

## 2.1 Introduction

A brief review of different techniques of thermodynamic measurements has been given in Chapter 1. It has already been pointed that emf technique based on fused salt electrolyte galvanic cell should be preferred for activity and partial molar quantities measurements in metallic systems. In this chapter, the experimental procedure and the details of activity measurements will be discussed. Specific details of the technique and the characteristics of the particular system have been given in the respective chapters. Activity of Indium in ternary systems; viz., Bi-In-Sn has been measured by emf technique based on molten salt electrolyte. Integral and Partial molar excess thermodynamic properties of zinc in Bi-In-Sn are calculated from the measured activities. Later thermodynamic properties of relevant binary system and ternary Bi-In-Sn system have been measured by a drop calorimetric technique. When thermodynamic data are not available with sufficient degree of accuracy one would, to start with, search for a suitable technique to determine these experimentally. Confidence in and reliability of the data are considerably increased if the quantities are measured by two or more independent techniques. So, enthalpy is measured by Calorimeter and free energy by emf techniques.

## 2.2 Materials

All pure metals Indium, Tin, Bismuth were obtained from Johnson Mathew (United Kingdom) and other raw materials for experiment from different supplier. The typical purity, sources, chemical compositions and other details of the principal elements of all raw materials is given in Table 2. 1.

**Table 2.1** Purity, Sources and Physical state of Materials

Material	Purity (%) ~Grade	Supplier	Physical state
Indium	99.999	JM, UK	Ingots
Bismuth	99.999	JM, UK	Lumps
Tin	99.999	JM, UK	Shots
InCl	AR	Loba-Chemie, INDIA	Powder
KCl	AR	Qualigens, INDIA	Powder
LiCl	AR	Reidel, GERMANY	Powder
Argon gas	IOL AR 1*	IOL, INDIA	Gas
Al <sub>2</sub> O <sub>3</sub>	99.99999%	NIST	Needle

JM = Johnson Matthey, UK

AR = Analytical Grade

IOL = Indian Oxygen Limited, India

NIST = National Institute of Standards and Technology

\* Oxygen content less than 2 ppm.

The specific elements in stoichiometric proportions, weighed to an accuracy of  $10^{-5}$  g were sealed in transparent quartz capsules under vacuum of better than  $10^{-5}$  mmHg. A vacuum pumping system ( Hind High Vacuum, India Model: VS 114PD) was used to generate vacuum.

### 2.3 Electrochemical Methods

The use of electrochemical technique in connection with thermodynamic and kinetic measurements is well established. In these techniques the thermodynamic properties are obtained by measuring the emf of a suitable electrochemical cell. A large number of investigations were carried out at the end of the nineteenth century on the aqueous

electrolytes and till the middle of the current century by molten salt electrolyte. In the last five decades a large numbers of system have been investigated by using solid electrolytes after Kiukkola and Wagner [Kiukkola and Wagner (1957)] introduced calcia stabilized zirconia solid electrolytes for thermodynamic measurements.

### 2.3.1 General Principles

Consider a simple galvanic cell consisting of a metal A, a fused electrolyte (AM) and alloys of the system A-B-C:



The half-cell reaction at different electrode may be written as:



The virtual cell reaction for the passage of coulombs of charge is:



The activity of component A in the multicomponent system A-B-C at temperature T, given by the relation:

$$\ln a_A = -\frac{nF}{RT} \dots\dots \text{valid only if transport no. of } A^+ \text{ cation is unity} \quad (2.5)$$

Where n is the number electron participated in the electrochemical reaction ‘F’ is the Faraday constant and E is the emf of the cell (2.1) in volt. From the activity values measured for different composition at different temperatures, partial and integral excess thermodynamic properties can be estimated.

### 2.3.2 Theoretical Considerations

Though the above cell (2.1) seems to be fairly simple, a number of theoretical considerations [Bass (1964), Oriani (1956), Taylor (1927), Wagner and Werner (1963)] and careful planning is required to arrive at the correct reversible emf to obtain accurate thermodynamic data. The criteria for the reversibility are (a) emf should be constant at a given temperature; (b) the path followed by the emf vs. temperature plot should be same during heating and cooling cycles. and (c) if a small current is passed through the cell externally, the emf should come back to initial emf after removal of the external source and an instrument having much larger impedance should be used for the measurement of emf of the cells.

In order to achieve reversibility of the cell following general considerations should be kept in mind:

- a) The electrolyte should show exclusively ionic conduction. In case any electronic conduction occurs in the cell, equation (1.11) has to be modified by more elaborate relations derived by Kiukkola and Wagner [Kiukkola and Wagner (1957)]. This correction requires the specified knowledge of the participating ion in the cell.
- b) The participating ion should be only in one valence state which means that the presence of any oxidizing or reducing agent in the cell must be avoided.
- c) The temperature range of operation must be high enough to enable diffusion to equalize activity gradient between the interior and at the surface of the alloy or compound electrode. According to Oriani [Oriani (1956)] an operating temperature level more than 0.3 to 0.4 of the melting point of the electrode is suitable.
- d) In the molten salt electrolyte galvanic cell, the salts used should have low melting and high boiling point. The vapour pressure of the salts should be low in the temperature range of operation.

- e) The presence of concentration gradient or liquid junction in the electrolyte can alter the cell emf because of the irreversible nature of diffusion occurring in the electrolyte.
- f) Transfer of materials from one part of the cell to another caused by flow of current, diffusion or physical mixing can cause the cell to have a mixed potential, resulting from the local shifts in electrolyte composition.
- g) An exchange reaction may take place between the alloy and adjacent electrolyte:



In order to avoid this exchange reaction, metal A should be less noble than the alloy component C in the Alloy A-B-C due to exchange reaction the emf may change from the normal value.

- h) It is important that no thermal gradient should exist in the region of the cell containing electrode and electrolyte in order to avoid irreproducible thermo-emf.
- i) The electrode contact wires, as far as possible, must be identical. In case of different lead wires, a correction factor for thermo-emf should be employed. The correction factor must be determined in a separate experiment without electrolyte in the temperature range of operation. The lead wire must be insoluble in electrode material to avoid altering the composition. A liquid metal with a high surface tension may not have good contact with the lead wires and hence an error of several millivolts in the cell emf may result.

#### 2.4 Experimental Set-up

A eutectic melt of LiCl and KCl together with 5 wt% InCl was used as the molten salt electrolyte to determine activity of Indium in the ternary systems, In–Sn–Bi. The eutectic point in the LiCl-KCl system occurs at 633 K and 43 wt% LiCl [Kleppa

(1956)].

#### 2.4.1 The Galvanic Cell Assembly

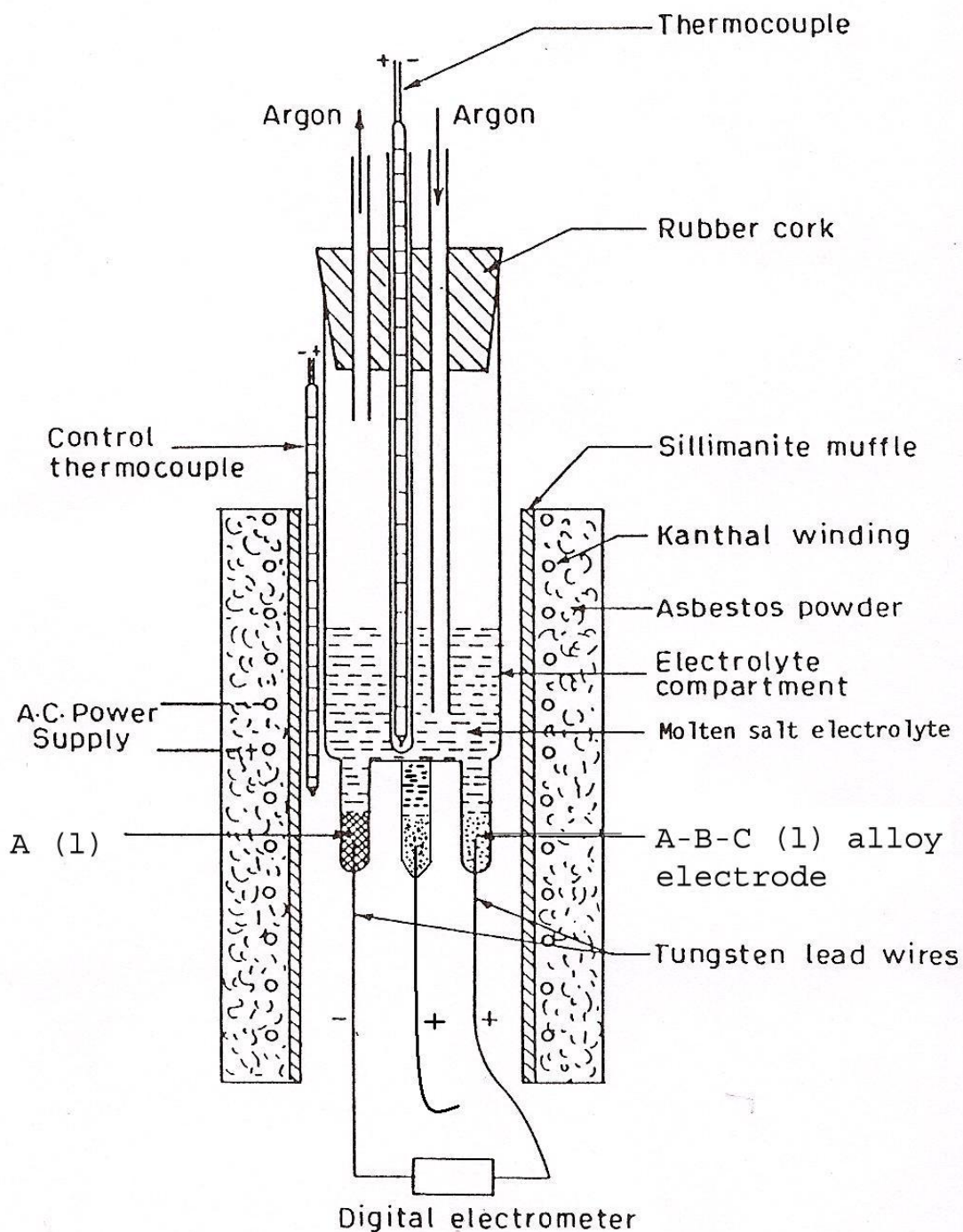
The experimental cell assembly, schematically shown in Fig. 2.1, was made of BOROSIL glass (81% Si, 14% boric oxide, 2% sodium oxide and 2-3% aluminium oxide). The assembly used for the investigation of In-Sn-Bi systems had six lower limbs (6 mm I. D). These limbs are present at the bottom of the electrolyte compartment of 50 mm dia. A tungsten lead wire of 0.4 mm dia and 20 cm length was sealed to the glass limb. One of the six limbs contained Indium as an electrode and the other were meant for the alloy electrode under study. The top of the cell assembly was covered with a rubber cork with three holes to allow of an argon inlet tube, a thermocouple well (one end-closed BOROSIL glass tube of 5mm I. D.) and an argon outlet tube. The thermocouple well as well as the inlet tube reached up to the bottom of the cell assembly. The plan of the cell assembly is shown in Figure 2.1.

#### 2.4.2 Furnace and Measuring Instruments

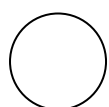
For heating of the electrochemical cells a Kanthal (A-I grade) wound silica tube furnace of 55 cm height and 60 mm I. D. was used. This furnace had constant temperature zone (within  $\pm 0.5$  K) of at least 15 cm long. The temperature of the furnace was controlled by PID based Digital Temperature Controller (Servotronics, India; Model: 192) with an accuracy of better than  $\pm 0.5$  K. The control thermocouple was placed in the gap between cell assembly and the furnace muffle. The temperature of the cell was measured by a pre-calibrated chromel-alumel thermocouple. The cold junction of the thermocouple was kept in ice-water mixture (i.e. at 273 K).

The open circuit emf of the cell across the tungsten lead wires was measured by a high impedance Electrometer (Keithley, USA; Model: 617) at the input impedance of more than  $2 \times 10^{12} \Omega$ . The electrometer was capable of measuring 0.01mV and was also used

to measure temperature of the cell.



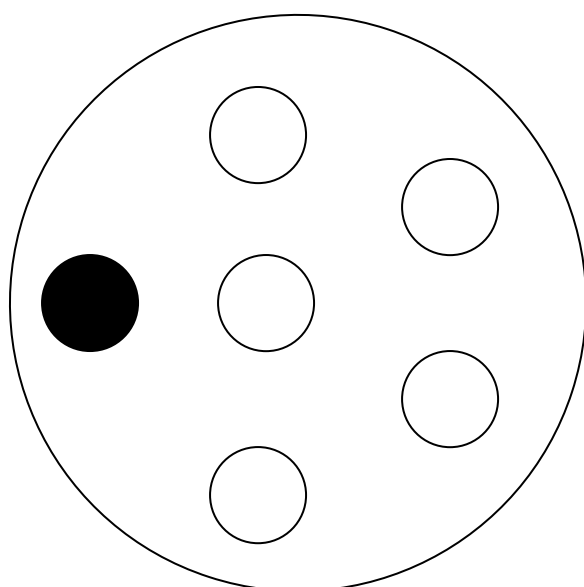
**Figure 2.1** Molten salt electrolyte galvanic cell assembly



Alloy Electrodes



Reference Electrode (Pure Indium)



**Figure 2. 2** Plan of the Galvanic cell assembly for the activity measurement



### 2. 4. 3 Experimental Procedure

In the beginning of the experiments, the electrodes were formed by charging desired metals in the specific limbs using long funnels. The reference electrode was formed by charging small pieces of pure metallic Indium in one of the limbs through a long funnel. Rests of the five limbs were charged with small pieces of bismuth, indium and tin (frozen prior to charging) in appropriate proportions corresponding the alloy composition through the long funnel to form the alloy electrodes.

The LiCl-KCl + 5 wt % InCl electrolyte was made from powders of LiCl, KCl and InCl in appropriate proportions (31.0, 39.9 and 3.5 g). It was then mixed and melted in a separate glass tube. The fused mass was solidified by cooling to 400 K and then crushed into small pieces and quickly transferred into the reaction chamber of the cell which was held in position into the tube furnace. This method of preparation of electrolyte prevented the absorption of moisture from the atmosphere particularly by LiCl and InCl which are highly hygroscopic.

The upper portion of the cell assembly was covered with a rubber cork along with thermocouple well, argon inlet and outlet tubes. The flushing of argon gas were started and continued for about 1 hr prior to heating and then furnace was heated to the desired temperature. During the initial stages of the experiment, a slow stream of argon gas was passed for about 5 hrs and then flow was stopped and the outlet was sealed airtight. Any leakage in the system was checked by counting the number of bubbles at the inlet and outlet of the assembly.

The cell was allowed to attained equilibrium over a period of 24 hrs. The emf of the cell was measured after 24 hours and after that emf values remained constant for over 30 hrs within  $\pm 0.02\text{mV}$ . After measuring emf at one temperature, the temperature of the cell was changed either by heating or cooling depending on the respective cycles.

To reestablish the equilibrium at the new temperature, sufficient time was allowed. The measurement of emf of the electrochemical cells was carried out during heating as well as cooling. At each temperature the reversibility of the cell was checked by short circuiting the two electrodes for short time. The emf values were taken to be reliable only when, after separating the lead wires, the cell emf returned back to the original value. Other precautions regarding the reversibility of the cell as outlined in Section 1.4.6.2 were adopted. Apart from measuring the emf values repeatedly by approaching both from higher and lower temperature sides, each complete experiment was repeated to check the reproducibility of results.

#### 2. 4. 4 Method of Calculation

The activity values of one component in the multicomponent solutions were calculated from equation (1. 12). The appropriate value of 'n' taken was consistent with the conducting ions and 'F' was taken 96,508 J Volt<sup>-1</sup>. From the emf data obtained at different temperatures, the integral excess molar and partial excess molar thermodynamic properties of the ternary systems were calculated by using appropriate equations. Partial molar thermodynamic properties of a single component in the multicomponent solution were also computed from the emf data. The activities of In in Bi-In-Sn systems were computed. From the activity of indium the partial excess molar free energy and enthalpy of mixing were computed as follows

$$\bar{G}_i^{xs} = RT \ln \left( \frac{a_i}{x_i} \right) \dots\dots\dots (2.7)$$

The integral excess molar free energy of the solution as a function of composition of indium for the Bi-In-Sn systems was calculated from equation (2.15). Partial excess molar free energy of indium was obtained from equation (2.7).

The activities of the other two components at the base of the ternary triangle were

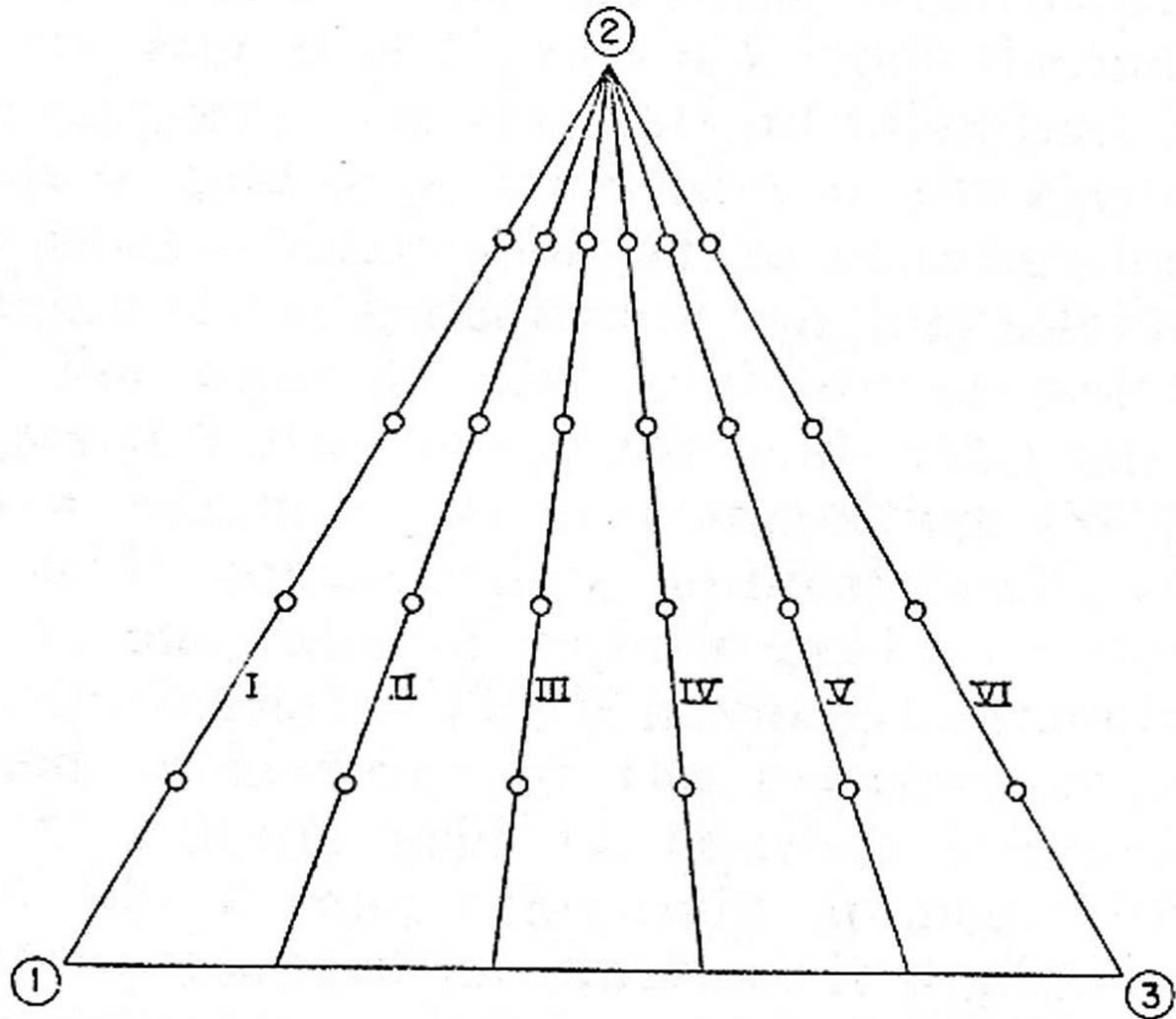
calculated from the partial excess molar free energy using equation (2.7).

**Darken's treatment of ternary system** [Darken (1950)] has suggested a method for calculation of activities components present at the base of the ternary triangle from the partial molar property of the component present at the apex of the triangle. Darken's treatment has been summarized in the following paragraphs. If  $\Delta Q$  is an integral molar property of the ternary system and  $\Delta Q_1$ ,  $\Delta Q_2$  and  $\Delta Q_3$  are the partial molar properties of components 1, 2 and 3 (shown in Figure 2.3), respectively, the integral and partial quantities are related as follows:

$$\Delta Q = x_1 \Delta \bar{Q}_1 + x_2 \Delta \bar{Q}_2 + x_3 \Delta \bar{Q}_3 \quad \dots\dots\dots (2.8)$$

The equation (2.8) is differentiated partially with respect to  $x_2$  at constant  $x_1/x_3$ ,

$$\text{giving} \left( \frac{\partial \Delta Q}{\partial x_2} \right)_{x_1/x_3} = x_1 \left( \frac{\partial \Delta \bar{Q}_1}{\partial x_2} \right)_{x_1/x_3} - \frac{x_1}{1-x_2} \Delta \bar{Q}_1 + x_2 \left( \frac{\partial \Delta \bar{Q}_2}{\partial x_2} \right)_{x_1/x_3} + \Delta \bar{Q}_2 + x_3 \left( \frac{\partial \Delta \bar{Q}_3}{\partial x_2} \right)_{x_1/x_3} - \frac{x_3}{1-x_2} \Delta \bar{Q}_3 \quad \dots\dots\dots (2.9)$$



**Figure 2.3** Illustrations on triangular coordinates of compositions to be investigated in ternary system.

According to Gibbs — Duhem equation ( $x_1\Delta\bar{Q}_1 + x_2\Delta\bar{Q}_2 + x_3\Delta\bar{Q}_3 = 0$ ) the sum of the first, third and fifth terms in the equation (2.9) is zero. Thus we have

$$\left(\frac{\partial\Delta Q}{\partial x_2}\right)_{x_1/x_3} = -\frac{x_1}{1-x_2}\Delta\bar{Q}_1 + \Delta\bar{Q}_2 - \frac{x_3}{1-x_2}\Delta\bar{Q}_3 \quad \dots\dots\dots (2.10)$$

On rearrangement of equation (2.10), it gives

$$\Delta\bar{Q}_2 = \Delta Q + (1 - x_2) \left(\frac{\partial\Delta Q}{\partial x_2}\right)_{x_1/x_3} \quad \dots\dots\dots (2.11)$$

The equation (2.11) is extensively used for computing partial molar quantity from the integral quantities by slope - intercept method. Dividing equation (2.11) by  $(1 - x_2)^2$  and rearranging terms, we get

$$\left[ \frac{\partial}{\partial x_2} \left( \frac{\Delta Q}{(1-x_2)^2} \right) \right]_{x_1/x_3} = \Delta \bar{Q}_2 / (1 - x_2)^2 \dots\dots\dots (2.12)$$

Equation (2.12) can be integrated graphically by two different methods along the line with constant value of  $x_1 / x_3$ . The first method is to integrate along the line with constant ratio of molar fraction of component 1 and 3 ( $x_1 / x_3$ ) from  $x_2 = 0$  to  $x_2 = x_2$ . The equation obtained for computing the integral quantity of the solution is

$$\Delta Q = (1 - x_2) \left[ \int_0^{x_2} \frac{\Delta \bar{Q}_2}{(1-x_2)^2} dx_2 + \Delta Q_{Binary\ 1-3} \right]_{x_1/x_3} \dots\dots\dots (2.13)$$

Above equation is similar to the expression for a true binary system with the addition of the integration constant =  $\Delta Q_{Binary\ 1-3}$  which is the value of  $\Delta Q$  for the binary 1 - 3 (where  $x_2= 0$ ), and the integration is to be done along a fixed cross section. The integral properties of the ternary solution can be computed by the Equation (2.13) by measuring the partial properties of component 2 as a function of composition  $x_2$ . The second approach is to integrate equation (2. 12) from  $x_2 = 1$  to  $x_2= x_2$ . The desired form of the equation for calculating the integral quantity is

$$\Delta Q = (1 - x_2) \left[ \int_1^{x_2} \frac{\Delta \bar{Q}_2}{(1-x_2)^2} dx_2 \right]_{x_1/x_3} + x_1 [\Delta \bar{Q}_1]_{x_2=1} + x_3 [\Delta \bar{Q}_3]_{x_2=1} \dots\dots\dots (2.14)$$

The last two terms in the above equation is the contribution from the infinitely dilute binary solution of 1-2 and 3-2, respectively. The terms

$[\Delta\bar{Q}_1]_{x_2=1}$  and  $[\Delta\bar{Q}_3]_{x_2=1}$  are obtained from the corresponding binaries as follows

$$\int_0^1 \frac{\Delta\bar{Q}_2}{(1-x_2)^2} dx_2 \dots\dots\dots (2.15)$$

The Equation (2.13) can be applied to the excess molar free energy of mixing for the ternary solution as:

$$G^{xs} = (1-x_2) \left[ \int_0^{x_2} \frac{\bar{G}_2^{xs}}{(1-x_2)^2} dx_2 + G_{Binary1-3}^{xs} \right]_{x_1/x_3} \dots\dots\dots (2.16)$$

This is used for computing  $G^{xs}$  for a ternary composition from the knowledge of (i)  $\bar{G}_2^{xs}$  for ternary compositions of constant  $x_1/x_3$  (ii)  $G^{xs}$  for binary system with the same ratio  $x_1/x_3$ .

If the  $G^{xs}$  for binary 1-3 is not available then equation (2. 7) can be used to calculate the integral quantity for the ternary solution:

$$G^{xs} = (1-x_2) \left[ \int_1^{x_2} \frac{\bar{G}_2^{xs}}{(1-x_2)^2} dx_2 \right]_{x_1/x_3} + x_1 [\bar{G}_1^{xs}]_{x_2=1} + x_3 [\bar{G}_3^{xs}]_{x_2=1} \dots\dots\dots (2.17)$$

The partial molar properties of the components in the ternary solution are calculated from integral properties by slope-intercept method Equation (2.11).

### Gibbs free energy Modeling

The Gibbs energy of a phase present at equilibrium in a ternary system is a function of composition. It can be expressed in terms of the Gibbs energy of the boundary binary systems using the Muggianu extrapolation formula [Muggianu et al. (1975)].

$$G = \sum_i x_i 0_{G_i} + RT \sum_i x_i (\ln x_i) + \sum_i \sum_{j \neq i} x_i x_j L_{i,j} + \sum_i \sum_{j \neq i} \sum_{k \neq j} x_i x_j x_k L_{i,j,k} \dots (2.18)$$

Where  $G_i$  is the Gibbs energy of the pure component  $i$  in the same state as the concerned phase,  $x_i$  the mol fraction of component  $i$ , and  $L_{i,j}$  binary interaction parameter which are temperature and composition dependent. The ternary interaction parameter  $L_{i,j,k}$  has the following dependence.

$$L_{i,j,k} = x_i L_i + x_j L_j + x_k L_k \dots\dots\dots$$

(2.19)

Where the parameters  $L_i$ ,  $L_j$  and  $L_k$  may have a temperature dependence.

## 2.5 Calorimetric technique and procedure

### 2.5.1 Drop calorimeter

Enthalpy of mixing of the binary and ternary solutions was measured using drop calorimetric method by MHTC 96 line evo from Setaram, France. The temperature of the calorimeter is measured by the thermopile consisting of 20 thermocouples. A Graphite resistance furnace is provided for heating up to the maximum temperature of 1593 K. From the top the calorimeter, samples are dropped by an automatic dropping device. Maximum of 23 samples can be dropped successively into the calorimeter in a certain interval of time. An alumina tube guides the sample into the crucible inside the calorimeter. A vacuum pump is used to evacuate air from the furnace and calorimeter chamber. The argon gas is purged continuously into the calorimeter to prevent the oxidation of metals and alloys placed in the crucible. Data acquisition and processing was done by the software supplied by the manufacturer.

### 2.5.2 Experimental Procedure

#### 2.5.2.1 Starting up the instrument

Calorimeter is started by switching on power. The switch is located on back side of the calorimeter. Inlet gas pressure is maintained around 3 to 3.5 bar. Water tap is turned on for cooling.

### 2.5.2.2 Starting up the Calisto software

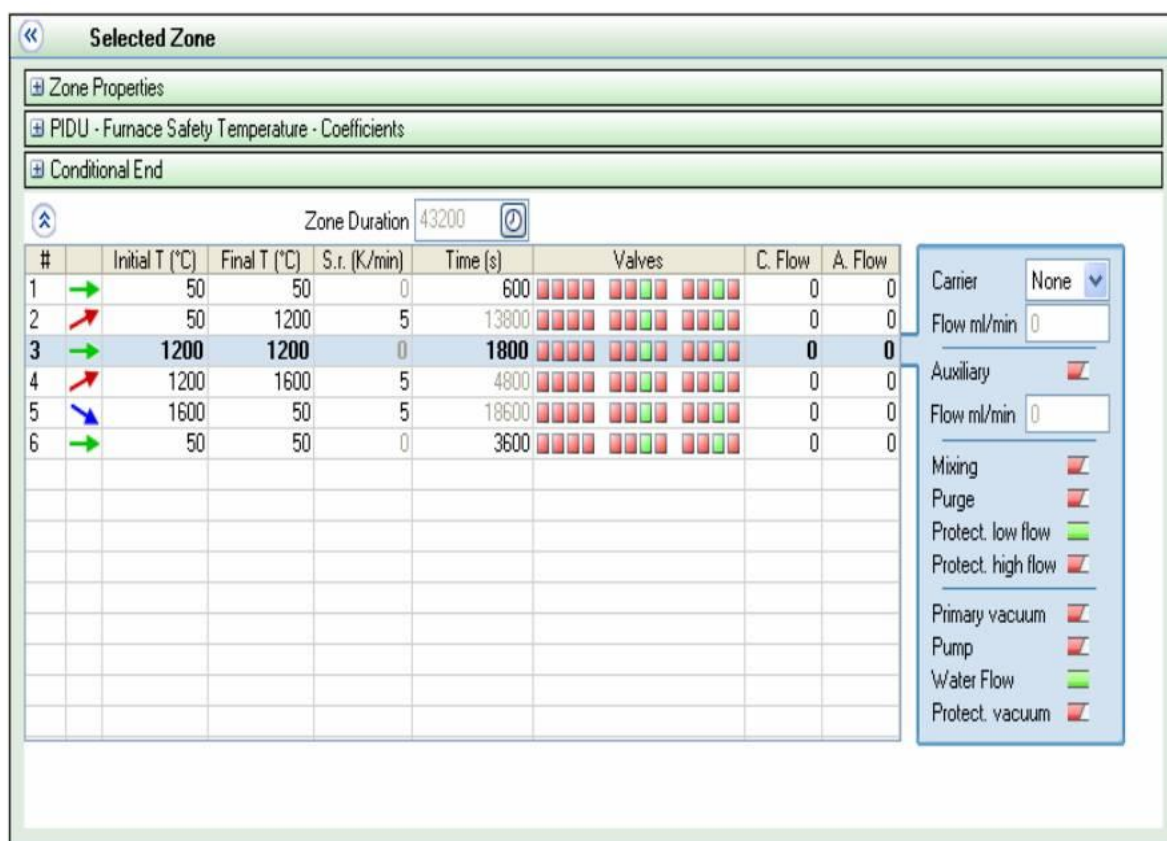
The Computer is switched on and then waited for 5 minutes. Calisto software is started by clicking data acquisition icon on the desktop. Program experiment or MHTC96 CS Evolution window is opened by clicking window tab in the top menu.

### 2.5.2.3 Programming the experiment

A new experiment is selected by clicking program experiments window. In right side a new experiment is created (see Figure 2.4). In Experiment Properties tab name of the experiment is changed, type of crucible is selected and mass of the sample is entered. In the procedure tab settings for procedure summary as well as for procedure properties like experiment group, end / pause mode are selected. In procedure properties sample and furnace temperature, carrier gas and

Safety temperatures are selected. By right clicking on the experiment name three standard zones are created (Heating zone, Isothermal zone and cooling zone). By clicking on serial no. tab sequences are added to the standard zones. During first zone (heating zone) furnace is heated at a given rate up to the desired temperature and samples are melted down in crucible. During second zone (isothermal zone) furnace is maintained at constant temperature and samples are dropped into the crucible. The time between each drop is generally 35 to 40 minutes. Extra time of 30 minutes is provided for stabilization in the starting of isothermal zone and 10 minutes after last drop for complete melting and mixing. In third zone (cooling zone) furnace is cooled to room temperature at a given rate. In this zone 10 minutes are given after cooling for stabilization and after that gas flow, water flow are closed.





**Figure 2.4** Experiment Programming

### 2.5.2.4 Sample Loading

Samples are loaded into alumina crucible by lifting up the dropping tube by pressing the Black button on the front left side of the calorimeter. Again by pressing the button dropping tube is moved down. Samples to be dropped are loaded into the Multi-Sample Introducer. Time interval is set between each drop.

### 2.5.2.5 Starting the experiment

After everything is ready the experiment is started by clicking start button under window tab. After finishing the experiment, the files are opened in Calisto processing software and area of each peak is measured.

### 2.5.2.6 Area measurement

After finishing the experiment the files are opened in Calisto processing software. Area of each peak is measured using baseline integration option under math tab. starting and end points of the peaks are selected for measuring area of individual peaks.

### 2.5.2.7 Necessity of calibration

The aim is to calibrate the transducer so as to transform the electrical signal  $S$  (in micro volts) into thermal power  $P$  (in mw). Heat related to thermal effect can thus be linked to mass variation that really produced a reaction during transformation. The coefficient of calibration  $K$  is then determined as:

$$S = K \times P \quad \dots\dots\dots (2.20)$$

This coefficient of calibration  $K$  varies with various parameters:

- The sample shape and mass.
- The properties of the transducer.
- The experimenting temperature.
- The properties of the crucible.
- The properties and flow-rate of the sweeping gas.

So, four samples of synthetic  $\alpha$ - $\text{Al}_2\text{O}_3$  is dropped at the end of each run so as to obtain the calibration constant at that particular flow rate, temperature and pressure. But this can be done in two ways generally. They are

1. Calibration with single standard
2. Calibration with multiple standards

**2.5.2.8 Calibration with a single standard**

If the transformation takes place within a limited temperature range, a single coefficient of calibration can be used when choosing the standard with the melting point closest to the sample transformation temperature.

Let H be the fusion heat content of the metal standard chosen (in J / g).

Let m be the mass of standard analyzed (in g).

Let S be the area of the fusion peak (in  $\mu\text{V} \cdot \text{s}$ ).

Then, the coefficient of calibration at the standard's melting point is given by:

$$K = \frac{S}{H} \times \frac{1}{m} \quad \text{in } \mu\text{V}/\text{W} \quad \dots\dots\dots (2.21)$$

It is recommended to express K in  $\mu\text{V}/\text{mW}$ .

For any peak area A (in  $\mu\text{V} \cdot \text{s}$ ) combined with the corresponding transformation Q (in Joule), the formula is:

$$Q = \frac{A}{K} \quad \dots\dots\dots (2.22)$$

**2.5.2.9 Calibration with multiple standards**

In practice, calibration with a single standard is not very accurate as the coefficient of calibration varies with temperature. Various metal standards are recommended so as to plot a variation curve of the coefficient of calibration in function of temperature. Choose at least five standards for a correct determining.

Let H be the fusion heat content of the standard i (in J/g), let  $m_i$  the mass of standard analyzed (in grams), let  $S_i$  be the area of the fusion peak (in  $\mu\text{V} \cdot \text{s}$ ), then the coefficient of calibration  $K_i$  at the standard's melting point  $T_{\text{em}}$  is given by:

$$K_i = \frac{S_i}{H_i} \times \frac{1}{m} \text{ in } \mu\text{V/W} \dots\dots\dots (2.23)$$

A table ( $T_{\text{eim}}$ ,  $K_i$ ) can be obtained and the variation  $K = f(T_{\text{eim}})$  can be plotted. The calibration curve reveals the instrument's coefficient of calibration at any temperature. It is recommended to write down this variation in the form of a polynomial function of the fourth degree:

$$K = A_0 + A_1 \cdot T_{\text{eim}1} + A_2 \cdot T_{\text{eim}2} + A_3 \cdot T_{\text{eim}3} + A_4 \cdot T_{\text{eim}4} \dots\dots\dots (2.24)$$

Regression software is needed for this work. The coefficients  $A_0$ ,  $A_1$ ,  $A_2$ ,  $A_3$  and  $A_4$  thus determined are entered in the software's Sensitivity page for automatically transforming the DTA signal.

### 2.5.2.10 Enthalpy calculations

The enthalpy change for each drop (integrated heat flow at constant pressure) is given by:

$$\Delta H_{\text{Reaction}, \text{In}, i} = (\Delta H_{\text{Signal}, \text{In}, i} \cdot K) - (\Delta H_{\text{In}, i}^{T_D \rightarrow T_M} \cdot n_{\text{In}, i}) \dots\dots\dots (2.25)$$

Where  $n_{\text{In}, i}$  is the moles of the indium dropped at  $i$ -Th drop.  $\Delta H_{\text{Signal}, \text{In}, i}$  is the heat effect due to single  $i$ -th drop of indium sample to the bath;  $K$  is the calibration constant;  $\Delta H_{\text{In}, i}^{T_D \rightarrow T_M}$  is the enthalpy increment of 1 mole of indium from drop temperature  $T_D$  (in Kelvins) to the bath temperature  $T_M$ , in the  $i$ -th measurement. The enthalpy increment of indium  $\Delta H_{\text{In}, i}^{T_D \rightarrow T_M}$  was computed using the heat capacity data of pure elements from Kubaschewski and Alcock [Kubaschewski, O. and Alcock (1979)].

Because of the relatively small mass added the partial enthalpy ( $\Delta \bar{H}_{\text{In}, i}^m$ ) can be directly calculated as:

$$\Delta \bar{H}_{m,i} \approx \Delta H_{Reaction,In,i} / n_{In,i} \dots\dots\dots (2.26)$$

In each of measurements, certain quantities of the liquid Bi-Sn binary alloys are used. Therefore, the enthalpy of mixing of binary alloys should be suitably added in the ternary enthalpy of mixing expression. The integral molar enthalpies of mixing, ( $\Delta_{mix}H$ ) was calculated by (Eq. (2.31)) as given below:

$$\Delta_{mix}H = [\{\Delta_{mix}H_{Bi-Sn} \times (n_{Bi} + n_{Sn})\} + \sum_i \Delta H_{Reaction,In,i}] / (n_{In} + n_{Bi} + n_{Sn}) \dots\dots\dots (2.27)$$

The molar enthalpy difference ( $H_{Sample,T_C} - H_{Sample,T_D}$ ) for Indium was calculated using the following relation.

$$(H_{Sample,T_C} - H_{Sample,T_D}) = \int_{T_D}^{T_C} C_P dT \dots\dots\dots (2.28)$$

$$(H_{Sample,T_C} - H_{Sample,T_D}) = \int_{T_D}^{T_{Tr}} C_P dT + \Delta H_{T_{Tr}} + \int_{T_{Tr}}^{T_m} C_P dT + \Delta H_{T_f} + \int_{T_m}^{T_C} C_P dT \dots\dots\dots (2.29)$$

Where,

$T_D$  = Temperature of the sample before dropping.

$T_{Tr}$  = Transition Temperature

$\Delta H_{T_{Tr}}$  = Latent heat of transition\*

$T_m$  = Melting Point

$\Delta H_{T_f}$  = Latent heat of melting

$T_C$  = Bath temperature.

The general expression for  $C_p$  as a function of temperature is as follows [Kubaschewski et al (1967)].

$$C_p = a + bT + cT^{-2} \dots\dots\dots(2.30)$$

Where a, b and c are the empirical constants and T is temperature in Kelvin. Values of a, b and c are referred from [Kubaschewski et al (1967)]. If the experiment is carried out at calorimeter temperature of 730 K and drop temperature of 293K. The expression is expressed as equation. (2.31).

$$(H_{Sample,T_C} - H_{Sample,T_D}) = \int_{293}^{730} C_p dT = 16219.8897 \text{ J/mole} \dots\dots\dots (2.31)$$

Alpha alumina ( $\alpha\text{-Al}_2\text{O}_3$ ) needles were used for the calibration of the heat flow peak for each experiment. Alpha alumina is very stable and does not react with the molten alloy of In-Bi-Sn. The molar enthalpy increment for  $\alpha\text{-Al}_2\text{O}_3$  was computed from the data available for Standard Reference Material 720 Synthetic Sapphire certificate issued by National Bureau of Standards Certificate, Washington.

#### 2.5.2.11 Calibration constant (K) calculation

The heat flow peaks were calibrated by dropping three to four needles of synthetic sapphire into the molten bath of alloys. The calibration constant is given by:

$$\Delta H_{Signal} = n_i (H_{Sample,T_C} - H_{Sample,T_D}) \dots\dots\dots (2.32)$$

$$K = \frac{A}{\Delta H_{Signal}} \dots\dots\dots (2.33)$$

Where  $n_i$  is the moles of dropped  $\alpha\text{-Al}_2\text{O}_3$  samples. A is peak area in microvolt-second ( $\mu\text{V}\cdot\text{s}$ ).  $\Delta H_{Signal}$  is the enthalpy increment in joule by  $n_i$  moles of  $\alpha\text{-Al}_2\text{O}_3$ .