



## Analysis of calorimetric measurement bismuth and tin system

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### Abstract

Lead-free soldering alloys with low melting point suitable for use in soldering joints are very essential. Use of lead as a solder is considered dangerous for the environment due to the huge number of printed circuit board and electronic devices, pipe joints etc. needed to be recycled from dumps.

In this work the metallic samples were prepared from Bi in the mass range from 0.75gm. Samples of Sn were dropped into the bath of pure Bi by using an automatic dropping device. System required 40min time interval after every sample of dropped. Calorimetric measurements was done at temperature 830K. The Integral and partial enthalpy of mixing was calculated at this temperatures. The Integral enthalpy of mixing in Bi- Sn system at 830K is endothermic in nature throughout the composition and its maximum value at  $X_{Sn} = 0.6$ , is 1005.9061 respectively.

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*Key words:* Drop Calorimeter, Calisto Software, Sapphire, Enthalpy

### 1. Introduction

Development of new lead-free solder requires a data base. The database will help us to avoid complicated and time consuming experiments. Information on thermodynamic properties such as mixing enthalpies is indispensable for the accurate thermodynamic optimization of phase diagrams, for the development of a lead-free solder database, and for the prediction of physical and chemical properties, such as surface tension and viscosity.

It is not possible so far to substitute lead by any single metal in the conventional lead-tin solder. So the attempt has been made to substitute lead by more than one metal. The systems are called multicomponent metallic solution. Like In- Sn-Bi, In-Sn-Zn, and In-Sn-Bi-Zn

Higher temperatures dramatically reduce the firmness of the solder joint during thermal cycling, due to greater plastic deformation of the solder and recrystallization and grain growth inside the solder. At such high temperatures, the mechanical properties of the conventional alloys Sn62/Pb36/Ag2 (melting point 179°C) and Sn63/Pb37 (melting point 183°C) deteriorate. In the manufacturing environment, the only risk is caused by breathing in floating, dried powder particles, or through the occurrence of gross mistakes in safety measures. A greater danger lies in the contamination of groundwater and soil by electronic

scrap (disposal of electronic circuit and solder dross). Several proposals have been made to ban the use of lead in electronics.

### 2. Experimental Setup & Procedure

- All experimental measurements were performed by using the calorimetric drop method. Calorimetric measurements were carried out by using the MHTC96 high temperature drop calorimeter from Setaram, France.
- It is a calorimeter with a thermopile of 20 thermocouples and a graphite tube resistance furnace operating up to 1723K. Control and data evaluation were performed using the software provided by the manufacturer. To prevent oxidation of the samples all measurements were taken in a atmosphere of flowing argon.
- All measurements were carried out in an alumina crucible.
- A motorized dropping device is placed on the top of the calorimeter. 23 samples can be installed at a time into it. It also consists of a vacuum pump.
- An alumina tube connects the furnace to the dropping

device. Sample is dropped from dropping device to the alumina crucible (placed in the furnace) by this tube.

- Control and data evaluation were performed using the software provided by the manufacturer.

The starting materials are the metals reagent grade as powder. In (purity > 99.9%; 1µm<Ø<2µm), Bi (purity > 99.95%; Ø< 25µm) and Sn (purity > 99.9985%; Ø<20µm). The Stoichiometric mixtures, in the appropriate molar ratio were carefully homogenized inside a glove box under purified argon gas in an agate mortar and compacted into 6mm diameter pellets. The pellets were cut into pieces and transferred from the glove box to the calorimeter using a special Ar-tight container in order to prevent any oxidation with air atmosphere. The Ar gas pressure and time in Analysis chamber is 1.5 bar & 15 min. while for furnace it is 1.5bar & 2 min 30 sec.

The starting samples were placed alternatively in the container with reference α-alumina used for calibration The enthalpy variations of α-alumina between room and experimental temperatures are well established by Sabbah et al. [1]



Figure 1: Drop Calorimeter Device

### 3. Governing Equation

#### 3.1 Heat capacity

If there is not a transition or reaction occurring within the sample on the temperature range, the following heat relation is obtained:

$$(H_{Sample,T_c} - H_{Sample,T_D}) = \int_{T_D}^{T_c} C_p dT$$

It is needed to repeat sample drops at different temperatures in order to determine the variation of heat versus sample temperature. From the derivation of this curve according to temperature the variation of the sample heat capacity is obtained on the measured temperature range.

#### 3.2 Determination of enthalpy of transition

For the temperature range under investigation, the sample can undergo a structure change (melting, crystallization, phase transition ...). The measured heat will contain the heat capacity contribution before and after the transformation and the corresponding heat of transition

$$(H_{Sample,T_c} - H_{Sample,T_D}) = \int_{T_D}^{T_{Tr}} C_p dT + \Delta H_{T_{Tr}} + \int_{T_{Tr}}^{T_c} C_p dT + \Delta H_{T_f} + \int_{T_m}^{T_c} C_p dT$$

To obtain the heat of transition, the Cp variation has to be calculated before and transition. The difference between the two curves provides the heat value.

Where

- $T_D$  = Dropping (Room) Temperature
- $T_{Tr}$  = Transformation Temperature
- $\Delta H_{T_{Tr}}$  = Enthalpy change during transformation
- $T_m$  = Melting Point
- $\Delta H_{T_f}$  = Enthalpy change during melting
- $T_c$  = Temperature of the Calorimeter at which experiment is carried out.

Transformation phase may or may not be present in the system. Cp was calculated using the following relation taken from the Metallurgical Thermochemistry book [27].

$$C_p = a + bT$$

Where a and b are the constants and T is temperature in Kelvin. Values of a and b are taken from the book. All the experiments was carried out at calorimeter temperature of 830 K and drop temperature was 293K.

$$(H_{Sample,T_c} - H_{Sample,T_D}) = \int_{T_D}^{T_c} C_p dT = 16219.8897 \text{ J/mole}$$

Alpha alumina (α-Al2O3) was used for the calibration of the calorimeter for each experiment. Alpha alumina does not react with the molten alloy of In-Bi-Sn due to its high melting point. Molecular weight of the α-Al2O3 = 101.9613. ΔH Reaction for α-Al2O3 is zero. The molar enthalpy difference for α-Al2O3 Standard Reference Material 720 was taken from Standard Reference Material

720 Synthetic Sapphire certificate issued by National Bureau of Standards Certificate, Washington.

$$(H_{Sample,T_C} - H_{Sample,T_D}) = 45533 \text{ J/mole}$$

### 3.3 Enthalpy calculation

The measured enthalpy (integrated heat flow at constant pressure) is given by

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

Where  $n_i$  the number of moles of the added sample is  $H_{sample, T_c}$  enotes molar enthalpies at calorimetric temperature and  $H_{sample, T_D}$  denotes molar enthalpies at drop (room) temperature.  $\Delta H_{Reaction}$  is the enthalpy of reaction due to addition of  $n_i$  number of moles.

Because of the relatively small mass added the Partial enthalpy can be directly calculated as

$$\Delta \bar{H}_i = \frac{\Delta H_{Reaction}}{n_i}$$

The integral enthalpy of mixing was calculated by summarizing the respective reaction enthalpies and division by the total molar amount of substance.

$$\Delta H_{mix} = \frac{\Sigma \Delta H_{Reaction}}{(n_{Crucible} + \Sigma n_i)}$$

#### 4.1.4 Calibration constant (K) calculation

Calibration constant was calculated using area under the peak of dropped  $\alpha\text{-Al}_2\text{O}_3$  samples

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

$$K = \frac{A}{\Delta H_{Signal}}$$

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

## 4. Results & Discussion

Molten Bi Held at temperature 830 K according to pre-set time range in program and Sn is dropped in the crucible at a regular interval of 40 mins with the help of motorizing dropping device.

The experimental values are compared with the literature and found some scatter due to difference in experimental constraints.

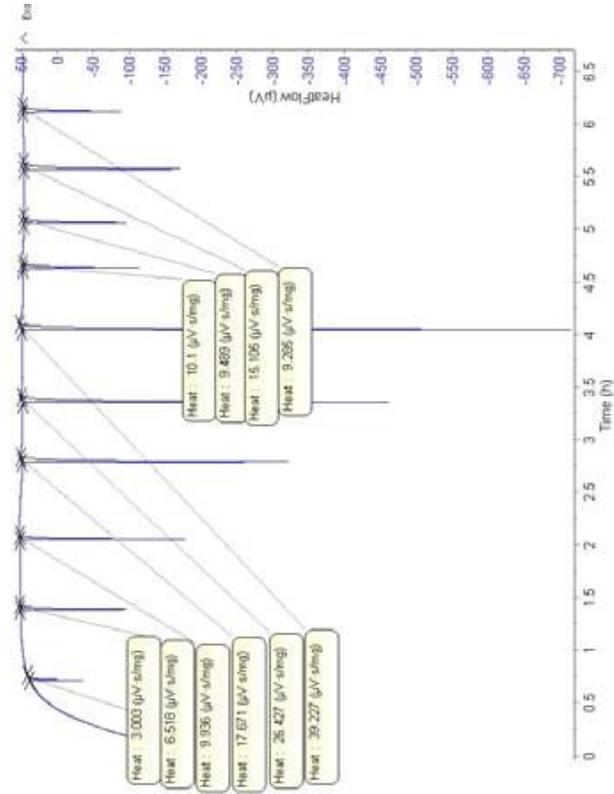


Figure 2: Peak areas with enthalpy values

Table 1 Molar mixing Enthalpies with composition

| Xsn    | $\Delta H_{MIX}$ (Joule/mole) |
|--------|-------------------------------|
| 0.1    | 40.27759                      |
| 0.2    | 151.754                       |
| 0.3    | 292.1128                      |
| 0.4    | 469.3475                      |
| 0.5    | 570.039                       |
| 0.6    | 605.922                       |
| 0.7389 | 569.9107                      |
| 0.8093 | 450.1246                      |
| 0.832  | 392.1039                      |
| 0.8498 | 339.8457                      |
| 0.8642 | 286.1929                      |
| 0.8861 | 229.9907                      |
| 0.8946 | 165.0691                      |
| 0.9019 | 85.15358                      |

Calibration constant was calculated using area under the peak of dropped  $\alpha\text{-Al}_2\text{O}_3$  samples

Table 2: Partially Enthalpies with 730 K composition [5]

| X <sub>sn</sub> | Partial Enthalpy (J/mole) |
|-----------------|---------------------------|
| 0.1             | 1352.665878               |
| 0.2             | 606.035198                |
| 0.3             | 515.5397029               |
| 0.4             | 945.0941891               |
| 0.5             | 883.0229295               |
| 0.6             | 667.9512507               |
| 0.7389          | 535.4989169               |
| 0.7796          | 106.1237565               |
| 0.832           | -3.890277147              |
| 0.8642          | -30.5927125               |
| 0.8946          | -104.2914341              |
| 0.9019          | -370.2476901              |

Table - 3: Integral Enthalpies of mixing at 830K

| X <sub>sn</sub> | ΔH <sub>MIX</sub> (J/mol)   |
|-----------------|-----------------------------|
|                 | Experimental values at 830K |
| 0.1             | 234.92128                   |
| 0.2126          | 570                         |
| 0.40295         | 745                         |
| 0.6             | 1005.9061                   |
| 0.7             | 915.2765                    |
| 0.78            | 678.7265                    |
| 0.86            | 423.5942                    |
| 0.91            | 263.36614                   |

Table - 4: Comparison of Enthalpies of mixing at 730K and 608K

|     | ΔH <sub>MIX</sub> (J/Mole)  |                            |
|-----|-----------------------------|----------------------------|
|     | Experimental values at 730K | Theoretical Values at 608K |
| 0.1 | 135.2776                    | 20.91                      |
| 0.2 | 221.754                     | 62.73                      |
| 0.3 | 292.1128                    | 83.64                      |
| 0.4 | 469.3475                    | 104.55                     |
| 0.5 | 589.039                     | 154.55                     |
| 0.6 | 612.922                     | 346.37                     |
| 0.7 | 570.678                     | 104.55                     |
| 0.8 | 400.126                     | 62.64                      |
| 0.9 | 165.1536                    | 2091                       |

Table 4: Variation of mixing enthalpies with X<sub>sn</sub>

| X <sub>sn</sub> | ΔH <sub>partial</sub> (J/mol) |
|-----------------|-------------------------------|
|                 | Experimental values at 830K   |
| 0.1             | 2364.1027                     |
| 0.2126          | 2058.12752                    |
| 0.40295         | 1158.32547                    |
| 0.6             | 628.76927                     |
| 0.7             | 137.91588                     |
| 0.78            | -89.168                       |
| 0.86            | -122.07893                    |
| 0.91            | -98.79091                     |

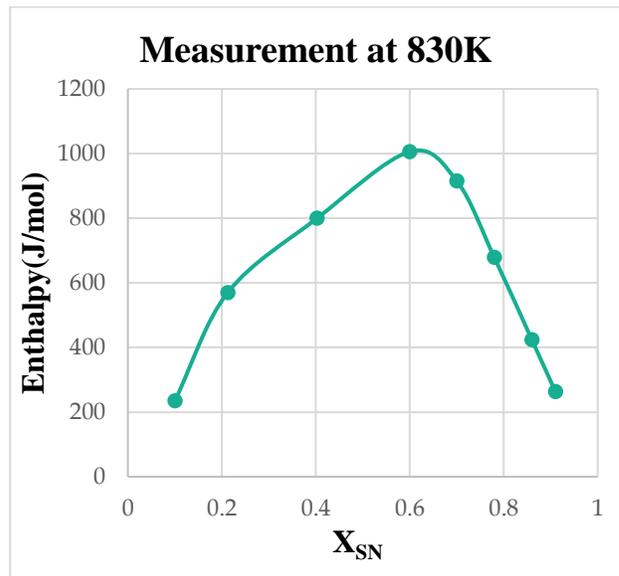


Figure 3. Comparison of Model values [3] to experimental values Partial Enthalpy values at 830K

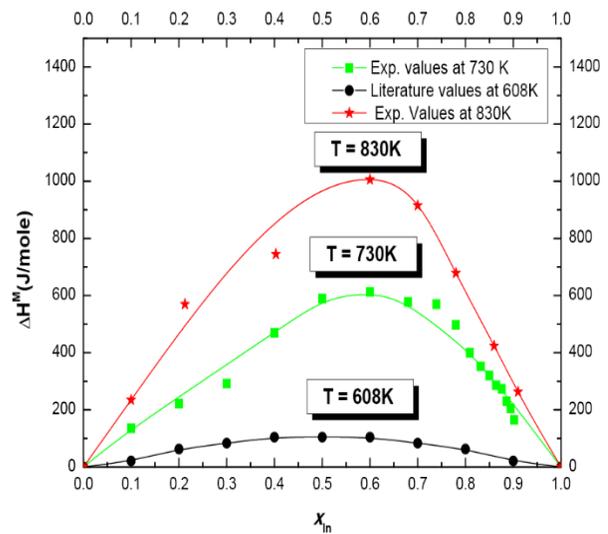


Figure 4: Comparison data analysis between Literature data & our experimental data

We find that first the value of Enthalpy is increasing with composition of Sn and at  $X_{Sn} = 0.59$ , the value of Enthalpy is Maximum for all the temperatures. This is an agreement with the literature. That means at this point reaction is more Endothermic in nature and after this composition Enthalpy goes on decreasing as shown in Fig. R. Hultgren et [3] have got the maximum value of enthalpy at  $X_{Sn} = 0.6$  is  $\Delta H_{mix} = 146.37$  J/mol at 608K. we have obtained the maximum values of enthalpy at  $X_{Sn} = 0.6$  is  $H_{mix} = 1005.9061$  J/mol at 830K, and is  $\Delta H_{mix} = 612.33$  J/mol at 730 K [5]. It has been observed that enthalpy of mixing in the system Bi- Sn is more endothermic in nature with the temperature.

It is observed that partial enthalpy of mixing decreases temperature. The experimental values show some scatter from the literature [3, 4]. The reason for the scatter may be due to different techniques used for the experimental measurement in the Bi-Sn system. The second reason may be the experiments are carried out at different temperatures. For example the Partial enthalpies values obtained from the literature are calculated values from EMF measurement but our values are obtained directly from the enthalpy measurement by calorimeter at 730K and 830 K.

## 5. Conclusion

The Enthalpy change of Bi- Sn system is measured at temperature 608K & 830K by Drop calorimetric technique

and following conclusions are made The Integral enthalpy of mixing in Bi- Sn system at 608K and 830K is endothermic in nature throughout the composition and its maximum value at  $X_{Sn} = 0.6$ , is 346.37 J/mol and 1005.9061 respectively.

The partial molar enthalpy of Sn is endothermic in nature and decreases with the composition of tin for most of the composition except Sn rich composition.

The experimental values are compared with the literature and found some scatter due to difference in experimental constraints.

## References

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