	-	-
	300	11.37	13.07	-	-	8.67	-
	350	10.18	11.63	12.13	-	8.73	-
	400	9.82	11.29	12.19	-	8.79	9.24
	425	-	-	-	9.77	-	-
	450	9.55	11.16	12.25	9.81	8.86	9.31
$\bar{C}_{\text{pSn(l)}}$ Cals/mole/°C	300	6.89	-	-	-	6.32	-
	450	6.85*	-	-	6.5	6.28*	-

* The same values were used for 350 and 400°C.

APPENDIX IVExpressions for Fitting Curves through Given Sets of Points with Minimum Standard Deviation

The standard deviation from the mean value is given by the following expression:

$$\sigma = \sqrt{\frac{1}{n} \sum_{1}^n (x - \bar{x})^2} \quad \text{AIV.1.}$$

Where $\bar{x}$ = the mean value, and n = total number of values.

Consider the equation,

$$Y = a + bx + cx^2$$

to be fitted into the points (x, y) .

$$\therefore \sigma = \sqrt{\frac{1}{n} \sum_{1}^n [(a + bx + cx^2) - y]^2},$$

$$\text{or } f(\sigma) = \frac{1}{2} \sum [a + bx + cx^2 - y]^2.$$

Three partial differentiations will then yield three equations, which when solved will yield the following results.

When $a = 0$

$$y = bx + cx^2 \quad \text{AIV.2.}$$

$$b = \frac{\sum x^4 \cdot \sum xy - \sum x^3 \cdot \sum x^2 y}{\sum x^4 \cdot \sum x^2 - (\sum x^3)^2} \quad \text{AIV.3.}$$

$$c = \frac{\sum x^2 \cdot \sum x^2 y - \sum x^3 \cdot \sum xy}{\sum x^4 \cdot \sum x^2 - (\sum x^3)^2} \quad \text{AIV.4.}$$

When $c = 0$

$$y = a + bx$$

AIV.5.

$$a = \frac{\sum y \sum x^2 - \sum x \sum xy}{n \sum x^2 - (\sum x)^2}$$

AIV.6.

$$b = \frac{n \sum xy - \sum x \sum y}{n \sum x^2 - (\sum x)^2}$$

AIV.7.

When $a = 0, c = 0$ $y = bx$

AIV.8.

$$b = \frac{\sum xy}{\sum x^2}$$

AIV.9.

When it is parabolic i.e.

$$y = b(x - \bar{x})^2$$

AIV.10.

$$b = \frac{\sum (x - \bar{x})^2 y}{\sum (x - \bar{x})^4}$$

AIV.11.

DEFINITION OF SYMBOLS

a	Activity
At%	Atomic percent
C	Heat capacity
C _v	Heat capacity at constant volume
C _p	Heat capacity at constant pressure
C _p _f	Average value of the heat capacity of the calorimeter containing the specimen
e	i) Energy of interaction between two atoms ii) Emissivity
G	Gibbs free energy
H	Enthalpy
i, j	Number of species
K	Heat transfer coefficient, i.e. rate of heat exchange between two surfaces when the temperature difference is unity
k	i) Boltzmann's constant ii) Ratio of the heat transfer coefficient and the average heat capacity of the calorimeter
k'	Heat transfer coefficient due to conduction and convection
(l)	Liquid state.
m	Number of additions made to the calorimeter.

N	i) Avogadro's number ii) With a subscript it represents number of atoms
n	Number of moles
P	Pressure
Q	Heat absorbed by a mole of specimen on solution in the calorimeter
q	Heat absorbed
R	Gas constant
r	Distance between two atoms
S	Entropy
(s)	Solid state
(sol'n)	In solution
T	Temperature in $^{\circ}\text{K}$ unless specified
ΔT_{cor}	$\Delta T_{\text{ob}} + k \int_{t_0}^{t_{\text{ob}}} \Delta T dt$
t	Time
U	Internal energy
V	Volume
w	Excess interaction energy of an unlike pair of atoms, i.e. $w = (e_{ij} - \frac{1}{2}e_{ii} - \frac{1}{2}e_{jj})$
x	Mole fraction
z	Co-ordination number
$z\bar{x}$	Number of unlike atom pairs in quasi-chemical theory

- Indicates the partial values
- α
 - i) Volume coefficient of expansion
 - ii) $\frac{\Delta G_1}{(1-x_1)^2}$
- β
 - i) Compressibility
 - ii) A complex function in the Quasi-chemical theory
 - iii) $\frac{\Delta \bar{H}_1}{(1-x_1)^2}$
- γ_e A constant in the expression for electronic specific heat
- Δ Increase in a property
- δ A parameter in the Average Potential Model
i.e. $(\frac{e_{jj}^*}{e_{ii}^*} - 1)$
- η Viscosity
- θ
 - i) A parameter in the Average Potential Model, i.e. $(\frac{e_{ij}^* - \frac{1}{2}e_{ii}^* - \frac{1}{2}e_{jj}^*}{e_{ii}^*})$
 - ii) Angle
 - iii) Thermoelectric power of a thermocouple
- λ Wave length
- ρ
 - i) A parameter in the Average Potential Model, i.e. $(\frac{r_{jj}^*}{r_{ii}^*} - 1)$
 - ii) Resistivity.
- Σ Summation
- σ Standard deviation

Subscripts

Anh	Anharmonic contribution
c	Calibrating Addition
dil	It is used along with C and is defined by $(C_p - C_v) = C_{dil}$
e	Equilibrium value
i, j	Different species
k	kth reading
o	Initial reading
ob	Chosen value or observed value
s	Surrounding
sp	Specimen
T	At temperature 'T'
x	At composition 'x'

Superscripts

av	Average value
e	Excess over the ideal value
m, r	Value at the end of the mth (or rth) addition
o	i) Standard state ii) Temperature
*	A characteristic value

List of Diagrams.

- Fig. 2.3.1. Equilibrium Diagram of Au-Sn System
(After Hansen).
- Fig. 2.4.1. Viscosity of Au-Sn Alloys.
- Fig. 2.4.2. Resistivity of Liquid Au-Sn Alloys.
- Fig. 2.5.1. Values of $\left(\frac{\sin \Theta}{\lambda}\right)$ at which peaks occur
in Liquid Au-Sn Alloys.
- Fig. 2.6.1. Behaviour of Partial Entropies of Liquid
Au-Sn Alloys (After Kleppa).
- Fig. 3.2.1. The Thermostat.
- Fig. 3.3.1. Control Heater System.
- Fig. 3.5.1. Crucible Assembly.
- Fig. 3.5.2. Molybdenum Stirrer.
- Fig. 3.5.3. Specimen Addition Mechanism.
- Fig. 3.6.1. Thermocouple Clip.
- Fig. 3.6.2. Temperature Profile Inside the Bottle
and the Effect of Annealing Cr/Al
Thermocouples.
- Fig. 4.2.1. Variation of $\Delta H_{\text{Au(s)}, x_{\text{Au}} \rightarrow 0}$ with
Temperature.
- Fig. 4.3.1. Enthalpies of Liquid Au-Sn Alloys.
- Fig. 4.3.2. Experimental and Computed Values of $\Delta H_{\text{Sn(l)}}$
at 400 and 450°C.

- Fig. 4.3.3. Experimental and Computed Values of $\Delta\bar{H}_{\text{Au}(1)}$ at 400 and 450°C.
- Fig. 4.3.4. Experimental and Computed Values of $\Delta\bar{H}_{\text{Sn}(1)}$ and $\Delta\bar{H}_{\text{Au}(1)}$ at 350°C.
- Fig. 4.3.5. Change of $\Delta\bar{H}_{\text{Sn}(1)}$ with Temperature.
- Fig. 4.3.6. Change of $\Delta\bar{H}_{\text{Au}(1)}$ with Temperature.
- Fig. 4.3.7. Heat Capacities of Liquid Au-Sn Alloys at 425°C.
- Fig. 5.3.1. Applicability of Different Models of Solution to Liquid Au-Sn System.
- Fig. 5.4.1. Excess Entropies of Liquid Au-Sn System at 450°C.
- Fig. AI.1. Composition Dependence of Heats of Solution of Solid Copper and Nickel in Liquid Tin at 350°C.
- Fig. AI.2. Heats of Formation of Cu-Ni Alloys.
- Fig. AII.1. Plot of $\log_{10}\Delta T$ against Time, Run 13.2.
- Fig. AII.2. Plot of $\log_{10}\Delta T$ against Time, Run 34.4.

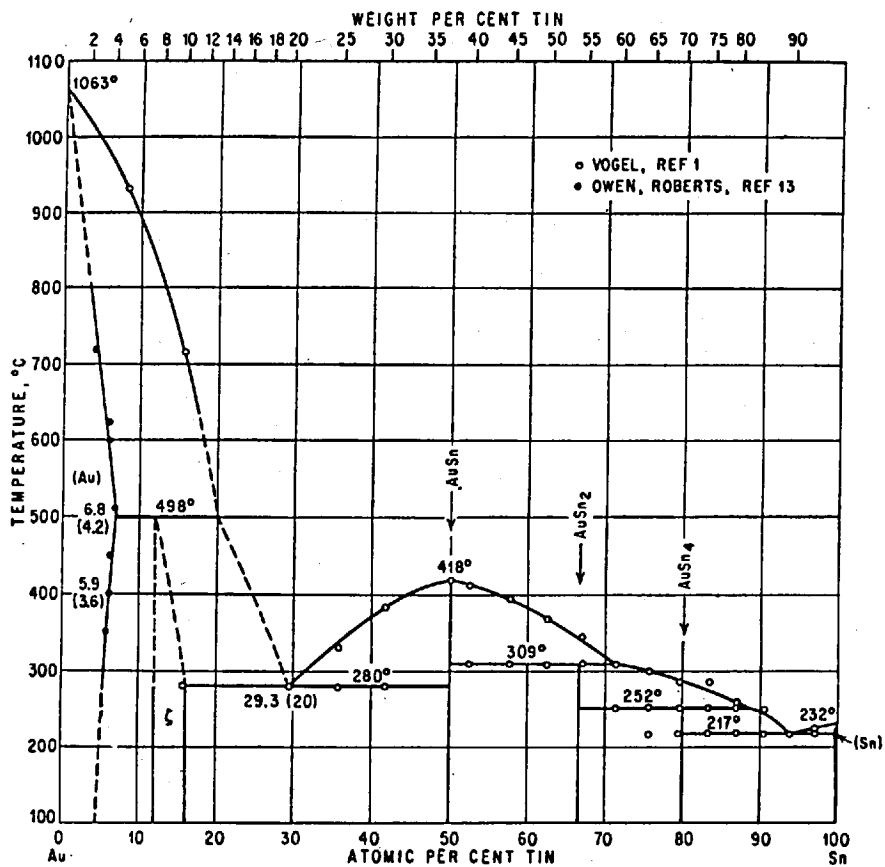


FIG. 2.3.1. EQUILIBRIUM DIAGRAM OF Au-Sn SYSTEM.
(AFTER HANSEN)

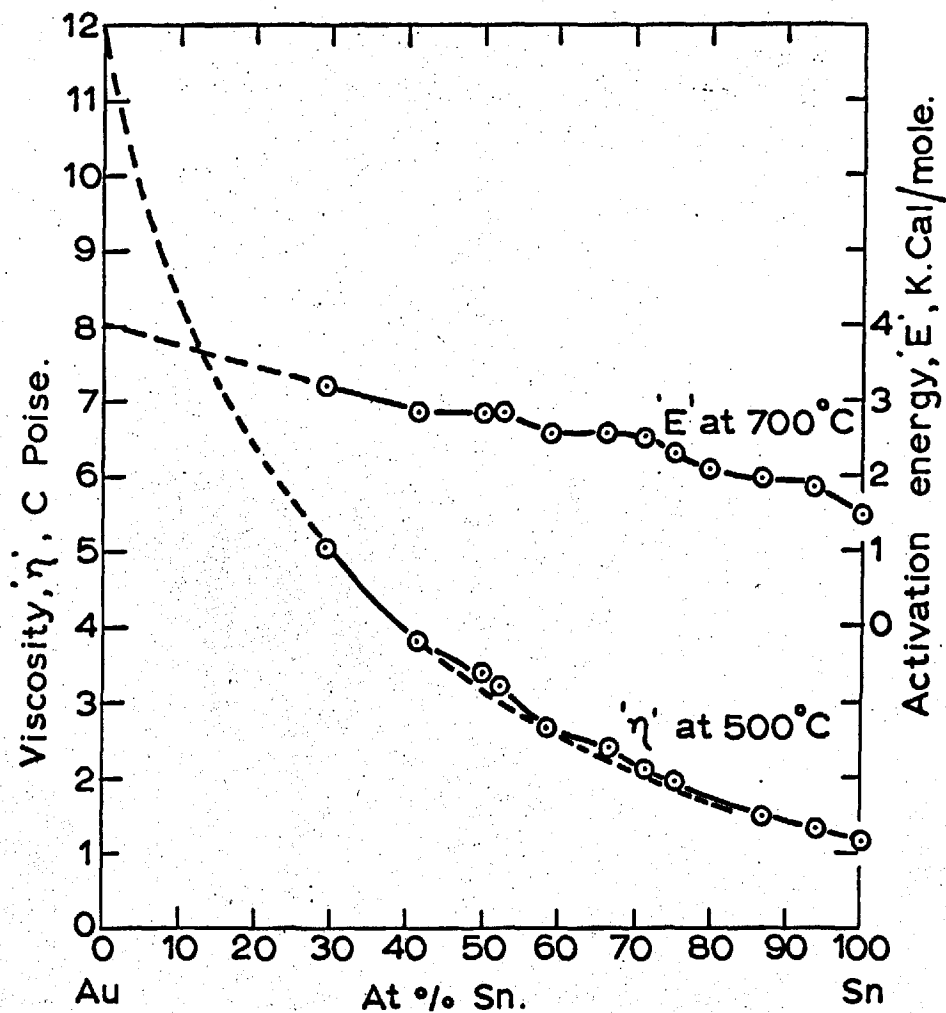


FIG. 2.4.1. VISCOSITY OF Au-Sn ALLOYS.

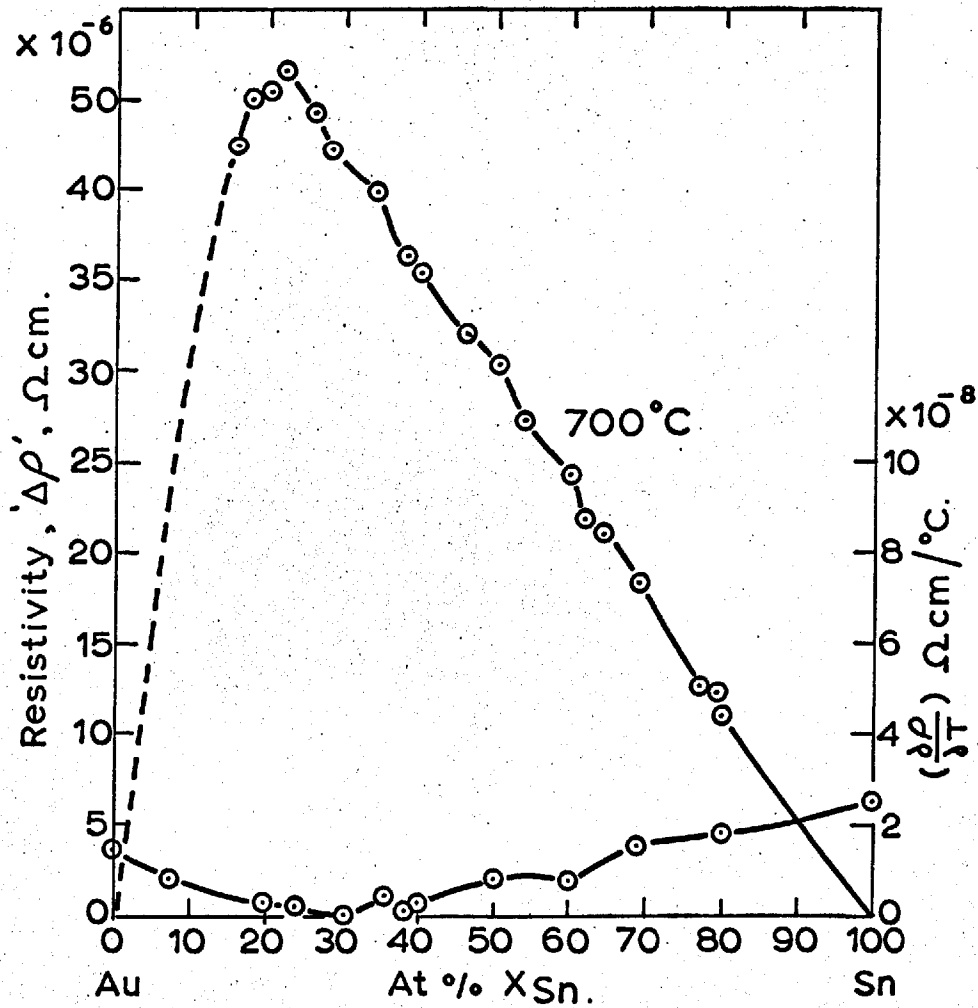


FIG. 2.4.2. RESISTIVITY OF LIQUID
Au - Sn ALLOYS.

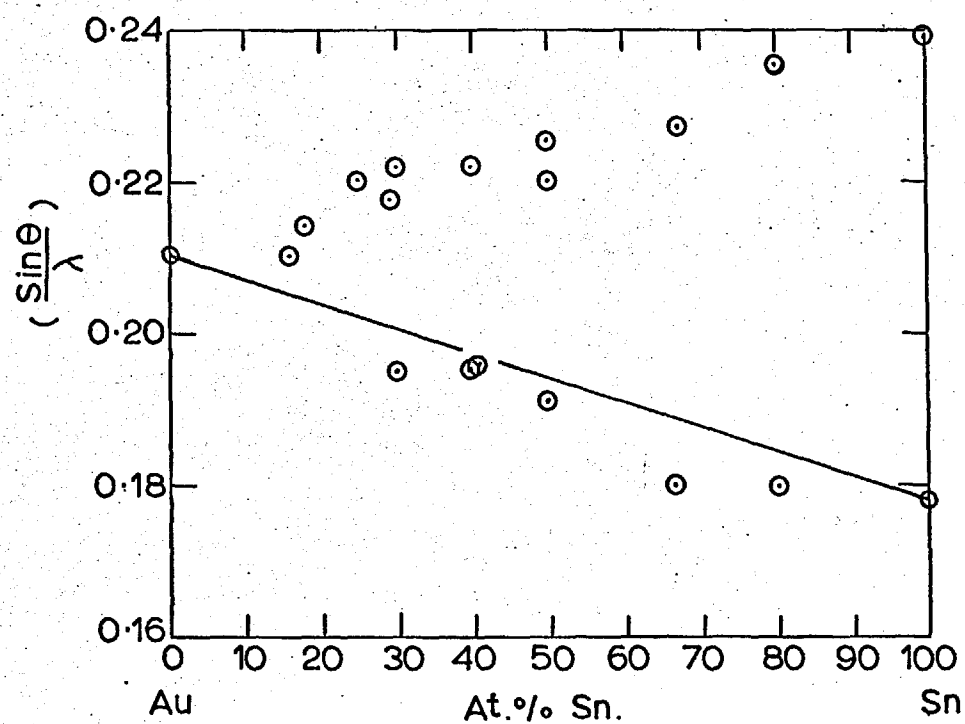


FIG. 2.5.1. VALUES OF $(\frac{\sin \theta}{\lambda})$ AT WHICH PEAKS OCCUR IN LIQUID Au-Sn ALLOYS.

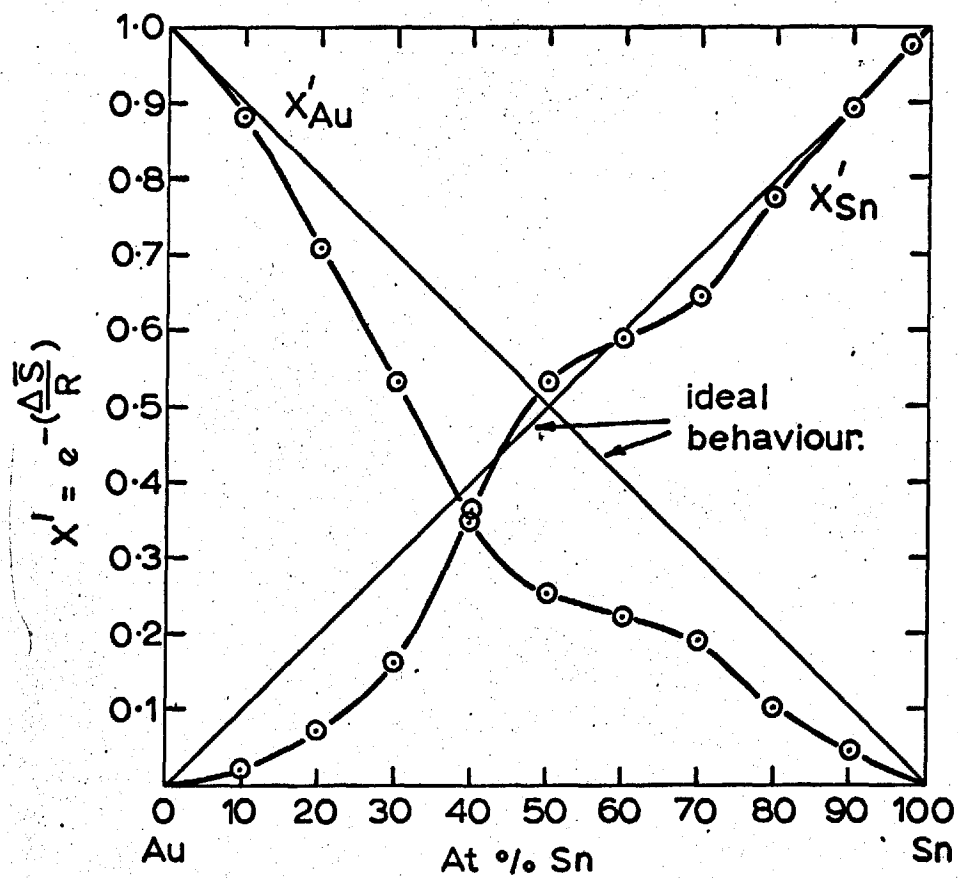


FIG. 2.6.1. BEHAVIOUR OF PARTIAL ENTROPIES OF LIQUID Au-Sn ALLOYS (AFTER KLEPPA).

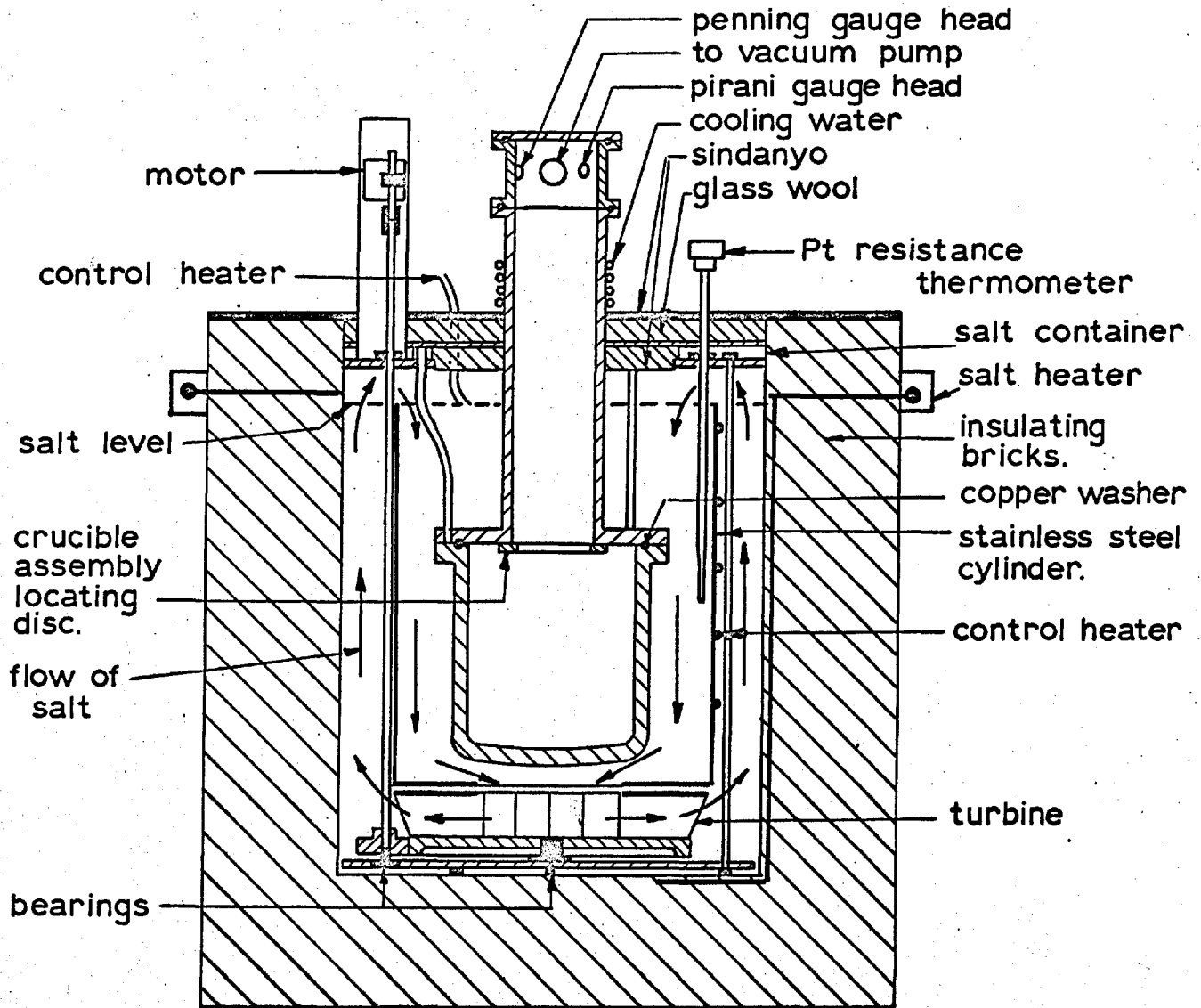


FIG. 3.2.1. THE THERMOSTAT.

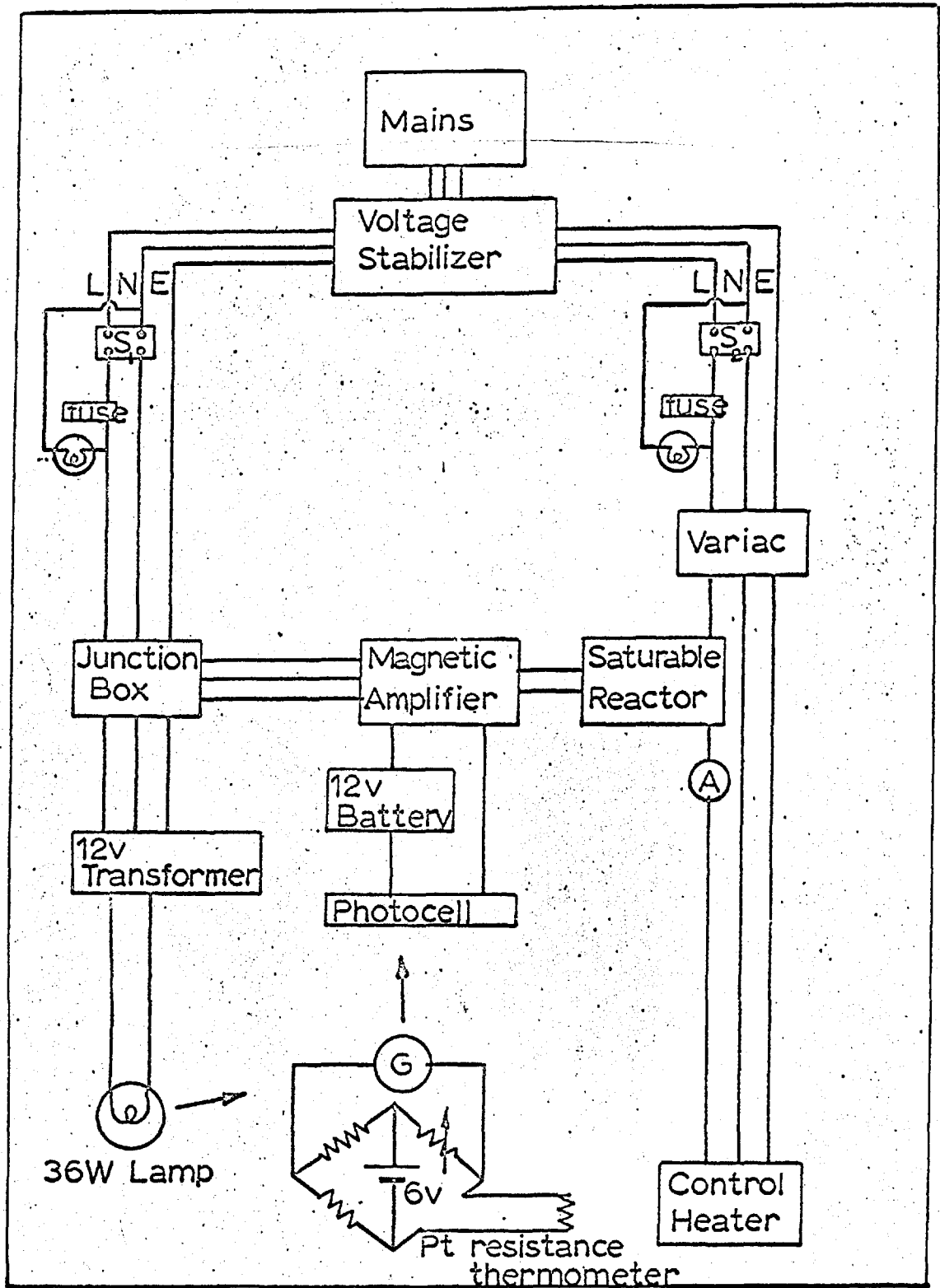


FIG. 3.3.1. CONTROL HEATER SYSTEM.

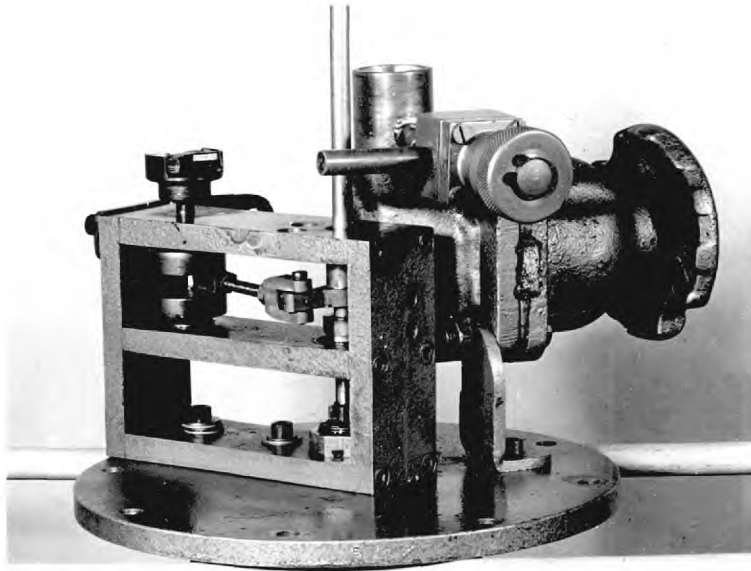


FIG.3.5.1. CRUCIBLE ASSEMBLY

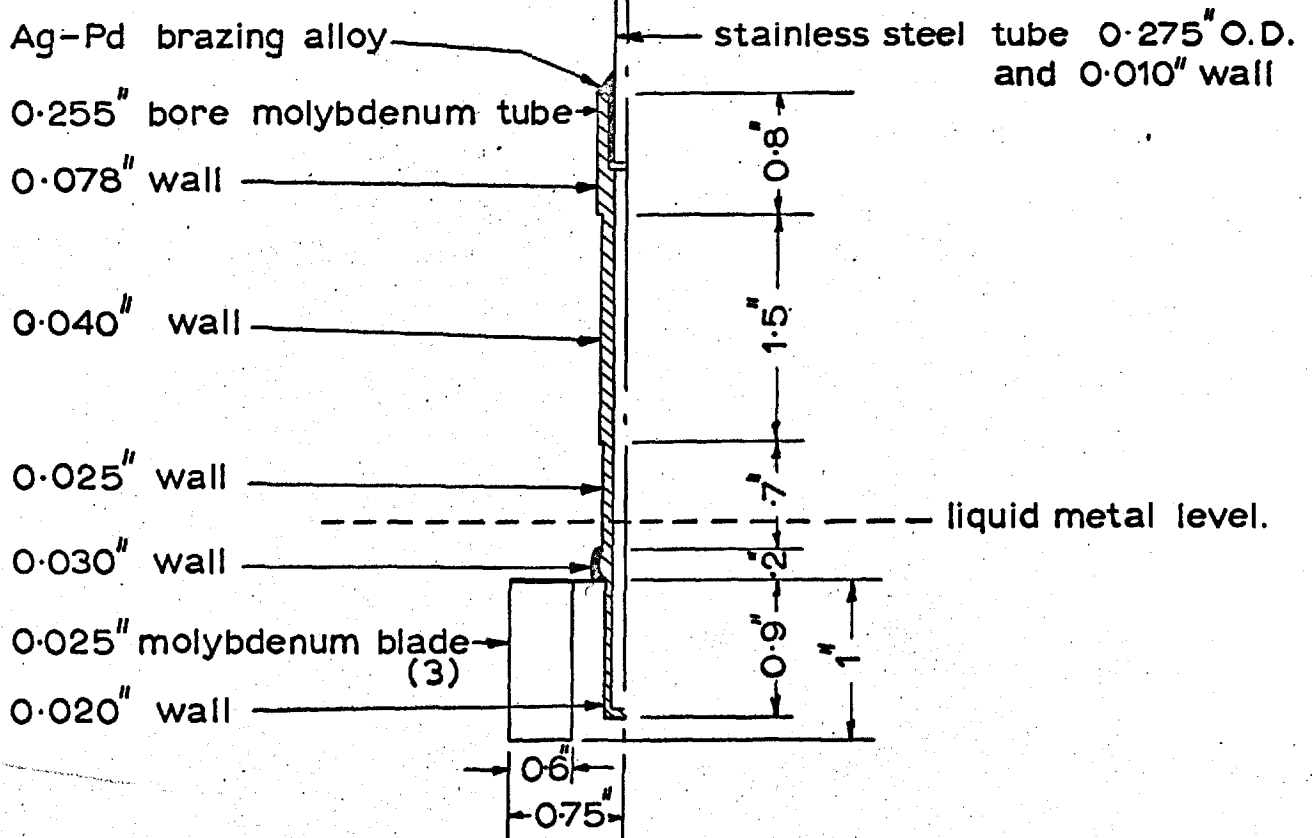


FIG. 3.5.2. MOLYBDENUM STIRRER

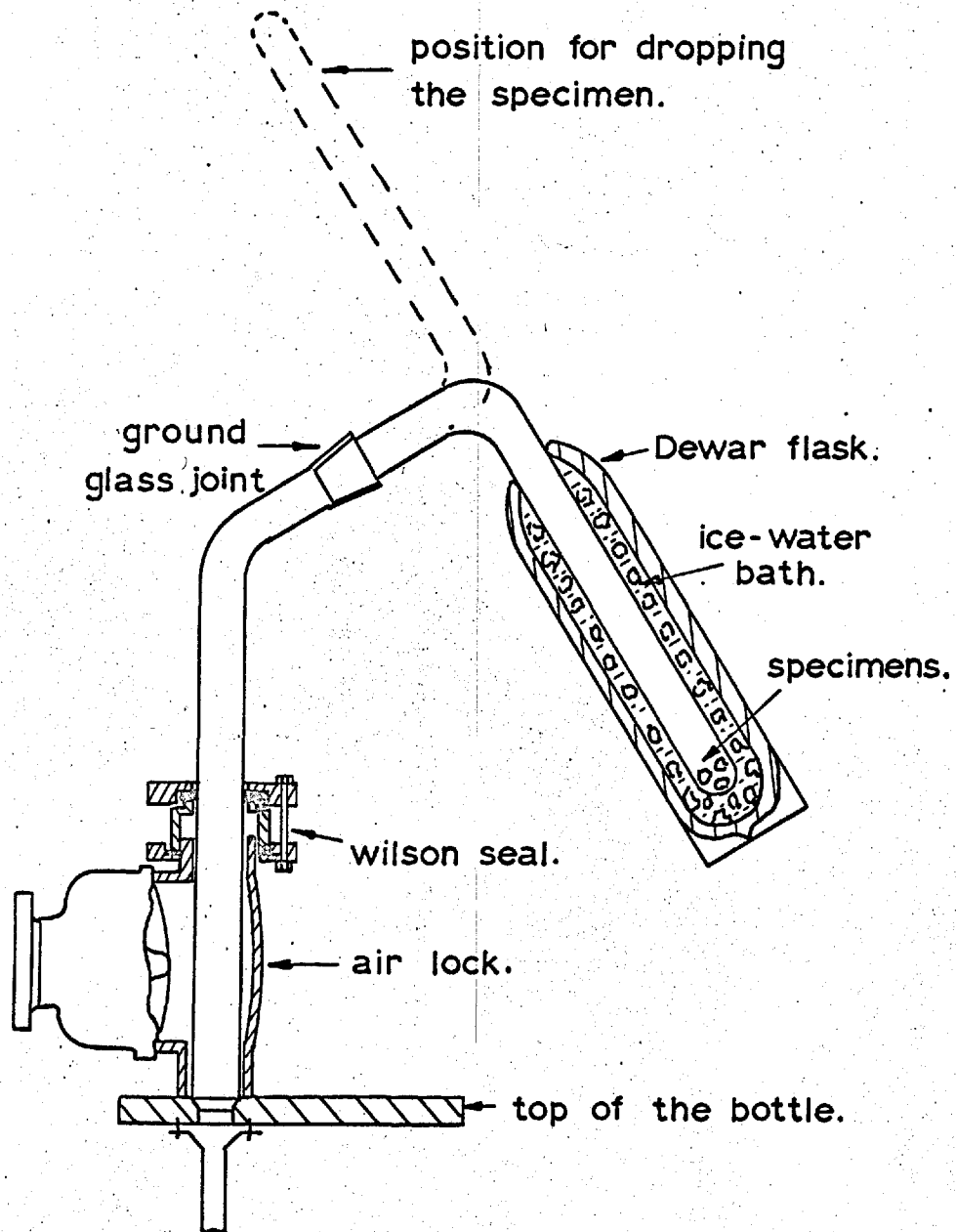


FIG. 3.5.3. SPECIMEN ADDITION MECHANISM.

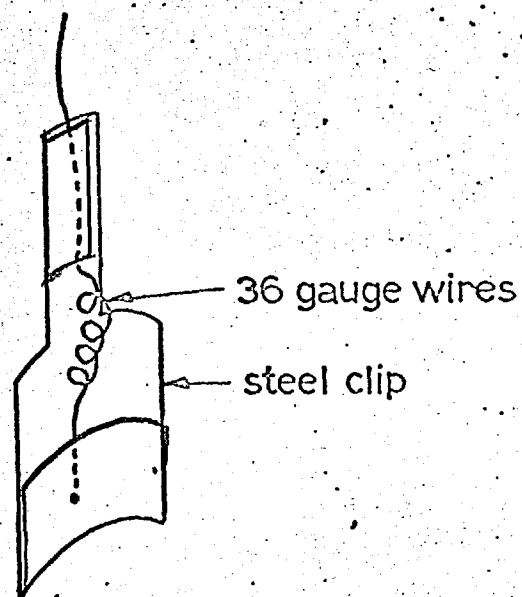


FIG. 3.6.1.

THERMOCOUPLE CLIP.

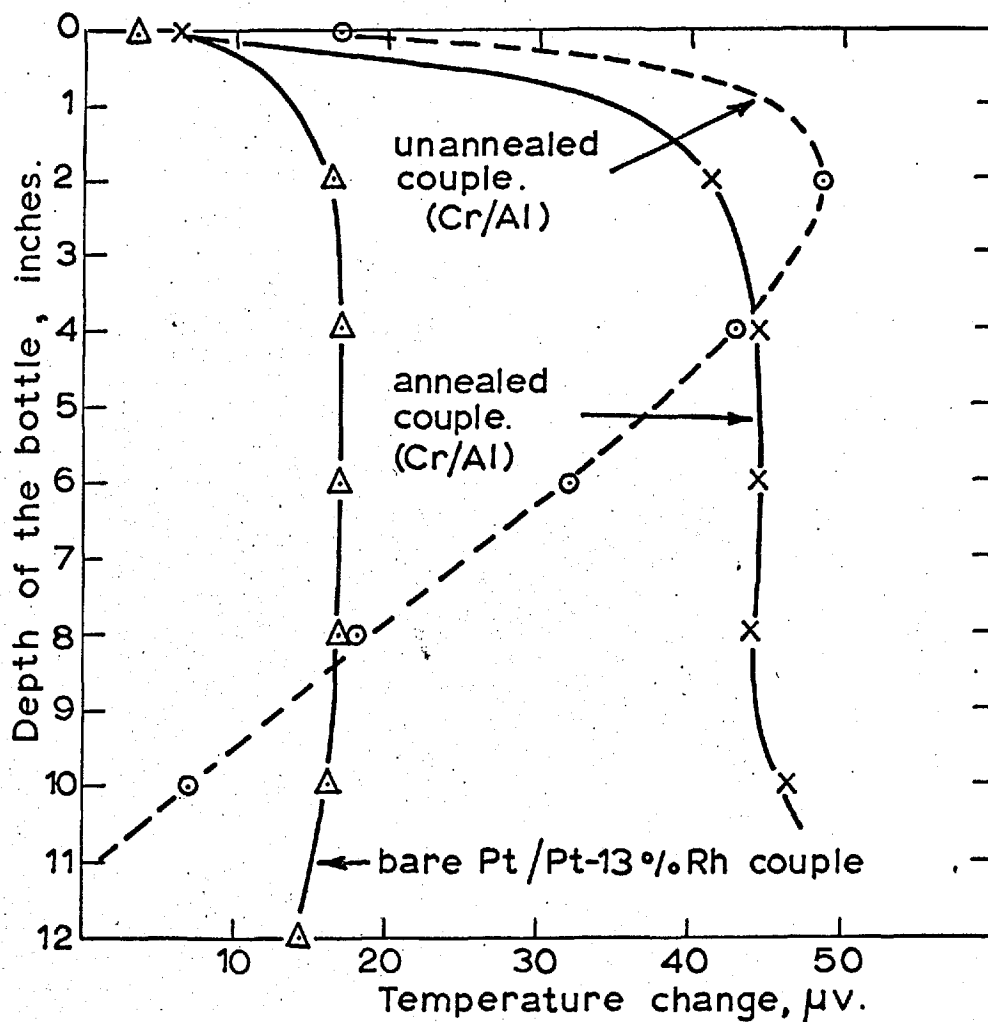


FIG. 3.6.2. TEMPERATURE PROFILE INSIDE THE BOTTLE AND THE EFFECT OF ANNEALING Cr/Al THERMOCOUPLES.



FIG. 4.2.1. VARIATION OF $\Delta \bar{H}_{Au}(s)$, $X_{Au} \rightarrow 0$ WITH TEMPERATURE.

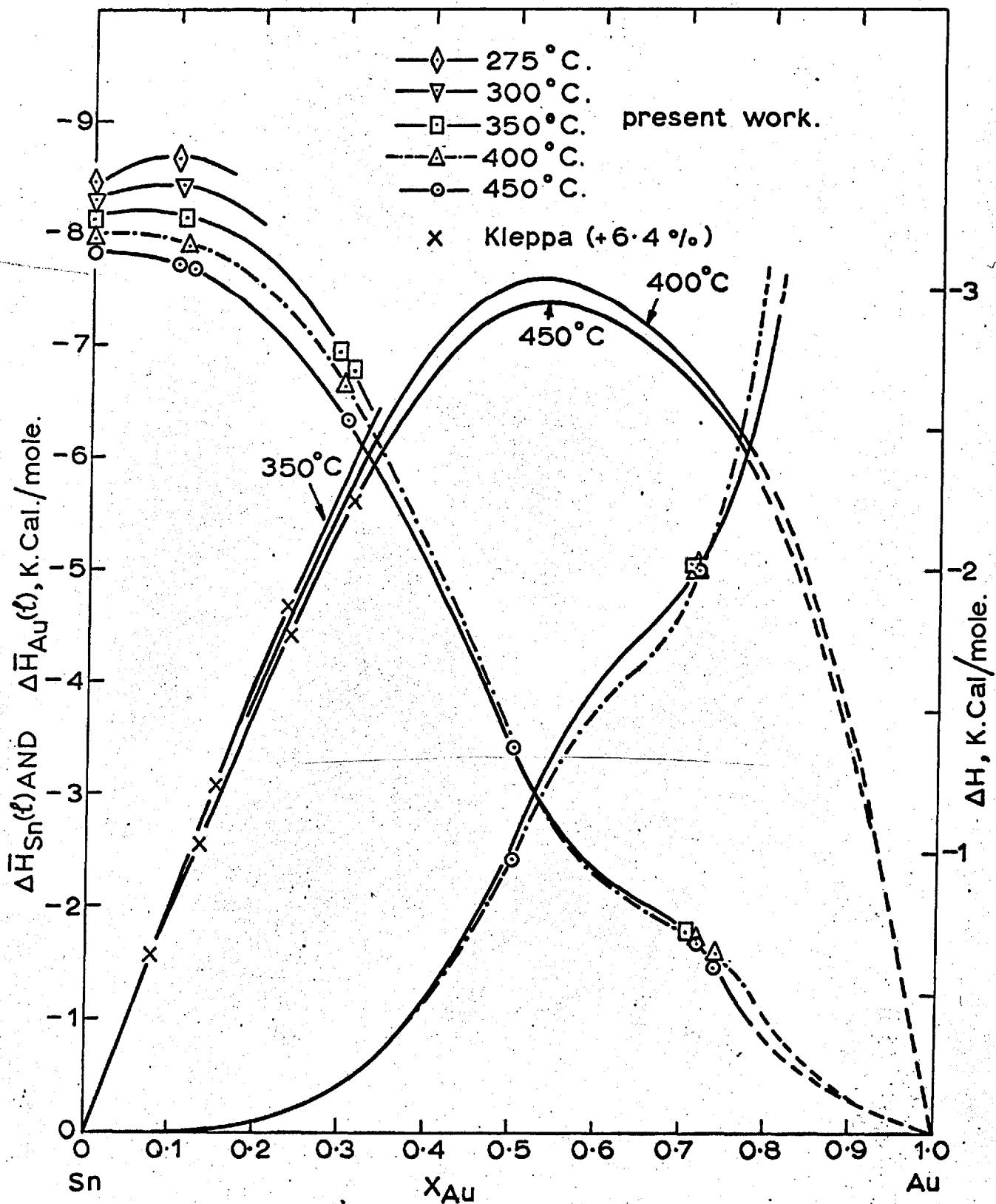


FIG. 4.3.1. ENTHALPIES OF LIQUID Au-Sn ALLOYS.

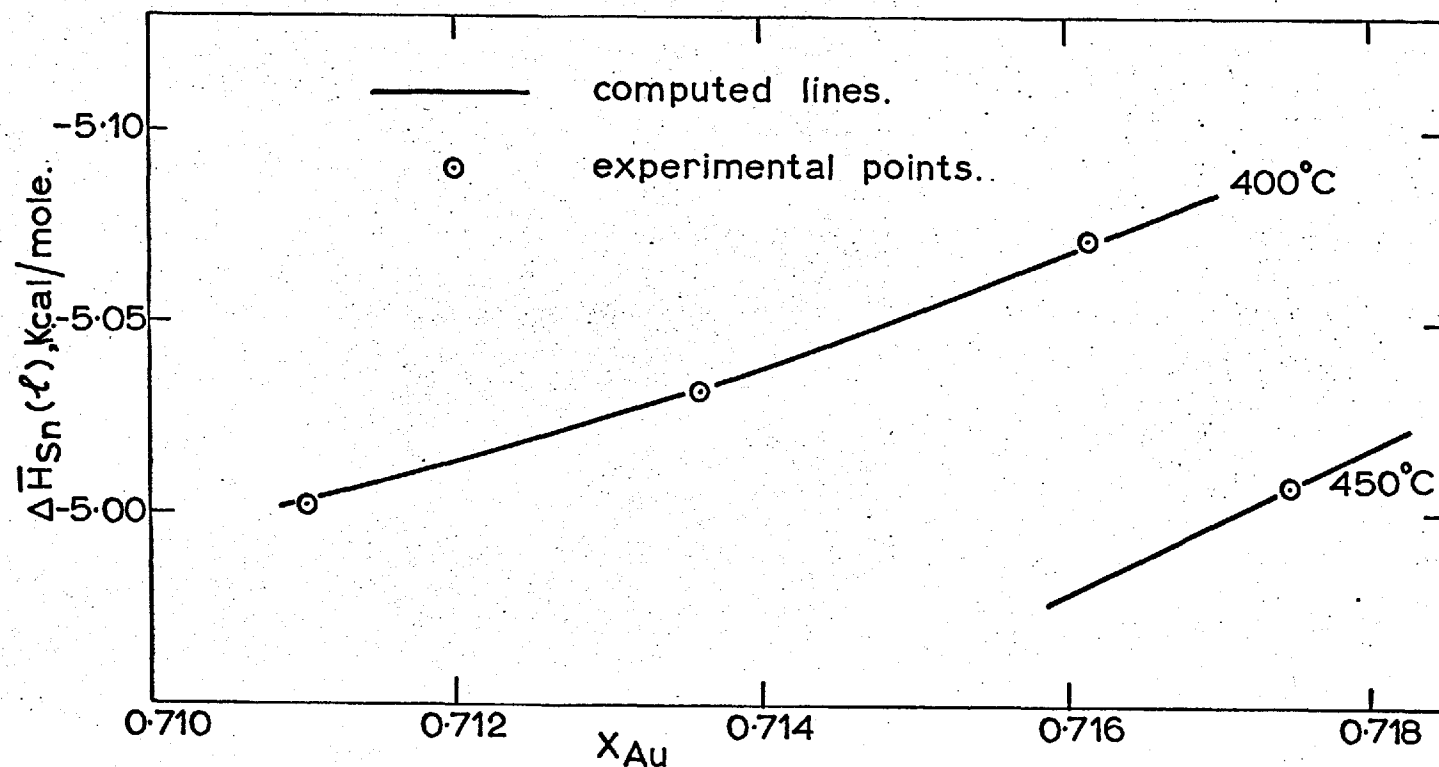


FIG. 4.3.2. EXPERIMENTAL AND COMPUTED VALUES OF $\Delta \bar{H}_{Sn}(l)$ AT 400 & 450°C.

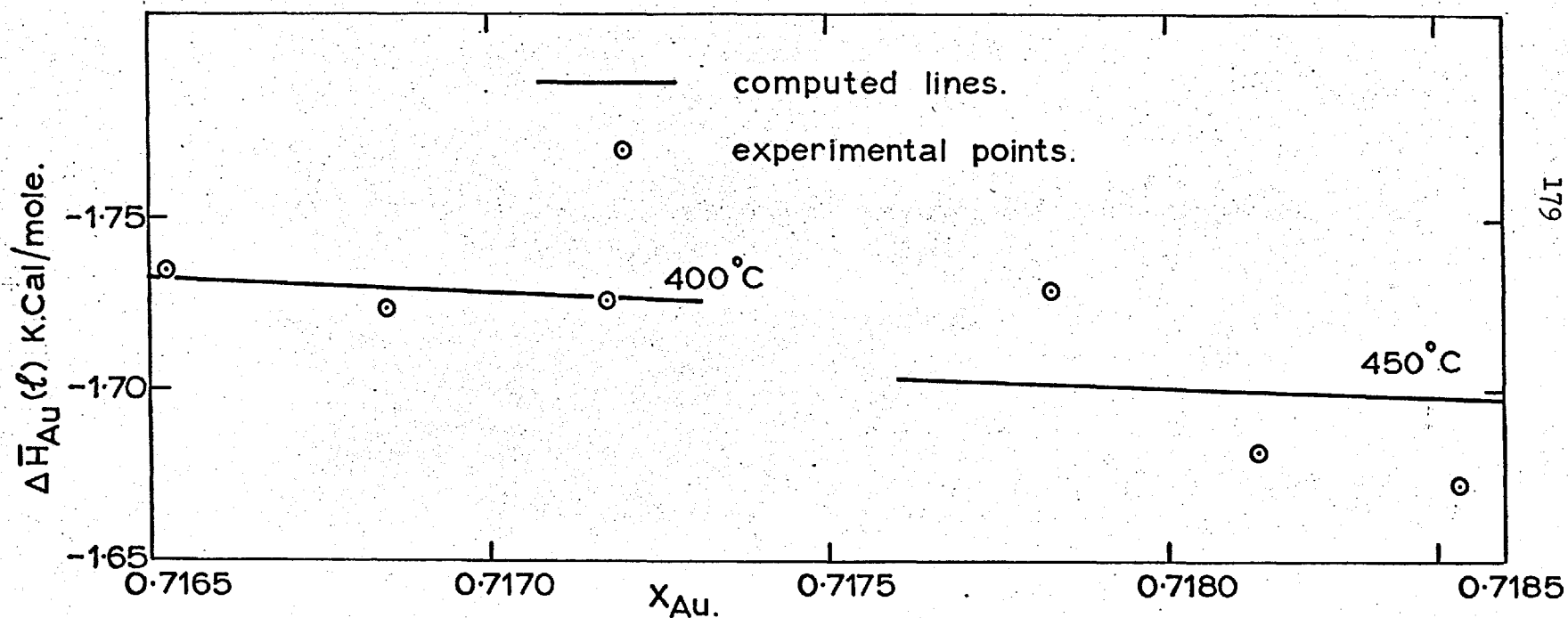


FIG. 4.3.3. EXPERIMENTAL AND COMPUTED VALUES FOR $\Delta \bar{H}_{Au}(l)$ AT 400 & 450°C.

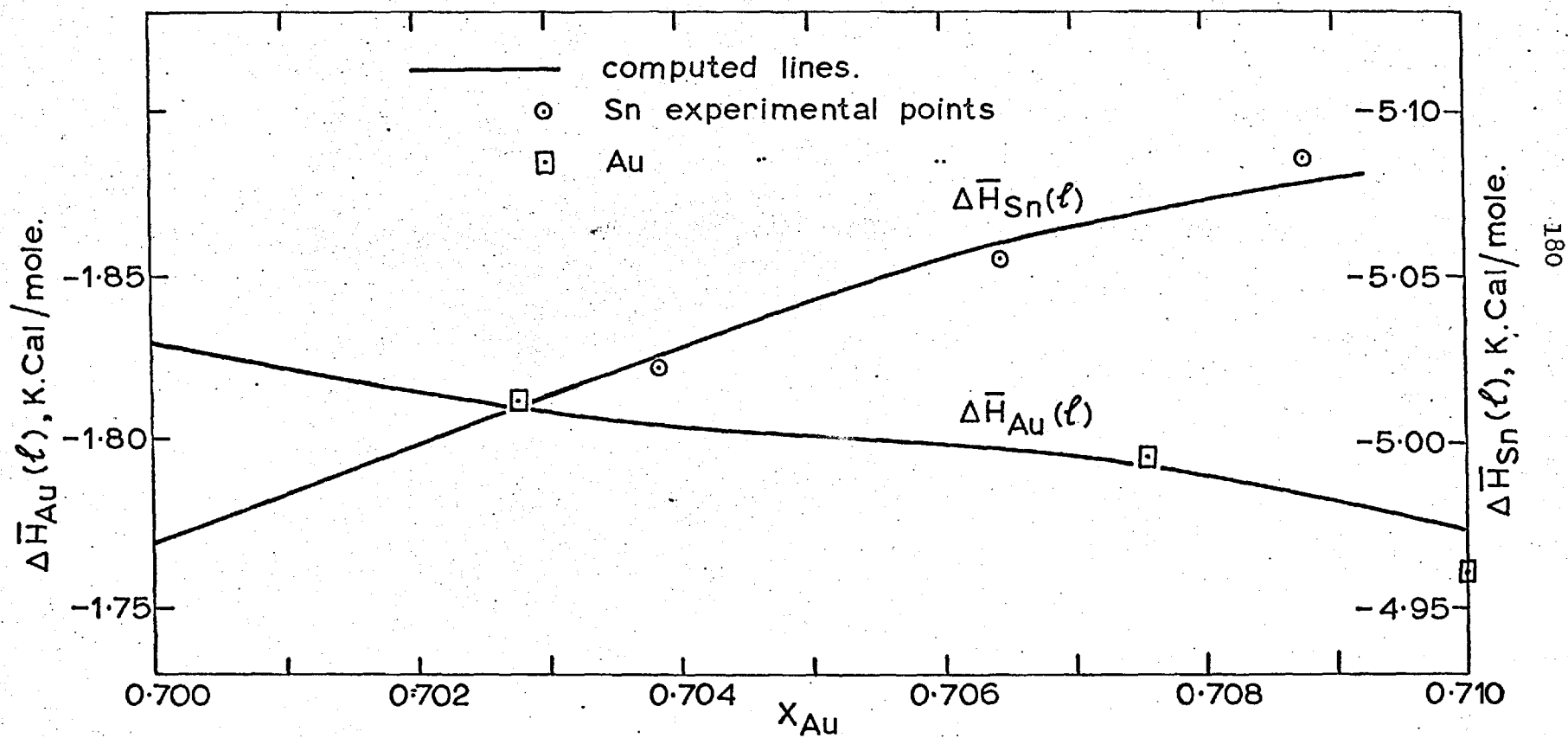
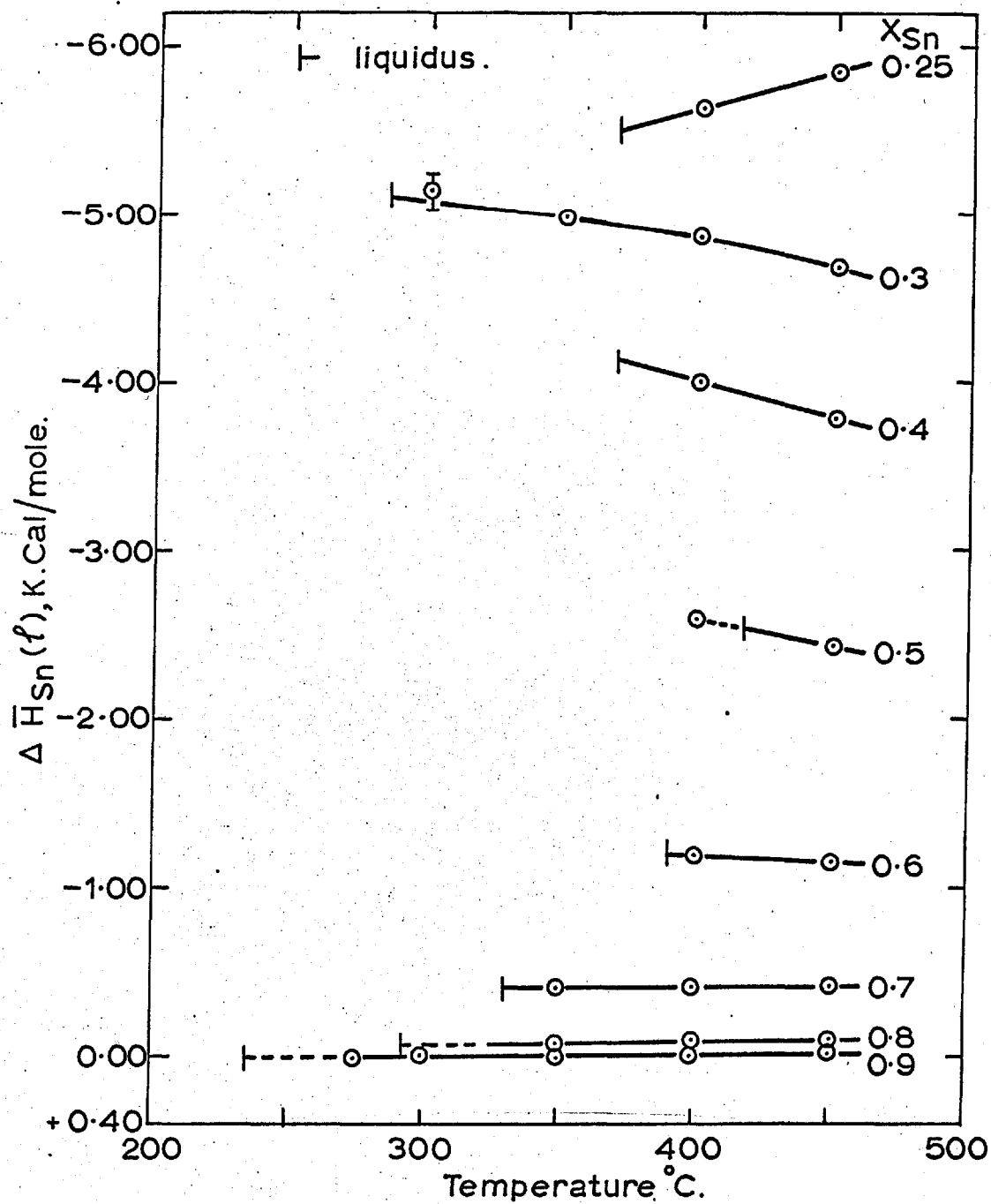
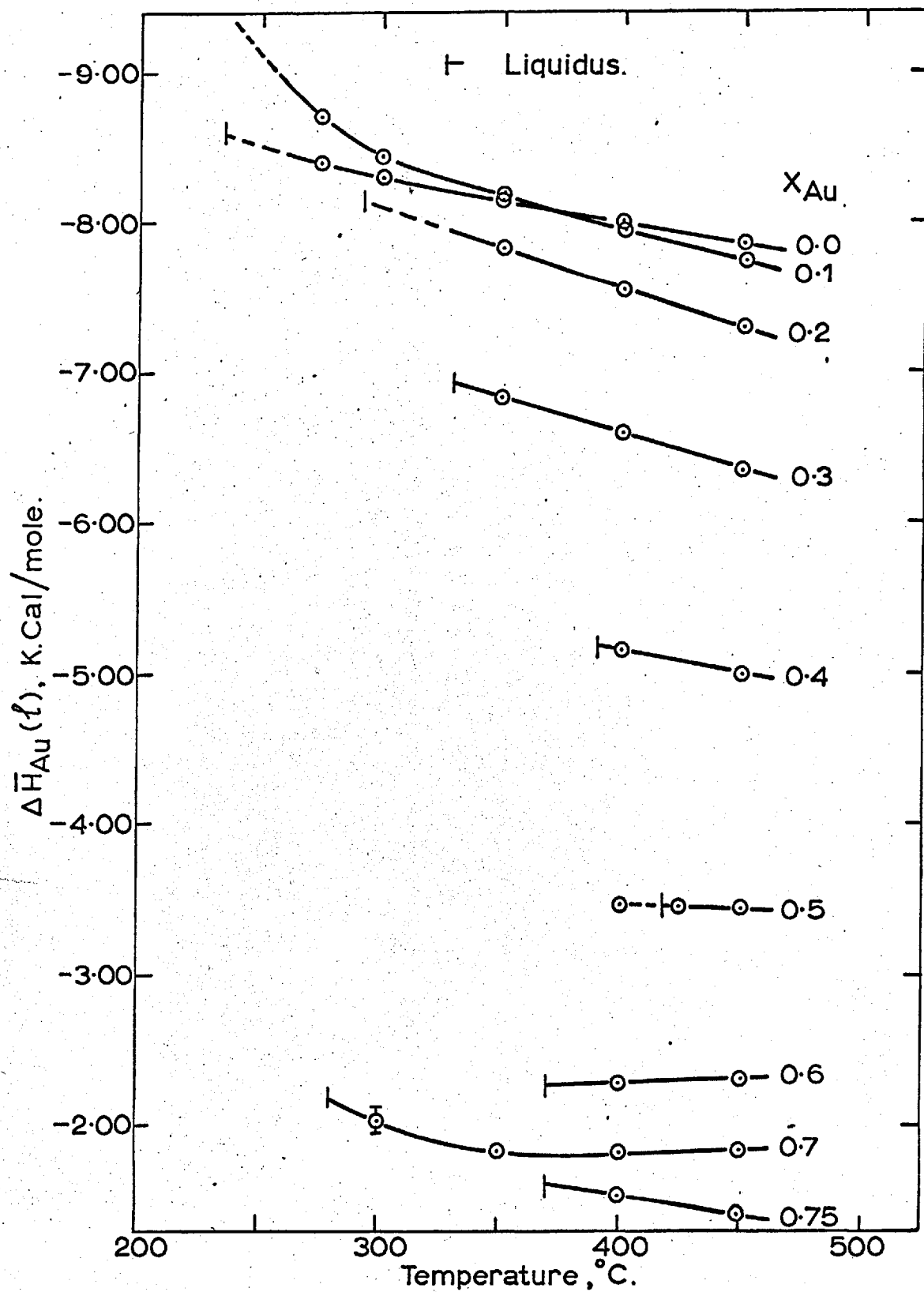


FIG. 4.3.4. EXPERIMENTAL AND COMPUTED VALUES OF $\Delta \bar{H}_{Sn}(l)$ AND $\Delta \bar{H}_{Au}(l)$ AT 350°C.

FIG. 4.3.5. CHANGE OF $\Delta \bar{H}_{Sn}(l)$ WITH TEMPERATURE.

FIG. 4.3.6. CHANGE OF $\Delta \bar{H}_{Au}(l)$ WITH TEMPERATURE.

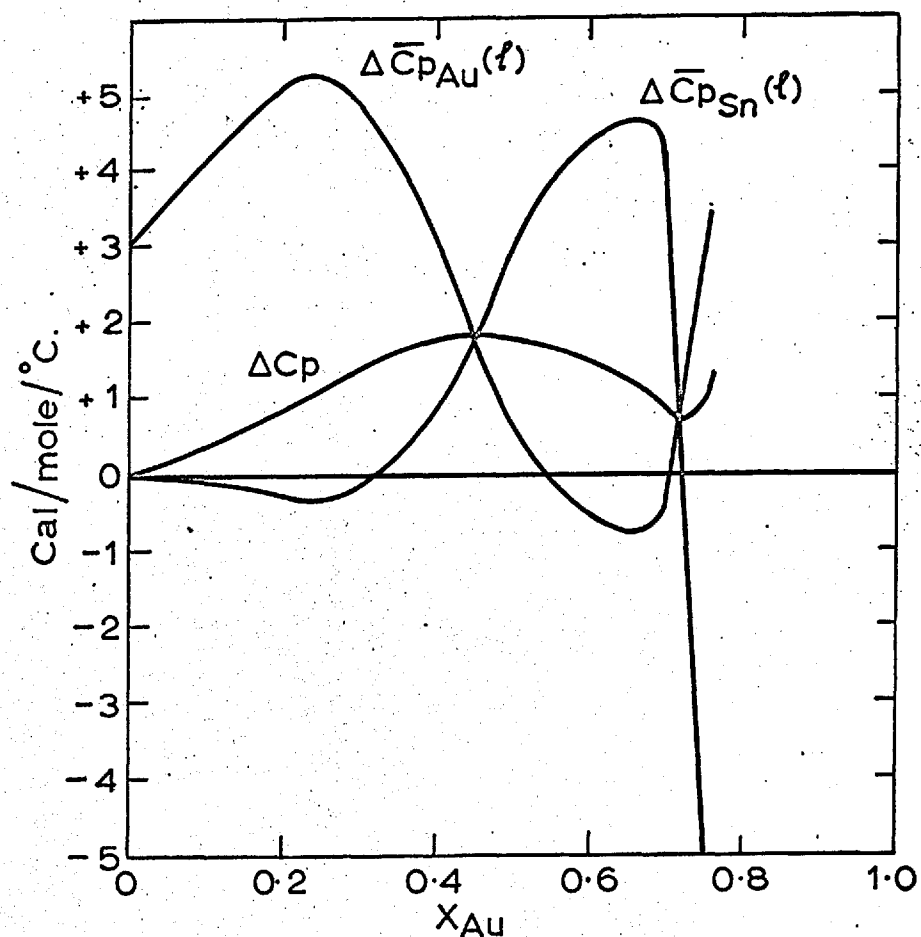


FIG. 4.3.7. HEAT CAPACITIES OF LIQUID Au - Sn ALLOYS AT 425 °C.

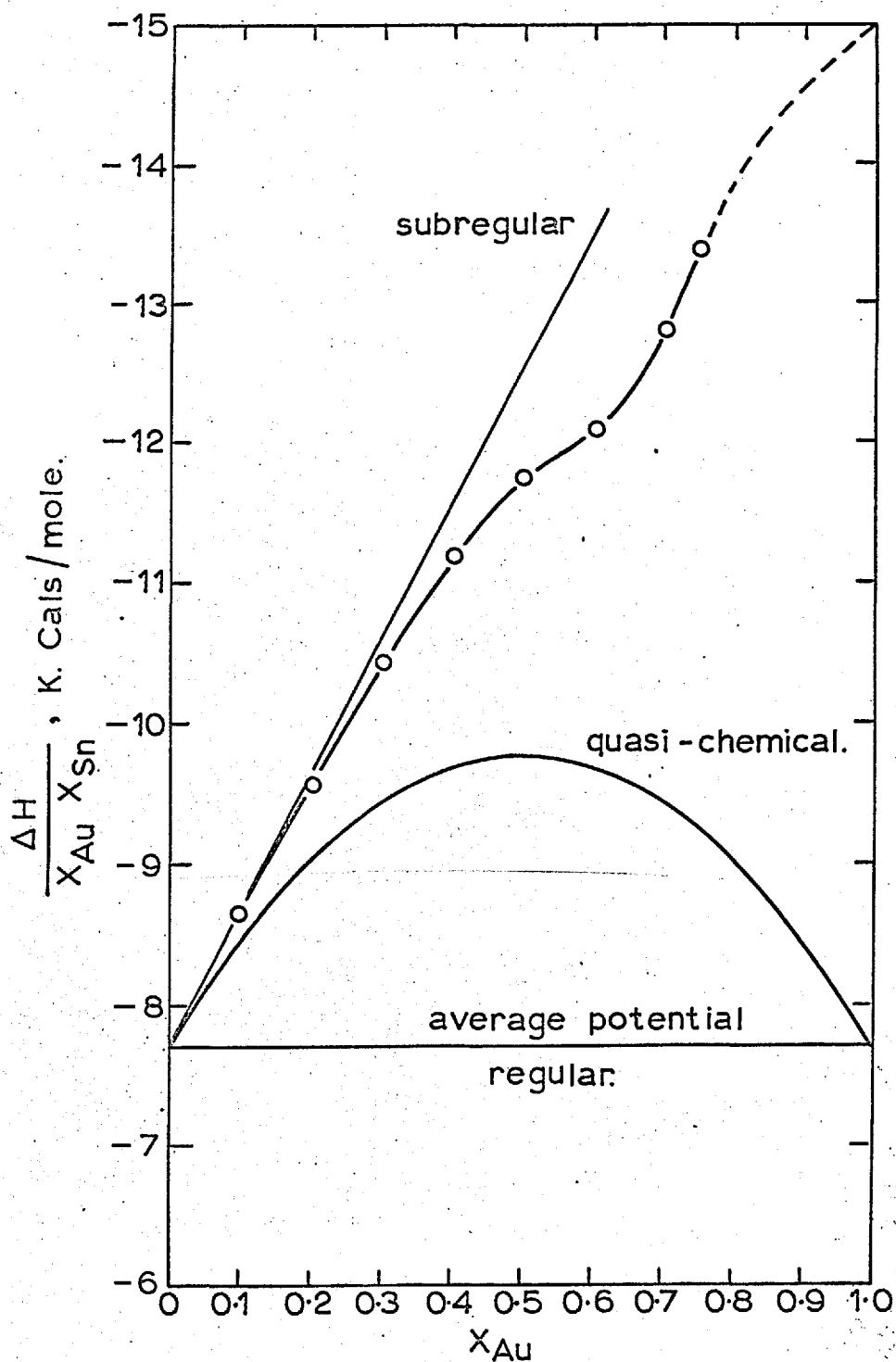


FIG. 5.3.1. APPLICABILITY OF DIFFERENT MODELS OF SOLUTION TO LIQUID Au-Sn SYSTEM.

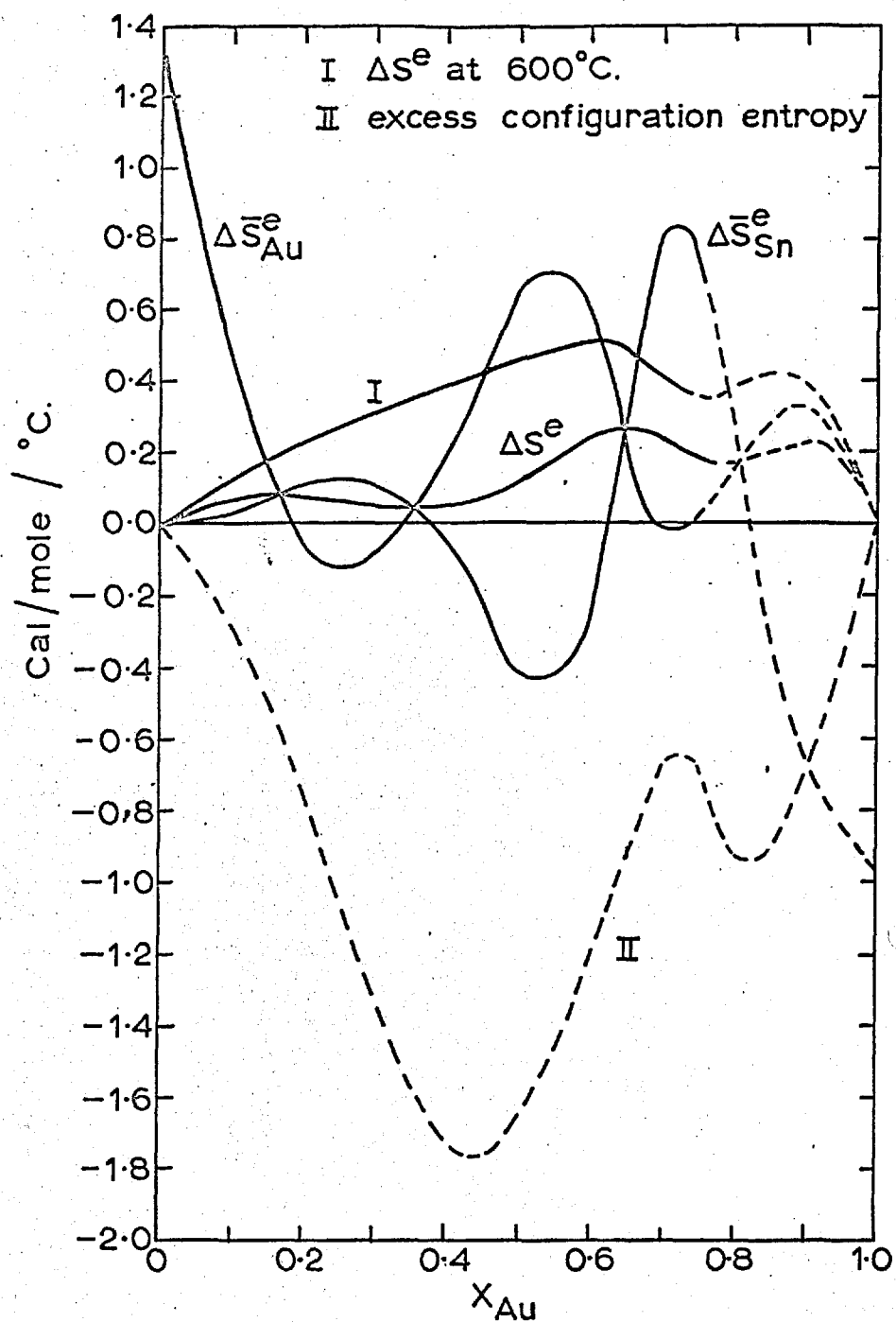


FIG. 5.4.1. EXCESS ENTROPIES OF LIQUID Au-Sn SYSTEM AT 450°C.

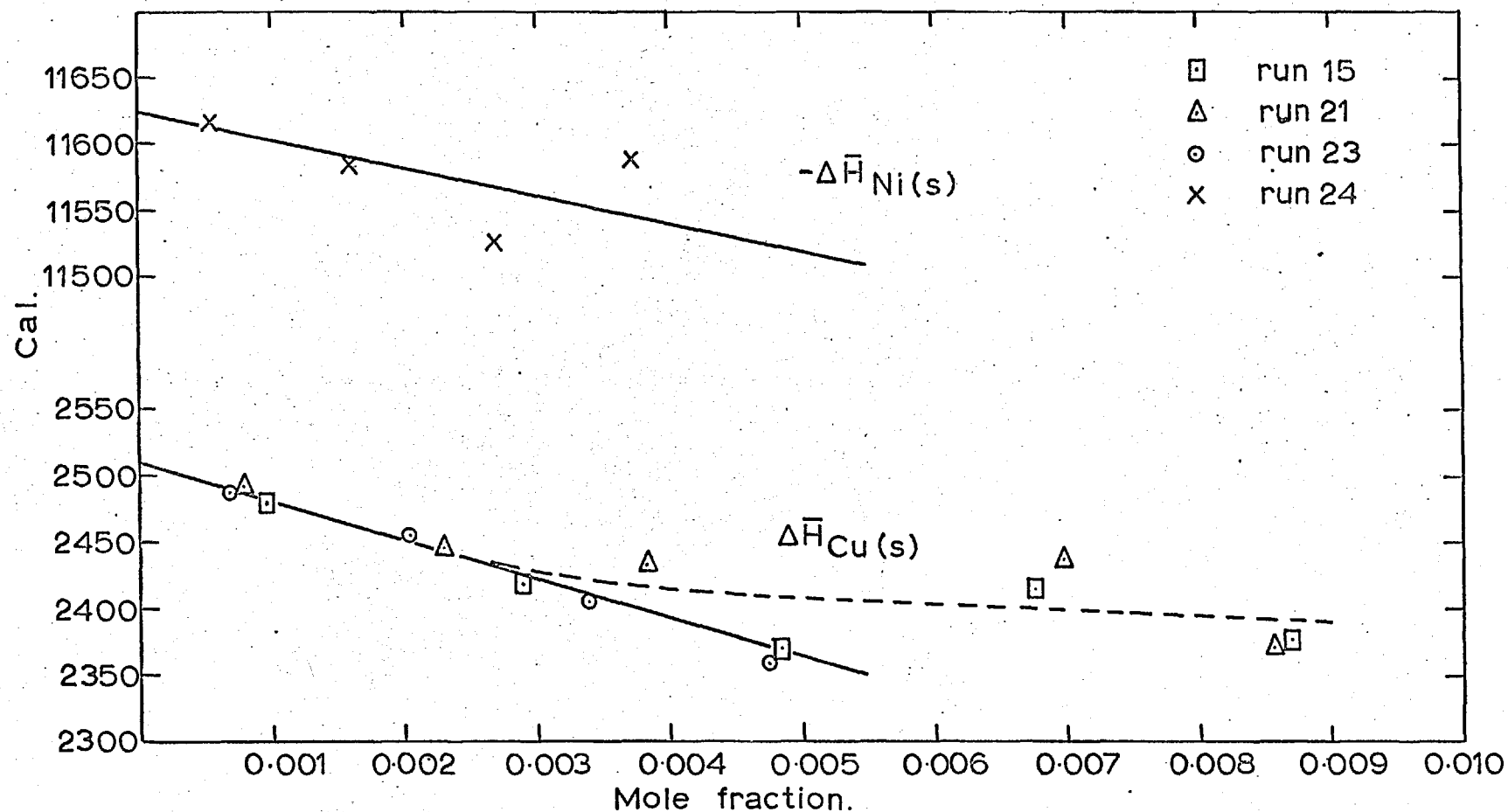


FIG. A1.1. COMPOSITION DEPENDENCE OF HEATS OF SOLUTION OF SOLID COPPER AND SOLID NICKEL IN LIQUID TIN AT 350°C.

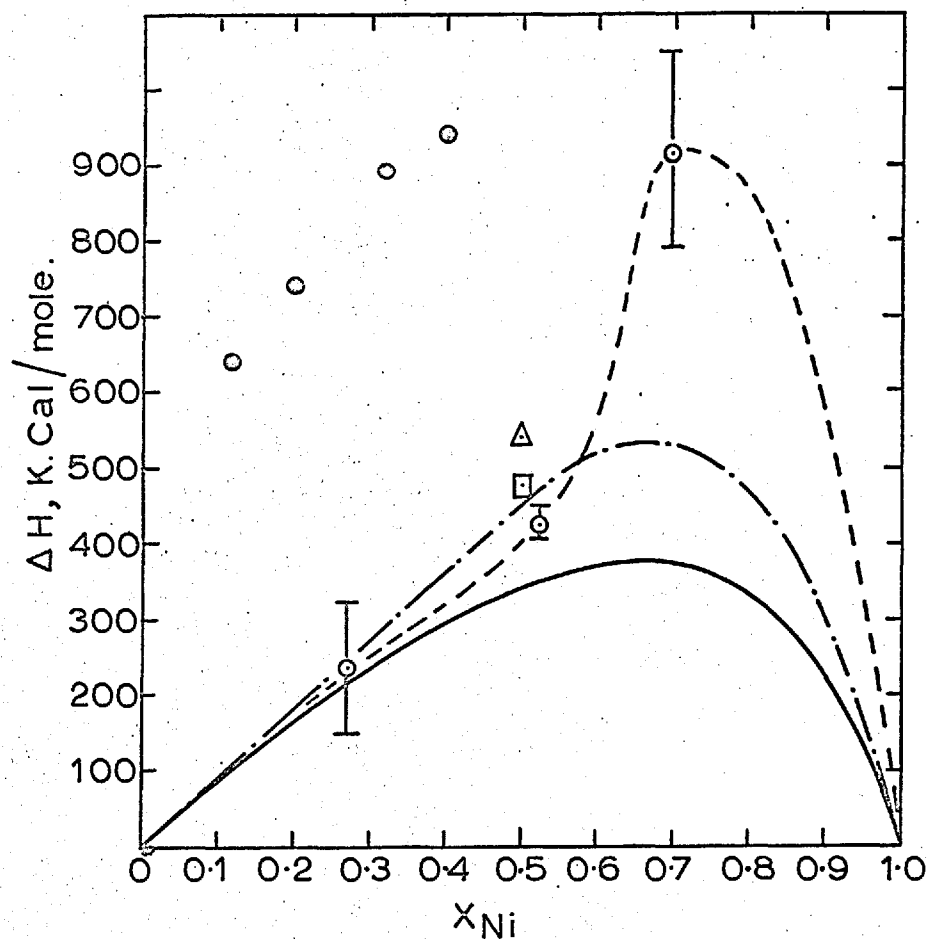


FIG. AI.2. HEATS OF FORMATION OF
Cu-Ni ALLOYS.

present work	○	0°C.
Leach et al	○	0°C.
Pratt	◻	500°C.
Oriani et al	—	640°C.
Kubaschewski et al	Δ	722°C.
Rapp et al	----	850°C.

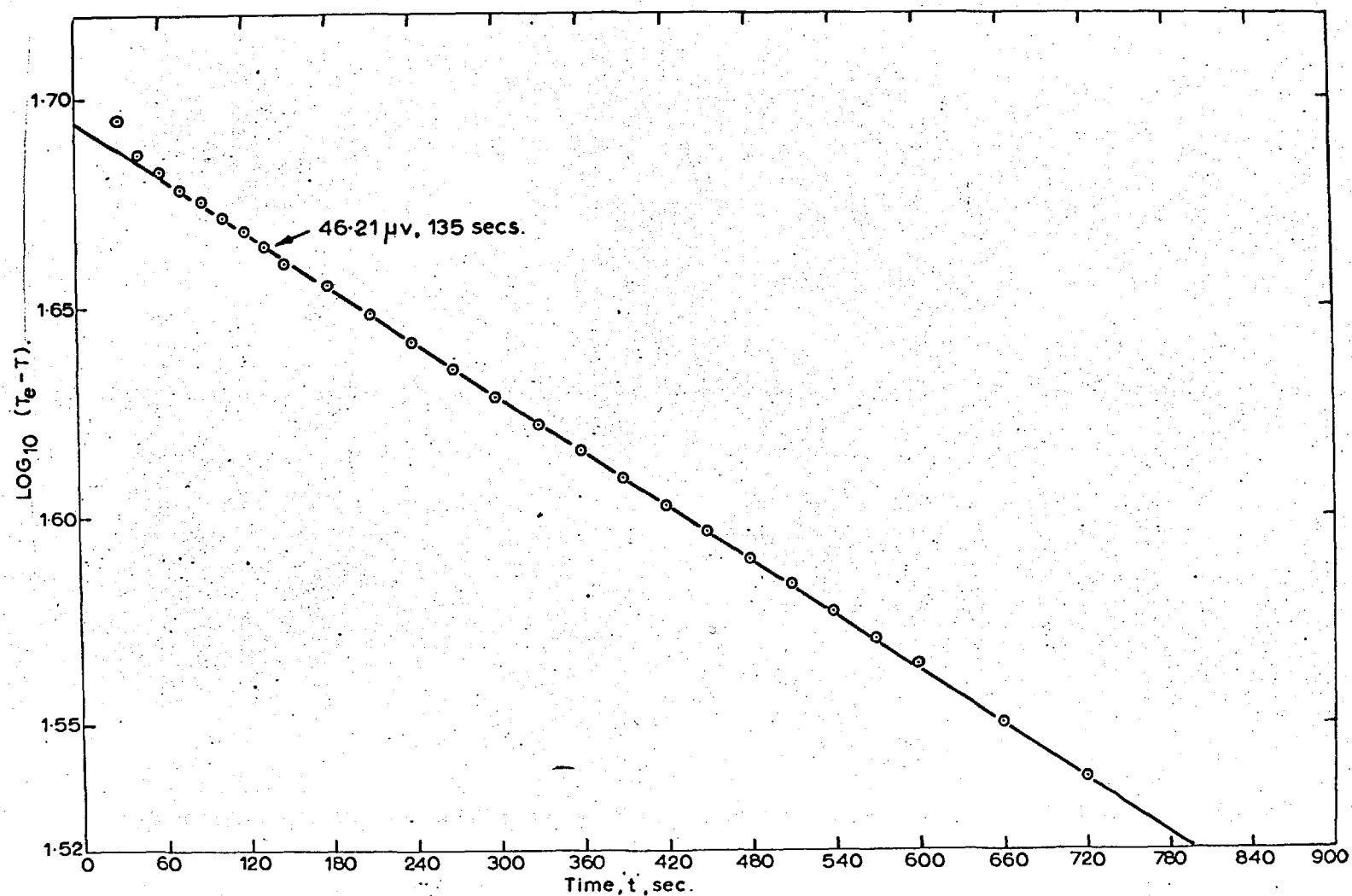


FIG. AII-1. PLOT OF $\text{LOG}_{10} \Delta T$ AGAINST TIME. RUN 13.2.

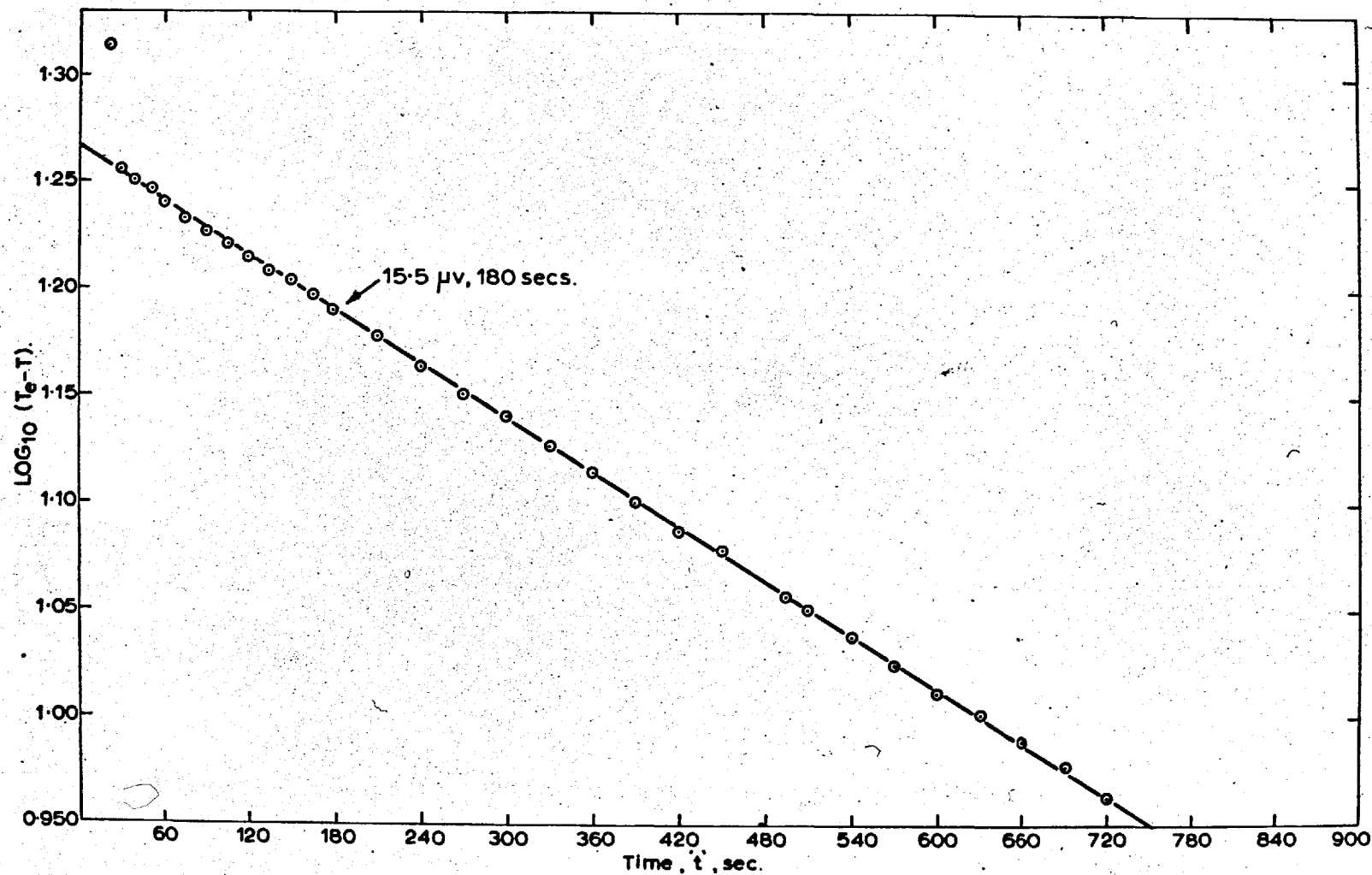


FIG. AII - 2. PLOT OF $\text{LOG}_{10} \Delta T$ AGAINST TIME RUN 34.4.