CHAPTER-4

ENTHALPIES OF MIXING IN Sn-Ga-In TERNARY SYSTEM

4.1 Introduction

In recent times, the harmful consequences that lead-containing materials have had on the environment and health have led to a rising demand for the development of lead-free alternatives that are friendlier to the environment. Conventional solders containing lead and tin, that are used in a wide range of electronic applications are an example of material that raises serious concerns. It is now absolutely necessary to look for lead-free solder alternatives that have characteristics that are comparable to those of Pb-Sn solder to solve this problem. As a possible replacement for traditional solders that contains lead, the alloy system consisting of tin (Sn), gallium (Ga), and indium (In) is the main objective of this research. Because of its superior ability to transmit electricity and its good resistance to corrosion, gallium stands out as a potentially useful choice. In addition, gallium's melting point of 29.76 °C, which is substantially lower than most other metals, making it a potential candidate for our study. This lowers the melting point of the alloy system as a whole. Notably, preceding studies have shown the positive effects of adding gallium into lead-free solders, improving mechanical characteristics and better wettability [145], [146], [150]**.** Aside from gallium, indium is an essential component in this alloy system. Having a melting point that is just 156.6 °C lower than gallium's, indium helps to lower the alloy's total melting point and provides excellent resistance to corrosion. Despite the fact that the value of electrical conductivity of indium is not even close to that of copper [67], [148], [149], [151], the addition of this element considerably improves the wetting behaviors of the alloy. This results in improvement in the strength of solder bond and hence making the solder more reliable. Tin, which is another crucial component of the system, has a melting point of just 213.93 °C and a boiling temperature that is 2270 °C. Tin's melting point is lower than lead's melting point, but it has a higher boiling point. The alloy's overall performance is further

enhanced by the fact that it has high electrical conductivity and is resistant to corrosion [140], [152], [153]. A lead-free solder replacement that has characteristics that are equivalent to those of typical lead-tin solder may be developed by using gallium, indium, and tin. This is a fascinating path to investigate. The outcomes of this study will, eventually, add to the continuous efforts that are being put forth in the development of environmentally friendly and sustainable materials for the electronics sector. In order to build an alloy comprising Sn, Ga, and In that may replace conventional Sn based solder, the first step is to determine the thermodynamic parameters of the alloy, which is then followed by the construction of phase diagram. It is challenging to discover any alloy that is capable of satisfying all of the criteria for a lead-free solder. According to the research that has been done, there is no calorimetric data that can be used for making direct measurements of enthalpies of mixing for this ternary system. Because of this, the determination of the enthalpy of mixing for this ternary system is aimed at providing an alternative to applications using lead-based solder. The ultimate objective of this study is to find a way to replace toxic lead-based solder with a non-toxic replacement that retains all of the desirable characteristics of the conventional solder.

The literature review suggests that there is no calorimetric data available for the Sn-Ga-In system. Therefore, we have undertaken to investigate this system. In this chapter, we used a drop calorimeter to determine the partial and integral enthalpies of mixing for Sn-Ga-In ternary alloy system along six of the cross sections (see **Figure 4.1** for more information) at different temperatures of 673 K, 723 K, and 773 K. Pieces of pure tin were dropped into molten $Ga_{0.25}In_{0.75}$, $Ga_{0.50}In_{0.50}$, $Ga_{0.75}In_{0.25}$ alloys and pieces of pure Indium were dropped into $Ga_{0.25}Sn_{0.75}$, $Ga_{0.50}Sn_{0.50}$, $Ga_{0.75}Sn_{0.25}$. Molar enthalpies of mixing were calculated from the partial molar enthalpies. Plotting iso-enthalpy curves was then accomplished using

integral mixing enthalpy. It was discovered that the temperature affected the mixing enthalpies. Based on ternary enthalpy values, the substitutional solution RKM model was used to determine the interaction parameter; to get these parameters, least square fitting was employed. 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. These models use the binary interaction parameters and these parameters are deduced from the literature [155] . When the values getting from RKM model and measured experimental values are compared, it is found that there is a good agreement between them.

4.2 Experimental details

4.2.1 Materials

To investigate the thermodynamic behavior, a calorimetric analysis of a ternary alloy was conducted, employing high-purity metals—specifically, Ga, In, and Sn. Calibration was performed using α-Al_2O_3 needles sourced from the National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland, USA. To ensure cleanliness, the metals underwent a thorough cleaning with n-hexane in a supersonic bath. Subsequently, the metals were vacuum-dried within an antechamber glove box to eliminate any residual solvent. Following this, the metals were segmented into smaller pieces and accurately weighed to the precision of 10^{-4} g. The specifications for the pure metals and the use of protective Argon gas are detailed in **Table 4.1**.

Table 4.1 The materials used for this study.

Materials	Source	Initial purity (wt.%)
Indium(rod)	Alfa Aesar, Germany	99.999
Argon gas	Indian oxygen limited,	99.999 (vol %)
Tin (shots)	Alfa Aesar, Germany	99.999
Gallium(lumps)	Alfa Aesar, Germany	99.999

4.2.2 Calorimetric Measurements

Throughout this experimental investigation, a drop calorimeter (model number-MHTC 96 LINE EVO) manufactured by SETARAM Instruments in France was employed to gather enthalpy data related to the studied system. Ensuring constant cooling, a graphite tube type resistance furnace with a water-flowing arrangement around its exterior was utilized, and temperature monitoring inside was achieved through a thermopile equipped with 56 pairs of S-type thermocouples. The furnace's maximum operating temperature is 1593 K. To automate the introduction of metals into the crucible, a motorized device specifically designed for dropping was utilized. Calibration reference for the heat flow curve was established by dropping four pieces of α-Al_2O_3 needles at the conclusion of each sample series. The CALISTO software comprehensively monitors the calorimeter. Before the experiment commenced, specific amounts of two of the three metals were placed in the crucible with an outer diameter of 12 mm and a length of 60 mm. The CALISTO software regulated both the gas circulation and the water cooling system. Pre-programming included parameters such as the rate of heating and cooling, holding duration, and the rate of gas flow. Throughout the experiment, a continuous supply of argon at a rate of

approximately 30 mL/min was maintained to prevent oxidation of the alloys. Argon served dual roles as a carrier and protective gas during the entire experiment. Upon reaching the designated holding temperature, the automated motorized dropping system introduced the first sample into the crucible. The dropping device, equipped with a timer set to automatically release the sample every half an hour, ensured a systematic approach. The data acquisition software continuously recorded heat signals at 673 K, 723 K, and 773 K. Following the completion of all sample drops, α-Al_2O_3 standard samples were introduced to calibrate the heat signals towards the experiment's conclusion. Calorimetric investigation of the Sn-Ga-In ternary alloy system was executed employing the methodology outlined above. Pure tin specimens were introduced into molten $Ga_{0.25}In_{0.75}$, $Ga_{0.50}In_{0.50}$, $Ga_{0.75}In_{0.25}$ alloys, while pure indium pieces were dropped into $Ga_{0.25}Sn_{0.75}$, $Ga_{0.50}Sn_{0.50}$, $Ga_{0.75}Sn_{0.25}$ alloys. This study encompassed a total of six isopleths. A thermal equilibration process lasting approximately 16 hours was implemented to establish a stable baseline before introducing the sample material. To assess the negligible weight loss due to evaporation, the combined mass of both the crucible and samples was measured before and after the experiments. To ensure reproducibility, each experiment was conducted twice with identical variables. The acquired heat signals underwent integration using the CALISTO Data Processing software, which facilitated the determination of enthalpy values. Using the CALISTO data processing program, we were able to successfully integrate the peaks that appeared in the heat flow curve. The value of the heat signal that was obtained from the α-Al_2O_3 needle drops served as the basis for the calculation of the calibration constant (K). Calculating the

enthalpy, or heat effect, for each given heat signal requires the multiplication of the integral values of that signal by a known value (K).

Here, the reaction enthalpy **($\Delta H_{Reaction,X,i}$)** which is a function of heat effect **($\Delta H_{Signal,X,i} \cdot K$)** and the enthalpy**($\Delta H_{X,i}^{T_D \rightarrow T_M}$)** increment of the sample to be dropped, is calculated by **Equation 4.1** when species ***X*** is dropped from drop temperature **(T_D)** to bath temperature **(T_M)**.

$$\Delta H_{Reaction,X,i} = (\Delta H_{Signal,X,i} \cdot K) - (\Delta H_{X,i}^{T_D \rightarrow T_M} \cdot n_{X,i}) \quad \textbf{(4.1)}$$

Where $n_{X,i}$ (no. of moles) is the number of species ***X*** that was dropped into the liquid bath with the assistance of an automated dropping system, and each peak is associated with a distinct $\Delta H_{Signal,X,i}$ value, which is the integrated area (in µVs). It was computed using baseline integration methods for every peak. The change in the molar enthalpy of species ***X*** is represented by $\Delta H_{X,i}^{T_D \rightarrow T_M}$ and may be evaluated with the use of enthalpy data found in the literature [98] for each species within the appropriate temperature range.

Although a very small amount of species ***X*** was added in with the liquid metal in the crucible, **Equation 4.2** may be used to calculate the partial enthalpy $\Delta \bar{H}_{X,i}$ **:**

$$\Delta \bar{H}_{X,i} \approx \Delta H_{Reaction,X,i} / n_{X,i} \quad \textbf{(4.2)}$$

For each measurement, two of the three metals were added to the crucible in precise proportions before the third was added at the designated temperature. Pieces of pure tin were dropped into molten $Ga_{0.25}In_{0.75}$, $Ga_{0.50}In_{0.50}$, $Ga_{0.75}In_{0.25}$ alloys and pieces of pure Indium into $Ga_{0.25}Sn_{0.75}$, $Ga_{0.50}Sn_{0.50}$, $Ga_{0.75}Sn_{0.25}$. The integral molar mixing enthalpy **(ΔH_{mix})** of ternary system can be calculated by using **Equation 4.3**.

$$\Delta H_{mix} = \frac{(n_{binary}) * (\Delta_{mix} H_{respective\ binary}) + \sum \Delta H_{Reaction}}{(n_{binary} + \sum n_{X,i})} \quad \textbf{(4.3)}$$

Here $\boldsymbol{n_{binary}}$ = total no. of moles of two base metals in crucible

$\Delta_{mix}\boldsymbol{H_{respective\ binary}}$= enthalpy of mixing value for the initial composition of binary in the crucible

The literature [98] was referred to get In and Sn's enthalpy increase from room temperature to drop temperature, which was then included into **Equation 4.1**. 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. The experimental error of the calorimeter is anywhere from ten to twelve percent. It was discovered that the mistake in calibration brought on by dropping α-Al_2O_3 needles fell within a region that was no more than 1.5%.

4.3 Results and Discussion

4.3.1 Experimental Results

The partial and integral enthalpy of mixing values for the given ternary system at temperature of 673 K,723 K and 773 K were shown in the **Table 4.2 and 4.3** respectively. All the series of measurements are listed in **Table 4.4.** These experimental values are used to find the ternary interaction parameter values as given in **Table 4.5**.

Table 4.2 Integral and partial mixing enthalpies of Sn-Ga-In alloys when Sn dropped.

Added moles n_{Sn}	Mole fraction (x_{Sn})	Standard uncertainties $u(x_{Sn})$	Heat effect ($\Delta H_{Signal} \cdot K$) (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-1)	Integral Enthalpy ΔH_{mix} (J mol-1)
Series 1: $(Ga_{0.25}In_{0.75})_{1-x}Sn_x$ alloys; Starting amount: n_{Ga} = 0.003032 mol, n_{In} = 0.009192 mol ; Argon at pressure p = 1 bar; K = 0.002279 JµVs^{-1}, T_M = 673 K, T_D = 298 K, $\Delta H_{Sn}^{T_D \rightarrow T_M}$ = 17839.353 (J mol^{-1}), $\Delta mix H_{Ga-In}$ = 1295.775 (J mol^{-1})							
0.000564	0.0441	0.0005	10.878	0.007	0.817	1449	1303
0.000464	0.0776	0.0008	8.246	0.014	-0.031	-67	1255
0.000437	0.1070	0.0009	7.584	0.007	-0.212	-485	1199
0.000447	0.1353	0.0002	8.195	0.015	0.221	494	1177
0.000462	0.1626	0.0004	8.386	0.011	0.144	312	1149
0.000449	0.1876	0.0001	7.505	0.013	-0.505	-1125	1082
0.000477	0.2126	0.0005	8.228	0.014	-0.281	-589	1030
0.000469	0.2357	0.0004	7.893	0.015	-0.474	-1011	970
0.000446	0.2564	0.0003	7.793	0.007	-0.163	-365	934

0.000511	**0.2788**	**0.0008**	**8.730**	**0.014**	**-0.386**	**-755**	**883**
0.000464	0.2980	0.0003	7.918	0.007	-0.359	-774	839
0.000435	0.3151	0.0007	7.066	0.015	-0.694	-1595	780
0.000421	0.3309	0.0006	7.543	0.011	0.033	78	764
0.000422	0.3460	0.0008	7.209	0.013	-0.319	-756	729
0.000466	0.3619	0.0005	7.777	0.014	-0.536	-1150	684
0.000462	0.3770	0.0008	8.103	0.015	-0.139	-301	660
0.000472	0.3916	0.0009	8.096	0.007	-0.324	-686	629
0.000418	0.4040	0.0002	7.379	0.014	-0.078	-187	612
0.000506	0.4183	0.0004	8.510	0.007	-0.517	-1022	573
0.000314	0.4269	0.0001	5.413	0.015	-0.189	-602	555
0.001685	0.4689	0.0005	29.162	0.011	-0.897	-532	476
0.001828	0.5079	0.0004	31.848	0.013	-0.762	-417	410
0.001661	0.5388	0.0003	28.844	0.014	-0.787	-474	355
0.001767	0.5676	0.0008	31.385	0.015	-0.137	-78	328
0.001470	0.5890	0.0003	26.287	0.007	0.063	43	314
0.001752	0.6119	0.0007	30.779	0.014	-0.476	-272	281

Series 2: $(Ga_{0.25}In_{0.75})_{1-x}Sn_x$ alloys; Starting amount: n_{Ga} = 0.003032 mol, n_{In} = 0.009192 mol ;Argon at pressure p = 1 bar ;K = 0.002365 JμVs^{-1},T_M = 723 K, T_D = 298 K, $\Delta H_{Sn}^{T_D \rightarrow T_M}$ = 19266.2743 (J mol^{-1}), $\Delta mixH_{Ga-In}$ = 1246.684 (J mol^{-1})							
0.000555	0.0434	0.0004	10.066	0.015	-0.627	-1130	1143
0.000464	0.0769	0.0001	8.941	0.013	0.001	2	1103
0.000437	0.1064	0.0002	7.818	0.012	-0.601	-1375	1024
0.000448	0.1348	0.0004	7.936	0.004	-0.695	-1551	943
0.000461	0.1621	0.0006	7.814	0.002	-1.068	-2317	840
0.000449	0.1871	0.0003	7.856	0.013	-0.795	-1771	762
0.000477	0.2121	0.0005	8.021	0.014	-1.169	-2451	663
0.000469	0.2352	0.0003	8.404	0.007	-0.632	-1348	604
0.000447	0.2560	0.0002	7.912	0.015	-0.700	-1566	545
0.000510	0.2784	0.0004	9.274	0.007	-0.552	-1082	496
0.000465	0.2977	0.0001	7.835	0.015	-1.124	-2417	418
0.000434	0.3148	0.0002	7.651	0.013	-0.711	-1638	368
0.000421	0.3306	0.0004	7.082	0.012	-1.029	-2444	303
0.000422	0.3457	0.0006	7.668	0.004	-0.462	-1095	272
0.000466	0.3616	0.0003	8.298	0.002	-0.680	-1459	230
0.000463	0.3767	0.0005	8.473	0.013	-0.447	-965	201

0.000471	0.3913	0.0003	8.454	0.014	-0.620	-1316	166
0.000418	0.4037	0.0002	6.917	0.007	-1.136	-2718	107
0.000507	0.4181	0.0004	10.416	0.015	0.648	1278	135
0.000314	0.4267	0.0001	5.067	0.007	-0.983	-3131	87
0.001685	0.4687	0.0002	29.873	0.015	-2.591	-1538	-32
0.001743	0.5061	0.0004	33.123	0.013	-0.458	-263	-48
0.001662	0.5372	0.0006	30.986	0.012	-1.035	-623	-84
0.001766	0.5662	0.0003	33.168	0.004	-0.856	-485	-109
0.001470	0.5877	0.0005	28.359	0.002	0.038	26	-103
0.001752	0.6107	0.0003	32.655	0.013	-1.100	-628	-132
Series 3: $(Ga_{0.25}In_{0.75})_{1-x}Sn_x$ alloys; Starting amount: n_{Ga} = 0.003032 mol, n_{In} = 0.009192 mol; Argon at pressure p = 1 bar; K = 0.002323 JμVs^{-1}, T_M = 773 K, T_D = 298 K, $\Delta H_{Sn}^{T_D \rightarrow T_M}$ = 20699.9793 (J mol^{-1}), $\Delta mixH_{Ga-In}$ = 997.551 (J mol^{-1})							
0.000547	0.0428	0.0002	9.829	0.012	-1.494	-2731	838
0.000464	0.0764	0.0005	8.308	0.014	-1.297	-2795	710
0.000437	0.1059	0.0004	8.471	0.015	-0.575	-1316	646
0.000447	0.1342	0.0001	8.068	0.013	-1.185	-2651	541
0.000462	0.1616	0.0002	9.147	0.012	-0.416	-900	496
0.000449	0.1867	0.0004	8.193	0.004	-1.101	-2452	408

0.000477	0.2117	0.0007	8.547	0.002	-1.327	-2782	309
0.000469	0.2349	0.0003	8.667	0.011	-1.041	-2220	235
0.000446	0.2556	0.0004	8.750	0.014	-0.482	-1081	199
0.000511	0.2781	0.0002	9.430	0.007	-1.148	-2247	126
0.000464	0.2974	0.0005	9.247	0.011	-0.358	-772	102
0.000435	0.3145	0.0004	8.019	0.007	-0.985	-2264	44
0.000421	0.3303	0.0001	7.588	0.012	-1.127	-2677	-19
0.000422	0.3454	0.0002	8.835	0.014	0.100	237	-13
0.000466	0.3614	0.0004	9.189	0.015	-0.457	-981	-37
0.000462	0.3764	0.0007	8.764	0.013	-0.799	-1729	-76
0.000472	0.3911	0.0003	8.736	0.012	-1.034	-2191	-126
0.000418	0.4035	0.0004	7.638	0.004	-1.015	-2428	-173
0.000506	0.4179	0.0002	9.548	0.002	-0.926	-1830	-213
0.000314	0.4265	0.0005	5.949	0.011	-0.551	-1755	-236
0.001685	0.4685	0.0004	33.220	0.014	-1.659	-985	-291
0.001744	0.5059	0.0001	35.311	0.007	-0.790	-453	-302
0.001661	0.5370	0.0002	32.515	0.011	-1.868	-1125	-354
0.001767	0.5661	0.0004	36.013	0.007	-0.564	-319	-352
0.001470	0.5876	0.0007	29.732	0.012	-0.697	-474	-358

0.001752	0.6106	0.0003	36.463	0.014	0.197	112	-331
Series 4: $(Ga_{0.50}In_{0.50})_{1-x}Sn_x$ alloys; Starting amount: n_{Ga} = 0.004912 mol, n_{In} = 0.004887 mol; Argon at pressure p = 1 bar, K = 0.002428 JμVs^{-1}, T_M = 673 K, T_D = 298 K, $\Delta H_{Sn}^{T_D \rightarrow T_M}$ = 17839.353 (J mol^{-1}), $\Delta mixH_{Ga-In}$ = 1448.184 (J mol^{-1})							
0.000399	0.0391	0.0001	6.487	0.011	-0.631	-1581	1330
0.000490	0.0832	0.0002	8.480	0.013	-0.261	-533	1244
0.000471	0.1219	0.0006	8.480	0.011	0.078	166	1199
0.000495	0.1592	0.0005	8.389	0.015	-0.441	-891	1110
0.000575	0.1987	0.0003	9.796	0.012	-0.462	-803	1020
0.000451	0.2272	0.0005	7.639	0.015	-0.407	-902	952
0.000606	0.2625	0.0004	10.348	0.007	-0.463	-764	873
0.000480	0.2882	0.0002	8.211	0.002	-0.352	-733	817
0.000506	0.3134	0.0005	9.086	0.013	0.059	117	793
0.000442	0.3340	0.0004	7.440	0.016	-0.445	-1007	738
0.000464	0.3544	0.0001	7.802	0.007	-0.475	-1024	685
0.000428	0.3721	0.0002	7.368	0.011	-0.267	-624	649
0.000451	0.3897	0.0006	7.932	0.013	-0.114	-253	623
0.001697	0.4481	0.0005	29.735	0.011	-0.538	-317	534
0.001704	0.4964	0.0003	30.406	0.015	0.008	5	487

0.001723	0.5374	0.0005	31.442	0.012	0.705	409	481
0.001819	0.5740	0.0004	32.997	0.015	0.547	301	467
0.001784	0.6046	0.0002	32.012	0.007	0.187	105	441
0.001629	0.6290	0.0005	30.262	0.002	1.202	738	459
Series 5: $(Ga_{0.50}In_{0.50})_{1-x}Sn_x$ alloys; Starting amount: n_{Ga} = 0.004017 mol, n_{In} = 0.004008 mol ;Argon at pressure p = 1 bar ;K = 0.002364 JμVs^{-1}, T_M = 723 K, T_D = 298 K, $\Delta H_{Sn}^{T_D \rightarrow T_M}$= 19266.2743 (J mol^{-1}), $\Delta mixH_{Ga-In}$ = 1333.420 (J mol^{-1})							
0.000362	0.0432	0.0007	6.526	0.007	-0.448	-1238	1222
0.000444	0.0913	0.0003	8.001	0.012	-0.553	-1245	1098
0.000509	0.1408	0.0007	9.608	0.011	-0.199	-391	1017
0.000504	0.1848	0.0005	8.508	0.014	-1.202	-2385	843
0.000428	0.2188	0.0003	6.935	0.014	-1.311	-3063	680
0.000474	0.2532	0.0001	8.363	0.012	-0.769	-1622	579
0.000531	0.2884	0.0001	9.988	0.011	-0.242	-456	530
0.000529	0.3203	0.0004	8.795	0.012	-1.397	-2641	388
0.000508	0.3483	0.0006	9.193	0.002	-0.594	-1169	324
0.000433	0.3704	0.0003	8.179	0.002	-0.163	-376	300
0.000433	0.3911	0.0004	7.205	0.015	-1.137	-2626	204
0.000506	0.4136	0.0005	9.644	0.014	-0.105	-208	189

0.000499	0.4343	0.0002	9.186	0.009	-0.428	-858	152
0.001636	0.4928	0.0005	30.820	0.015	-0.700	-428	92
0.001723	0.5426	0.0003	31.960	0.005	-1.236	-717	12
0.001483	0.5782	0.0001	29.292	0.015	0.720	486	49
0.001664	0.6122	0.0002	31.479	0.011	-0.580	-349	17
Series 6: $(Ga_{0.50}In_{0.50})_{1-x}Sn_x$ alloys; Starting amount: n_{Ga} = 0.004125 mol, n_{In} = 0.004120 mol ;Argon at pressure p = 1 bar ;K = 0.002391 JμVs^{-1},T_M = 773 K, T_D = 298 K$\Delta H_{Sn}^{T_D \rightarrow T_M}$= 20699.9793 (J mol^{-1}), $\Delta mixH_{Ga-In}$ = 1228.286 (J mol^{-1})							
0.000459	0.0527	0.0004	10.166	0.011	0.665	1449	1240
0.000481	0.1023	0.0002	9.415	0.015	-0.542	-1127	1116
0.000450	0.1443	0.0003	9.234	0.012	-0.081	-180	1055
0.000526	0.1886	0.0005	10.424	0.014	-0.464	-882	955
0.000502	0.2268	0.0006	10.526	0.015	0.135	269	923
0.000441	0.2575	0.0003	8.318	0.013	-0.811	-1839	813
0.000506	0.2898	0.0007	10.581	0.012	0.107	211	787
0.000424	0.3149	0.0003	7.708	0.004	-1.069	-2521	670
0.000431	0.3385	0.0009	7.749	0.011	-1.173	-2722	553
0.000468	0.3625	0.0005	9.383	0.015	-0.305	-652	510
0.000463	0.3845	0.0004	8.975	0.012	-0.609	-1315	446

0.000472	0.4055	0.0004	8.885	0.014	-0.885	-1875	367
0.000544	0.4279	0.0002	11.010	0.015	-0.251	-461	336
0.000441	0.4449	0.0003	8.429	0.013	-0.700	-1587	279
0.000466	0.4618	0.0005	9.074	0.012	-0.572	-1227	233
0.001580	0.5121	0.0006	32.268	0.004	-0.438	-277	185
0.001599	0.5543	0.0003	30.874	0.011	-2.225	-1391	49
0.001615	0.5901	0.0007	32.021	0.015	-1.409	-872	-25
0.001402	0.6168	0.0003	28.706	0.012	-0.315	-225	-38
Series 7: $(Ga_{0.75}In_{0.25})_{1-x}Sn_x$ alloys; Starting amount: n_{Ga} = 0.008531 mol, n_{In} = 0.002844 mol; Argon at pressure p = 1 bar; K = 0.002235 JμVs^{-1}, T_M = 673 K, T_D = 298 K, $\Delta H_{Sn}^{T_D \rightarrow T_M}$ = 17839.353 (J mol^{-1}), $\Delta mixH_{Ga-In}$ = 1027.310 (J mol^{-1})							
0.000529	0.0444	0.0001	8.594	0.003	-0.843	-1594	911
0.000558	0.0872	0.0006	8.911	0.012	-1.043	-1869	786
0.000522	0.1239	0.0003	9.213	0.011	-0.099	-190	747
0.000361	0.1476	0.0007	6.452	0.017	0.012	33	728
0.000539	0.1807	0.0005	9.057	0.012	-0.558	-1035	659
0.000369	0.2019	0.0002	6.438	0.013	-0.145	-393	632
0.000551	0.2316	0.0003	10.132	0.013	0.303	550	629
0.000525	0.2579	0.0002	8.860	0.014	-0.506	-964	575

0.000452	0.2792	0.0007	8.061	0.005	-0.002	-4	558
0.000517	0.3021	0.0003	8.947	0.004	-0.276	-534	523
0.000424	0.3198	0.0004	7.969	0.013	0.405	955	534
0.000505	0.3397	0.0003	9.662	0.014	0.653	1293	556
0.000431	0.3558	0.0002	7.320	0.007	-0.369	-856	522
0.000452	0.3719	0.0004	8.249	0.017	0.186	412	519
0.000598	0.3920	0.0006	11.330	0.007	0.662	1107	538
0.001237	0.4297	0.0001	22.421	0.015	0.354	286	522
0.001642	0.4731	0.0002	30.912	0.011	1.620	987	558
0.001580	0.5090	0.0004	29.071	0.013	0.885	560	558
0.001605	0.5408	0.0008	29.591	0.015	0.959	598	560
0.001645	0.5694	0.0004	31.411	0.017	2.065	1255	604
0.001678	0.5951	0.0005	32.142	0.013	2.208	1316	646
0.001588	0.6168	0.0004	29.342	0.010	1.013	638	646
Series 8: $(Ga_{0.75}In_{0.25})_{1-x}Sn_x$ alloys; Starting amount: n_{Ga} = 0.008531 mol, n_{In} = 0.002844 mol; Argon at pressure p = 1 bar; K = 0.002366 JμVs^{-1}, T_M = 723 K ,T_D = 298 K, , $\Delta H_{Sn}^{T_D \rightarrow T_M}$ = 19266.2743 (J mol^{-1}), $\Delta mixH_{Ga-In}$ = 943.148 (J mol^{-1})							
0.000537	0.0451	0.0005	9.878	0.015	-0.468	-872	861
0.000550	0.0872	0.0004	14.542	0.014	0.049	89	827

0.000522	0.1239	0.0001	13.767	0.015	0.012	23	795
0.000361	0.1476	0.0002	8.848	0.013	-0.665	-1842	724
0.000539	0.1807	0.0007	13.381	0.012	-0.822	-1525	636
0.000369	0.2019	0.0006	10.165	0.004	0.441	1195	651
0.000551	0.2316	0.0003	13.443	0.002	-1.076	-1953	554
0.000525	0.2579	0.0004	13.999	0.011	0.165	314	546
0.000452	0.2792	0.0005	11.715	0.014	-0.196	-434	518
0.000525	0.3024	0.0004	13.166	0.007	-0.668	-1272	460
0.000424	0.3201	0.0001	12.058	0.015	0.885	2087	501
0.000506	0.3400	0.0002	12.749	0.014	-0.585	-1156	453
0.000431	0.3561	0.0007	11.673	0.015	0.316	733	459
0.000451	0.3722	0.0006	11.523	0.013	-0.361	-800	428
0.000598	0.3922	0.0003	15.793	0.012	0.035	59	416
0.001237	0.4299	0.0004	32.809	0.004	0.213	172	401
0.001643	0.4733	0.0005	44.449	0.002	1.154	702	424
0.001579	0.5092	0.0004	41.613	0.011	0.005	3	395
0.001605	0.5410	0.0001	44.052	0.014	1.759	1096	441
0.001645	0.5695	0.0002	43.206	0.007	-0.141	-86	408
0.001678	0.5952	0.0007	45.116	0.015	0.899	536	416

0.001588	0.6169	0.0006	42.704	0.014	0.859	541	422
Series 9: $(Ga_{0.75}In_{0.25})_{1-x}Sn_x$ alloys; Starting amount: n_{Ga} = 0.008531 mol, n_{In} = 0.002844 mol ;Argon at pressure p = 1 bar ; K = 0.002235 JμVs^{-1}, T_M = 773 K T_D = 298 K, $\Delta H_{Sn}^{T_D \rightarrow T_M}$ = 20699.9793 (J mol^{-1}), $\Delta mixH_{Ga-In}$ = 916.001 (J mol^{-1})							
0.000521	0.0438	0.0002	12.589	0.009	1.804	3463	1028
0.000557	0.0866	0.0003	13.811	0.013	2.281	4095	1165
0.000523	0.1234	0.0005	11.881	0.011	1.055	2017	1199
0.000360	0.1471	0.0004	8.515	0.015	1.063	2953	1246
0.000539	0.1802	0.0001	11.217	0.014	0.060	111	1202
0.000370	0.2015	0.0002	7.398	0.015	-0.261	-705	1153
0.000551	0.2312	0.0007	12.336	0.013	0.930	1688	1173
0.000525	0.2576	0.0006	11.133	0.012	0.266	507	1150
0.000451	0.2788	0.0003	9.524	0.004	0.188	417	1129
0.000517	0.3017	0.0004	10.882	0.002	0.180	348	1104
0.000424	0.3194	0.0002	7.735	0.011	-1.042	-2458	1014
0.000506	0.3394	0.0003	11.775	0.014	1.301	2571	1060
0.000431	0.3555	0.0005	9.017	0.007	0.095	220	1039

0.000451	0.3716	0.0004	9.421	0.015	0.085	188	1018
0.000599	0.3917	0.0001	11.743	0.007	-0.656	-1095	950
0.001236	0.4294	0.0002	26.445	0.015	0.860	696	934
0.001643	0.4729	0.0007	34.002	0.011	-0.008	-5	863
0.001579	0.5088	0.0006	33.204	0.013	0.519	329	826
0.001605	0.5407	0.0003	32.194	0.014	-1.029	-641	731
0.001645	0.5693	0.0004	33.563	0.015	-0.488	-297	667
0.001678	0.5950	0.0005	34.951	0.013	0.216	129	635
0.001588	0.6167	0.0003	31.337	0.012	-1.535	-967	549

[a]Standard uncertainties u are: $u(T_M)$ = 0.2 K, $u(p)$ = 17 kPa, $u(n_{In})$ = 0.000002 mol , $u(n_{Sn})$ = 0.000004 mol ,$u(n_{Ga})$ = 0.000003 mol, $u(\Delta H_{Reaction})$ = 0.002 J; Series 1: $u(\Delta_{mix}H)$ = 130 J mol^{-1}, $u(K)$ = 0.000001 J/μV s; Series 2: $u(\Delta_{mix}H)$ = 114 Jmol^{-1}, $u(K)$ = 0.000007 J/μVs ;Series 3: $u(\Delta_{mix}H)$ = 83 Jmol^{-1},$u(K)$ = 0.000003 J/μV s; Series 4: $u(\Delta_{mix}H)$ = 132 J mol^{-1}; $u(K)$ = 0.000001 J /μV s; Series 5: $u(\Delta_{mix}H)$ = 122 J mol^{-1}, $u(K)$ = 0.000002 J/μV s; Series 6: $u(\Delta_{mix}H)$ = 123 J mol^{-1}, $u(K)$ = 0.000002 J/μV s; Series 7: $u(\Delta_{mix}H)$ =91 J mol^{-1},$u(K)$ = 0. 000004 J/μV s; Series 8: $u(\Delta_{mix}H)$ = 86 J mol^{-1}, $u(K)$ = 0. 000002 J/μVs; Series 9: $u(\Delta_{mix}H)$ = 124 J mol^{-1}, $u(K)$ = 0. 000007 J/μV s;K = Calibration constant

Table 4.3 Integral and partial mixing enthalpies of Sn-Ga-In alloys when In dropped.

Added moles n_{In}	Mole fraction (x_{In})	Standard uncertainties u(x_{In})	Heat effect H_{Signal}· 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^{-1})	Integral Enthalpy ΔH_{mix} (J mol^{-1})
Series 1: $(Ga_{0.25}Sn_{0.75})_{1-x}In_x$ alloys; Starting amount: n_{Ga} = 0.006233 mol, n_{Sn} = 0.018715 mol; Argon at pressure p = 1 bar; K = 0.002216 JμVs^{-1}, T_D = 298 K, T_M = 673 K, $\Delta H_{In}^{T_D \rightarrow T_M}$=14100 (J mol^{-1}), $\Delta mix H_{Ga-Sn}$ =1106.147 (J mol^{-1})							
0.000853	0.0331	0.0003	8.857	0.009	-3.170	-3716	947
0.001252	0.0778	0.0005	11.227	0.011	-6.426	-5133	665
0.002171	0.1463	0.0004	27.885	0.014	-2.726	-1256	523
0.002064	0.2026	0.0005	26.933	0.007	-2.169	-1051	419
0.002215	0.2554	0.0003	33.148	0.014	1.916	865	448
0.002192	0.3011	0.0007	33.183	0.007	2.276	1038	485
0.003193	0.3585	0.0005	48.053	0.015	3.032	950	523
0.003070	0.4054	0.0004	45.530	0.011	2.243	731	538
0.002179	0.4348	0.0003	33.666	0.013	2.942	1350	578
0.002329	0.4631	0.0005	34.007	0.009	1.168	502	574
0.004004	0.5057	0.0004	61.061	0.011	4.605	1150	620

0.003860	0.5408	0.0005	55.360	0.014	0.934	242	593
0.002554	0.5614	0.0003	35.655	0.007	-0.356	-139	560
0.003065	0.5838	0.0007	46.292	0.014	3.075	1003	583
0.003277	0.6054	0.0005	47.399	0.007	1.193	364	571
Series 2: $(Ga_{0.25}Sn_{0.75})_{1-x}In_x$ alloys; Starting amount: n_{Ga} = 0.006232 mol, n_{Sn} = 0.018715 mol; Argon at pressure p = 1 bar; K = 0.002216 JμVs^{-1}, T_M = 723 K, T_D = 298 K, $\Delta H_{In}^{T_D \rightarrow T_M}$ = 15558.0555 (J mol^{-1}), $\Delta mixH_{Ga-Sn}$ = 1019.846 (J mol^{-1})							
0.000809	0.0314	0.0002	7.167	0.011	-5.419	-6698	777
0.001253	0.0763	0.0005	10.100	0.013	-9.394	-7497	394
0.002171	0.1451	0.0004	27.314	0.014	-6.463	-2977	143
0.002064	0.2015	0.0001	27.128	0.015	-4.984	-2415	-26
0.002215	0.2544	0.0002	35.474	0.013	1.013	457	6
0.002191	0.3002	0.0004	32.693	0.012	-1.395	-637	-34
0.003194	0.3578	0.0006	49.524	0.004	-0.168	-53	-35
0.003069	0.4048	0.0003	51.426	0.002	3.678	1198	55
0.002179	0.4342	0.0005	36.474	0.013	2.573	1181	111
0.002330	0.4626	0.0003	37.215	0.011	0.965	414	126
0.004004	0.5053	0.0002	65.369	0.013	3.075	768	177
0.003860	0.5405	0.0002	61.684	0.014	1.630	422	194

0.002553	0.5611	0.0005	43.577	0.015	3.857	1511	254
0.003065	0.5836	0.0004	47.735	0.013	0.050	16	241
0.003277	0.6052	0.0001	53.291	0.012	2.307	704	265
Series 3: $(Ga_{0.25}Sn_{0.75})_{1-x}In_x$ alloys Starting amount: n_{Ga} = 0.006233 mol, n_{Sn} = 0.018715 mol; Argon at pressure p = 1 bar; K = 0.002226 JμVs^{-1}, T_M = 773 K, T_D = 298 K, $\Delta H_{In}^{T_D \rightarrow T_M}$ = 17012 (J mol^{-1}), $\Delta mixH_{Ga-Sn}$ = 723.217 (J mol^{-1})							
0.000835	0.0324	0.0004	9.124	0.014	-5.081	-6085	503
0.001253	0.0772	0.0001	18.417	0.015	-2.899	-2314	372
0.002171	0.1458	0.0002	29.487	0.013	-7.446	-3430	90
0.002064	0.2022	0.0004	31.031	0.012	-4.082	-1978	-47
0.002215	0.2550	0.0007	35.423	0.004	-2.259	-1020	-111
0.002191	0.3007	0.0003	34.223	0.002	-3.050	-1392	-190
0.003194	0.3582	0.0004	55.215	0.011	0.879	275	-152
0.003069	0.4052	0.0003	49.587	0.014	-2.623	-855	-203
0.002179	0.4345	0.0002	36.889	0.007	-0.180	-83	-197
0.002330	0.4629	0.0004	41.948	0.014	2.310	991	-138
0.004004	0.5055	0.0001	66.036	0.015	-2.080	-519	-168
0.003860	0.5407	0.0002	61.721	0.013	-3.945	-1022	-229
0.002553	0.5613	0.0004	48.082	0.012	4.650	1821	-137

0.003065	0.5837	0.0007	52.522	0.004	0.380	124	-123
0.003278	0.6053	0.0003	56.168	0.002	0.403	123	-110
Series 4: $(Ga_{0.50}Sn_{0.50})_{1-x}In_x$ alloys; Starting amount: n_{Ga} = 0.006920 mol, n_{Sn} = 0.006921 mol; Argon at pressure p = 1 bar; K = 0.002127 JμVs^{-1}, T_M = 673 K ,T_D = 298 K, $\Delta H_{In}^{T_D \rightarrow T_M}$ = 14100 (J mol^{-1}), $\Delta mixH_{Ga-Sn}$ = 1017.403 (J mol^{-1})							
0.001183	0.0787	0.0004	12.787	0.014	-3.893	-3291	678
0.001125	0.1429	0.0003	14.268	0.007	-1.595	-1418	532
0.001110	0.1980	0.0002	15.360	0.014	-0.291	-262	481
0.001074	0.2450	0.0005	16.921	0.015	1.778	1655	550
0.001318	0.2957	0.0007	22.158	0.013	3.574	2712	695
0.000984	0.3292	0.0001	15.105	0.012	1.231	1251	721
0.001554	0.3762	0.0002	24.511	0.004	2.600	1673	788
0.001484	0.4153	0.0006	24.615	0.002	3.691	2487	895
0.002144	0.4639	0.0005	34.762	0.011	4.532	2114	996
0.002099	0.5042	0.0003	32.527	0.014	2.931	1396	1026
0.002307	0.5420	0.0005	34.864	0.007	2.335	1012	1025
0.002201	0.5731	0.0004	34.551	0.014	3.517	1598	1064
0.002295	0.6013	0.0002	35.692	0.015	3.332	1452	1089
0.001426	0.6171	0.0005	20.295	0.013	0.188	132	1052

Series 5: $(Ga_{0.50}Sn_{0.50})_{1-x}In_x$ alloys; Starting amount: n_{Ga} = 0.006920 mol, n_{Sn} = 0.006921 mol; Argon at pressure p=1 bar; K = 0.002216 JμVs^{-1}, T_M = 723 K, T_D = 298 K, $\Delta H_{In}^{T_D \rightarrow T_M}$ = 15558.0555 (J mol^{-1}), $\Delta mixH_{Ga-Sn}$ = 1172.614 (J mol^{-1})							
0.001174	0.0782	0.0008	12.157	0.007	-6.108	-5203	674
0.001125	0.1424	0.0006	13.069	0.012	-4.434	-3941	352
0.001111	0.1977	0.0004	17.035	0.011	-0.250	-225	315
0.001074	0.2447	0.0005	17.522	0.014	0.813	757	341
0.001317	0.2953	0.0004	20.723	0.012	0.233	177	330
0.000985	0.3290	0.0001	17.235	0.015	1.910	1939	407
0.001553	0.3760	0.0007	24.705	0.013	0.543	350	403
0.001484	0.4151	0.0004	25.848	0.012	2.760	1860	494
0.002145	0.4637	0.0005	36.401	0.004	3.029	1412	571
0.002099	0.5040	0.0003	36.308	0.003	3.652	1740	659
0.002306	0.5419	0.0002	37.883	0.015	2.006	870	675
0.002202	0.5730	0.0003	35.419	0.017	1.160	527	665
0.002295	0.6013	0.0001	39.308	0.007	3.602	1569	724
0.001425	0.6170	0.0005	23.479	0.013	1.309	919	732

Series 6: $(Ga_{0.50}Sn_{0.50})_{1-x}In_x$ alloys; Starting amount: n_{Ga} = 0.006920 mol, n_{Sn} = 0.006921 mol; Argon at pressure p = 1 bar; K = 0.002226 JμVs^{-1}, T_M = 773 K, T_D = 298 K, $\Delta H_{In}^{T_D \rightarrow T_M}$ = 17012 (J mol^{-1}), $\Delta mixH_{Ga-Sn}$ = 1377.370 (J mol^{-1})							
0.001200	0.0798	0.0004	18.933	0.005	-1.481	-1234	1169
0.001125	0.1438	0.0003	16.207	0.011	-2.932	-2606	906
0.001111	0.1989	0.0007	19.202	0.015	0.302	272	865
0.001074	0.2458	0.0005	18.005	0.012	-0.266	-248	800
0.001317	0.2963	0.0004	19.832	0.014	-2.573	-1954	616
0.000985	0.3298	0.0002	16.323	0.015	-0.434	-441	566
0.001553	0.3767	0.0003	25.965	0.013	-0.455	-293	505
0.001485	0.4158	0.0005	25.740	0.012	0.477	321	494
0.002144	0.4643	0.0006	35.669	0.004	-0.805	-375	422
0.002099	0.5045	0.0003	35.804	0.002	0.096	46	394
0.002306	0.5423	0.0007	40.684	0.014	1.454	631	412
0.002202	0.5734	0.0003	37.648	0.014	0.188	85	389
0.002295	0.6015	0.0009	39.247	0.007	0.204	89	370
0.001425	0.6173	0.0005	23.895	0.015	-0.347	-244	345

Series 7: $(Ga_{0.75}Sn_{0.25})_{1-x}In_x$ alloys; Starting amount: n_{Ga} = 0.011893 mol, n_{Sn} = 0.003977 mol; Argon at pressure p = 1 bar; K = 0.002127 JμVs^{-1}, T_M = 673 K, T_D = 298 K, $\Delta H_{In}^{T_D \rightarrow T_M}$ = 14100 (J mol^{-1}), $\Delta mixH_{Ga-Sn}$ = 713.531 (J mol^{-1})							
0.000846	0.0506	0.0003	11.190	0.005	-0.739	-874	633
0.001412	0.1246	0.0006	19.357	0.017	-0.552	-391	553
0.001763	0.2022	0.0001	26.516	0.014	1.658	940	588
0.001774	0.2675	0.0005	30.231	0.015	5.218	2941	780
0.002469	0.3424	0.0004	42.097	0.012	7.284	2950	1002
0.002761	0.4099	0.0002	45.201	0.013	6.271	2271	1133
0.000861	0.4282	0.0003	13.095	0.013	0.955	1109	1132
0.003506	0.4924	0.0005	58.541	0.012	9.106	2597	1296
0.002372	0.5282	0.0007	36.978	0.007	3.533	1489	1310
0.002886	0.5654	0.0003	46.544	0.002	5.851	2027	1367
0.003409	0.6025	0.0004	51.746	0.012	3.679	1079	1342
0.003108	0.6312	0.0003	47.508	0.014	3.685	1186	1331
0.003124	0.6562	0.0003	47.222	0.009	3.174	1016	1309
0.003678	0.6816	0.0004	55.035	0.013	3.175	863	1277
0.001919	0.6934	0.0004	28.513	0.007	1.455	758	1257

Series 8: $(Ga_{0.75}Sn_{0.25})_{1-x}In_x$ alloys: Starting amount: n_{Ga} = 0.011893 mol, n_{Sn} = 0.003977 mol; Argon at pressure p = 1 bar; K = 0.002216 JμVs^{-1}, T_M = 723 K, T_D = 298 K, $\Delta H_{In}^{T_D \rightarrow T_M}$ = 15558.0555(J mol^{-1}), $\Delta mixH_{Ga-Sn}$ = 758.548 (J mol^{-1})							
0.000793	0.0476	0.0005	10.476	0.008	-1.862	-2348	611
0.001439	0.1233	0.0002	39.047	0.013	1.128	784	624
0.001763	0.2011	0.0003	47.757	0.012	1.300	737	634
0.001809	0.2678	0.0004	50.096	0.015	2.427	1342	693
0.002468	0.3426	0.0004	70.320	0.017	5.286	2142	842
0.002762	0.4101	0.0002	77.062	0.015	4.281	1550	914
0.000860	0.4284	0.0002	24.985	0.017	2.323	2701	970
0.003507	0.4925	0.0007	99.125	0.012	6.712	1914	1076
0.002363	0.5282	0.0005	64.859	0.004	2.592	1097	1077
0.002886	0.5654	0.0003	80.003	0.003	3.954	1370	1100
0.003409	0.6025	0.0003	93.255	0.011	3.424	1004	1092
0.003108	0.6312	0.0003	87.042	0.014	5.143	1655	1133
0.003124	0.6562	0.0004	84.658	0.007	2.337	748	1107
0.003678	0.6816	0.0005	100.344	0.015	3.425	931	1094

Series 9: $(Ga_{0.75}Sn_{0.25})_{1-x}In_x$ alloys; Starting amount: n_{Ga} = 0.011893 mol, n_{Sn} = 0.003977 mol; Argon at pressure p = 1 bar; K = 0.002137 JμVs^{-1}, T_M = 773 K, T_D = 298 K, $\Delta H_{In}^{T_D \rightarrow T_M}$ = 17012 (J mol^{-1}), $\Delta mixH_{Ga-Sn}$ = 821.455 (J mol^{-1})							
0.000793	0.0476	0.0005	16.011	0.005	2.520	3178	934
0.001413	0.1220	0.0002	28.821	0.011	4.783	3385	1125
0.001763	0.2001	0.0004	34.123	0.013	4.131	2343	1233
0.001809	0.2669	0.0005	32.205	0.015	1.430	790	1196
0.002468	0.3419	0.0007	43.986	0.015	2.000	810	1157
0.002762	0.4096	0.0001	46.655	0.015	-0.332	-120	1026
0.000860	0.4279	0.0003	16.917	0.014	2.287	2659	1076
0.003507	0.4921	0.0005	61.124	0.013	1.463	417	1002
0.002363	0.5278	0.0006	39.412	0.005	-0.787	-333	908
0.002886	0.5651	0.0003	51.819	0.003	2.722	943	911
0.003409	0.6023	0.0004	59.182	0.011	1.188	348	863
0.003108	0.6310	0.0002	56.931	0.017	4.058	1306	895
0.003123	0.6560	0.0002	51.138	0.007	-1.990	-637	791
0.003679	0.6814	0.0004	63.745	0.017	1.158	315	756
0.001919	0.6932	0.0005	33.230	0.007	0.584	304	739

[a]**Standard uncertainties u are: $u(T_M)$ = 0.2 K, $u(p)$ = 10 kPa, $u(n_{Sn})$ = 0.000003 mol, $u(n_{Ga})$ = 0.000002 mol, $u(n_{In})$ = 0.000004 mol, $u(\Delta H_{Reaction})$ = 0.002 J; Series 1: $u(\Delta_{mix}H)$ = 90 J mol^{-1},$u(K)$ = 0.000003 J /μV s; Series 2: $u(\Delta_{mix}H)$ =71 Jmol^{-1},$u(K)$ = 0.000001 J /μV s , Series 3: $u(\Delta_{mix}H)$ = 51 J mol^{-1}, $u(K)$ = 0.000004 J /μV s; Series 4: $u(\Delta_{mix}H)$ = 65 J mol^{-1}, $u(K)$ = 0.000003 J /μV s, Series 5:$u(\Delta_{mix}H)$ = 73 J mol^{-1}, (K) = 0.000002 J /μV s^{1}; Series 6: $u(\Delta_{mix}H)$ = 116 J mol^{-1}, $u(K)$ = 0.000002 J /μV s; Series 7: $u(\Delta_{mix}H)$ =135 J mol^{-1}, $u(K)$ = 0.000004 J /μV s; Series 8: $u(\Delta_{mix}H)$ = 108 J mol^{-1}, $u(K)$ = 0.000003 J /μV s; Series 9: $u(\Delta_{mix}H)$ = 120 J mol^{-1}, $u(K)$ = 0. 000002 J /μV s ;K = Calibration constant**

Table 4.4 List of all series of measurements along different isopleths and at different temperatures.

	Series	Composition	Temperature	Drop element
As listed in table 4.2	1	$x_{Ga} : x_{In} = 1:3$	673 K	Sn
	2	$x_{Ga} : x_{In} = 1:3$	723 K	Sn
	3	$x_{Ga} : x_{In} = 1:3$	773 K	Sn
	4	$x_{Ga} : x_{In} = 1:1$	673 K	Sn
	5	$x_{Ga} : x_{In} = 1:1$	723 K	Sn
	6	$x_{Ga} : x_{In} = 1:1$	773 K	Sn
	7	$x_{Ga} : x_{In} = 3:1$	673 K	Sn
	8	$x_{Ga} : x_{In} = 3:1$	723 K	Sn
	9	$x_{Ga} : x_{In} = 3:1$	773 K	Sn
As listed in table 4.3	**1**	$x_{Ga} : x_{Sn} = 1:3$	673 K	In
	2	$x_{Ga} : x_{Sn} = 1:3$	723 K	In
	3	$x_{Ga} : x_{Sn} = 1:3$	773 K	In
	4	$x_{Ga} : x_{Sn} = 1:1$	673 K	In
	5	$x_{Ga} : x_{Sn} = 1:1$	723 K	In
	6	$x_{Ga} : x_{Sn} = 1:1$	773 K	In
	7	$x_{Ga} : x_{Sn} = 3:1$	673 K	In
	8	$x_{Ga} : x_{Sn} = 3:1$	723 K	In
	9	$x_{Ga} : x_{Sn} = 3:1$	773 K	In

4.3.1 Theoretical Models

Using different theoretical models, one may extrapolate the thermodynamic features of ternary or higher order systems from data on binary systems. Ansara and Dupin's theoretical model is a major contribution [143]. Luef et al. [127] have also used the Redlich-Kister-Muggianu polynomial for substitutional solutions. To determine the ternary interaction parameters, we performed a least-squares fit to the available data using **Equation 4.4.**

$$\Delta H_{mix} = \sum_i \sum_{j>i} \left[x_i x_j \sum_v L_{i:j}^{(v)} (x_i - x_j)^v \right] + x_i x_j x_k (L_{i:j:k}^0 x_{Sn} + L_{i:j:k}^1 x_{Ga} + L_{i:j:k}^2 x_{In}) \quad \text{.....(4.4)}$$

where $L_{i:j}^{(v)}$ (v= 0, 1, 2, …) are the interaction parameters(binary) of the binary systems and $L_{i:j:k}^{v}$ (ν= 0, 1, 2,…) are the interaction parameters(ternary). The experimentally determined mixing enthalpy is then compared with the estimated values, with just the binary contributions being taken into consideration. **Table 4.4** contains the results of the binary interaction parameter that was derived from the data that was accessible in the literature for all binary systems [155]. The difference between the two values shows the contribution of the ternary interaction to this system, which may then be optimized using **Equation 4.4**.

Table 4.5 Binary interaction parameters as a function of temperature(T).

Interaction parameter	Order(v)	(J/mol)
L^{v}_{Ga-Sn} [155]	*0*	**14.40*T*-5653**
	1	**0.12T^2-167.45*T*+58125**
	2	**-86.90*T*+62076**
	3	**96.93*T*-67943**
L^{v}_{Ga-In} [155]	*0*	**-8.83*T*+11735**
	1	**13.21*T*-10519**
	2	**-0.33T^2+470.04*T*-164828**
	3	**1.06T^2-1542.22*T*+559523**
L^{v}_{In-Sn} [155]	*0*	**-731**
	1	**-305**
	2	**-813**
	3	**-657**
$L^{v}_{Ga-In-Sn}$	*0*	**-312.393*T*+183220**
	1	**654.2*T*- 481046**
	2	**-528.873*T*+393622**

Table 4.6 Integral enthalpy of mixing values at the sites of intersection **a, b, c, d, e, f, g, h** also sees **Figure 4.1**.

Intersection	Integral enthalpy of mixing (J/mol)					
	673 K		**723 K**		**773 K**	
	Sn drops	**In drops**	**Sn drops**	**In drops**	**Sn drops**	**In drops**
a	441	419	17	-26	-25	-46
b	555	578	87	111	-213	-197
c	522	532	401	352	934	906
d	738	721	388	407	533	566
e	1082	1089	762	724	309	370
f	632	588	651	634	1153	1233
g	1110	1132	1017	970	1055	1076
h	1255	1257	1103	1094	710	739

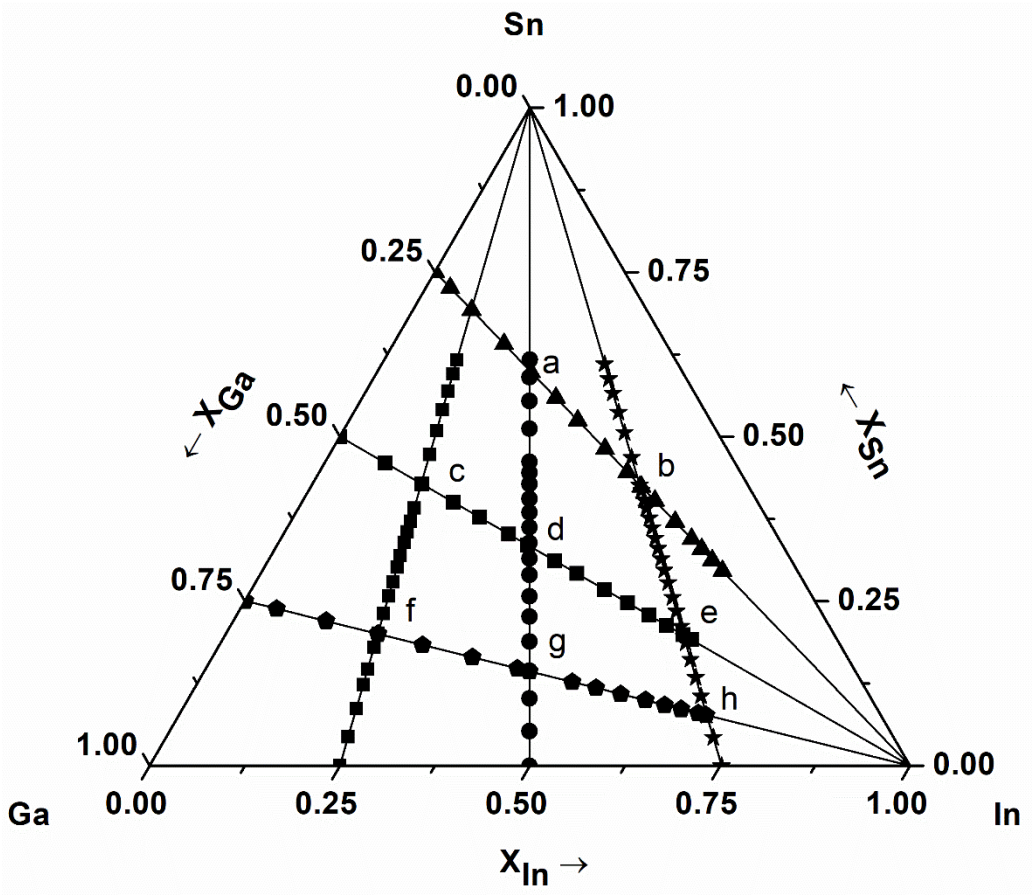

Fig. 4.1 Measured cross-sections (intersections **a** to **h** indicated, see **Table 4.6**) and alloy compositions in the Sn-Ga-In ternary system.

The enthalpies of mixing along six of the cross sections depicted in **Figure 4.1** for Sn-Ga-In Ternary alloy systems were determined at different temperatures of 673 K, 723 K, and 773 K. Pieces of pure tin were dropped into molten $Ga_{0.25}In_{0.75}$, $Ga_{0.50}In_{0.50}$, $Ga_{0.75}In_{0.25}$ alloys and pieces of pure Indium was dropped into $Ga_{0.25}Sn_{0.75}$, $Ga_{0.50}Sn_{0.50}$, $Ga_{0.75}Sn_{0.25}$ alloys. The closeness of readings near the intersection points on the six cross-sections indicates the quality of our experimental data (see **Table 4.6** and **Figure 4.1**). However, systemic errors, such as those resulting from insufficient mixing reactions, cannot be completely ruled out.

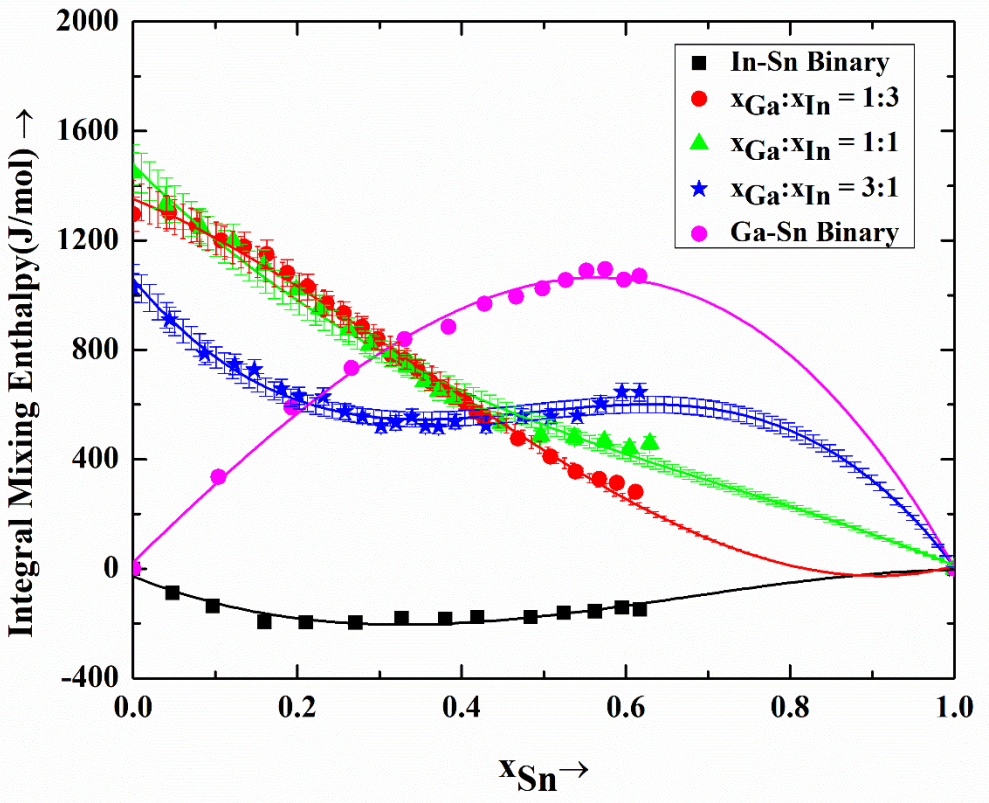

Fig. 4.2 Plot representing the enthalpies of mixing of the given ternary alloy system corresponding to cross-section of $(Ga_{0.25}In_{0.75})_{1-x}Sn_x$; circle, $(Ga_{0.50}In_{0.50})_{1-x}Sn_x$; triangle and $(Ga_{0.75}In_{0.25})_{1-x}Sn_x$; star at 673 K, In-Sn binary data from the literature [155] ; square ,Ga-Sn binary data from the literature [155]; half-filled circle and solid line represents RKM fitted polynomial curve.

As shown in **Figure 4.2**, the mixing enthalpy values for the two sections $(Ga_{0.50}In_{0.50})_{1-x}Sn_x$ and $(Ga_{0.75}In_{0.25})_{1-x}Sn_x$ are endothermic in nature but for section $(Ga_{0.25}In_{0.75})_{1-x}Sn_x$ it is showing exothermic nature for the composition of Sn ranging from 0.75 to 1. Exothermic or negative value of mixing enthalpy in this range tells about the region where the alloy is supposed to be more stable. Also it suggests that there is finite amount of interatomic interaction among three metals in this range as there is good chance of Gibb's energy to be negative as enthalpy is negative although it also depends on sign of entropy as well.

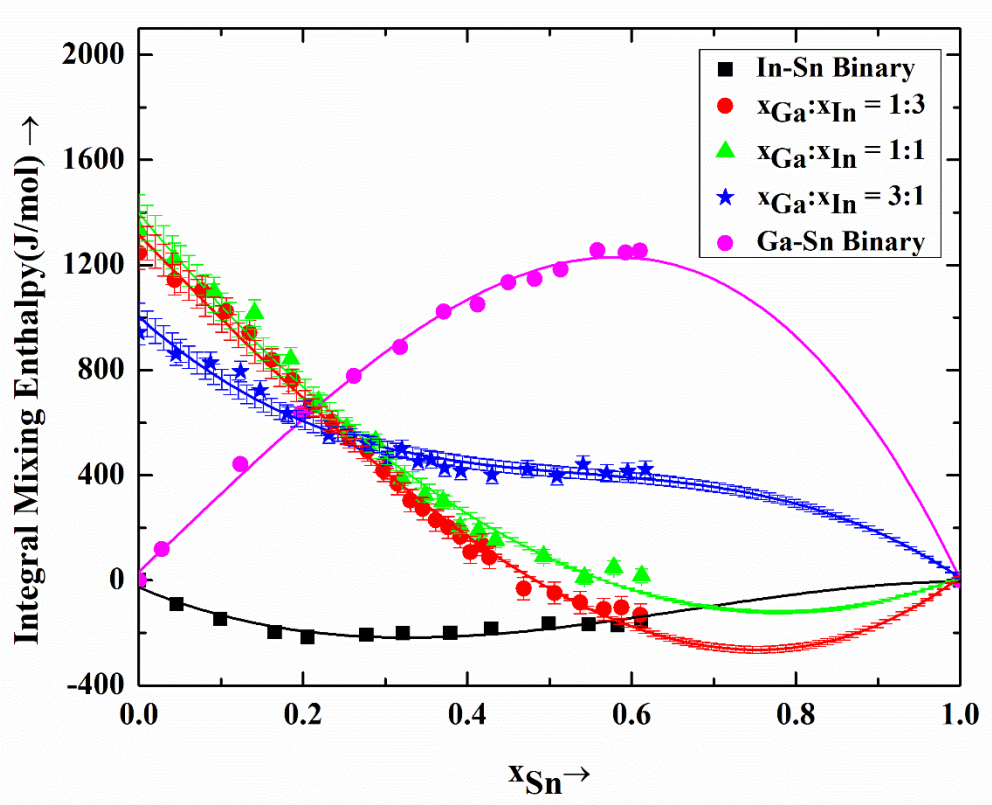

Fig. 4.3 Plot representing the enthalpies of mixing of the given ternary alloy system corresponding to cross-section of $(Ga_{0.25}In_{0.75})_{1-x}Sn_x$; circle, $(Ga_{0.50}In_{0.50})_{1-x}Sn_x$; triangle and $(Ga_{0.75}In_{0.25})_{1-x}Sn_x$; star at 723 K, In-Sn binary data from the literature [155]; square, Ga-Sn binary data from the literature [155]; half-filled circle and solid line represents RKM fitted polynomial curve.

Referring to **Figure 4.3**, the integral mixing enthalpy values for the section $(Ga_{0.25}In_{0.75})_{1-x}Sn_x$,$(Ga_{0.50}In_{0.50})_{1-x}Sn_x$ are getting negative or exothermic for the composition range of x_{Sn} between 0.5 to 1 but remains endothermic for the section $(Ga_{0.75}In_{0.25})_{1-x}Sn_x$. Exothermic or negative value of mixing enthalpy in this range tells about the region where the alloy is supposed to be more stable. Also it suggests that there is finite amount of interatomic interaction among three metal atoms in this range as there is good chance of Gibb's energy to be negative as enthalpy is negative although it also depends on sign of entropy as well. As mixing enthalpy values are small as compared to positive enthalpy values in this system, the stability of the alloys will mostly depend on the entropy of mixing.

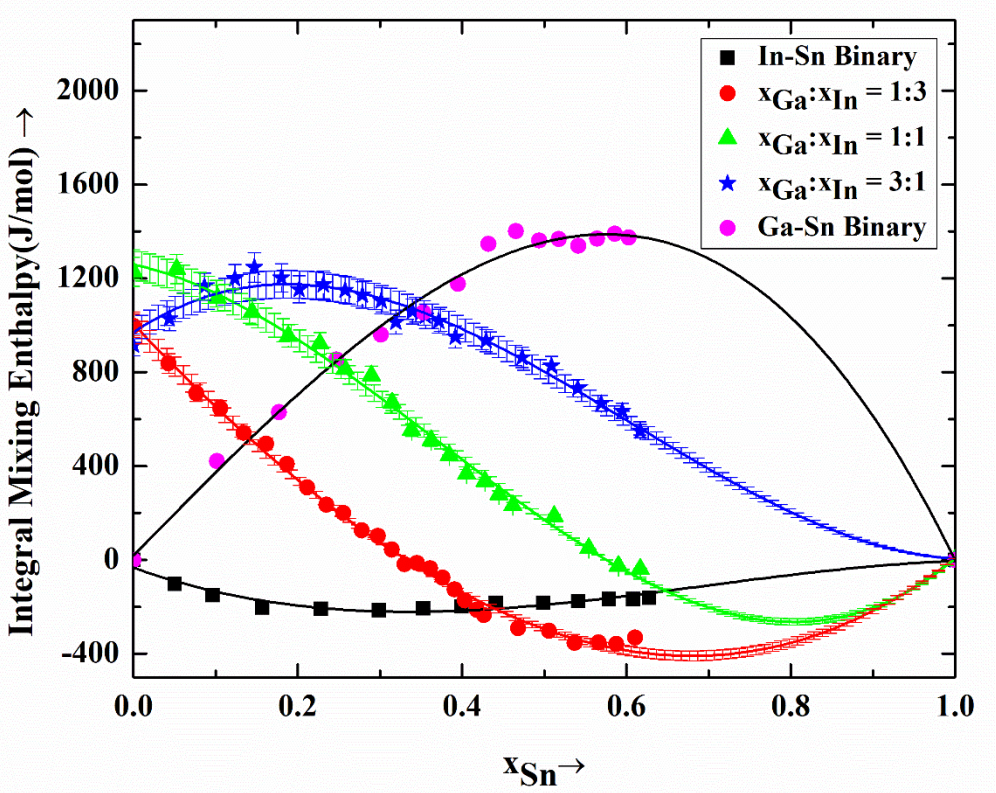

Fig. 4.4 Plot representing the enthalpies of mixing of the given ternary alloy system corresponding to cross-section of $(Ga_{0.25}In_{0.75})_{1-x}Sn_x$; circle, $(Ga_{0.50}In_{0.50})_{1-x}Sn_x$; triangle and $(Ga_{0.75}In_{0.25})_{1-x}Sn_x$; star at 773 K, In-Sn binary data from the literature [155]; square , Ga-Sn binary data from the literature [155]; half filled circle and solid line represents RKM fitted polynomial curve.

Referring to **Figure 4.4**, the integral mixing enthalpy values are positive for the section $(Ga_{0.75}In_{0.25})_{1-x}Sn_x$ throughout the composition of x_{Sn} but for two sections $(Ga_{0.25}In_{0.75})_{1-x}Sn_x$, $(Ga_{0.50}In_{0.50})_{1-x}Sn_x$, the values of integral mixing enthalpy are found to be negative or exothermic for the composition range of x_{Sn} between 0.3 to 1 and between 0.5 to 1 respectively. Exothermic or negative value of mixing enthalpy in this range tells about the region where the alloy is supposed to be more stable. Also it suggests that there is finite amount of interatomic interaction among three metal atoms in this range as there is good chance of Gibb's energy to be negative as enthalpy is negative although it also depends on sign of entropy as well. This is a non-ideal system departing very little from ideal enthalpy of mixing.

From **Figures 4.2,4.3** and **4.4**, it can be inferred that as the temperature increases from 673 K to 773 K, the two sections $(Ga_{0.25}In_{0.75})_{1-x}Sn_x$ and $(Ga_{0.50}In_{0.50})_{1-x}Sn_x$ are getting exothermic for large range of x_{Sn}. Addition of Sn makes the alloy more stable and it is also desired for the solder applications.

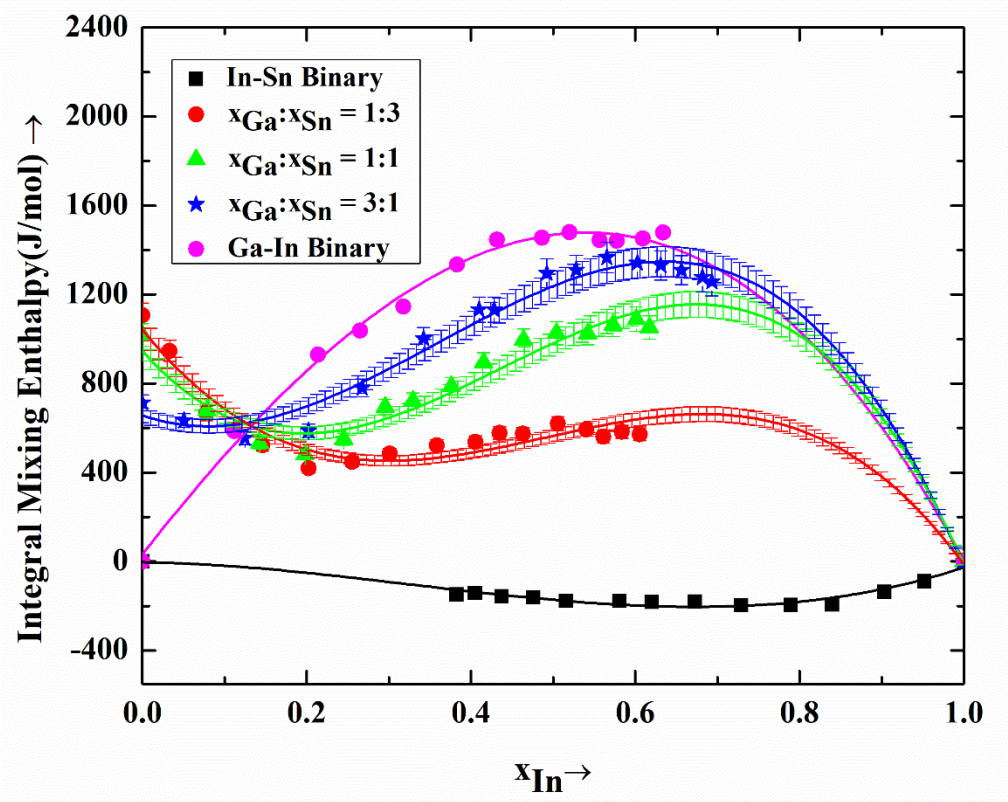

Fig. 4.5 Plot representing the enthalpies of mixing of the given ternary alloy system corresponding to cross-section of $(Ga_{0.25}Sn_{0.75})_{1-x}In_x$; circle, $(Ga_{0.50}Sn_{0.50})_{1-x}In_x$; triangle and $(Ga_{0.75}Sn_{0.25})_{1-x}In_x$; star, In-Sn binary data from the literature [155]; square, Ga-In binary data from the literature [155]; half-filled circle at 673 K and solid line represents RKM fitted polynomial curve.

Figure 4.5 illustrates that all three isopleths are endothermic in nature with respect to composition of In (x_{In}) and as the x_{Ga}/x_{Sn} value increases the enthalpy of mixing values are getting more positive (endothermic) with respect to the composition of In (x_{In}). So, there may be a chance of less tendency for the atoms to be mixed in this system at 673 K.

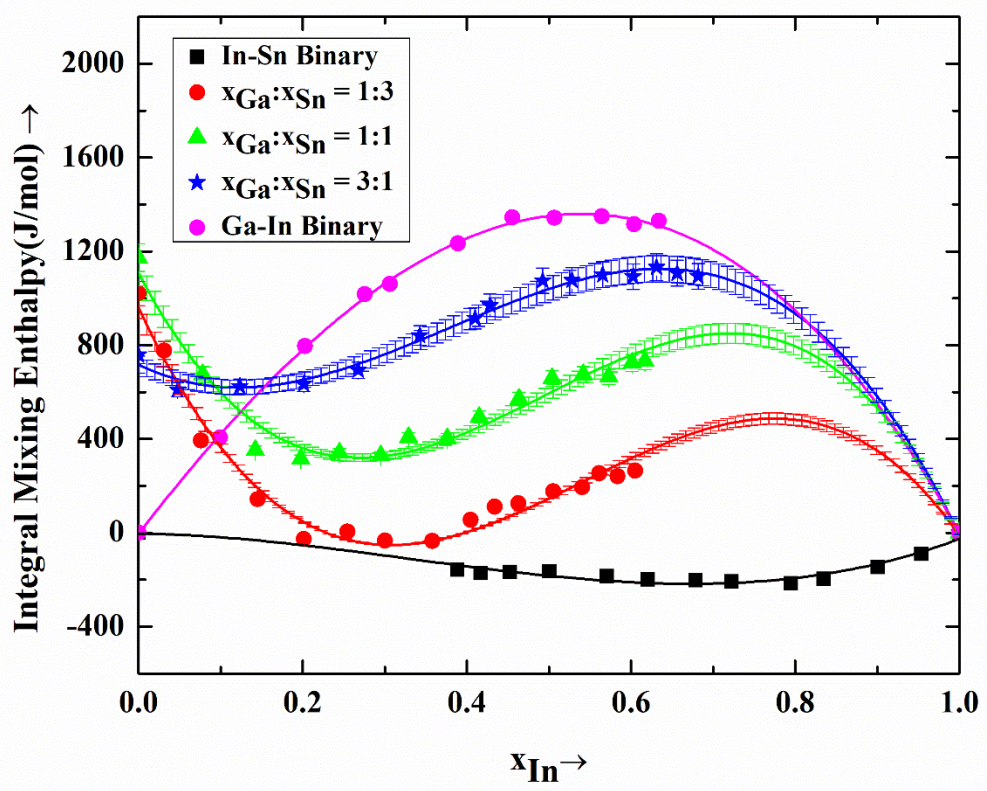

Fig. 4.6 Plot representing the enthalpies of mixing of the given ternary alloy system corresponding to cross-section of $(Ga_{0.25}Sn_{0.75})_{1-x}In_x$; circle, $(Ga_{0.50}Sn_{0.50})_{1-x}In_x$; triangle and $(Ga_{0.75}Sn_{0.25})_{1-x}In_x$; star at 723 K, In-Sn binary data from the literature [155]; square ,Ga-In binary data from the literature [155]; half-filled circle and solid line represents RKM fitted polynomial curve.

Figure 4.6 illustrates the variation in mixing enthalpies with the indium composition for three different isopleths $(Ga_{0.25}Sn_{0.75})_{1-x}In_x$, $(Ga_{0.50}Sn_{0.50})_{1-x}In_x$ and $(Ga_{0.75}Sn_{0.25})_{1-x}In_x$ and two binaries at 723 K. For three isopleths and the Ga-In binary, the mixing enthalpies are endothermic for the entire composition of In except for the isopleth $(Ga_{0.25}Sn_{0.75})_{1-x}In_x$, where values are slightly negative in the range of x_{In} =0.2-0.4. Also it suggests that there is finite amount of interatomic interaction among three metal atoms in this range as there is good chance of Gibb's energy to be negative as enthalpy is negative although it also depends on sign of entropy as well.

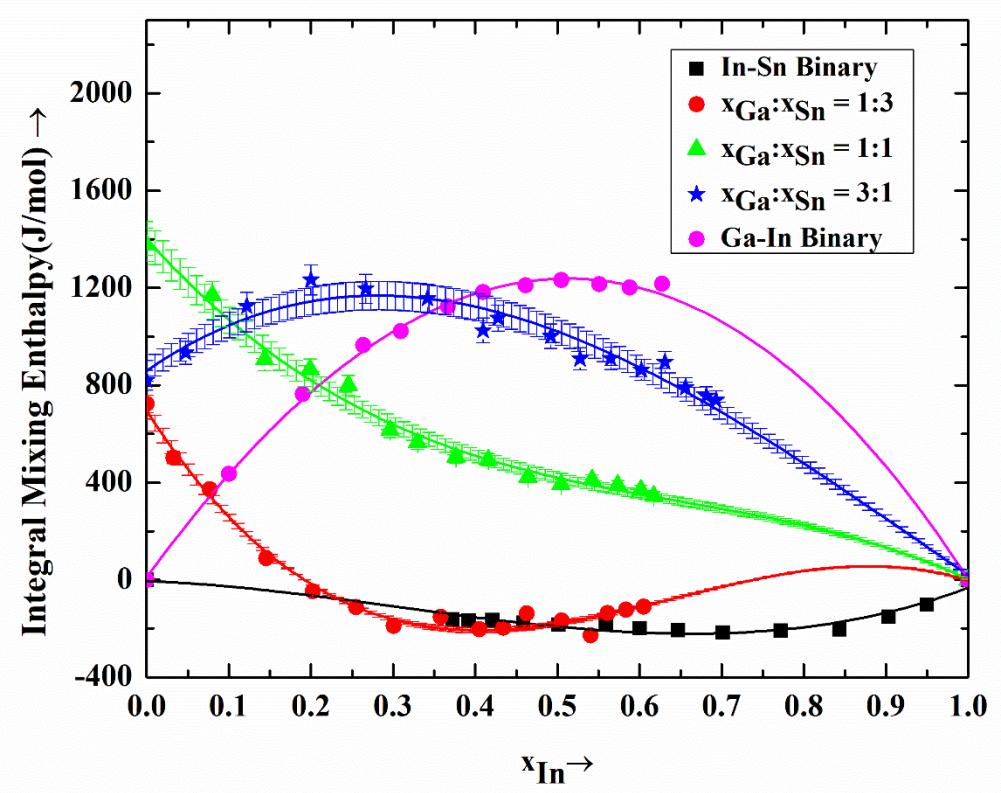

Fig. 4.7 Plot representing the enthalpies of mixing of the given ternary alloy system corresponding to cross-section of $(Ga_{0.25}Sn_{0.75})_{1-x}In_x$; circle, $(Ga_{0.50}Sn_{0.50})_{1-x}In_x$; triangle and $(Ga_{0.75}Sn_{0.25})_{1-x}In_x$; star at 773 K, In-Sn binary data from the literature [155]; square, Ga-In binary data from the literature [155]; half-filled circle and solid line represents RKM fitted polynomial curve.

Figure 4.7 shows the nature of plots of mixing enthalpies for three isopleths $(Ga_{0.25}Sn_{0.75})_{1-x}In_x$, $(Ga_{0.50}Sn_{0.50})_{1-x}In_x$ and $(Ga_{0.75}Sn_{0.25})_{1-x}In_x$ and two binaries In-Sn and Ga-In at 773 K. For two isopleths $(Ga_{0.50}Sn_{0.50})_{1-x}In_x$ and $(Ga_{0.75}Sn_{0.25})_{1-x}In_x$ the mixing enthalpies are endothermic for entire In composition, but for isopleth $(Ga_{0.25}Sn_{0.75})_{1-x}In_x$ the values of mixing enthalpies are negative or exothermic in nature in the range of x_{In} =0.15-1. Also it suggests that there is finite amount of interatomic interaction among three metal atoms in this range as there is good chance of Gibb's energy to be negative as enthalpy is negative although it also depends on sign of entropy as well.

From **Figures 4.5, 4.6** and **4.7**, it can be inferred that as the temperature increases from 673 K to 773 K, the enthalpies of mixing become more exothermic for $(Ga_{0.25}Sn_{0.75})_{1-x}In_x$ isopleth.

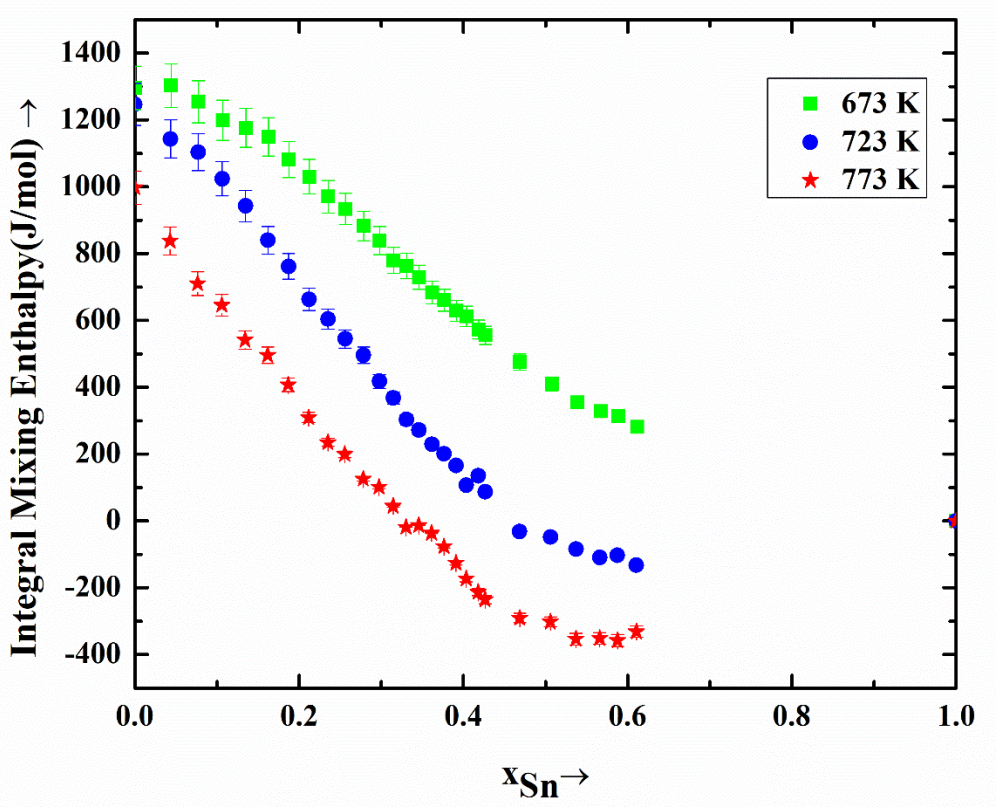

Fig. 4.8 Plot representing the enthalpies of mixing of the given ternary alloy system for the cross-section of $(Ga_{0.25}In_{0.75})_{1-x}Sn_x$.

Figure 4.8 illustrates the effect of temperature on the enthalpy of mixing for isopleth $(Ga_{0.25}In_{0.75})_{1-x}Sn_x$ at different mole fraction of Sn. Also, it can be inferred from above plot that enthalpy curves at 673 K, 723 K, and 773 K are not close to one another. This confirms that the enthalpies of mixing of ternary Sn-Ga-In system is not independent of temperature. So, temperature has a very important role to play on mixing of Ga, Sn and In atoms. The degree of mixing is better for the given isopleth at 773 K as the enthalpy of mixing values are most negative at 773 K.

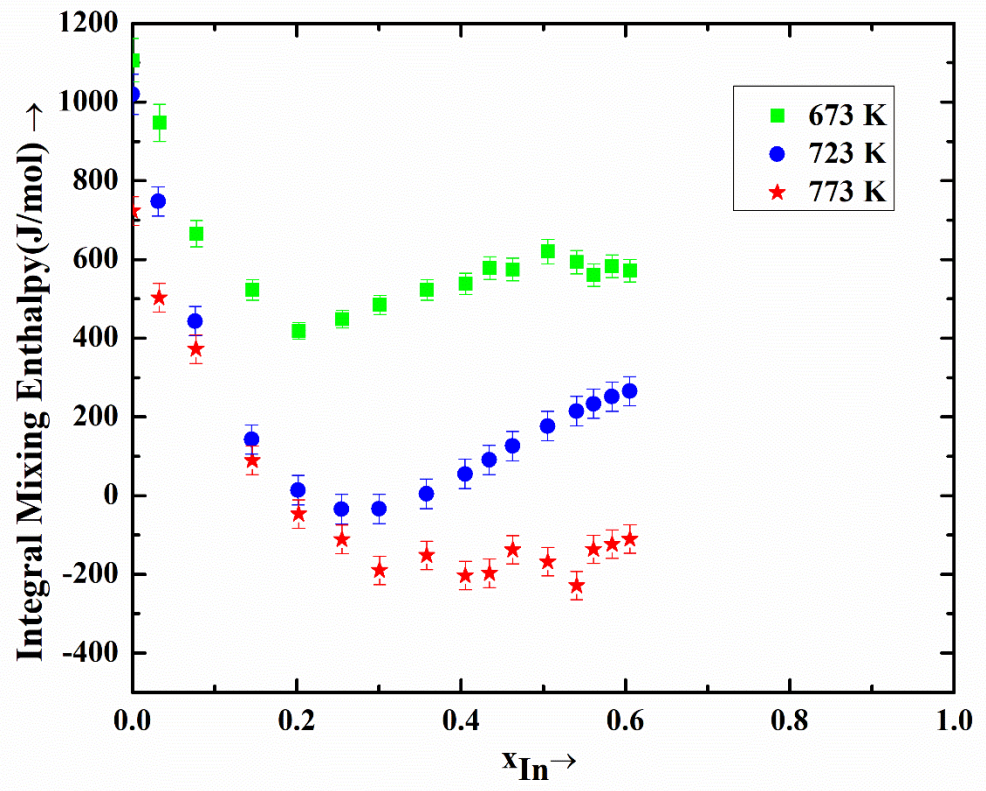

Fig. 4.9 Plot representing the enthalpies of mixing of the given ternary alloy system for the cross-section of $(Ga_{0.25}Sn_{0.75})_{1-x}In_{x.}$

The influence of temperature on the enthalpy of mixing for isopleth $(Ga_{0.25}Sn_{0.75})_{1-x}In_x$ at various mole fractions of In is shown in **Figure 4.9**. The above figure also suggests that the enthalpy curves at 673 K, 723 K, and 773 K are not close to one other. This demonstrates that the ternary Sn-Ga-In system's enthalpies of mixing are not temperature-independent. Therefore, temperature has a significant impact on how Ga, Sn, and In atoms combine. The degree of mixing is better for the given isopleth at 773 K as the enthalpy of mixing values are most negative at 773 K.

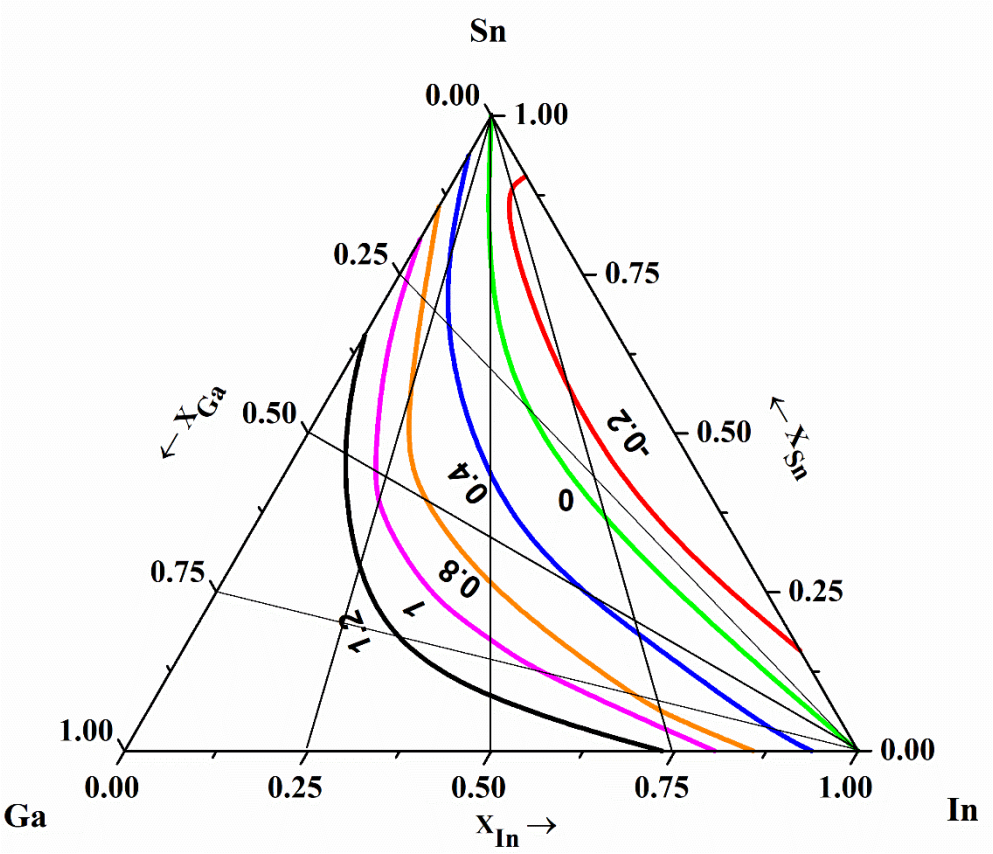

Fig. 4.10 Plot representing different Iso-enthalpy curves of given liquid ternary alloy at 773 K; values are in kJ/mol.

There are six iso-enthalpies curves i.e. -0.2 kJ/mol, 0 kJ/mol ,0.4 kJ/mol ,0.8 kJ/mol ,1 kJ/mol, 1.2 kJ/mol as shown in the **Figure 4.10**. Along each curve enthalpy value is constant. To generate these plots, the values of molar mixing enthalpy with respect to amount of the species which is to be dropped are used. The behavior of both the binaries Ga-Sn and Ga-In affects the majority of the iso-enthalpy curves because In-Sn system is slightly negative or exothermic in nature. It is seen that enthalpy of mixing becomes positive from In-Sn binary towards Gallium corner. As gallium composition increases the enthalpy of mixing increases. All the iso-enthalpy curves are oriented towards In-Sn binary. Therefore, the stability of the alloy is maximum for the composition close to In-Sn binary.

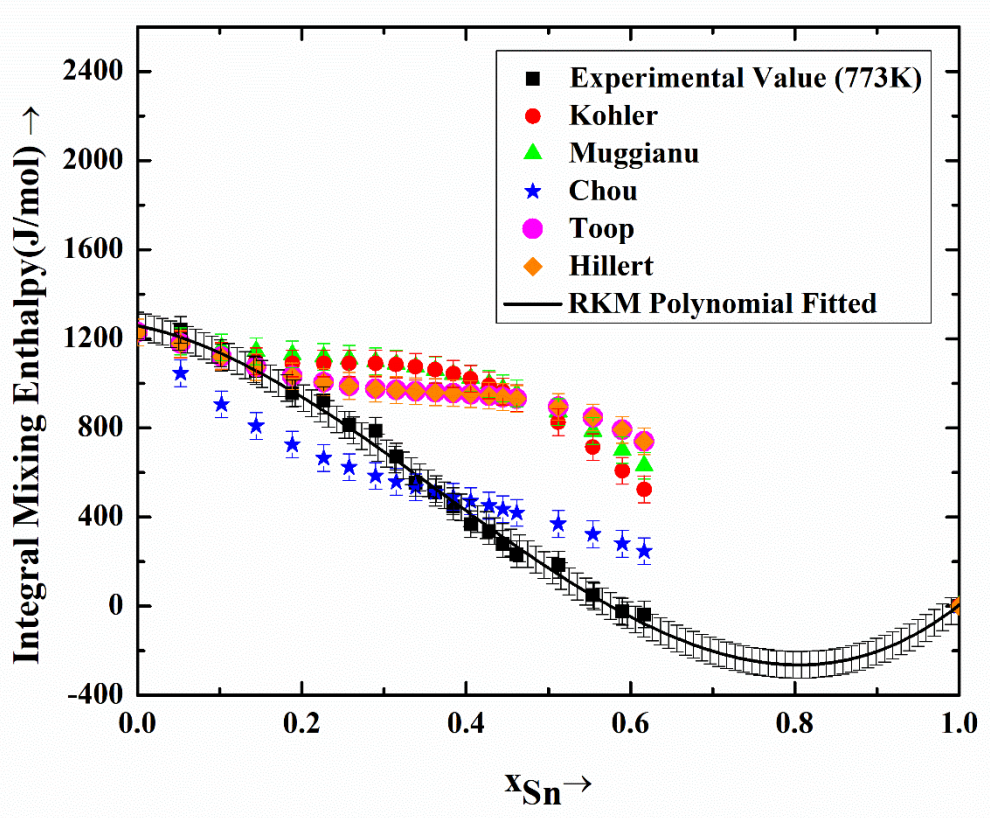

Fig. 4.11 Experimental and calculated integral enthalpy of mixing for the isopleth $(Ga_{0.50}In_{0.50})_{1-x}Sn_x$ by using the five geometric models (Kohler, Muggianu, Chou, Toop and Hillert) at 773 K along with RKM Polynomial fitted Curve.

Five extrapolation geometric models (Kohler, Muggianu, Chou, Toop and Hillert) were used to predict the enthalpy of mixing values of ternary Sn-Ga-In 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 In-Sn, Ga-In and Ga-Sn were taken from the data available in literature [155] and given in the **Table 4.5**.

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

4.3.2.1 Kohler model [141]

$$\Delta H^{mix}_{Sn-Ga-In} = \left[(x_{Ga} + x_{Sn})^2 \Delta H^{mix}_{Ga-Sn}\left(\frac{x_{Sn}}{x_{Sn}+x_{Ga}}; \frac{x_{Ga}}{x_{Sn}+x_{Ga}}\right) + (x_{Sn} + x_{In})^2 \Delta H^{mix}_{In-Sn}\left(\frac{x_{Sn}}{x_{Sn}+x_{In}}; \frac{x_{In}}{x_{Sn}+x_{In}}\right) + (x_{Ga} + x_{In})^2 \Delta H^{mix}_{Ga-In}\left(\frac{x_{Ga}}{x_{Ga}+x_{In}}; \frac{x_{In}}{x_{Ga}+x_{In}}\right)\right]$$

. . ….. **(4.5)**

4.3.2.2 Muggianu model [141]

$$\Delta H^{mix}_{Sn-Ga-In} = \left[\left(\frac{4x_{Ga}x_{Sn}}{[1-(x_{Ga}-x_{Sn})^2]}\right)\Delta H^{mix}_{Ga-Sn}\left(x_{Sn} + \frac{x_{In}}{2}; x_{Ga} + \frac{x_{In}}{2}\right) + \left(\frac{4x_{Ga}x_{In}}{[1-(x_{Ga}-x_{In})^2]}\right)\Delta H^{mix}_{Ga-In}\left(x_{Ga} + \frac{x_{Sn}}{2}; x_{In} + \frac{x_{Sn}}{2}\right) + \left(\frac{4x_{In}x_{Sn}}{[1-(x_{In}-x_{Sn})^2]}\right)\Delta H^{mix}_{In-Sn}\left(x_{In} + \frac{x_{Ga}}{2}; x_{Sn} + \frac{x_{Ga}}{2}\right)\right]$$

…….. **(4.6)**

4.3.2.3 Chou model [141]

$$\Delta H^{mix}_{Sn-Ga-In} = \left[\left(\frac{x_{Ga}}{1-x_{Sn}}\right)\Delta H^{mix}_{Ga-Sn}(x_{Sn}; x_{Ga}) + \left(\frac{x_{In}}{1-x_{Ga}}\right)\Delta H^{mix}_{Ga-In}(x_{Ga}; x_{In}) + \left(\frac{x_{Sn}}{1-x_{In}}\right)\Delta H^{mix}_{In-Sn}(x_{Sn}; x_{In})\right]$$

…….. **(4.7)**

4.3.2.4 Toop model [141]

$$\Delta H^{mix}_{Sn-Ga-In} = \left[\left(\frac{x_{Ga}}{1-x_{Sn}}\right)\Delta H^{mix}_{Ga-Sn}(x_{Sn}; 1-x_{Sn}) + (x_{Ga} + x_{In})^2 \Delta H^{mix}_{Ga-In}\left(\frac{x_{Ga}}{x_{Ga}+x_{In}}; \frac{x_{In}}{x_{Ga}+x_{In}}\right) + \left(\frac{x_{In}}{1-x_{Sn}}\right)\Delta H^{mix}_{In-Sn}(x_{Sn}; 1-x_{Sn})\right]$$

…….. **(4.8)**

4.3.2.5 Hillert model [141]

$$\Delta H^{mix}_{Sn-Ga-In} = \left[\left(\frac{x_{Ga}}{1-x_{Sn}}\right)\Delta H^{mix}_{Ga-Sn}(x_{Sn}; 1-x_{Sn}) + \left(\frac{4x_{Ga}x_{In}}{[1-(x_{Ga}-x_{In})^2]}\right)\Delta H^{mix}_{Ga-In}\left(x_{Ga} + \frac{x_{Sn}}{2}; x_{In} + \frac{x_{Sn}}{2}\right) + \left(\frac{x_{In}}{1-x_{Sn}}\right)\Delta H^{mix}_{In-Sn}(x_{Sn}; 1-x_{Sn})\right]$$

…… **(4.9)**

A comparison of experimental data with all geometric model data along with RKM modelled fitted data at 773 K is shown in **Figure 4.11** for the isopleth $(Ga_{0.50}In_{0.50})_{1-x}Sn_x$. RKM modelled polynomial fitted data fits well to the experimental data. The experimental data differing between x_{Sn} = 0.2 to 0.6 compared with the model predications. This variation in data is due to the different geometries followed by the different models. This may be due to difference in the size of atoms in the given system. Binary and ternary interaction parameter values are shown in **Table 4.5**. Large value of ternary interaction parameters shows that there is strong interaction among three elements, that's why we are getting large values of three L parameters. Therefore, we could infer that ternary contribution is quite significant in this ternary system and also referring to **Figures 4.8 and 4.9**, the experimental values are not close to each other so temperature dependence is there. A comparison of experimental data and the data predicted from CALPHAD technique [144] with all geometric model data along with RKM modelled fitted data at 773 K is shown in **Figure 4.12** for the isopleth $(Ga_{0.75}Sn_{0.25})_{1—x}In_x$. 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 ±5%.

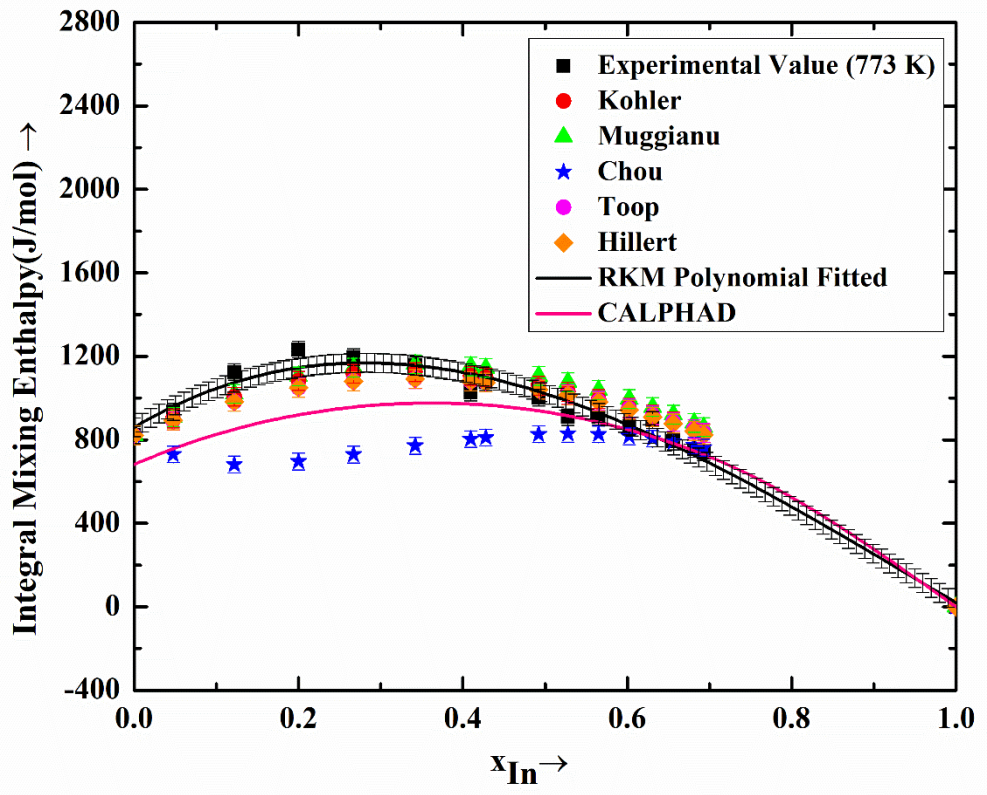

Fig. 4.12 Experimental and calculated integral enthalpy of mixing for the isopleth $(Ga_{0.75}Sn_{0.25})_{1-x}In_x$ by using the five geometric models (Kohler, Muggianu, Chou, Toop and Hillert) at 773 K along with RKM Polynomial fitted Curve and data predicted from CALPHAD technique [144].

4.4 Conclusions

Partial mixing enthalpy and integral mixing enthalpy values were derived from this study on Sn-Ga-In Ternary alloy systems by using drop calorimeter along six of the cross sections (**see Figure 4.1**) at temperatures ranging from 673 K to 773 K. It was found that mixing enthalpies were temperature dependent. 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.