

*CHAPTER 5*

**ENTHALPIES OF  
MIXING IN  
Sn-Bi-Sb  
TERNARY  
SYSTEM**



## 5.1 Introduction

The best soldering materials in the electronics sector are lead-tin alloys because of their exceptional mechanical, chemical, and physical properties. It is very reliable and easily manufactured. It has dominated the soldering industry for many years and hasn't been improved much. However, finding a new alternative solder alloy to replace lead has been difficult due to its excellent properties except environmental and health hazards. Due to the development of current, advanced technology, most of the electronic items, including mobile phones, etc., have been miniaturized. This technology has grown and advanced quite quickly. Electronic products lose their effectiveness after a short span of time. As a result, a lot of electronic garbage is produced [1]–[8]. The majority of old gadgets are thrown away in landfills, where the lead eventually seeps into the soil and contaminates groundwater. The European Union is making a lot of effort to enforce the lead ban on devices. In June 2000, the EU approved the Waste of Electrical and Electronic Equipment (WEEE) Directive and the Regulation on the Restrictions of the Use of Certain Hazardous Substances (RoHS) [9], [10]. There is a big motivation in the electronic industry to shift from lead-tin to lead-free solders. In recent years, Electronic assembly manufacturing has undergone considerable modifications. To enable lead-free solder in electronics, some manufacturers have already begun to adapt the design. Accurate phase diagram determination and thermodynamic property measurements are the initial stages in the creation of novel solder alloys (lead-free). Many experts in this field have suggested the creation of a thermodynamic database for solder systems that is free of lead. So that's why it is very important to carry out experiments on this type of alloy system to generate a reliable database of thermodynamic properties. The literature review suggests that there are very little calorimetric data available for the Sn-Bi-Sb system. Therefore, in this chapter we have conducted calorimetric measurements of the Sn-Bi-

Sb system along five of the cross sections (see **Figure 5.1**) in the temperature range of 923 K-1023 K by MHTC 96 LINE EVO calorimeter. Pieces of pure tin were dropped into molten  $\text{Sb}_{0.25}\text{Bi}_{0.75}$ ,  $\text{Sb}_{0.50}\text{Bi}_{0.50}$ ,  $\text{Sb}_{0.75}\text{Bi}_{0.25}$  alloys; Bismuth into  $\text{Sb}_{0.50}\text{Sn}_{0.50}$  and Antimony into  $\text{Bi}_{0.50}\text{Sn}_{0.50}$ . From the calorimetric data, partial and integral thermodynamic properties were determined. The integral mixing enthalpy plots was used to generate iso-enthalpy curves. The substitutional solution Redlich-Kister-Muggianu (RKM) model was used to derive the interaction parameter based on ternary enthalpy values and to get these parameters we use least square fitting. Comparisons are made between the estimated and measured values.

## 5.2 Experimental details

### 5.2.1 Materials

The binary and ternary alloys formed in this study were made from pure metals (Sn, Bi, and Sb).  $\alpha\text{-Al}_2\text{O}_3$  needles from the NIST in Gaithersburg, Maryland, the United States, were used as the calibration reference. Metals were cleaned with n-hexane in a supersonic bath and then vacuum-dried in a glove box antechamber to eliminate any remaining solvent. They were then divided into small bits and precisely weighed to the accuracy of  $10^{-4}$  gm. **Table 5.1** lists the specifications for pure metals and compounds.

**Table 5.1** The materials used for this study.

Materials	Initial purity (wt.%)	Source
<b>Argon gas</b>	99.999 (vol. %)	Indian oxygen limited, India
<b>Antimony(lumps)</b>	99.999	Johnson Matthey(JM), UK
<b>Bismuth(lumps)</b>	99.999	JM, UK
<b>Tin (shots)</b>	99.999	JM, UK

### 5.2.2 Calorimetric Measurements

In this investigation, to get enthalpy values of the given system we have used a drop calorimeter (MHTC 96 LINE EVO) made by SETARAM Instruments, France. It is equipped with a furnace of resistance type made up of graphite tube and having an arrangement for flow of water throughout outer section of the furnace for continuous cooling and a thermopile of 56 pairs of S-type thermocouples. The furnace can operate at a maximum temperature of 1593 K. There is a motorized dropping apparatus that helps in dropping the metals automatically into the crucible. For the calibration of the calorimeter, four pieces of NIST SRM 720 (National Institute of Standards and Technology, Gaithersburg, MD)  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> needles were dropped at the end of each sample series. The NIST, USA has certified that these needles adhere to its standards. CALISTO software completely monitors the calorimeter. A specified amount of base metal was added to the crucible having outer diameter of 12 mm and length of 60 mm before the trials began. The CALISTO software managed the flow of gas and the water cooling system. Prior to the start of the trials, everything needs to be programmed like what will the rate of heating and cooling and for how much time we have to hold the temperature and what will be the rate of gas flow. To create a completely inert atmosphere, firstly we flush out all the air from the crucible and protective tube (space between outer wall and inner wall of furnace) by using vacuum pumping system and then argon gas was passed through the crucible. Throughout the studies, a steady supply of argon (about 30 mL/min) kept the alloy inert from oxidizing. Here, Argon gas takes the fumes during heating process from furnace. So, Argon gas behaves as carrier gas as well as protective gas too. There was 30 minutes' gap in between two successive drops and then the heat signals were

recorded. At 923 K, 973 K, and 1023 K, we conducted calorimetric analyses of the Sn-Bi-Sb system along five of the cross sections (see **Figure 5.1**). Pieces of pure tin were dropped into molten  $\text{Sb}_{0.25}\text{Bi}_{0.75}$ ,  $\text{Sb}_{0.50}\text{Bi}_{0.50}$ ,  $\text{Sb}_{0.75}\text{Bi}_{0.25}$  alloys; Bismuth into  $\text{Sb}_{0.50}\text{Sn}_{0.50}$  and Antimony into  $\text{Bi}_{0.50}\text{Sn}_{0.50}$ . Prior to introducing the sample material, the system underwent a roughly 16-hour thermal equilibration process to establish a stable baseline. The entire mass of the crucible and the samples were weighed before and after the measurements to confirm that there was only a little weight loss due to evaporation. Every experiment was repeated twice while holding the parameters constant. The CALISTO Data Processing software was then used to integrate the recorded heat signals and estimate the enthalpy values. The heat signal value associated with the  $\alpha\text{-Al}_2\text{O}_3$  needle drops served as the basis for determining the calibration constant (K). After being multiplied by the calibration constant, the integral values of each heat signal were then converted to enthalpy that we call it as heat effect. Here, we are interested in knowing the reaction enthalpy ( $\Delta H_{\text{Reaction},X,i}$ ) which can be evaluated by using **Equation 5.1** in which the term heat effect ( $\Delta H_{\text{Signal},X,i} \cdot K$ ) and the change in enthalpy ( $\Delta H_{X,i}^{T_D \rightarrow T_M}$ ) by dropping the species X from drop temperature ( $T_D$ ) to bath temperature ( $T_M$ )

$$\Delta H_{\text{Reaction},X,i} = (\Delta H_{\text{Signal},X,i} \cdot K) - (\Delta H_{X,i}^{T_D \rightarrow T_M} \cdot n_{X,i}) \quad (5.1)$$

where  $n_{X,i}$  representing the amount of species X (no. of moles) which was dropped by the help of automatic dropping device in the liquid bath and corresponding to every peak we get a  $\Delta H_{\text{Signal},X,i}$  which is the integrated area (microvolts-seconds) we get after integrating the peaks corresponding to each drop by using baseline integration tool.  $\Delta H_{X,i}^{T_D \rightarrow T_M}$  represents change in the molar

enthalpy of species **X** and this change can be calculated by the help of enthalpy data available in the literature for each species corresponding to given temperature range.

To calculate the partial enthalpy  $\Delta\bar{H}_{X,i}$  we can use the **Equation 5.2** as we were adding very small amount of species X in the base liquid metal :

$$\Delta\bar{H}_{X,i} \approx \Delta H_{Reaction,X,i}/n_{X,i} \quad (5.2)$$

Each measurement involved adding specific amounts of one of the three metals to the crucible, then dropping the remaining two metals at the specified temperature. In this instance, Bi was placed into the crucible and Sb was then dropped and then Sn were dropped in the binary Bi-Sb; Sb was placed into the crucible and Sn was then dropped and then Bi were dropped in the binary Sb-Sn; and Sn was placed into the crucible and Bi was then dropped and then Sb were dropped in the binary Bi-Sn. According to (**Equation 5.3**), the integral molar mixing enthalpy  $\Delta H_{mix}$  is computed as given below:

$$\Delta H_{mix} = \frac{\sum \Delta H_{Reaction}}{(n_{crucible} + \sum n_i)} \quad (5.3)$$

Bi, Sn, and Sb's enthalpy increment from room temperature to drop temperature was acquired from the literature [98], [153] and used in **Equation 5.1**. Errors in calorimetric measurements can come from a number of different places, including the calorimeter's construction type, calibration, heat flow curve baseline integration, degree of solute solubility in the solvent, and impurity concentration. The calorimeter's overall experimental uncertainty ranges from 10 to 12 percent. It was determined that the calibration error caused by the dropping  $\alpha\text{-Al}_2\text{O}_3$  needles was less than  $\pm 1.5\%$ .

### 5.3 Results and Discussion

### 5.3.1 Experimental Results

**Tables 5.2, 5.3, and 5.4** provide the molar integral enthalpies which was derived by the help of **Equation 5.3** for the given ternary system along five sections considering various compositions. **Tables 5.2, 5.3, and 5.4** additionally include partial mixing enthalpies values also with variation in composition of different species. These experimental values are used to find the ternary interaction parameter values as given in **Table 5.6**.

**Table 5.2** Integral and partial mixing enthalpies of Sn-Bi-Sb alloys when Sn dropped.

Added moles	Mole fraction ( $x_{\text{Sn}}$ )	Standard uncertainties $u(x_{\text{Sn}})$	Heat effect $H_{\text{Signal}} \cdot K$ (J)	Standard uncertainties $u(\Delta H_{\text{Signal}} \cdot K)$ (J)	Heat of Reaction $\Delta H_{\text{Reaction}}$ (J)	Partial Enthalpy $\Delta \bar{H}_{x,i}$ (J mol <sup>-1</sup> )	Integral Enthalpy $\Delta H_{\text{mix}}$ (J mol <sup>-1</sup> )
<b>Series 1: (Sb<sub>0.25</sub>Bi<sub>0.75</sub>)<sub>1-x</sub>Sn<sub>x</sub> alloys; Atmosphere: Argon at pressure <math>p = 0.1</math> MPa; Starting amount <math>n_{\text{Bi}} = 0.002586</math> mol, <math>K=0.001899 \text{ J} \mu \text{Vs}^{-1}</math>, <math>T_{\text{D}} = 298</math> K, <math>T_{\text{M}} = 923</math> K, <math>\Delta H_{\text{Sn}}^{T_{\text{D}} \rightarrow T_{\text{M}}} = 24115</math> (J mol<sup>-1</sup>), <math>\Delta H_{\text{Sb}}^{T_{\text{D}} \rightarrow T_{\text{M}}} = 37089.563</math> (J mol<sup>-1</sup>);</b>							
$n_{\text{Sb}}$							
<b>0.000853</b>	0	0.0002	33.067	0.005	1.430	1676	415.886
$n_{\text{Sn}}$							
<b>0.000489</b>	0.1245	0.0007	11.523	0.005	-0.269	-550	295.527
<b>0.000486</b>	0.2209	0.0004	11.333	0.009	-0.387	-796	175.399
<b>0.000391</b>	0.2843	0.0002	8.980	0.011	-0.449	-1148	67.535
<b>0.000421</b>	0.3419	0.0001	9.736	0.014	-0.416	-988	-17.449
<b>0.000853</b>	0.4343	0.0003	20.123	0.007	-0.447	-524	-88.479
<b>0.001567</b>	0.5502	0.0005	36.966	0.014	-0.822	-525	-177.930
<b>0.001613</b>	0.6286	0.0004	38.343	0.007	-0.554	-343	-206.679
<b>0.001637</b>	0.6844	0.0005	39.285	0.015	-0.191	-117	-193.219

<b>0.001579</b>	0.7243	0.0003	37.906	0.011	-0.172	-109	-182.528
<b>0.002081</b>	0.7637	0.0007	50.045	0.013	-0.138	-66	-165.912
<b>0.001555</b>	0.7865	0.0005	37.436	0.014	-0.063	-41	-153.819
<b>0.001707</b>	0.8070	0.0004	41.075	0.015	-0.089	-52	-144.088
<b>0.001489</b>	0.8219	0.0001	35.605	0.013	-0.302	-203	-148.610
<b>0.002082</b>	0.8392	0.0003	50.318	0.012	0.111	53	-128.931
<b>0.001572</b>	0.8502	0.0004	38.074	0.004	0.165	105	-112.932
<b>0.001643</b>	0.8602	0.0006	39.334	0.002	-0.287	-175	-117.055
<b>0.001504</b>	0.8683	0.0003	36.536	0.013	0.267	178	-100.101
<b>0.001716</b>	0.8764	0.0001	41.346	0.014	-0.035	-20	-95.160
<b>0.002339</b>	0.8860	0.0002	56.133	0.007	-0.272	-116	-96.814
<b>0.002044</b>	<b>0.8932</b>	0.0004	49.595	0.015	0.304	149	-81.236
<b>Series 2: (Sb<sub>0.25</sub>Bi<sub>0.75</sub>)<sub>1-x</sub>Sn<sub>x</sub> alloys; Atmosphere: Argon at pressure <math>p = 0.1</math> MPa; Starting amount <math>n_{Bi} = 0.002593</math> mol, <math>K = 0.001911 \text{ J}\mu\text{V s}^{-1}</math>, <math>T_D = 298 \text{ K}</math>, <math>T_M = 973 \text{ K}</math>, <math>\Delta H_{Sn}^{T_D \rightarrow T_M} = 26351 \text{ (J mol}^{-1}\text{)}</math>, <math>\Delta H_{Sb}^{T_D \rightarrow T_M} = 38658.938 \text{ (J mol}^{-1}\text{)}</math></b>							
<b><math>n_{Sb}</math></b>							
<b>0.000855</b>	0	0.0003	34.494	0.011	1.441	1685	418.021
<b><math>n_{Sn}</math></b>							
<b>0.000421</b>	0.1088	0.0005	10.909	0.007	-0.185	-439	324.604

<b>0.000421</b>	0.1963	0.0003	10.750	0.015	-0.344	-817	212.632
<b>0.000422</b>	0.2683	0.0002	10.625	0.011	-0.495	-1173	88.481
<b>0.000421</b>	0.3283	0.0005	10.661	0.013	-0.433	-1029	-3.182
<b>0.000842</b>	0.4229	0.0004	21.726	0.014	-0.462	-549	-80.032
<b>0.001685</b>	0.5499	0.0001	43.514	0.015	-0.887	-526	-178.162
<b>0.001685</b>	0.6310	0.0002	43.820	0.013	-0.581	-345	-208.239
<b>0.001685</b>	0.6874	0.0004	44.210	0.012	-0.191	-113	-193.786
<b>0.001684</b>	0.7288	0.0006	44.195	0.004	-0.180	-107	-182.231
<b>0.001685</b>	0.7605	0.0003	44.291	0.002	-0.110	-65	-168.539
<b>0.001685</b>	0.7856	0.0005	44.323	0.013	-0.078	-46	-155.718
<b>0.001685</b>	0.8060	0.0003	44.320	0.014	-0.081	-48	-145.551
<b>0.001684</b>	0.8228	0.0002	44.043	0.007	-0.332	-197	-149.986
<b>0.001685</b>	0.8369	0.0005	44.547	0.015	0.146	87	-131.131
<b>0.001685</b>	0.8489	0.0004	44.554	0.007	0.153	91	-114.768
<b>0.001685</b>	0.8593	0.0001	44.110	0.015	-0.291	-173	-118.736
<b>0.001685</b>	0.8684	0.0002	44.681	0.011	0.280	166	-100.397
<b>0.001684</b>	0.8763	0.0004	44.337	0.013	-0.038	-23	-95.701
<b>0.001685</b>	0.8834	0.0006	44.136	0.014	-0.265	-157	-99.222

<b>0.001685</b>	0.8897	0.0003	44.710	0.015	0.309	183	-83.991
<b>Series 3: (Sb<sub>0.25</sub>Bi<sub>0.75</sub>)<sub>1-x</sub>Sn<sub>x</sub> alloys; Atmosphere: Argon at pressure <math>p = 0.1</math> MPa; Starting amount <math>n_{\text{Bi}} = 0.002586</math> mol, <math>K = 0.002037 \text{ J}\mu\text{V s}^{-1}</math>, <math>T_{\text{D}} = 298 \text{ K}</math>, <math>T_{\text{M}} = 1023 \text{ K}</math>, <math>\Delta H_{\text{Sn}}^{T_{\text{D}} \rightarrow T_{\text{M}}} = 27340 \text{ (J mol}^{-1}\text{)}</math>, <math>\Delta H_{\text{Sb}}^{T_{\text{D}} \rightarrow T_{\text{M}}} = 40228.313 \text{ (J mol}^{-1}\text{)}</math></b>							
<b><math>n_{\text{Sb}}</math></b>							
<b>0.000854</b>	0	0.0002	35.807	0.014	1.452	1700	422.021
<b><math>n_{\text{Sn}}</math></b>							
<b>0.000489</b>	0.1245	0.0009	13.114	0.008	-0.255	-521	304.744
<b>0.000424</b>	0.2097	0.0003	11.267	0.012	-0.325	-767	200.295
<b>0.000362</b>	0.2704	0.0002	9.448	0.011	-0.449	-1240	89.633
<b>0.000382</b>	0.3251	0.0005	10.030	0.012	-0.414	-1084	1.702
<b>0.000910</b>	0.4273	0.0004	24.383	0.014	-0.496	-545	-81.132
<b>0.001520</b>	0.5430	0.0001	40.705	0.015	-0.852	-561	-177.867
<b>0.001473</b>	0.6178	0.0002	39.712	0.013	-0.560	-380	-211.044
<b>0.001569</b>	0.6745	0.0004	42.700	0.012	-0.196	-125	-198.251
<b>0.001479</b>	0.7145	0.0007	40.258	0.004	-0.178	-120	-188.636
<b>0.001461</b>	0.7454	0.0003	39.842	0.002	-0.102	-70	-175.835
<b>0.001649</b>	0.7731	0.0004	44.997	0.011	-0.087	-53	-162.390
<b>0.001588</b>	0.7946	0.0003	43.324	0.014	-0.092	-58	-152.526

<b>0.001495</b>	0.8114	0.0002	40.554	0.007	-0.319	-213	-157.524
<b>0.001546</b>	0.8261	0.0004	42.396	0.011	0.128	83	-138.748
<b>0.001717</b>	0.8400	0.0004	47.097	0.007	0.154	90	-120.479
<b>0.001572</b>	0.8509	0.0001	42.687	0.015	-0.291	-185	-124.897
<b>0.001592</b>	0.8605	0.0002	43.794	0.011	0.269	169	-105.944
<b>0.001673</b>	0.8694	0.0004	45.762	0.013	0.022	13	-98.374
<b>0.001664</b>	0.8772	0.0006	45.163	0.014	-0.331	-199	-104.325
<b>0.002733</b>	0.8881	0.0003	75.013	0.015	0.293	107	-85.531
<b>0.002338</b>	0.8960	0.0005	63.965	0.013	0.044	19	-78.168
<b>Series 4: (Sb<sub>0.50</sub>Bi<sub>0.50</sub>)<sub>1-x</sub>Sn<sub>x</sub> alloys; Atmosphere: Argon at pressure <math>p = 0.1</math> MPa; Starting amount <math>n_{\text{Bi}} = 0.001804</math> mol, <math>K = 0.001986 \text{ J}\mu\text{Vs}^{-1}</math>, <math>T_{\text{D}} = 298 \text{ K}</math>, <math>T_{\text{M}} = 923 \text{ K}</math>, <math>\Delta H_{\text{Sn}}^{T_{\text{D}} \rightarrow T_{\text{M}}} = 24115 \text{ (J mol}^{-1}\text{)}</math>, <math>\Delta H_{\text{Sb}}^{T_{\text{D}} \rightarrow T_{\text{M}}} = 37089.563 \text{ (J mol}^{-1}\text{)}</math></b>							
<b><math>n_{\text{Sb}}</math></b>							
<b>0.001808</b>	0	0.0003	69.072	0.015	2.014	1114	557.499
<b><math>n_{\text{Sn}}</math></b>							
<b>0.000510</b>	0.1237	0.0004	10.665	0.005	-1.634	-3204	92.212
<b>0.000401</b>	0.2014	0.0003	8.718	0.012	-0.952	-2374	-126.503
<b>0.000563</b>	0.2898	0.0002	12.371	0.011	-1.206	-2142	-349.553
<b>0.000331</b>	0.3332	0.0005	7.168	0.013	-0.814	-2459	-478.446

<b>0.000912</b>	0.4293	0.0007	20.702	0.011	-1.291	-1416	-613.483
<b>0.000898</b>	0.5002	0.0001	20.770	0.015	-0.885	-986	-659.743
<b>0.000897</b>	0.5554	0.0002	20.998	0.012	-0.633	-706	-664.837
<b>0.001006</b>	0.6044	0.0006	23.979	0.015	-0.281	-279	-622.341
<b>0.000994</b>	0.6432	0.0005	23.375	0.007	-0.595	-599	-619.996
<b>0.001537</b>	0.6902	0.0003	36.678	0.002	-0.387	-252	-571.493
<b>0.001485</b>	0.7252	0.0005	35.561	0.013	-0.250	-168	-525.914
<b>0.001522</b>	0.7537	0.0004	36.232	0.016	-0.471	-309	-503.477
<b>0.001641</b>	0.7785	0.0002	39.736	0.007	0.163	99	-442.832
<b>0.001817</b>	0.8007	0.0005	44.269	0.015	0.452	249	-373.513
<b>0.001500</b>	0.8160	0.0004	35.570	0.007	-0.603	-402	-375.666
<b>0.001584</b>	0.8297	0.0001	38.582	0.015	0.384	242	-329.526
<b>0.001699</b>	0.8423	0.0002	39.593	0.011	-1.378	-811	-365.215
<b>0.001694</b>	0.8532	0.0004	41.740	0.013	0.889	525	-303.940
<b>0.001683</b>	0.8626	0.0006	40.568	0.014	-0.018	-11	-285.158
<b>0.001711</b>	0.8710	0.0003	41.248	0.015	-0.013	-8	-268.197
<b>0.001689</b>	0.8783	0.0005	40.697	0.013	-0.033	-20	-254.054
<b>0.001803</b>	0.8853	0.0003	43.504	0.012	0.025	14	-238.706

<b>0.001740</b>	0.8913	0.0002	41.990	0.004	0.030	17	-225.330
<b>Series 5: (Sb<sub>0.50</sub>Bi<sub>0.50</sub>)<sub>1-x</sub>Sn<sub>x</sub> alloys; Atmosphere: Argon at pressure <math>p = 0.1</math> MPa; Starting amount <math>n_{sb} = 0.001795</math> mol, <math>K = 0.001984 \text{ J } \mu\text{Vs}^{-1}</math>, <math>T_D = 298 \text{ K}</math>, <math>T_M = 973 \text{ K}</math>, <math>\Delta H_{Sn}^{T_D \rightarrow T_M} = 26351 \text{ (J mol}^{-1}\text{)}</math>, <math>\Delta H_{Bi}^{T_D \rightarrow T_M} = 31240.188 \text{ (J mol}^{-1}\text{)}</math></b>							
<b>nBi</b>							
<b>0.001776</b>	0	0.0002	57.491	0.013	2.008	1131	562.233
<b>nSn</b>							
<b>0.000430</b>	0.1075	0.0008	9.865	0.007	-1.466	-3409	135.552
<b>0.000464</b>	0.2002	0.0003	11.108	0.012	-1.119	-2412	-129.272
<b>0.000450</b>	0.2734	0.0004	10.847	0.013	-1.011	-2247	-323.049
<b>0.000439</b>	0.3330	0.0005	10.542	0.014	-1.026	-2337	-488.278
<b>0.000913</b>	0.4302	0.0004	22.755	0.014	-1.303	-1427	-624.997
<b>0.001127</b>	0.5170	0.0001	28.604	0.015	-1.094	-971	-677.689
<b>0.000902</b>	0.5696	0.0001	23.177	0.011	-0.592	-656	-675.395
<b>0.001098</b>	0.6199	0.0004	28.659	0.012	-0.274	-250	-625.561
<b>0.000711</b>	0.6466	0.0006	18.285	0.004	-0.451	-634	-626.263
<b>0.001340</b>	0.6880	0.0003	34.993	0.002	-0.317	-237	-580.567
<b>0.001438</b>	0.7228	0.0004	37.650	0.015	-0.243	-169	-534.680
<b>0.001386</b>	0.7497	0.0003	36.066	0.014	-0.456	-329	-514.657

<b>0.001467</b>	0.7731	0.0002	38.843	0.007	0.186	127	-454.885
<b>0.001681</b>	0.7950	0.0005	44.750	0.015	0.454	270	-384.907
<b>0.001678</b>	0.8130	0.0003	43.586	0.005	-0.631	-376	-384.112
<b>0.001896</b>	0.8299	0.0001	50.328	0.015	0.367	194	-331.932
<b>0.001695</b>	0.8426	0.0002	43.241	0.011	-1.424	-840	-369.935
<b>0.001872</b>	0.8546	0.0003	50.244	0.012	0.915	489	-304.458
<b>0.001875</b>	0.8649	0.0006	49.386	0.017	-0.022	-12	-283.694
<b>0.001769</b>	0.8734	0.0003	46.581	0.015	-0.034	-19	-267.106
<b>0.001971</b>	0.8816	0.0004	51.914	0.016	-0.024	-12	-250.468
<b>0.001819</b>	0.8884	0.0003	47.961	0.012	0.029	16	-235.309
<b>Series 6: (Sb<sub>0.50</sub>Bi<sub>0.50</sub>)<sub>1-x</sub>Sn<sub>x</sub> alloys; Atmosphere: Argon at pressure <math>p = 0.1</math> MPa; Starting amount <math>n_{sb} = 0.001836</math> mol, <math>K = 0.002004 \text{ J}\mu\text{Vs}^{-1}</math>, <math>T_D = 298 \text{ K}</math>, <math>T_M = 1023 \text{ K}</math>, <math>\Delta H_{Sn}^{T_D \rightarrow T_M} = 27340 \text{ (J mol}^{-1}\text{)}</math>, <math>\Delta H_{Bi}^{T_D \rightarrow T_M} = 32830.488 \text{ (J mol}^{-1}\text{)}</math></b>							
<b><math>n_{Bi}</math></b>							
<b>0.001814</b>	0	0.0004	61.626	0.013	2.071	1142	567.478
<b><math>n_{Sn}</math></b>							
<b>0.000452</b>	0.1102	0.0004	10.793	0.005	-1.565	-3462	123.469
<b>0.000446</b>	0.1974	0.0003	11.113	0.011	-1.081	-2424	-126.395
<b>0.000398</b>	0.2620	0.0007	9.954	0.015	-0.927	-2329	-303.701

<b>0.000530</b>	0.3335	0.0005	13.271	0.012	-1.219	-2300	-496.972
<b>0.000767</b>	0.4153	0.0004	19.840	0.014	-1.130	-1473	-616.843
<b>0.000920</b>	0.4904	0.0002	24.188	0.015	-0.965	-1049	-672.320
<b>0.001047</b>	0.5554	0.0003	27.846	0.013	-0.779	-744	-681.431
<b>0.001154</b>	0.6102	0.0005	31.210	0.012	-0.340	-295	-633.798
<b>0.001053</b>	0.6496	0.0006	28.155	0.004	-0.634	-602	-630.634
<b>0.001416</b>	0.6915	0.0003	38.387	0.002	-0.326	-230	-582.703
<b>0.001499</b>	0.7262	0.0007	40.741	0.014	-0.242	-161	-535.313
<b>0.001646</b>	0.7563	0.0003	44.479	0.014	-0.523	-318	-511.402
<b>0.001737</b>	0.7816	0.0009	47.691	0.007	0.201	116	-446.221
<b>0.001842</b>	0.8033	0.0005	50.886	0.015	0.526	286	-373.611
<b>0.001857</b>	0.8212	0.0004	50.075	0.007	-0.695	-374	-373.665
<b>0.001828</b>	0.8359	0.0001	50.418	0.015	0.440	241	-323.154
<b>0.002001</b>	0.8494	0.0002	53.110	0.011	-1.597	-798	-362.371
<b>0.001794</b>	0.8598	0.0004	50.099	0.013	1.051	586	-297.046
<b>0.001732</b>	0.8686	0.0006	47.318	0.014	-0.035	-20	-279.782
<b>0.001761</b>	0.8764	0.0003	48.195	0.015	0.049	28	-261.441
<b>0.001782</b>	0.8834	0.0005	48.696	0.013	-0.024	-13	-247.302

<b>0.001826</b>	0.8899	0.0003	49.954	0.012	0.031	17	-232.739
<b>Series 7: (Sb<sub>0.75</sub>Bi<sub>0.25</sub>)<sub>1-x</sub>Sn<sub>x</sub> alloys; Atmosphere: Argon at pressure <math>p = 0.1</math> MPa; Starting amount <math>n_{sb} = 0.003269</math> mol, <math>K = 0.001912 \text{ J}\mu\text{V s}^{-1}</math>, <math>T_D = 298 \text{ K}</math>, <math>T_M = 923 \text{ K}</math>, <math>\Delta H_{Sn}^{T_D \rightarrow T_M} = 24115 \text{ (J mol}^{-1}\text{)}</math>, <math>\Delta H_{Bi}^{T_D \rightarrow T_M} = 29649.888 \text{ (J mol}^{-1}\text{)}</math></b>							
<b><math>n_{Bi}</math></b>							
<b>0.001084</b>	0	0.0002	33.955	0.011	1.815	1674	417.008
<b><math>n_{Sn}</math></b>							
<b>0.000510</b>	0.1049	0.0004	9.684	0.005	-2.615	-5127	-164.573
<b>0.000545</b>	0.1951	0.0006	11.029	0.012	-2.114	-3879	-538.871
<b>0.000476</b>	0.2602	0.0002	9.695	0.014	-1.784	-3748	-798.353
<b>0.000453</b>	0.3131	0.0007	9.639	0.017	-1.285	-2837	-944.150
<b>0.000877</b>	0.3966	0.0004	19.208	0.012	-1.941	-2213	-1098.386
<b>0.001011</b>	0.4708	0.0002	22.780	0.015	-1.600	-1583	-1157.940
<b>0.000585</b>	0.5059	0.0003	13.663	0.013	-0.444	-759	-1131.438
<b>0.000791</b>	0.5466	0.0004	18.041	0.012	-1.034	-1307	-1145.957
<b>0.000976</b>	0.5884	0.0007	22.802	0.005	-0.734	-752	-1109.589
<b>0.000827</b>	0.6183	0.0003	19.458	0.002	-0.485	-586	-1071.649
<b>0.001375</b>	0.6594	0.0005	32.552	0.013	-0.606	-441	-1003.773
<b>0.001546</b>	0.6961	0.0003	37.088	0.014	-0.194	-125	-908.958

<b>0.001635</b>	0.7273	0.0002	38.783	0.007	-0.645	-394	-856.296
<b>0.001683</b>	0.7533	0.0004	40.319	0.013	-0.267	-159	-789.711
<b>0.001694</b>	0.7749	0.0004	40.270	0.007	-0.581	-343	-750.570
<b>0.001854</b>	0.7946	0.0001	44.942	0.015	0.233	126	-673.909
<b>0.001694</b>	0.8098	0.0002	40.297	0.011	-0.554	-327	-648.254
<b>0.001855</b>	0.8241	0.0004	45.102	0.013	0.369	199	-584.722
<b>0.001528</b>	0.8343	0.0006	36.796	0.014	-0.052	-34	-552.676
<b>0.001561</b>	0.8436	0.0004	36.755	0.017	-0.889	-570	-553.621
<b>0.001578</b>	0.8520	0.0005	38.851	0.013	0.798	506	-496.777
<b>0.001808</b>	0.8605	0.0004	43.888	0.010	0.288	159	-458.789
<b>0.001515</b>	0.8670	0.0002	36.193	0.004	-0.341	-225	-447.970
<b>0.001659</b>	0.8734	0.0005	39.985	0.002	-0.022	-13	-426.994
<b>0.001622</b>	0.8791	0.0004	39.068	0.013	-0.047	-29	-409.079
<b>0.001824</b>	0.8849	0.0001	44.014	0.014	0.028	15	-388.598
<b>0.001612</b>	0.8896	0.0002	38.819	0.007	-0.054	-33	-374.106
<b>Series 8: (Sb<sub>0.75</sub>Bi<sub>0.25</sub>)<sub>1-x</sub>Sn<sub>x</sub> alloys; Atmosphere: Argon at pressure <math>p = 0.1</math> MPa; Starting amount <math>n_{sb} = 0.003285</math> mol, <math>K = 0.002048 \text{ J } \mu\text{Vs}^{-1}</math>, <math>T_D = 298 \text{ K}</math>, <math>T_M = 973 \text{ K}</math>, <math>\Delta H_{Sn}^{T_D \rightarrow T_M} = 26351 \text{ (J mol}^{-1}\text{)}</math>, <math>\Delta H_{Bi}^{T_D \rightarrow T_M} = 31240.19 \text{ (J mol}^{-1}\text{)}</math></b>							
<b><math>n_{Bi}</math></b>							

<b>0.001086</b>	0	0.0004	35.765	0.008	1.838	1692	420.432
<b>nSn</b>							
<b>0.000417</b>	0.0871	0.0007	8.673	0.009	-2.315	-5552	-99.676
<b>0.000220</b>	0.1272	0.0002	4.770	0.013	-1.027	-4668	-300.249
<b>0.000476</b>	0.2030	0.0003	10.635	0.011	-1.908	-4008	-622.186
<b>0.000546</b>	0.2751	0.0005	12.692	0.015	-1.696	-3106	-847.151
<b>0.000256</b>	0.3046	0.0004	6.153	0.014	-0.593	-2316	-906.882
<b>0.000482</b>	0.3542	0.0001	11.711	0.015	-0.990	-2054	-988.576
<b>0.000503</b>	0.3988	0.0002	12.045	0.013	-1.210	-2406	-1086.704
<b>0.000372</b>	0.4281	0.0007	9.265	0.012	-0.538	-1446	-1104.138
<b>0.001282</b>	0.5103	0.0006	31.935	0.004	-1.847	-1441	-1152.507
<b>0.001059</b>	0.5622	0.0003	26.920	0.002	-0.986	-931	-1129.049
<b>0.001286</b>	0.6122	0.0004	33.023	0.011	-0.864	-672	-1076.825
<b>0.001576</b>	0.6597	0.0003	40.803	0.014	-0.726	-461	-1001.240
<b>0.001832</b>	0.7022	0.0002	47.880	0.007	-0.395	-216	-903.171
<b>0.001552</b>	0.7307	0.0005	40.561	0.015	-0.336	-216	-837.524
<b>0.002336</b>	0.7646	0.0004	60.753	0.007	-0.803	-344	-775.410
<b>0.002959</b>	0.7969	0.0001	77.928	0.015	-0.045	-15	-670.879

<b>0.002403</b>	0.8173	0.0002	62.692	0.011	-0.629	-262	-629.802
<b>0.002589</b>	0.8352	0.0004	68.569	0.013	0.346	134	-555.256
<b>0.002276</b>	0.8482	0.0006	59.884	0.014	-0.091	-40	-514.545
<b>0.002919</b>	0.8622	0.0003	75.849	0.015	-1.070	-367	-500.907
<b>0.002621</b>	0.8727	0.0005	69.967	0.013	0.901	344	-436.435
<b>0.002964</b>	0.8828	0.0003	78.434	0.012	0.330	111	-392.896
<b>0.002608</b>	0.8905	0.0002	68.322	0.004	-0.401	-154	-377.266
<b>Series 9: (Sb<sub>0.75</sub>Bi<sub>0.25</sub>)<sub>1-x</sub>Sn<sub>x</sub> alloys; Atmosphere: Argon at pressure <math>p = 0.1</math> MPa; Starting amount <math>n_{sb} = 0.002900</math> mol, <math>K = 0.002106 \text{ J}\mu\text{Vs}^{-1}</math>, <math>T_D = 298 \text{ K}</math>, <math>T_M = 1023 \text{ K}</math>, <math>\Delta H_{Sn}^{T_D \rightarrow T_M} = 27340 \text{ (J mol}^{-1}\text{)}</math>, <math>\Delta H_{Bi}^{T_D \rightarrow T_M} = 32830.488 \text{ (J mol}^{-1}\text{)}</math></b>							
<b><math>n_{Bi}</math></b>							
<b>0.000967</b>	0	0.0005	33.387	0.012	1.640	1696	424.125
<b><math>n_{Sn}</math></b>							
<b>0.000417</b>	0.0973	0.0004	9.129	0.006	-2.272	-5448	-147.426
<b>0.000476</b>	0.1876	0.0003	11.133	0.015	-1.881	-3952	-527.943
<b>0.000280</b>	0.2327	0.0005	6.473	0.011	-1.182	-4221	-733.064
<b>0.000376</b>	0.2860	0.0006	9.144	0.011	-1.136	-3021	-892.074
<b>0.001121</b>	0.4084	0.0007	28.065	0.014	-2.583	-2304	-1134.091
<b>0.000732</b>	0.4680	0.0001	19.113	0.014	-0.900	-1230	-1143.729

<b>0.001687</b>	0.5682	0.0002	44.392	0.013	-1.731	-1026	-1121.625
<b>0.001544</b>	0.6317	0.0004	41.273	0.011	-0.940	-609	-1046.173
<b>0.002283</b>	0.6975	0.0008	61.599	0.004	-0.818	-358	-923.373
<b>0.001701</b>	0.7330	0.0003	46.142	0.002	-0.363	-213	-839.946
<b>0.001611</b>	0.7597	0.0007	43.804	0.011	-0.241	-150	-770.874
<b>0.002045</b>	0.7868	0.0003	55.700	0.014	-0.210	-103	-695.527
<b>0.001021</b>	0.7982	0.0002	27.844	0.007	-0.070	-69	-662.103
<b>0.002908</b>	0.8248	0.0005	79.347	0.012	-0.158	-54	-582.028
<b>0.001459</b>	0.8356	0.0004	38.644	0.007	-1.245	-853	-598.863
<b>0.001532</b>	0.8457	0.0001	42.460	0.014	0.575	375	-539.319
<b>0.002215</b>	0.8582	0.0002	59.954	0.011	-0.604	-273	-517.646
<b>0.002894</b>	0.8718	0.0008	79.666	0.013	0.544	188	-449.970
<b>0.001568</b>	0.8782	0.0006	42.890	0.014	0.021	13	-427.060
<b>0.001656</b>	0.8842	0.0003	44.239	0.015	-1.036	-626	-436.904
<b>0.002472</b>	0.8922	0.0005	68.630	0.013	1.046	423	-377.645

<sup>a</sup>Standard uncertainties **u** are:  $u(T_M) = 0.1 \text{ K}$ ,  $u(p) = 11 \text{ kPa}$ ,  $u(n_{\text{Bi}}) = 0.000001 \text{ mol}$ ,  $u(n_{\text{Sn}}) = 0.000001 \text{ mol}$ ,  $u(n_{\text{Sb}}) = 0.000002 \text{ mol}$ ,  $u(\Delta H_{\text{Reaction}}) = 0.001 \text{ J}$ ; Series 1:  $u(K) = 0.000003 \text{ J}/\mu\text{V s}$ ,  $u(\Delta_{\text{mix}}H) = 20.0213 \text{ J mol}^{-1}$ ; Series 2:  $u(K) =$

**0.000002 J / $\mu$ V s ,  $u(\Delta_{\text{mix}}H) = 18.017 \text{ J mol}^{-1}$ , Series 3:  $u(K) = 0.000002 \text{ J /}\mu\text{V s}$ ,  $u(\Delta_{\text{mix}}H) = 21.018 \text{ J mol}^{-1}$ ; Series 4:  $u(K) = 0.000004 \text{ J /}\mu\text{V s}$ ,  $u(\Delta_{\text{mix}}H) = 45.017 \text{ J mol}^{-1}$ ; Series 5:  $u(K) = 0.000001 \text{ J /}\mu\text{V s}$ ,  $u(\Delta_{\text{mix}}H) = 43.014 \text{ J mol}^{-1}$ ; Series 6:  $u(K) = 0.000001 \text{ J /}\mu\text{V s}$ ,  $u(\Delta_{\text{mix}}H) = 46.017 \text{ J mol}^{-1}$ ; Series 7:  $u(K) = 0.000001 \text{ J /}\mu\text{V s}$ ,  $u(\Delta_{\text{mix}}H) = 75.012 \text{ J mol}^{-1}$ ; Series 8:  $u(K) = 0.000004 \text{ J /}\mu\text{V s}$ ,  $u(\Delta_{\text{mix}}H) = 78.025 \text{ J mol}^{-1}$ ; Series 9:  $u(K) = 0.000003 \text{ J /}\mu\text{V s}$ ,  $u(\Delta_{\text{mix}}H) = 80.007 \text{ J mol}^{-1}$**

**$T_D$  = Drop temperature in Kelvin,  $T_M$  = Bath temperature in Kelvin,  $n_{\text{sn}}$  = number of moles of tin,  $n_{\text{Bi}}$  = number of moles of bismuth,  $n_{\text{sb}}$  = number of moles of antimony,  $K$  = Calibration constant,  $\Delta H_{\text{Signal}}$  = the heat effect due to single drop of sample to the bath,  $\Delta_{\text{mix}}H$  = Integral enthalpy of mixing of Sn-Bi-Sb system**

**Table 5.3** Partial and integral mixing enthalpies of Sn-Bi-Sb alloys when Bi dropped.

Added moles	Mole fraction ( $x_{Bi}$ )	Standard uncertainties $u(x_{Bi})$	Heat effect $H_{Signal} \cdot K$ (J)	Standard uncertainties $u(\Delta H_{Signal} \cdot K)$ (J)	Heat of Reaction $\Delta H_{Reaction}$ (J)	Partial enthalpy $\Delta \bar{H}_{X,i}$ (J mol <sup>-1</sup> )	Integral enthalpy $\Delta H_{mix}$ (J mol <sup>-1</sup> )
<b>Series 1: (Sb<sub>0.50</sub>Sn<sub>0.50</sub>)<sub>1-x</sub>Bi<sub>x</sub> alloys; Atmosphere: Argon at pressure <math>p = 0.1</math> MPa; Starting amount <math>n_{Sb} = 0.001191</math> mol, <math>K = 0.001986 \text{ J} \mu\text{Vs}^{-1}</math>, <math>T_D = 298 \text{ K}</math>, <math>T_M = 923 \text{ K}</math>, <math>\Delta H_{Sn}^{T_D \rightarrow T_M} = 24115 \text{ (J mol}^{-1}\text{)}</math>, <math>\Delta H_{Bi}^{T_D \rightarrow T_M} = 29649.888 \text{ (J mol}^{-1}\text{)}</math></b>							
$n_{Sn}$							
<b>0.001179</b>	0	0.0002	25.060	0.013	-3.372	-2860	-1422.75
$n_{Bi}$							
<b>0.000290</b>	0.1090	0.0005	8.706	0.004	0.108	372	-1226.939
<b>0.000228</b>	0.1794	0.0003	7.150	0.012	0.390	1711	-995.116
<b>0.000319</b>	0.2610	0.0005	9.987	0.011	0.529	1658	-731.181
<b>0.000331</b>	0.3301	0.0004	10.509	0.013	0.695	2100	-466.359
<b>0.000517</b>	0.4155	0.0004	16.136	0.017	0.807	1561	-208.002
<b>0.000510</b>	0.4808	0.0001	15.832	0.015	0.711	1394	-28.980
<b>0.000510</b>	0.5330	0.0002	15.692	0.016	0.571	1120	86.473
<b>0.000572</b>	0.5803	0.0003	17.522	0.015	0.562	983	177.282

<b>0.000564</b>	0.6184	0.0006	17.059	0.004	0.336	596	215.188
<b>0.000873</b>	0.6654	0.0004	26.337	0.005	0.453	519	252.709
<b>0.000844</b>	0.7011	0.0005	25.341	0.013	0.316	374	265.665
<b>0.000864</b>	0.7304	0.0003	26.121	0.014	0.503	582	296.716
<b>0.000933</b>	0.7563	0.0002	27.591	0.007	-0.072	-77	260.837
<b>0.001031</b>	0.7797	0.0008	30.724	0.012	0.155	150	250.292
<b>0.000853</b>	0.7958	0.0004	25.389	0.007	0.098	115	240.369
<b>0.000900</b>	0.8105	0.0001	26.892	0.015	0.207	230	239.572
<b>0.000964</b>	0.8241	0.0004	28.526	0.012	-0.056	-58	218.267
<b>0.000963</b>	0.8358	0.0004	28.607	0.013	0.054	56	207.434
<b>0.000956</b>	0.8460	0.0006	28.388	0.014	0.043	45	197.362
<b>0.000972</b>	0.8552	0.0003	29.182	0.015	0.362	372	207.779
<b>0.000960</b>	0.8632	0.0005	28.163	0.013	-0.301	-314	178.876
<b>0.001024</b>	0.8708	0.0003	30.386	0.012	0.025	24	170.253
<b>0.000988</b>	0.8774	0.0002	28.926	0.004	-0.368	-372	142.556
<b>0.001441</b>	0.8859	0.0005	43.345	0.002	0.620	430	162.509
<b>Series 2: (Sb<sub>0.50</sub>Sn<sub>0.50</sub>)<sub>1-x</sub>Bi<sub>x</sub> alloys: Atmosphere: Argon at pressure <math>p = 0.1</math> MPa; Starting amount <math>n_{Sb} = 0.001191</math> mol, <math>K = 0.001984 \text{ J}\mu\text{Vs}^{-1}</math>, <math>T_D = 298 \text{ K}</math>, <math>T_M = 973 \text{ K}</math>, <math>\Delta H_{Sn}^{T_D \rightarrow T_M} = 26351 \text{ (J mol}^{-1}\text{)}</math>, <math>\Delta H_{Bi}^{T_D \rightarrow T_M} = 31240.188 \text{ (J mol}^{-1}\text{)}</math></b>							

<b><i>n</i>Sn</b>							
<b>0.001179</b>	0	0.0003	27.682	0.011	-3.386	-2872	-1428.779
<b><i>n</i>Bi</b>							
<b>0.000244</b>	0.0933	0.0004	7.621	0.007	-0.002	-8	-1295.942
<b>0.000151</b>	0.1429	0.0003	4.986	0.012	0.269	1781	-1128.080
<b>0.000369</b>	0.2438	0.0002	12.170	0.011	0.642	1740	-790.230
<b>0.000071</b>	0.2605	0.0007	2.396	0.015	0.178	2507	-717.174
<b>0.000332</b>	0.3299	0.0004	11.001	0.014	0.629	1895	-472.155
<b>0.000640</b>	0.4326	0.0004	21.052	0.017	1.058	1653	-146.463
<b>0.000513</b>	0.4947	0.0002	16.700	0.013	0.674	1314	13.120
<b>0.000623</b>	0.5539	0.0007	20.225	0.012	0.762	1223	155.011
<b>0.000664</b>	0.6035	0.0006	21.166	0.003	0.423	637	208.551
<b>0.000502</b>	0.6342	0.0004	15.993	0.002	0.310	618	240.311
<b>0.000816</b>	0.6751	0.0005	25.845	0.013	0.353	433	261.756
<b>0.000788</b>	0.7068	0.0002	25.122	0.014	0.505	641	298.738
<b>0.000833</b>	0.7342	0.0007	25.967	0.007	-0.056	-67	264.563
<b>0.000955</b>	0.7599	0.0005	30.006	0.012	0.172	180	256.424
<b>0.000953</b>	0.7810	0.0004	29.916	0.007	0.144	151	247.155

<b>0.001077</b>	0.8009	0.0001	33.906	0.015	0.260	241	246.588
<b>0.000963</b>	0.8158	0.0002	30.039	0.011	-0.045	-47	224.665
<b>0.001064</b>	0.8298	0.0004	33.318	0.013	0.078	73	213.104
<b>0.001065</b>	0.8419	0.0006	33.334	0.014	0.063	59	202.138
<b>0.001004</b>	0.8518	0.0003	31.745	0.015	0.380	378	213.219
<b>0.001120</b>	0.8615	0.0005	34.700	0.013	-0.289	-258	182.363
<b>0.001033</b>	0.8694	0.0003	32.295	0.012	0.024	23	173.345
<b>0.001493</b>	0.8793	0.0002	46.291	0.004	-0.351	-235	142.266
<b>Series 3: (Sb<sub>0.50</sub>Sn<sub>0.50</sub>)<sub>1-x</sub>Bi<sub>x</sub> alloys; Atmosphere: Argon at pressure <math>p = 0.1</math> MPa; Starting amount <math>n_{Sb} = 0.001191</math> mol, <math>K = 0.002004 \text{ J}\mu\text{Vs}^{-1}</math>, <math>T_D = 298 \text{ K}</math>, <math>T_M = 1023 \text{ K}</math>, <math>\Delta H_{Sn}^{T_D \rightarrow T_M} = 27340 \text{ (J mol}^{-1}\text{)}</math>, <math>\Delta H_{Bi}^{T_D \rightarrow T_M} = 32830.488 \text{ (J mol}^{-1}\text{)}</math></b>							
<b><math>n_{Sn}</math></b>							
<b>0.001179</b>	0	0.0004	28.834	0.011	-3.400	-2884	-1434.779
<b><math>n_{Bi}</math></b>							
<b>0.000257</b>	0.0978	0.0005	8.445	0.007	0.008	31	-1291.193
<b>0.000253</b>	0.1771	0.0007	8.741	0.015	0.435	1719	-1026.568
<b>0.000226</b>	0.2370	0.0002	7.828	0.011	0.408	1805	-820.816
<b>0.000177</b>	0.2781	0.0006	6.358	0.012	0.547	3090	-609.656
<b>0.000144</b>	0.3084	0.0004	5.201	0.014	0.473	3285	-446.165

<b>0.000522</b>	0.3998	0.0001	18.003	0.015	0.865	1657	-168.126
<b>0.000595</b>	0.4784	0.0007	20.277	0.013	0.743	1249	17.456
<b>0.000655</b>	0.5441	0.0004	22.199	0.017	0.695	1061	148.836
<b>0.000599</b>	0.5912	0.0006	20.069	0.004	0.404	674	203.211
<b>0.000804</b>	0.6410	0.0003	26.871	0.002	0.475	591	250.343
<b>0.000852</b>	0.6820	0.0005	28.333	0.016	0.361	424	270.189
<b>0.000934</b>	0.7175	0.0008	31.235	0.014	0.571	611	308.122
<b>0.000987</b>	0.7472	0.0002	32.354	0.007	-0.050	-51	270.441
<b>0.001046</b>	0.7726	0.0005	34.517	0.015	0.176	168	260.135
<b>0.001056</b>	0.7935	0.0004	34.818	0.007	0.149	141	249.208
<b>0.001038</b>	0.8106	0.0009	34.324	0.015	0.246	237	248.205
<b>0.001136</b>	0.8264	0.0002	37.250	0.011	-0.045	-40	224.238
<b>0.001020</b>	0.8385	0.0004	33.545	0.013	0.058	57	212.616
<b>0.000983</b>	0.8486	0.0006	32.313	0.014	0.041	42	201.843
<b>0.001001</b>	0.8577	0.0003	33.261	0.015	0.398	398	213.622
<b>0.001012</b>	0.8659	0.0005	32.885	0.013	-0.339	-335	182.221
<b>0.001037</b>	0.8733	0.0003	34.066	0.012	0.021	20	173.210

<sup>a</sup>Standard uncertainties  $u$  are:  $u(T_M) = 0.1 \text{ K}$ ,  $u(p) = 12 \text{ kPa}$ ,  $u(n_{\text{Bi}}) = 0.000002 \text{ mol}$ ,  $u(n_{\text{Sn}}) = 0.000001 \text{ mol}$ ,  $u(n_{\text{Sb}}) = 0.000002 \text{ mol}$ ,  $u(\Delta H_{\text{Reaction}}) = 0.001 \text{ J}$ ; Series 1:  $u(K) = 0.000002 \text{ J}/\mu\text{V s}$ ,  $u(\Delta_{\text{mix}}H) = 70.013 \text{ J mol}^{-1}$ ; Series 2:  $u(K) = 0.000002 \text{ J}/\mu\text{V s}$ ,  $u(\Delta_{\text{mix}}H) = 72.017 \text{ J mol}^{-1}$ , Series 3:  $u(K) = 0.000003 \text{ J}/\mu\text{V s}$ ,  $u(\Delta_{\text{mix}}H) = 75.018 \text{ J mol}^{-1}$ ;

<sup>b</sup> $T_D$  = Drop temperature in Kelvin,  $T_M$  = Bath temperature in Kelvin,  $n_{\text{Sn}}$  = number of moles of tin,  $n_{\text{Bi}}$  = number of moles of bismuth,  $n_{\text{Sb}}$  = number of moles of antimony,  $K$  = Calibration constant,  $\Delta H_{\text{Signal}}$  = the heat effect due to a single drop of sample to the bath,  $\Delta_{\text{mix}}H$  = Integral enthalpy of mixing of Sn-Bi-Sb system

**Table 5.4** Partial and integral mixing enthalpies of Sn-Bi-Sb alloys when Sb dropped.

Added moles	Mole fraction ( $x_{Sb}$ )	Standard uncertainties $u(x_{Sb})$	Heat effect $H_{Signal} \cdot K$ (J)	Standard uncertainties $u(\Delta H_{Signal} \cdot K)$ (J)	Heat of Reaction $\Delta H_{Reaction}$ (J)	Partial enthalpy $\Delta \bar{H}_{X,i}$ (J mol <sup>-1</sup> )	Integral enthalpy $\Delta H_{mix}$ (J mol <sup>-1</sup> )
<b>Series 1: (Bi<sub>0.50</sub>Sn<sub>0.50</sub>)<sub>1-x</sub>Sb<sub>x</sub> alloys; Atmosphere: Argon at pressure <math>p = 0.1</math> MPa; Starting amount <math>n_{Sn} = 0.001855</math> mol,</b>							
<b><math>K = 0.001986 \text{ J}\mu\text{Vs}^{-1}, T_D = 298 \text{ K}, T_M = 923 \text{ K}, \Delta H_{Sb}^{T_D \rightarrow T_M} = 37089.563 \text{ (J mol}^{-1}\text{)}, \Delta H_{Bi}^{T_D \rightarrow T_M} = 29649.888 \text{ (J mol}^{-1}\text{)}</math></b>							
$n_{Bi}$							
<b>0.001804</b>	0	0.0004	53.947	0.005	0.459	254.00	125.324
$n_{Sb}$							
<b>0.000497</b>	0.1196	0.0005	17.733	0.007	-0.701	-1410	-58.118
<b>0.000392</b>	0.1955	0.0007	13.779	0.013	-0.760	-1939	-220.361
<b>0.000548</b>	0.2820	0.0002	19.284	0.011	-1.041	-1900	-400.994
<b>0.000394</b>	0.3335	0.0004	14.063	0.016	-0.550	-1396	-472.399
<b>0.000889</b>	0.4264	0.0004	31.697	0.014	-1.276	-1435	-606.449

<b>0.000876</b>	0.4957	0.0001	31.717	0.015	-0.773	-882	-639.770
<b>0.000874</b>	0.5499	0.0003	32.239	0.017	-0.177	-203	-592.790
<b>0.000982</b>	0.5984	0.0004	35.752	0.012	-0.670	-682	-602.423
<b>0.000968</b>	0.6370	0.0006	35.716	0.004	-0.187	-193	-563.155
<b>0.001499</b>	0.6840	0.0007	55.716	0.003	0.119	79	-479.969
<b>0.001448</b>	0.7191	0.0005	53.488	0.013	-0.218	-151	-443.361
<b>0.001483</b>	0.7478	0.0003	55.079	0.014	0.075	51	-392.889
<b>0.001601</b>	0.7729	0.0002	59.509	0.007	0.129	81	-345.837
<b>0.00177</b>	0.7954	0.0005	65.804	0.015	0.155	88	-302.931
<b>0.001463</b>	0.8108	0.0004	54.779	0.007	0.517	353	-253.268
<b>0.001545</b>	0.8248	0.0001	57.056	0.015	-0.247	-160	-246.384
<b>0.001656</b>	0.8377	0.0002	61.559	0.011	0.139	84	-222.083
<b>0.001651</b>	0.8488	0.0004	61.374	0.013	0.139	84	-201.213

<b>0.001641</b>	0.8584	0.0006	60.992	0.014	0.128	78	-183.480
<b>0.001669</b>	0.8670	0.0003	62.031	0.015	0.129	77	-167.658
<b>0.001647</b>	0.8745	0.0005	61.200	0.013	0.113	69	-154.308
<b>0.001757</b>	0.8816	0.0003	65.278	0.012	0.112	64	-141.890
<b>0.001696</b>	0.8878	0.0002	63.000	0.004	0.096	57	-131.574
<b>Series 2: (Bi<sub>0.50</sub>Sn<sub>0.50</sub>)<sub>1-x</sub>Sb<sub>x</sub> alloys; Atmosphere: Argon at pressure <math>p = 0.1</math> MPa; Starting amount <math>n_{Sn} = 0.001855</math> mol,</b>							
<b><math>K = 0.001984 \text{ J}\mu\text{Vs}^{-1}, T_D = 298 \text{ K}, T_M = 973 \text{ K}, \Delta H_{Sb}^{T_D \rightarrow T_M} = 38658.938 \text{ (J mol}^{-1}\text{)}, \Delta H_{Bi}^{T_D \rightarrow T_M} = 31240.188 \text{ (J mol}^{-1}\text{)}</math></b>							
<b><math>n_{Bi}</math></b>							
<b>0.001804</b>	0	0.0006	56.827	0.015	0.470	261	128.324
<b><math>n_{Sb}</math></b>							
<b>0.000591</b>	0.1391	0.0005	22.005	0.008	-0.842	-1425	-87.534
<b>0.000280</b>	0.1923	0.0004	10.215	0.015	-0.610	-2179	-216.834
<b>0.00044</b>	0.2638	0.0002	16.060	0.013	-0.950	-2159	-388.699

<b>0.000121</b>	0.2813	0.0007	4.630	0.017	-0.048	-397	-388.833
<b>0.000395</b>	0.3330	0.0004	14.633	0.014	-0.637	-1613	-476.945
<b>0.001098</b>	0.4443	0.0007	41.120	0.016	-1.328	-1209	-599.142
<b>0.00088</b>	0.5098	0.0002	33.345	0.013	-0.675	-767	-618.919
<b>0.00107</b>	0.5712	0.0006	40.602	0.012	-0.763	-713	-630.771
<b>0.000693</b>	0.6034	0.0007	26.652	0.004	-0.139	-201	-598.484
<b>0.001307</b>	0.6526	0.0003	50.615	0.002	0.088	67	-515.849
<b>0.001402</b>	0.6934	0.0005	53.945	0.013	-0.255	-182	-476.607
<b>0.001352</b>	0.7246	0.0007	52.329	0.014	0.062	46	-423.485
<b>0.00143</b>	0.7514	0.0002	55.395	0.007	0.113	79	-374.636
<b>0.001639</b>	0.7763	0.0005	63.500	0.015	0.138	84	-328.685
<b>0.001636</b>	0.7966	0.0004	63.721	0.007	0.475	290	-272.382
<b>0.001848</b>	0.8156	0.0001	71.164	0.015	-0.278	-150	-261.028

<b>0.001652</b>	0.8298	0.0002	64.003	0.011	0.138	84	-234.552
<b>0.001826</b>	0.8431	0.0004	70.719	0.013	0.128	70	-210.684
<b>0.001828</b>	0.8545	0.0006	70.775	0.014	0.106	58	-191.159
<b>0.001724</b>	0.8638	0.0003	66.774	0.015	0.126	73	-174.200
<b>0.001922</b>	0.8729	0.0005	74.409	0.013	0.107	56	-158.869
<b>0.001774</b>	0.8803	0.0003	68.688	0.012	0.107	60	-146.148
<b>Series 3: (Bi<sub>0.50</sub>Sn<sub>0.50</sub>)<sub>1-x</sub>Sb<sub>x</sub> alloys; Atmosphere: Argon at pressure <math>p = 0.1</math> MPa; Starting amount <math>n_{Sn} = 0.001855</math> mol,</b>							
<b><math>K = 0.002004 \text{ J}\mu\text{Vs}^{-1}, T_D = 298 \text{ K}, T_M = 1023 \text{ K}, \Delta H_{Sb}^{T_D \rightarrow T_M} = 40228.313 \text{ (J mol}^{-1}\text{)}, \Delta H_{Bi}^{T_D \rightarrow T_M} = 32830.488 \text{ (J mol}^{-1}\text{)}</math></b>							
<b><math>n_{Bi}</math></b>							
<b>0.001804</b>	0	0.0004	59.710	0.015	0.484	268	132.325
<b><math>n_{Sb}</math></b>							
<b>0.000441</b>	0.1076	0.0005	17.115	0.007	-0.626	-1420	-34.595
<b>0.000434</b>	0.1930	0.0003	16.611	0.013	-0.848	-1954	-218.376

<b>0.000388</b>	0.2566	0.0007	14.746	0.011	-0.863	-2224	-376.474
<b>0.000304</b>	0.2998	0.0005	11.829	0.014	-0.400	-1316	-431.209
<b>0.000246</b>	0.3313	0.0003	9.553	0.017	-0.343	-1394	-474.417
<b>0.000897</b>	0.4255	0.0001	34.947	0.015	-1.138	-1269	-586.267
<b>0.001021</b>	0.5049	0.0004	40.233	0.011	-0.840	-823	-618.921
<b>0.001125</b>	0.5703	0.0005	44.712	0.012	-0.545	-484	-601.203
<b>0.001027</b>	0.6165	0.0006	41.041	0.004	-0.273	-266	-565.056
<b>0.00138</b>	0.6650	0.0007	55.350	0.002	-0.165	-120	-508.804
<b>0.001462</b>	0.7045	0.0005	58.781	0.013	-0.033	-23	-451.354
<b>0.001604</b>	0.7384	0.0008	64.251	0.014	-0.275	-171	-419.307
<b>0.001694</b>	0.7667	0.0002	68.245	0.007	0.098	58	-367.778
<b>0.001796</b>	0.7907	0.0005	72.404	0.015	0.154	86	-321.159
<b>0.001811</b>	0.8103	0.0007	73.373	0.007	0.520	287	-264.045

<b>0.001782</b>	0.8263	0.0001	71.394	0.015	-0.293	-164	-255.603
<b>0.001951</b>	0.8411	0.0002	78.616	0.011	0.131	67	-228.249
<b>0.001749</b>	0.8523	0.0004	70.500	0.013	0.141	81	-206.432
<b>0.001689</b>	0.8617	0.0006	68.089	0.014	0.143	85	-187.878
<b>0.001716</b>	0.8701	0.0003	69.164	0.015	0.132	77	-171.729
<b>0.001738</b>	0.8777	0.0005	70.036	0.013	0.119	68	-157.773
<b>0.00178</b>	0.8846	0.0003	71.731	0.012	0.125	70	-144.984

<sup>a</sup>Standard uncertainties  $u$  are:  $u(T_M) = 0.1$  K,  $u(p) = 10$  kPa,  $u(n_{Bi}) = 0.000003$  mol,  $u(n_{Sn}) = 0.000002$  mol,  $u(n_{Sb}) = 0.000005$  mol,  $u(\Delta H_{Reaction}) = 0.001$  J; Series 1:  $u(K) = 0.000002$  J /  $\mu$ V s,  $u(\Delta_{mix}H) = 60.013$  J mol<sup>-1</sup>; Series 2:  $u(K) = 0.000002$  J /  $\mu$ V s,  $u(\Delta_{mix}H) = 58.016$  J mol<sup>-1</sup>, Series 3:  $u(K) = 0.000003$  J /  $\mu$ V s,  $u(\Delta_{mix}H) = 62.008$  J mol<sup>-1</sup>;

<sup>b</sup> $T_D$  = Drop temperature in Kelvin,  $T_M$  = Bath temperature in Kelvin,  $n_{Sn}$  = number of moles of tin,  $n_{Bi}$  = number of moles of bismuth,  $n_{Sb}$  = number of moles of antimony,  $K$  = Calibration constant,  $\Delta H_{Signal}$  = the heat effect due to a single drop of sample to the bath,  $\Delta_{mix}H$  = Integral enthalpy of mixing of Sn-Bi-Sb system

5.3.2 Theoretical Models

The thermodynamic characteristics of various type of systems it may be ternary or higher order may be deduced from the data of different binaries using a variety of theoretical models. The theoretical model put forward by Ansara and Dupin is significant[143]. Redlich-Kister-Muggianu polynomial has also been employed by Luef et al.[156] for substitutional solutions. We have used the least squares fitting for the given data set as per **Equation 5.4**.

$$\Delta H_{mix} = \sum_i \sum_{j>i} \left[ x_i x_j \sum_v L_{i:j}^{(v)} (x_i - x_j)^v \right] + x_i x_j x_k (L_{i:j:k}^0 x_{Sn} + L_{i:j:k}^1 x_{Bi} + L_{i:j:k}^2 x_{Sb}) \dots\dots\dots \tag{5.4}$$

where  $L_{i:j}^{(v)}$  ( $v= 0, 1, 2, \dots$ ) are the interaction parameters(binary) of the binary systems and  $L_{i:j:k}^v$  ( $v= 0, 1, 2, \dots$ ) are the interaction parameters(ternary). The mixing enthalpy obtained experimentally is compared with the calculated values considering the binary contributions only. The difference gives the ternary interaction contribution in this system which is further optimized using **Equation 5.4**. Ternary mixing enthalpy for Sn-Bi-Sb system for the cross-sections of  $(Sb_{0.25}Bi_{0.75})_{1-x}Sn_x$ ,  $(Sb_{0.50}Bi_{0.50})_{1-x}Sn_x$ ,  $(Sb_{0.75}Bi_{0.25})_{1-x}Sn_x$ ,  $(Sb_{0.50}Sn_{0.50})_{1-x}Bi_x$ ,  $(Bi_{0.50}Sn_{0.50})_{1-x}Sb_x$  is represented in **Figure 11** along with the R-K Muggianu modeled data fitted curve at 973 K as per **Equation 5.4**. The binary interaction parameters and findings from this study are used to derive the ternary interaction parameters using the least square fit. The binary interaction parameters are taken from data in the literature [130] that was readily available. **Table 5.6** lists the interaction parameters for binary and ternary systems. The comparison between the experimental data with the values obtained from the R-K-Muggianu model considering the ternary interaction are shown in **Figure 5.11**. It is observed that both the values for the mixing enthalpies were in good

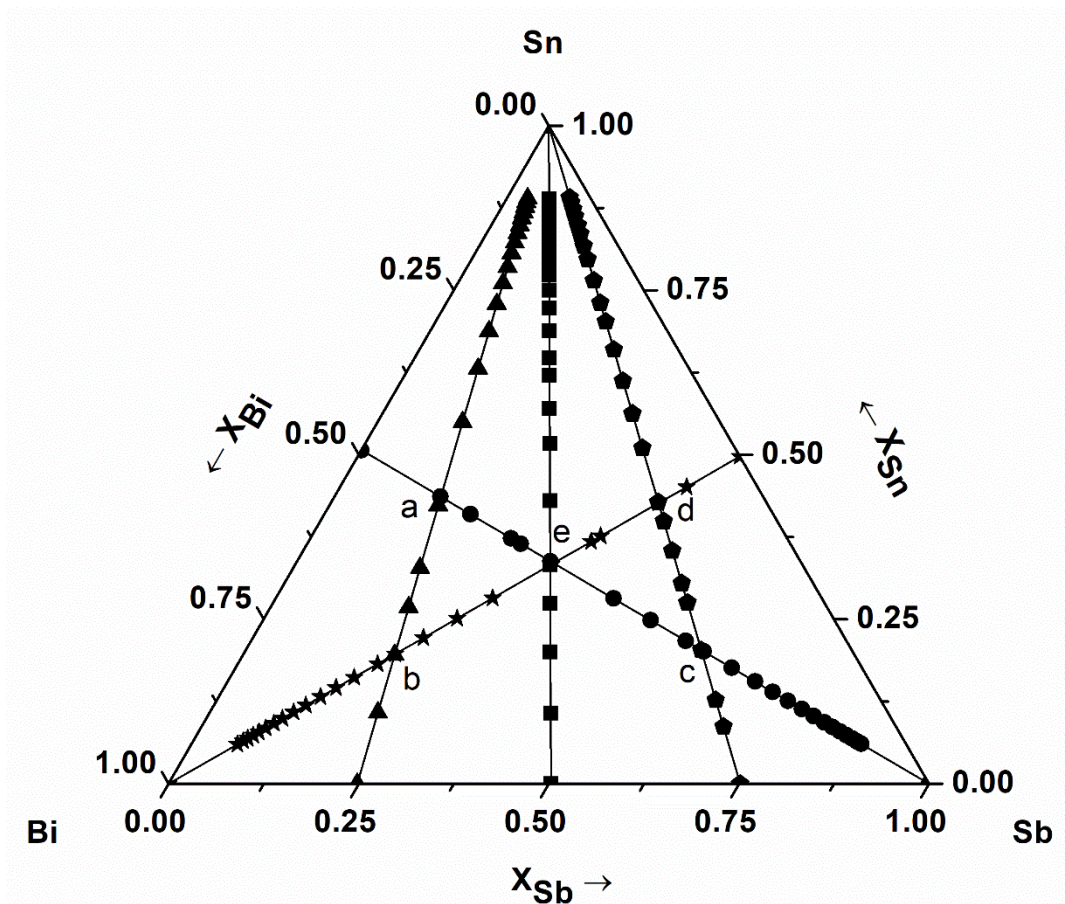
agreement except for a few compositions. Therefore, the R-K-Muggianu substitutional model is very well followed by this system in the temperature range of 923-1023 K.

**Table 5.5** Integral enthalpy of mixing values at the sites of intersection **a, b, c, d, and e**; also see **Figure 5.1**.

Intersection	Integral enthalpy of mixing in J/mol		
	Sn drops	Bi drops	Sb drops
a	-80.032		-87.534
b	212.632	208.551	
c	-622.186		-598.484
d	-1104.138	-1128.080	
e	-488.278	-472.155	-476.945

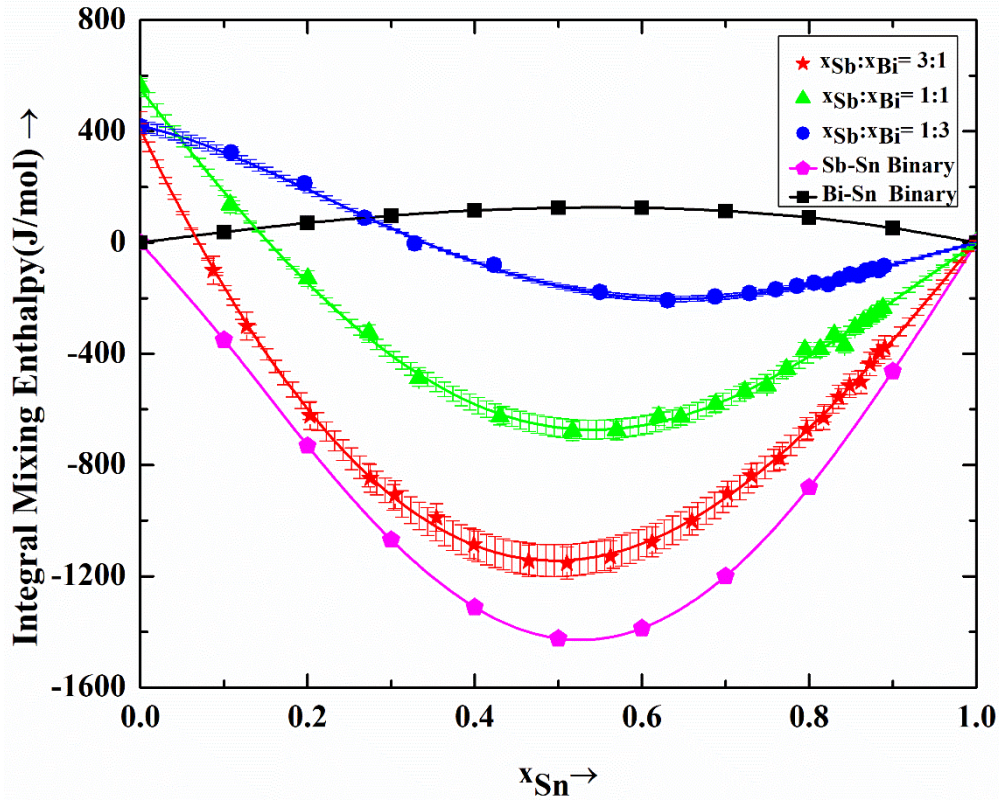
**Table 5.6.** Binary and Ternary interaction parameters.

Interaction parameter	$\nu$	(J/mol)
$L_{Bi-Sb}^{\nu}$ [130]	0	2230
$L_{Bi-Sn}^{\nu}$ [130]	0	500
	1	-100
$L_{Sb-Sn}^{\nu}$ [130]	0	-5695.1
	1	782.6
	2	1840.9
$L_{Sn-Bi-Sb}^{\nu}$	0	-4743.1
	1	11251.87
	2	-13969.1



**Fig.5.1** Measured cross-sections (intersections a to e indicated, see **Table 5.5**) and alloy compositions in the Sn-Bi-Sb ternary system.

The enthalpies of mixing of the five cross-sections depicted in **Figure 5.1** in the Sn-Bi-Sb ternary system were determined at 923 K, 973 K, and 1023 K. Pieces of pure tin were dropped into molten  $\text{Sb}_{0.25}\text{Bi}_{0.75}$ ,  $\text{Sb}_{0.50}\text{Bi}_{0.50}$ ,  $\text{Sb}_{0.75}\text{Bi}_{0.25}$  alloys; Bismuth into  $\text{Sb}_{0.50}\text{Sn}_{0.50}$  and Antimony into  $\text{Bi}_{0.50}\text{Sn}_{0.50}$  alloys. The closeness of readings near the intersection points on the five cross-sections indicates the quality of our experimental data (see **Table 5.5** and **Figure 5.1**). In each attempt, the variation is significantly reduced and hardly noticeable. However, systemic errors, such as those resulting from insufficient mixing reactions, cannot be completely ruled out.



**Fig. 5.2** Plot representing the enthalpies of mixing of the given ternary alloy system corresponding to cross-section of  $(\text{Sb}_{0.25}\text{Bi}_{0.75})_{1-x}\text{Sn}_x$ ; circle,  $(\text{Sb}_{0.50}\text{Bi}_{0.50})_{1-x}\text{Sn}_x$ ; triangle and  $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{1-x}\text{Sn}_x$ ; star at 973 K, Sb-Sn binary data from literature[130]; pentagon and Bi-Sn binary data from literature; square[130].

**Figure 5.2** illustrates the change in mixing enthalpies for three different isopleths and two binaries. For three isopleths and the Sb-Sn binary, the mixing enthalpies are exothermic across the Sn composition, but endothermic at low Sn composition end. For these three cross sections, we found that mixing enthalpy's minima to be exothermic in nature which makes the alloy more stable.

Mixing enthalpy's minima corresponding to the cross-sections  $(\text{Sb}_{0.25}\text{Bi}_{0.75})_{1-x}\text{Sn}_x$  is close to  $x_{\text{Sn}} \sim 0.62$  and for the cross-section  $(\text{Sb}_{0.50}\text{Bi}_{0.50})_{1-x}\text{Sn}_x$  is approximately equal to  $x_{\text{Sn}} \sim 0.55$  and if we consider the

cross section  $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{1-x}\text{Sn}_x$  it is almost symmetric about tin composition.

The enthalpy of mixing falls with increasing tin content and reaches a minimum at the tin composition indicated above. As the  $x_{\text{Sb}}/x_{\text{Bi}}$  ratio decreases, it can also be seen in **Figure 5.2** that the lowest value (minima) in the curve representing mixing enthalpy becoming less exothermic in nature. It reaches its peak at equi-atomic composition after that it decreases at the extremes. The Bi, Sb, and Sn atoms' interatomic interaction may have diminished as a result regardless of the mixing entropy's sign, the mixing enthalpy adds adversely to the Gibbs energy for the majority of the tin composition. The measured mixing enthalpy is found to be negative which suggests that the atoms in this system have finite amounts of interatomic interaction energy. This indicates that the heat is produced by mixing process making it more exothermic.

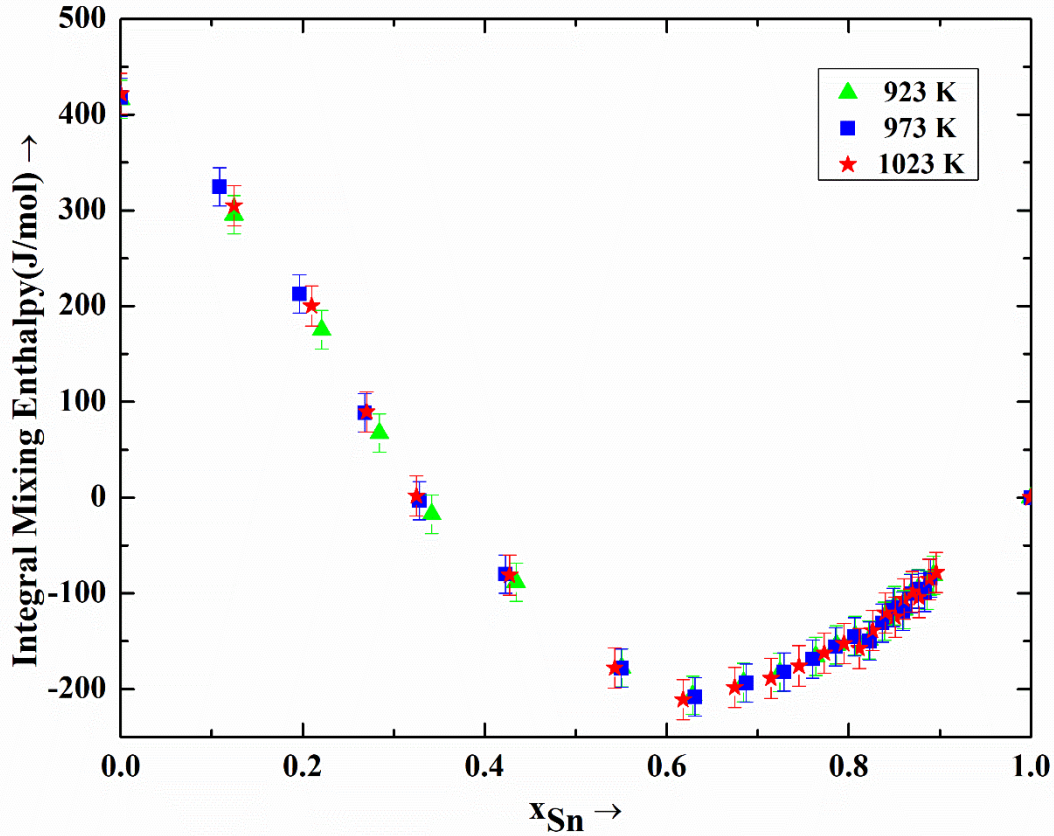


Fig. 5.3 Plot representing the enthalpies of mixing of the given ternary alloy system for the cross-section of  $(\text{Sb}_{0.25}\text{Bi}_{0.75})_{1-x}\text{Sn}_x$ .

Figure 5.3-5.5 illustrates the nature of mixing enthalpies with the variations in the composition of Sn. Additionally, it can be seen that the enthalpy curve at 923 K, 973 K, and 1023 K are quite close to one another. This makes the mixing enthalpy of Sn-Bi-Sb system's independent of temperature. Temperature has very little effect on how the Bi, Sn, and Sb atoms in this system interact with one another in the above temperature range. The degree of mixing is better when the curve is more symmetric. In the temperature range of 923 K–1023 K, the  $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{1-x}\text{Sn}_x$  alloy mixes better than the other two alloys.

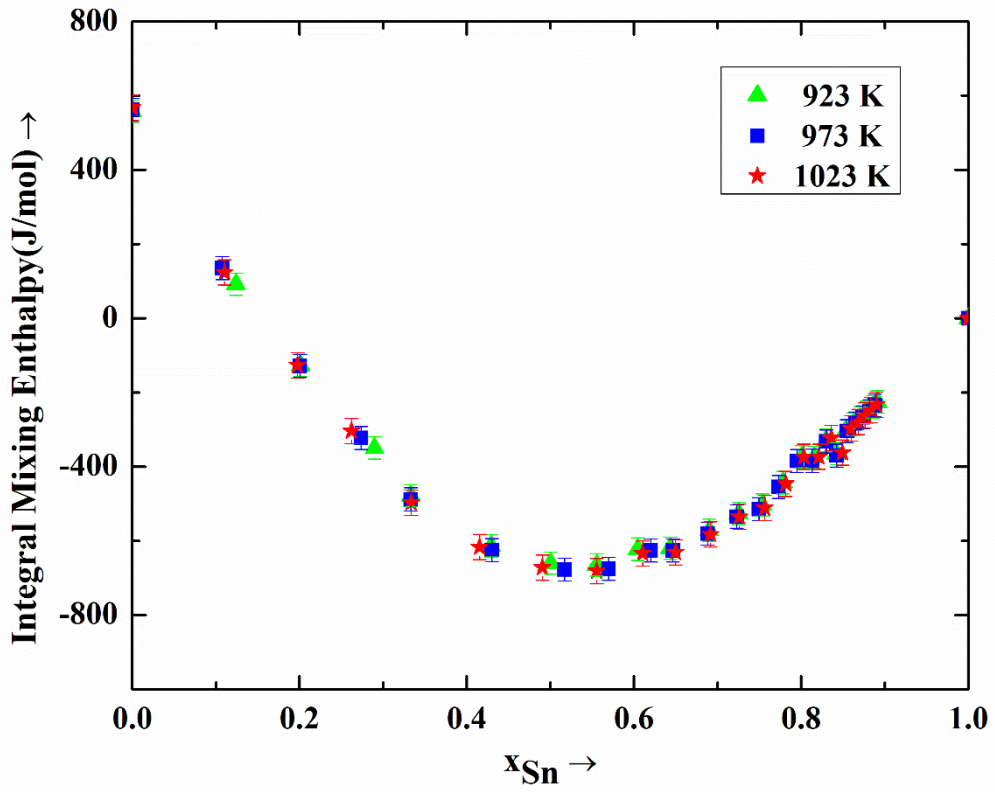


Fig. 5.4 Plot representing the enthalpies of mixing of the given ternary alloy system for the cross-section of  $(Sb_{0.50}Bi_{0.50})_{1-x}Sn_x$ .

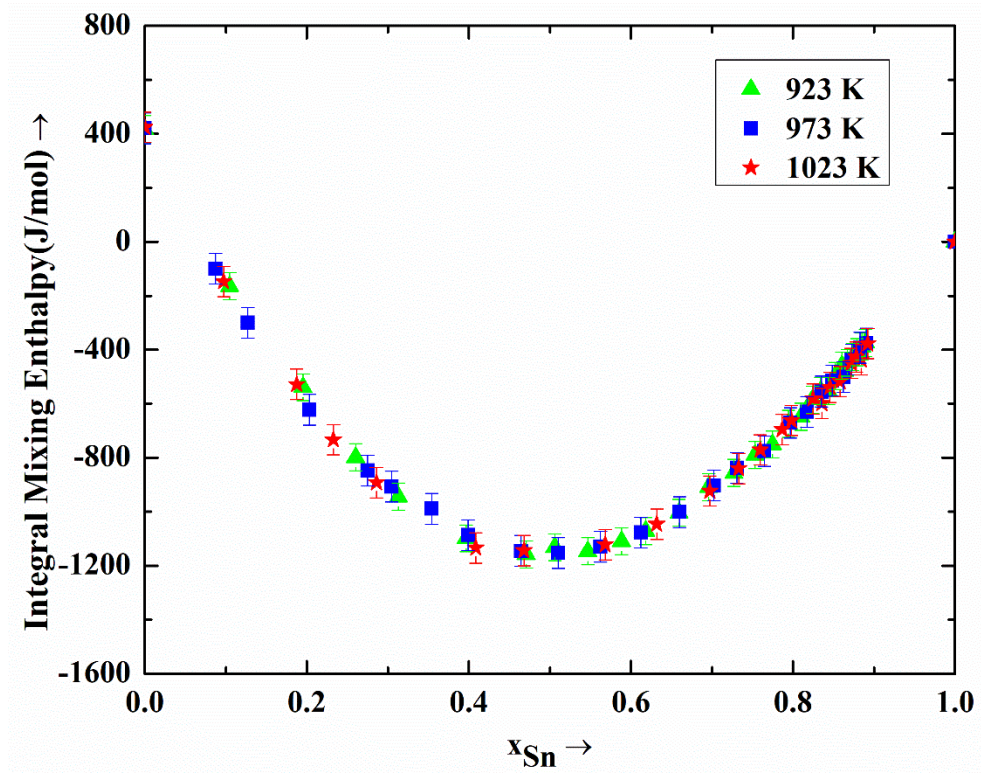
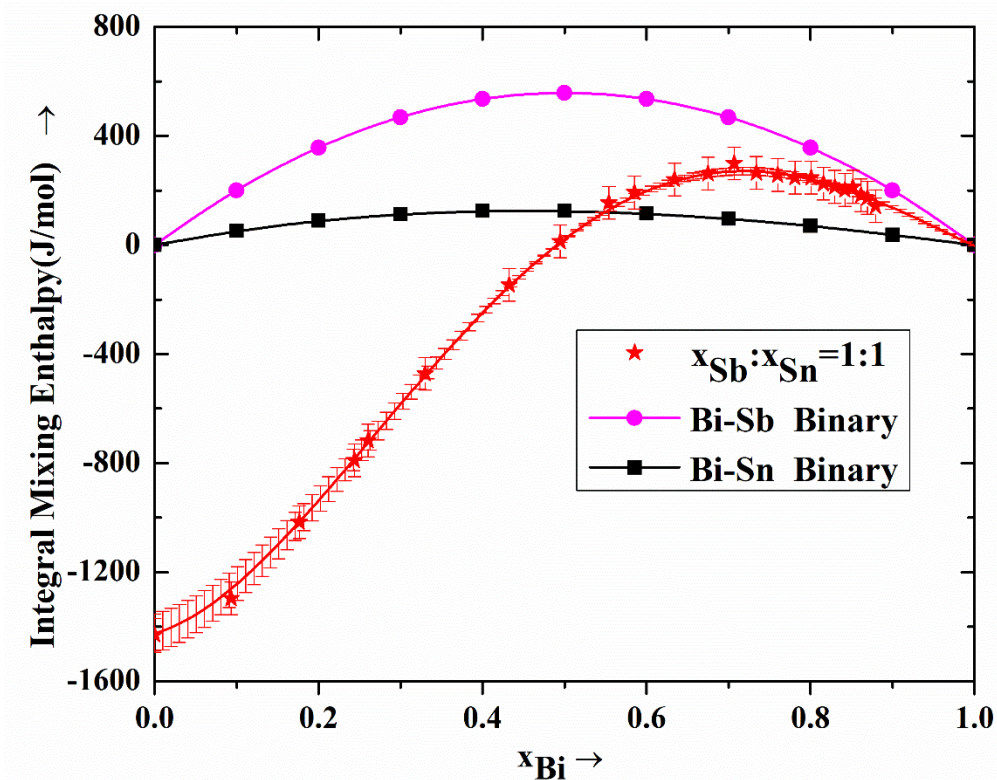


Fig. 5.5 Plot representing the enthalpies of mixing of the given ternary alloy system for the cross-section of  $(Sb_{0.75}Bi_{0.25})_{1-x}Sn_x$ .



**Fig. 5.6** Plot representing the enthalpies of mixing of the given ternary alloy system for the cross-section of  $(\text{Sb}_{0.50}\text{Sn}_{0.50})_{1-x}\text{Bi}_x$  at 973 K; star. Bi-Sb binary data from literature[130]; circle and Bi-Sn binary data from literature; square[130].

**Figure 5.6** illustrates the nature of mixing enthalpies with the variations in the composition of Bi. In the given cross-section, the mixing enthalpy maxima are endothermic in nature. The asymmetrical nature of the enthalpy of mixing curve and the large value of enthalpy of mixing makes the alloy less stable. The amount of heat needed to produce these alloys would depend on their composition. The enthalpy of mixing rises with bismuth concentration, reaching a peak around  $x_{\text{Bi}} \sim 0.72$ .

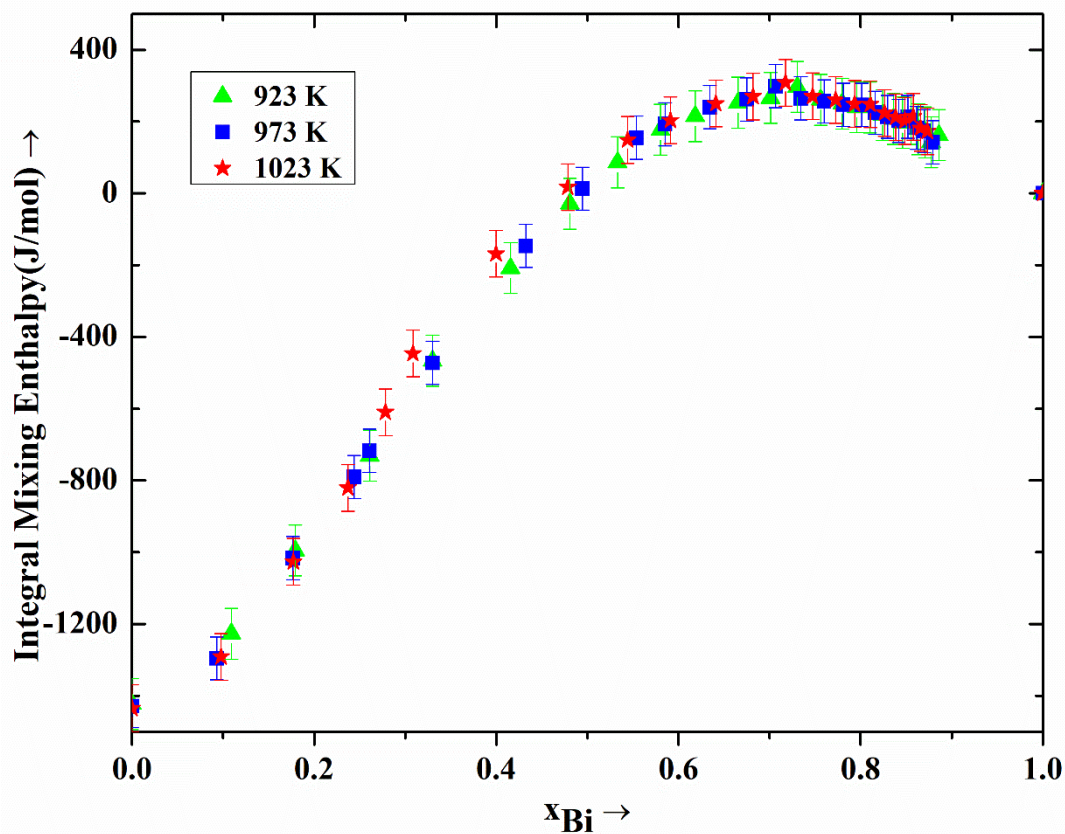
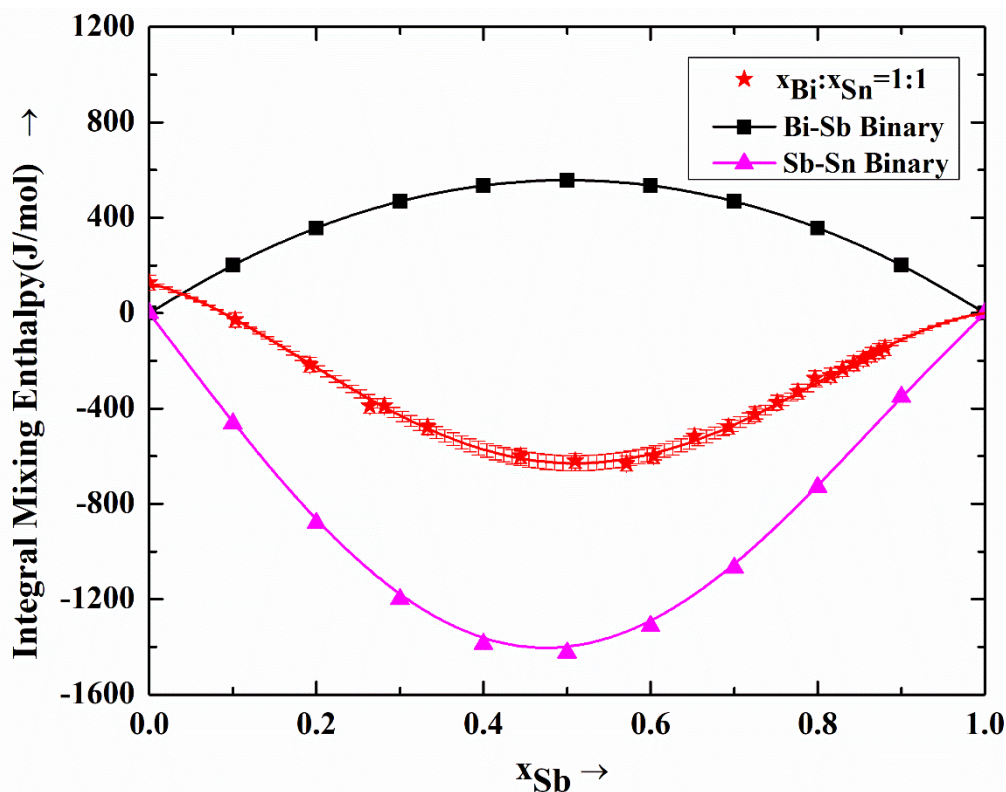


Fig. 5.7 Plot representing the enthalpies of mixing of the given ternary alloy system for the cross-section of  $(Sb_{0.50}Sn_{0.50})_{1-x}Bi_x$ .

Figure 5.7 further shows that the enthalpies of mixing plots for given ternary system at 923 K, 973 K, and 1023 K as a function of composition. These plots are quite close to each other. This might mean that in the Sn-Bi-Sb system, mixing enthalpy is almost independent of temperature and mixing behavior does not significantly alter with the variation of temperature.



**Fig. 5.8** Plot representing the enthalpies of mixing of the given ternary alloy system for the cross-section of  $(\text{Bi}_{0.50}\text{Sn}_{0.50})_{1-x}\text{Sb}_x$  at 973 K; star. Bi-Sb binary data from literature [130]; square and Sb-Sn binary data from literature; triangle [130].

**Figure 5.8** illustrates the relationship between mixing enthalpies with variation in Sb composition of the given ternary alloy system. In the given cross-section, minima of the mixing enthalpy are exothermic in nature which makes the alloy more stable. In the cross section  $(\text{Bi}_{0.50}\text{Sn}_{0.50})_{1-x}\text{Sb}_x$ , minima of enthalpy of mixing is almost symmetric with regard to antimony composition.

The enthalpy of mixing falls as antimony concentration rises, reaching minima at  $x_{\text{Sb}} \sim 0.50$ . It reaches its peak at equiatomic percent and then decreases at the end.

The Bi, Sb, and Sn atoms' interatomic attraction may have diminished as a result. Regardless of the mixing entropy's sign, the mixing enthalpy adds adversely to the Gibbs energy for the majority of the antimony composition. The measured mixing enthalpy is found to be negative which suggests that the atoms in this system have finite amounts of

interatomic interaction energy. Therefore, heat produced by mixing process is exothermic and is released during the mixing process.

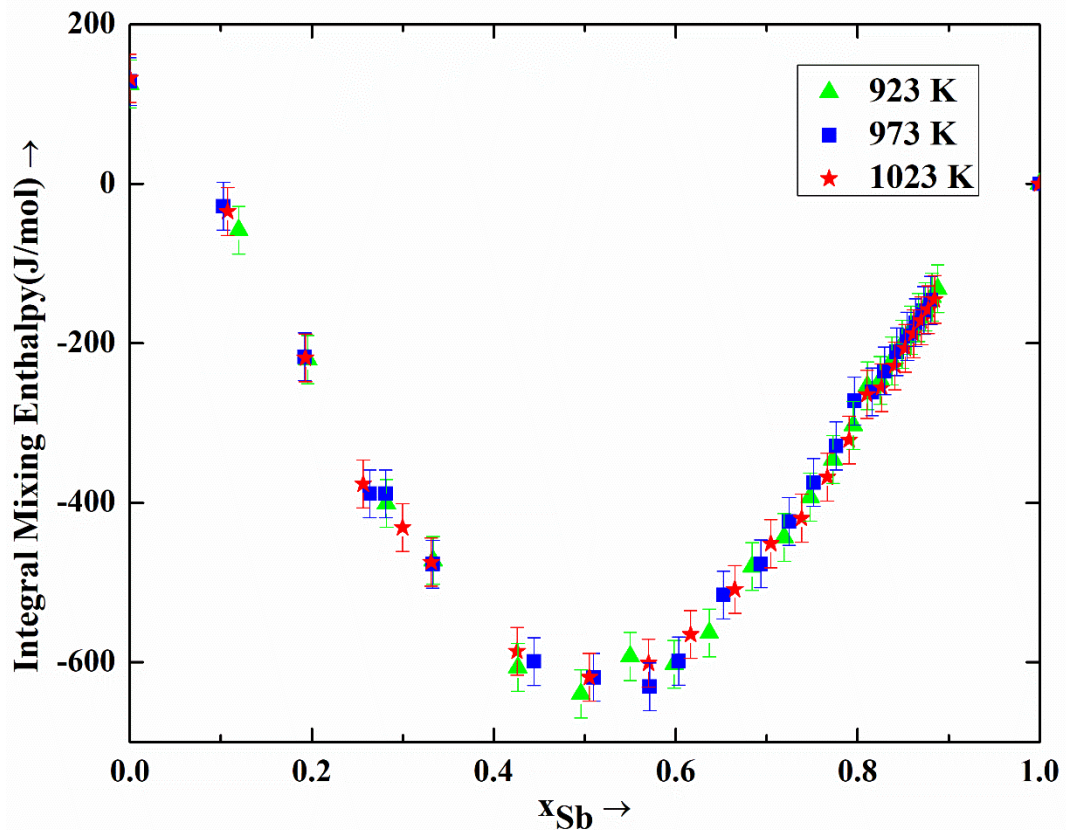
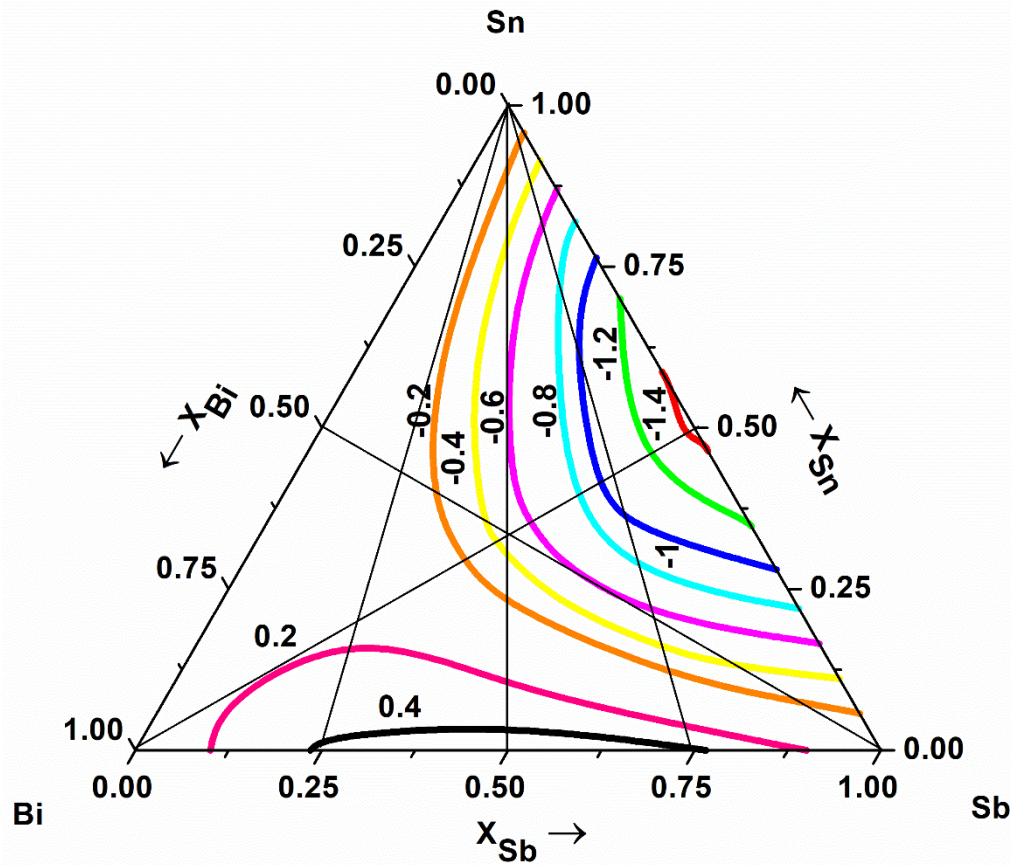


Fig. 5.9 Plot representing the enthalpies of mixing of the given ternary alloy system for the cross-section of  $(\text{Bi}_{0.50}\text{Sn}_{0.50})_{1-x}\text{Sb}_x$ .

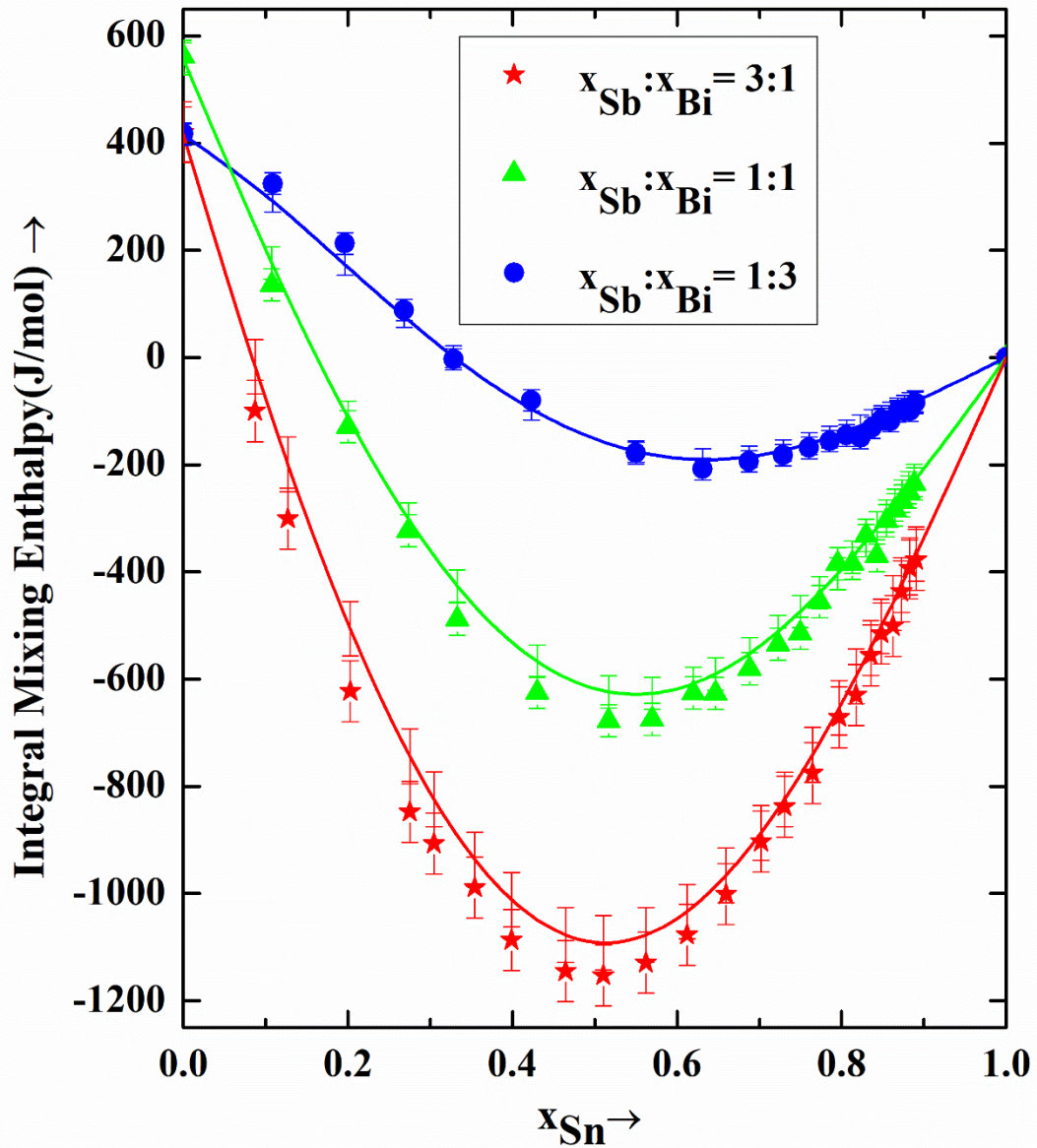
Figure 5.9 further shows that the plots at 923 K, 973 K, and 1023 K are quite near to one another. This suggests that the Sn-Bi-Sb system's enthalpy of mixing is nearly temperature-independent.



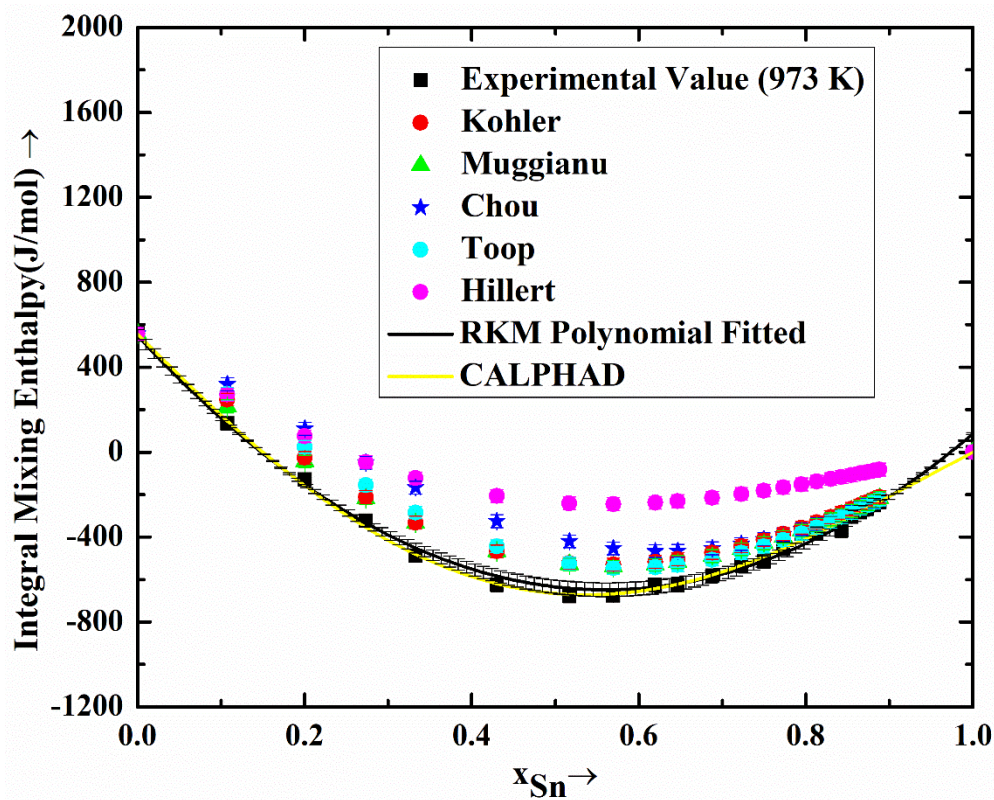
**Fig. 5.10** Plot representing different Iso-enthalpy curves of given liquid ternary alloy at 973 K; values are in kJ/mol.

The plots between molar enthalpy of mixing and the composition of dropping species was used to create the above curves. It is shown in **Figure 5.10** for nine iso-enthalpies i.e. 0.2 kJ/mol, 0.4 kJ/mol, -0.2 kJ/mol, -0.4 kJ/mol, -0.6 kJ/mol, -0.8 kJ/mol, -1.0 kJ/mol, -1.2 kJ/mol, and -1.4 kJ/mol. The mixing enthalpy is seen to be more negative when the alloy's composition is nearer to the Sb-Sn binary system and positive when it is nearer to the Bi-Sb binary system. This is so Sb-Sn binary system has the largest negative mixing enthalpy values among the three binaries, whereas the Bi-Sb alloys have the highest positive enthalpy of mixing values. The binary Sb-Sn affects the majority of the iso-enthalpy curves. This suggests that the Sb and Sn atoms

in the given ternary systems sub-lattice may have greater influence on the orientation of the enthalpy of mixing curves.



**Fig. 5.11** Comparison of mixing enthalpies between R-K Muggianu modeled data; bold line and experimental data of liquid Sn-Sb-Bi alloys along the cross-sections of  $(\text{Sb}_{0.25}\text{Bi}_{0.75})_{1-x}\text{Sn}_x$ ; circle,  $(\text{Sb}_{0.50}\text{Bi}_{0.50})_{1-x}\text{Sn}_x$ ; triangle and  $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{1-x}\text{Sn}_x$ ; star at 973 K.



**Fig. 5.12** Experimental and calculated integral enthalpy of mixing for the isopleth  $(\text{Bi}_{0.50}\text{Sb}_{0.50})_{1-x}\text{Sn}_x$  by using the five geometric models (Kohler, Muggianu, Chou, Toop and Hillert) at 973 K along with RKM Polynomial fitted Curve and data predicted from CALPHAD technique [144].

Five extrapolation geometric models (Kohler, Muggianu, Chou, Toop and Hillert) were used to predict the enthalpy of mixing values of ternary Sn-Bi-Sb system. Binary interaction parameter of all binaries were required to predict the thermodynamic properties of the given ternary system. Binary interaction parameter of all binary systems Bi-Sn, Sb-Sn and Bi-Sb were taken from the data available in literature [130] and given in the **Table 5.6**.

The various predictive extensions from the binary to ternary Sn-Bi-Sb System are shown below:

## 5.3.2.1 Kohler model [141]

$$\begin{aligned} \Delta H_{Sn-Bi-Sb}^{mix} = & \left[ (x_{Bi} + x_{Sn})^2 \Delta H_{Bi-Sn}^{mix} \left( \frac{x_{Sn}}{x_{Sn} + x_{Bi}}; \frac{x_{Bi}}{x_{Sn} + x_{Bi}} \right) + (x_{Sn} + \right. \\ & \left. x_{Sb})^2 \Delta H_{Sb-Sn}^{mix} \left( \frac{x_{Sn}}{x_{Sn} + x_{Sb}}; \frac{x_{Sb}}{x_{Sn} + x_{Sb}} \right) + (x_{Bi} + x_{Sb})^2 \Delta H_{Bi-Sb}^{mix} \left( \frac{x_{Bi}}{x_{Bi} + x_{Sb}}; \frac{x_{Sb}}{x_{Bi} + x_{Sb}} \right) \right] \\ \dots \end{aligned} \quad (4.5)$$

## 5.3.2.2 Muggianu model [141]

$$\begin{aligned} \Delta H_{Sn-Bi-Sb}^{mix} = & \left[ \left( \frac{4x_{Bi}x_{Sn}}{[1-(x_{Bi}-x_{Sn})^2]} \right) \Delta H_{Bi-Sn}^{mix} \left( x_{Sn} + \frac{x_{Sb}}{2}; x_{Bi} + \frac{x_{Sb}}{2} \right) + \right. \\ & \left( \frac{4x_{Bi}x_{Sb}}{[1-(x_{Bi}-x_{Sb})^2]} \right) \Delta H_{Bi-Sb}^{mix} \left( x_{Bi} + \frac{x_{Sn}}{2}; x_{Sb} + \frac{x_{Sn}}{2} \right) + \\ & \left. \left( \frac{4x_{Sb}x_{Sn}}{[1-(x_{Sb}-x_{Sn})^2]} \right) \Delta H_{Sb-Sn}^{mix} \left( x_{Sb} + \frac{x_{Bi}}{2}; x_{Sn} + \frac{x_{Bi}}{2} \right) \right] \\ \dots \end{aligned} \quad (4.6)$$

## 5.3.2.3 Chou model [141]

$$\begin{aligned} \Delta H_{Sn-Bi-Sb}^{mix} = & \left[ \left( \frac{x_{Bi}}{1-x_{Sn}} \right) \Delta H_{Bi-Sn}^{mix} (x_{Sn}; x_{Bi}) + \left( \frac{x_{Sb}}{1-x_{Bi}} \right) \Delta H_{Bi-Sb}^{mix} (x_{Bi}; x_{Sb}) + \right. \\ & \left. \left( \frac{x_{Sn}}{1-x_{Sb}} \right) \Delta H_{Sb-Sn}^{mix} (x_{Sn}; x_{Sb}) \right] \\ \dots \end{aligned} \quad (4.7)$$

## 5.3.2.4 Toop model [141]

$$\begin{aligned} \Delta H_{Sn-Bi-Sb}^{mix} = & \left[ \left( \frac{x_{Bi}}{1-x_{Sn}} \right) \Delta H_{Bi-Sn}^{mix} (x_{Sn}; 1 - x_{Sn}) + (x_{Bi} + \right. \\ & \left. x_{Sb})^2 \Delta H_{Bi-Sb}^{mix} \left( \frac{x_{Bi}}{x_{Bi} + x_{Sb}}; \frac{x_{Sb}}{x_{Bi} + x_{Sb}} \right) + \left( \frac{x_{Sb}}{1-x_{Sn}} \right) \Delta H_{Sb-Sn}^{mix} (x_{Sn}; 1 - x_{Sn}) \right] \\ \dots \end{aligned} \quad (4.8)$$

### 5.3.2.5 Hillert model [141]

$$\Delta H_{Sn-Bi-Sb}^{mix} = \left[ \left( \frac{x_{Bi}}{1-x_{Sn}} \right) \Delta H_{Bi-Sn}^{mix}(x_{Sn}; \mathbf{1} - x_{Sn}) + \left( \frac{4x_{Bi}x_{Sb}}{[1-(x_{Bi}-x_{Sb})^2]} \right) \Delta H_{Bi-Sb}^{mix} \left( x_{Bi} + \frac{x_{Sn}}{2}; x_{Sb} + \frac{x_{Sn}}{2} \right) + \left( \frac{x_{Sb}}{1-x_{Sn}} \right) \Delta H_{Sb-Sn}^{mix}(x_{Sn}; \mathbf{1} - x_{Sn}) \right]$$

.....

(4.9)

A comparison of experimental data with all geometric model data along with RKM modelled fitted data at 973 K is shown in **Figure 5.12** for the isopleth  $(\text{Bi}_{0.50}\text{Sb}_{0.50})_{1-x}\text{Sn}_x$ . RKM modelled polynomial fitted data fits well to the experimental data. Also the data predicted from CALPHAD technique [144] by using THERMOCALC software 2023 (database: SSOL5) is very close to the experimental data for most of the composition range. It's possible for calorimetric readings to be inaccurate for a variety of reasons, including the kind of calorimeter that was used, the techniques for calibrating it, the integration of the heat flow curve baseline, the solubility of the solute in the solvent, and the concentration of impurities. After performing each series twice, we found that the experimental error of the calorimeter is approximately  $\pm 5\%$ .

## 5.4 Conclusions

Integral and partial mixing enthalpies of Sn-Bi-Sb ternary system were investigated using drop calorimeter (MHTC 96 LINE EVO) in the temperature range of 923 K-1023 K along five of the cross-sections:  $(\text{Sb}_{0.25}\text{Bi}_{0.75})_{1-x}\text{Sn}_x$ ,  $(\text{Sb}_{0.50}\text{Bi}_{0.50})_{1-x}\text{Sn}_x$ ,  $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{1-x}\text{Sn}_x$ ,  $(\text{Sb}_{0.50}\text{Sn}_{0.50})_{1-x}\text{Bi}_x$ ,  $(\text{Bi}_{0.50}\text{Sn}_{0.50})_{1-x}\text{Sb}_x$  by drop methods. It has been found that the enthalpies of mixing are nearly temperature-independent. The curves representing iso-enthalpy were plotted using the mixing enthalpy values for the all five cross sections. Most of these curves were oriented towards Sb-Sn binary system. The substitutional solution RKM model was used to derive the interaction parameter based on ternary enthalpy values and to get these parameters least square fitting is used.

Additionally, the enthalpies of mixing of the given ternary have been calculated by using the Kohler, Muggianu, Chou, Toop and Hillert geometric models and compared with the experimental ones. It is also observed that the data predicted from CALPHAD technique [144] is very close to the experimental data for most of the composition range. These models use the binary interaction parameters and these parameters are deduced by using a Redlich-Kister polynomial fitting to accurately describe the binary interactions within each binary alloy system. When the values getting from RKM model and measured experimental values are compared, it is found that there is a good agreement between them.

