CHAPTER 3

ENTHALPIES OF MIXING IN Ga-In, Ga-Sn AND In-Sn BINARY SYSTEMS

3.1 Introduction

The main objective in exploring a lead-free solder system comprising Gallium, Indium, and Tin lies in the desire to mitigate health hazards related to lead exposure. In this Chapter, we focus on the alloy system composed of gallium (Ga), indium (In), and tin (Sn) as a potential alternative to conventional lead-based solders. Gallium emerges as a promising candidate due to its excellent electrical conductivity and high corrosion resistance. Moreover, the significantly low melting point of gallium at 29.76 °C makes it an appealing choice for our investigation, effectively lowering the overall melting point of the alloy system. Notably, previous research has demonstrated the advantageous effects of incorporating gallium into lead-free solders, leading to improvements in mechanical properties and enhanced wettability [145], [146]**.** In addition to gallium, indium plays a crucial role in this alloy system as it has relatively low melting point of 156.6 °C, indium contributes to reducing the overall melting point of the alloy while offering excellent resistance to corrosion. Although indium's electrical conductivity does not close to that of copper or silver [53], [67], [147]–[151]**,** its addition significantly enhances the wetting characteristics of the alloy, ensuring better adhesion and solder joint reliability. Tin, another essential component of the alloy system, possesses a relatively low melting point of 213.93 °C and a high boiling point of 2270 °C. Its excellent electrical conductivity and resistance to corrosion further add to the alloy's overall performance [140], [152]–[154].The combination of gallium, indium, and tin offers a promising avenue to explore a lead-free solder alternative with comparable properties to traditional Pb-Sn solder. Ultimately, the findings of this research will contribute to the ongoing efforts in developing sustainable and environmentally friendly materials for the electronics industry. The first step towards designing an alloy involving Ga, In and Sn that can replace Pb-Sn solder is the determination of thermodynamic properties and followed by the phase diagram. It is difficult to find any binary that can meet all the requirements of a lead-free solder. Recently, researchers have been computing the thermodynamic properties of the higher order system using the binary data. Therefore, thermodynamic measurements with better precision of binary systems are very important. It has been observed from the literature that very few literatures are available for the direct measurements of enthalpies of mixing by calorimetry for these binary systems. Therefore, measurement of enthalpy of mixing for some of the important binary systems targeted for lead free solder applications were taken up in this investigation. Enthalpy of mixing of the three of the binary systems: Ga-Sn, Ga-In and In-Sn were investigated by drop calorimetric technique using MHTC 96 LINE EVO calorimeter in the temperature range of 673 K-773 K. Experimental data from this study were used to find the interaction parameters by using R-K polynomial fitting. Comparison of enthalpy of mixing data of this study with literature were done to check the accuracy of data. In this study, we investigated the partial and integral enthalpy of mixing for Gallium-Indium (Ga-In), Gallium-Tin (Ga-Sn), and Indium-Tin (In-Sn) binary alloy systems by the help of drop calorimeter at different temperatures of 673 K, 723 K, and 773 K. The results demonstrate that the enthalpy of mixing exhibits certain variations with temperature and composition, providing insights into the interatomic interactions between the constituent elements in the alloy systems. Endothermic enthalpies of mixing were obtained for the Ga-Sn-and Ga-In system but slightly exothermic nature was observed for In-Sn system. After getting enthalpy data from the experiments, a Redlich-Kister polynomial fitting was employed to accurately describe the binary interactions within each alloy system. The variation of enthalpy of mixing was found to be temperature dependent for the Ga-In and Ga-Sn system but temperature independency was observed in In-Sn system. Binary interactions parameters for the Ga-Sn, Ga-In and In-Sn were determined at different temperatures. It was observed that interaction parameters are temperature dependent for the Ga-In and Ga-Sn system and independent for the In-Sn System. Comparison of partial molar and integral molar enthalpies of mixing obtained from this study with the literature were attempted. It was found that the results obtained in this study show very good agreement with the data available in literature.

3.2 Experimental

3.2.1 Materials

In order to study the thermodynamic behavior, drop calorimetric study of binary alloys were done by using pure metals (Ga, In, and Sn). As a standard for calibration, α-Al_2O_3 needles from the NIST (National Institute of Standards and Technology) in Gaithersburg, Maryland, United States were used. Here, α-Al_2O_3 needles were used because the enthalpy values of these needles are known. After being cleaned with n-hexane in a supersonic bath, metals were vacuum-dried in an antechamber glove box to remove any trace of the solvent that may have been left behind. All metals were initially in solid form. After that, they were cut up into smaller pieces and weighed to an accuracy of 10^{-4} g by using Sartorius balance type Cubis. The specifications for pure metals and protective Argon gas are listed in **Table 3.1**.

Table 3.1 The materials used for this study.

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

3.2.2 Calorimetric Measurements

During the course of this experiment, a drop calorimeter (model number MHTC 96 LINE EVO) that was manufactured in France by SETARAM Instruments is used in order to get enthalpy data pertaining to the system under consideration. A graphite tube resistance furnace with a water-flowing arrangement around the outside portion of the furnace ensures constant cooling, and a thermopile with 56 pairs of S-type thermocouples keeps track of temperatures inside. Thermocouple height is 213 mm. The thermopile made up of thermocouples distributed over the bottom and overall the side surface of the crucibles, provides good sensitivity, no matter how full is the measuring crucible. A sealed alumina tube crosses the furnace through the center of the heating element. It forms the experimenting chamber and enables insulation between the furnace’s atmosphere and that of the experimenting chamber. This tube is held at the top by furnace’s nose and at the bottom by the lower mounting plate which has rings for sealing. Proportional-Integral-Derivative (PID) controllers are there which takes the feedback from thermal sensors and accordingly it adjusts the heating rate to maintain the isothermal state. The utmost temperature at which the furnace can operate is 1593 K. The metals are dropped in an automated manner into the crucible with the help of a motorized device designed specifically for dropping. Dropping four pieces of α-Al_2O_3 needles at the completion of each sample series served as the calorimeter's calibration reference. The NIST, United States has certified that these needles conform to its specifications. The calorimeter is entirely monitored by the CALISTO software. A specified amount of one of the two metals was placed in the crucible having outer diameter of 12 mm and length of 60 mm before the trials began. The circulation of gas and the water cooling system were both regulated by the help of CALISTO software. Before beginning the trials, everything, including the rate of heating and cooling, the holding duration, and the rate of gas flow, was pre-programmed. During the entire duration of the experiment, an uninterrupted supply of argon at a rate of around 30 mL/min was kept going to make sure the alloys would not get oxidized. Argon gas is used in both the role of carrier and protective gas during the course of whole experiment. As soon as the temperature at which holding would occur had been reached, the first sample could be added into the crucible using the automated motorized dropping system. The motorized device for dropping also included a timer set to automatically drop the sample after every half an hour. The CALISTO data acquisition software recorded the heat signals continuously at 673 K, 723 K, and 773 K. After all the samples were dropped, α-Al_2O_3 standard samples were dropped towards the end of the experiments for the calibration of the heat signals. The peaks were integrated to find the area and the same were converted to enthalpy. Subsequently, the enthalpy of mixing was calculated from the partial enthalpy of mixing. Calorimetric studies of the Ga-In, Ga-Sn and In-Sn binary systems were conducted following the above procedure. Pieces of pure Indium into molten Gallium in Ga-In system, Tin into molten Gallium in Ga-Sn system and Tin into molten Indium in In-Sn system were dropped. An approximately 16-h long thermal equilibration process was performed on the system in order to create a stable baseline prior to the introduction of the sample material. Before and after the measurements, the total mass of both the crucible and the samples were weighed in order to validate the hypothesis that the amount of weight lost due to evaporation was negligible. For the purpose of verifying that the findings could be reliably reproduced, each experiment was carried out twice with the same set of variables. The acquired heat signals were then integrated with the help of the CALISTO Data Processing software, which was then utilized to determine the enthalpy values.

3.3 Results and Discussion

The heat flow curve's peaks were integrated with the aid of the CALISTO data processing software. The calibration constant (K) was determined based on the heat signal value corresponding to the α-Al_2O_3 needle drops. The integral values of each heat signal were multiplied by the calibration constant ***(K)*** to get the corresponding enthalpy, which is often referred to as the heat effect.

Here, the reaction enthalpy **($\Delta \boldsymbol{H}_{\boldsymbol{Reaction,X,i}}$)** which is a function of heat effect **($\Delta \boldsymbol{H}_{\boldsymbol{Signal,X,i}} \cdot \boldsymbol{K}$)** and the enthalpy**($\Delta \boldsymbol{H}_{\boldsymbol{X,i}}^{\boldsymbol{T_D} \to \boldsymbol{T_M}}$)** increment of the sample to be dropped, is calculated by **Equation 3.1** when species $\boldsymbol{X}$ is dropped from drop temperature **($\boldsymbol{T_D}$)** to bath temperature **($\boldsymbol{T_M}$)**.

$$\Delta \boldsymbol{H}_{\boldsymbol{Reaction,X,i}} = (\Delta \boldsymbol{H}_{\boldsymbol{Signal,X,i}} \cdot \boldsymbol{K}) \; - (\Delta \boldsymbol{H}_{\boldsymbol{X,i}}^{\boldsymbol{T_D} \to \boldsymbol{T_M}} \cdot \boldsymbol{n}_{\boldsymbol{X,i}}) \tag{3.1}$$

where $\boldsymbol{n}_{\boldsymbol{X,i}}$ (no. of moles) representing the amount of species $\boldsymbol{X}$ which was dropped in the liquid bath by the help of automatic dropping device and each peak corresponds to a unique $\Delta \boldsymbol{H}_{\boldsymbol{Signal,X,i}}$ value which is the integrated area(**µV/s**). It was calculated for each peak by baseline integration tools**.** $\Delta \boldsymbol{H}_{\boldsymbol{X,i}}^{\boldsymbol{T_D} \to \boldsymbol{T_M}}$ 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.

As a very little quantity of species $\boldsymbol{X}$ was introduced to liquid metal in the crucible, so **Equation 3.2** can be used to compute the partial enthalpy $\Delta \overline{\boldsymbol{H}}_{\boldsymbol{X,i}}$ **:**

$$\Delta \overline{\boldsymbol{H}}_{\boldsymbol{X,i}} \approx \; \Delta \boldsymbol{H}_{\boldsymbol{Reaction,X,i}} / \boldsymbol{n}_{\boldsymbol{X,i}} \tag{3.2}$$

Each measurement included carefully putting predetermined quantities of one of the two metals into the crucible, followed by the controlled introduction of the other metals at the designated temperature. Depending on the various binary systems, pieces of pure Indium were dropped into molten Gallium which is kept in crucible; Tin into molten Gallium and Tin into molten Indium. **Equation 3.3** gives the integral molar mixing enthalpy **(**$\Delta\boldsymbol{H_{mix}}$**)** as follows:

$$\Delta\boldsymbol{H_{mix}} = \frac{\sum \Delta\boldsymbol{H_{Reaction}}}{(\boldsymbol{n_{crucible}} + \sum \boldsymbol{n_i})} \qquad \textbf{(3.3)}$$

In and Sn's enthalpy increment from room temperature to drop temperature was acquired from the literature [98] and used in **Equation 3.1**. Integral molar and partial molar enthalpies of mixing of Ga-In, Ga-Sn and In-Sn binary systems were computed by above equations at 673 K ,723 K & 773 K represented in the **Table 3.2, 3.3** and **3.4**.

Calorimetric measurements may be susceptible to several causes of error, such as the type of calorimeter used, calibration procedures, integration of the heat flow curve baseline, solute solubility in the solvent, and concentration of impurities. The experimental uncertainty of the calorimeter varies between 10 and 12 percent. The calibration error resulting from the dropping of α-Al_2O_3 needles was found to be within a range of ± 1.5%.

Table 3.2 Partial and integral mixing enthalpies of Ga-In alloys when In dropped.

Added moles n_{In}	Mole fraction (x_{In})	Standard uncertainties $u(x_{In})$	Heat effect $H_{\mathrm{Signal}} \cdot K$ (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-In alloys; Atmosphere: Argon at pressure p = 0.1 MPa; Starting amount n_{Ga} = 0.015476 mol, K = 0.002402 J /μV s, T_D = 298 K, T_M = 673 K, $\Delta H_{In}^{T_D \to T_M}$ = 14100 (J mol^{-1})							
0.001951	0.1120	0.0002	37.712	0.011	10.203	5230	585.467
0.004205	0.2137	0.0005	39.872	0.012	8.091	3590	929.523
0.005578	0.2649	0.0007	22.922	0.014	3.563	2595	1038.122
0.007210	0.3178	0.0004	27.139	0.018	4.128	2529	1145.429
0.009609	0.3831	0.0005	41.307	0.015	7.481	3118	1334.101
0.011746	0.4315	0.0009	36.025	0.016	5.893	2758	1445.845
0.014681	0.4868	0.0003	45.876	0.014	4.492	1530	1454.095
0.016759	0.5199	0.0007	33.160	0.004	3.860	1858	1480.087
0.019429	0.5566	0.0004	40.347	0.003	2.700	1011	1444.244
0.021168	0.5777	0.0008	26.898	0.012	2.378	1367	1440.588
0.024138	0.6093	0.0005	46.599	0.015	4.722	1590	1451.781

0.026798	0.6339	0.0004	42.516	0.005	5.010	1883	1478.956
Series 2: Ga-In alloys; Atmosphere: Argon at pressure *p* = 0.1 MPa; Starting amount n_{Ga} = 0.013493 mol, *K* = 0.002397 J /*μ*V s, T_D = 298 K, T_M = 723 K, $\Delta H_{In}^{T_D \to T_M}$ = 15558.0555 (J mol^{-1})							
0.001489	0.0994	0.0001	29.243	0.012	6.077	4081	405.614
0.003433	0.2028	0.0002	37.640	0.011	7.395	3804	795.906
0.005130	0.2755	0.0004	31.891	0.017	5.489	3235	1018.157
0.005962	0.3065	0.0005	14.630	0.012	1.686	2026	1061.265
0.008603	0.3893	0.0003	47.713	0.015	6.624	2508	1234.196
0.011281	0.4554	0.0007	47.705	0.018	6.041	2256	1344.617
0.013865	0.5068	0.0002	43.645	0.017	3.443	1332	1343.483
0.017486	0.5644	0.0005	61.367	0.005	5.031	1389	1348.840
0.020543	0.6036	0.0003	50.584	0.004	3.023	989	1316.525
0.023369	0.6340	0.0007	48.184	0.010	4.217	1492	1329.985
Series 3: Ga-In alloys; Atmosphere: Argon at pressure *p* = 0.1 MPa; Starting amount n_{Ga} = 0.014304 mol, *K* = 0.002276 J /*μ*V s, T_D = 298 K, T_M = 773 K, $\Delta H_{In}^{T_D \to T_M}$ = 17012 (J mol^{-1})							
0.001599	0.1005	0.0004	34.138	0.011	6.936	4338	436.117
0.003355	0.1900	0.0003	36.417	0.012	6.544	3727	763.360
0.005119	0.2636	0.0007	35.267	0.015	5.258	2981	964.734
0.006408	0.3094	0.0005	24.368	0.017	2.440	1893	1022.475

0.008287	0.3668	0.0002	36.178	0.012	4.212	2242	1123.894
0.009928	0.4097	0.0004	31.183	0.016	3.266	1990	1182.556
0.012251	0.4613	0.0005	43.018	0.015	3.499	1506	1210.880
0.014578	0.5047	0.0006	43.012	0.003	3.425	1472	1231.897
0.017563	0.5511	0.0004	53.928	0.005	3.147	1054	1215.267
0.020448	0.5884	0.0005	52.126	0.012	3.046	1056	1202.043
0.024104	0.6276	0.0005	67.136	0.015	4.940	1351	1216.222

[a] **Standard uncertainties** u **are:** $u(T_M)$ **= 0.1 K,** $u(p)$ **= 15 kPa,** $u(n_{Ga})$ **= 0.000004 mol,** $u(n_{In})$ **= 0.000002 mol,** $u(\Delta H_{\mathrm{Reaction}})$ **= 0.004 J;**

Series 1: $u(K)$ **= 0.000005 J /μV s,** $u(\Delta_{mix}H)$ **= 130.013 J mol**$^{-1}$**;**

Series 2: $u(K)$ **= 0.000005 J /μV s ,** $u(\Delta_{mix}H)$ **= 112.017 J mol**$^{-1}$**,**

Series 3: $u(K)$ **= 0.000004 J /μV s,** $u(\Delta_{mix}H)$ **= 105.018 J mol**$^{-1}$**;**

Table 3.3. Partial and integral mixing enthalpies of Ga-Sn alloy when Sn dropped.

Added moles n_{Sn}	Mole fraction (x_{Sn})	Standard uncertainties $u(x_{Sn})$	Heat effect $H_{\text{Signal}}\cdot K$ (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-Sn alloys; Atmosphere: Argon at pressure p = 0.1 MPa; Starting amount n_{Ga} = 0.013622 mol, K = 0.002390 J /μV s, T_D = 298 K, T_M = 673 K, $\Delta H_{Sn}^{T_D\rightarrow T_M}$ = 17839.35 (J mol^{-1})							
0.001582	0.1041	0.0005	33.340	0.019	5.118	3235	336.612
0.003253	0.1928	0.0003	34.658	0.015	4.848	2901	590.601
0.004938	0.2661	0.0007	33.708	0.014	3.649	2166	733.550
0.006724	0.3305	0.0003	35.314	0.015	3.453	1933	838.907
0.008495	0.3841	0.0004	34.087	0.014	2.494	1408	884.458
0.010189	0.4279	0.0005	33.717	0.005	3.497	2064	968.418
0.011911	0.4665	0.0004	33.051	0.015	2.332	1354	994.458
0.013554	0.4987	0.0007	31.759	0.017	2.449	1491	1024.428
0.015172	0.5269	0.0006	31.410	0.019	2.546	1574	1055.301
0.016798	0.5522	0.0005	31.747	0.014	2.740	1685	1088.962
0.018418	0.5748	0.0003	30.840	0.017	1.940	1198	1094.458
0.020266	0.5980	0.0002	33.707	0.013	0.740	400	1056.612

0.021921	0.6167	0.0005	31.770	0.016	2.246	1357	1070.601
Series 2: Ga-Sn alloys; Atmosphere: Argon at pressure p = 0.1 MPa; Starting amount n_{Ga} = 0.014486 mol, K = 0.002429 J /μV s, T_D = 298 K, T_M = 723 K, $\Delta H_{Sn}^{T_D \rightarrow T_M}$ = 19266.2743 (J mol^{-1})							
0.000421	0.0282	0.0002	9.878	0.011	1.767	4197	118.558
0.002045	0.1237	0.0001	36.838	0.013	5.550	3417	442.648
0.003562	0.1974	0.0004	33.380	0.015	4.153	2738	635.536
0.005135	0.2617	0.0005	34.099	0.012	3.793	2411	777.908
0.006755	0.3180	0.0007	34.817	0.014	3.606	2226	888.317
0.008561	0.3715	0.0003	39.505	0.013	4.710	2608	1023.072
0.010175	0.4126	0.0007	33.399	0.017	2.303	1427	1049.522
0.011857	0.4501	0.0004	36.415	0.005	4.009	2383	1134.700
0.01349	0.4822	0.0007	33.664	0.007	2.202	1348	1147.155
0.015291	0.5135	0.0006	37.851	0.011	3.152	1750	1183.618
0.018329	0.5586	0.0009	64.489	0.017	5.958	1961	1255.612
0.021104	0.5930	0.0004	56.663	0.009	3.199	1153	1247.600
0.022688	0.6103	0.0008	32.760	0.012	2.242	1415	1254.752
Series 3: Ga-Sn alloys; Atmosphere: Argon at pressure p = 0.1 MPa; Starting amount n_{Ga} = 0.014523 mol, K = 0.002415 J /μV s, T_D = 298 K, T_M = 773 K, $\Delta H_{Sn}^{T_D \rightarrow T_M}$ = 20699.9793 (J mol^{-1})							
0.001643	0.1016	0.0002	40.822	0.015	6.812	4146	421.367

0.003127	0.1772	0.0003	35.012	0.017	4.293	2893	629.206
0.004769	0.2472	0.0005	39.370	0.015	5.381	3277	854.539
0.006258	0.3011	0.0007	34.286	0.012	3.464	2326	960.017
0.007922	0.3530	0.0005	38.165	0.013	3.720	2236	1054.561
0.009485	0.3951	0.0003	36.940	0.017	4.586	2934	1176.934
0.011053	0.4322	0.0007	38.648	0.012	6.190	3948	1346.821
0.012652	0.4656	0.0006	36.712	0.024	3.613	2260	1400.528
0.014178	0.4940	0.0003	32.595	0.012	1.007	660	1361.126
0.015582	0.5176	0.0005	31.167	0.011	2.104	1499	1367.552
0.017144	0.5414	0.0003	33.555	0.018	1.222	782	1338.693
0.018818	0.5644	0.0004	37.921	0.019	3.269	1953	1369.518
0.020548	0.5859	0.0007	38.896	0.017	3.085	1783	1389.910
0.022049	0.6029	0.0008	32.600	0.008	1.529	1019	1374.695

[a]Standard uncertainties u are: $u(T_M)$ = 0.1 K, $u(p)$ = 15 kPa, $u(n_{Ga})$ = 0.000001 mol, $u(n_{Sn})$ = 0.000002 mol , $u(\Delta H_{Reaction})$ = 0.001 J;

Series 1: $u(K)$ = 0.000005 J /μV s, $u(\Delta_{mix}H)$ = 105.213 J mol^{-1};

Series 2: $u(K)$ = 0.000005 J /μV s , $u(\Delta_{mix}H)$ = 118.017 J mol^{-1},

Series 3: $u(K)$ = 0.000002 J /μV s, $u(\Delta_{mix}H)$ =121.018 J mol^{-1};

Table 3.4 Partial and integral mixing enthalpies of In-Sn 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: In-Sn alloys; Atmosphere: Argon at pressure p = 0.1 MPa; Starting amount n_{In} = 0.007854 mol, K = 0.002379 J /μV s ,T_D = 298 K, T_M = 673 K, $\Delta H_{Sn}^{T_D\rightarrow T_M}$ = 17839.35 (J mol^{-1})							
0.000396	0.0480	0.0005	6.332	0.017	-0.732	-1848	-88.724
0.000842	0.0968	0.0004	7.508	0.014	-0.448	-1004	-135.733
0.001498	0.1602	0.0007	11.067	0.012	-0.636	-970	-194.164
0.002094	0.2105	0.0005	10.501	0.015	-0.131	-220	-195.752
0.002918	0.2709	0.0008	14.530	0.008	-0.170	-206	-196.546
0.003822	0.3273	0.0005	16.136	0.015	0.009	10	-180.502
0.004815	0.3801	0.0007	17.509	0.012	-0.205	-206	-182.565
0.005668	0.4192	0.0007	15.144	0.015	-0.073	-86	-176.444
0.00737	0.4841	0.0003	30.056	0.017	-0.307	-180	-176.868
0.008655	0.5243	0.0007	22.953	0.016	0.029	23	-161.363
0.010099	0.5625	0.0002	25.620	0.017	-0.140	-97	-156.163
0.011543	0.5951	0.0003	25.819	0.019	0.059	41	-141.508

0.012676	0.6174	0.0005	19.917	0.012	-0.295	-260	-148.055
Series 2: In-Sn alloys; Atmosphere: Argon at pressure p = 0.1 MPa; Starting amount n_{In} = 0.007229 mol, K = 0.002419 J /μV s, T_D = 298 K, T_M = 723 K, $\Delta H_{Sn}^{T_D \to T_M}$ = 19266.2743 (J mol^{-1})							
0.000351	0.0463	0.0005	6.072	0.017	-0.690	-1966	-91.063
0.000798	0.0994	0.0007	8.129	0.013	-0.483	-1081	-146.157
0.001434	0.1655	0.0006	11.725	0.012	-0.528	-830	-196.384
0.001866	0.2052	0.0001	8.060	0.018	-0.263	-609	-215.938
0.002774	0.2773	0.0004	17.388	0.013	-0.106	-117	-206.985
0.003425	0.3215	0.0003	12.461	0.017	-0.081	-124	-201.922
0.004418	0.3793	0.0005	18.955	0.013	-0.176	-177	-199.826
0.005439	0.4293	0.0007	19.660	0.019	-0.011	-11	-184.590
0.007209	0.4993	0.0006	34.072	0.013	-0.029	-16	-163.908
0.008747	0.5475	0.0008	29.331	0.017	-0.301	-196	-167.007
0.010106	0.5830	0.0003	25.873	0.012	-0.310	-228	-171.794
0.011382	0.6116	0.0004	24.635	0.013	0.051	40	-157.263
Series 3: In-Sn alloys; Atmosphere: Argon at pressure p = 0.1 MPa; Starting amount n_{In} = 0.008272 mol, K = 0.002334 J /μV s, T_D = 298 K, T_M = 773 K, $\Delta H_{Sn}^{T_D \to T_M}$ = 20699.9793 (J mol^{-1})							
0.000436	0.0501	0.0002	8.137	0.015	-0.888	-2037	-102.022
0.000883	0.0965	0.0004	8.754	0.019	-0.499	-1116	-151.497

0.001538	0.1568	0.0005	12.952	0.017	-0.606	-925	-203.208
0.002446	0.2282	0.0007	18.549	0.012	-0.247	-272	-209.038
0.003523	0.2987	0.0008	21.990	0.016	-0.304	-282	-215.649
0.004511	0.3529	0.0005	20.343	0.018	-0.109	-110	-207.533
0.005504	0.3995	0.0007	20.460	0.012	-0.095	-96	-199.446
0.006525	0.4410	0.0006	21.185	0.014	0.050	49	-182.356
0.008228	0.4987	0.0005	34.928	0.017	-0.324	-190	-183.164
0.009765	0.5414	0.0004	31.651	0.016	-0.165	-107	-176.719
0.011377	0.5790	0.0003	33.294	0.019	-0.074	-46	-165.943
0.012822	0.6079	0.0007	29.666	0.013	-0.245	-170	-166.190
0.013955	0.6278	0.0009	23.345	0.017	-0.108	-95	-162.608

Standard uncertainties u are: $u(T_M)$ = 0.1 K, $u(p)$ = 14 kPa, $u(n_{In})$ = 0.000001 mol, $u(n_{Sn})$ = 0.000001 mol, $u(\Delta H_{Reaction})$ = 0.004 J;

Series 1: $u(K)$ = 0.000005 J /μV s, $u(\Delta_{mix}H)$ = 20.513 J mol^{-1};

Series 2: $u(K)$ = 0.000005 J /μV s, $u(\Delta_{mix}H)$ = 19.015 J mol^{-1},

Series 3: $u(K)$ = 0.000002 J /μV s, $u(\Delta_{mix}H)$ = 21.128 J mol^{-1}

For substitutional solutions, Ansara and Dupin [143] offer the following Redlich-Kister polynomial, which was used to fit the experimental calorimetric data for the enthalpies of mixing of all the binaries at 623 K, 673 K, and 723 K. The data set was fitted using least squares fit in accordance with **Equation 3.4**.

$$\boldsymbol{\Delta H_{mix} = \sum_i \sum_{j>i} \left[x_i x_j \sum_v L_{i:j}^{(v)} \left(x_i - x_j\right)^v \right]} \tag{3.4}$$

where $L_{i:j}^{(v)}$(ν= 0, 1, 2, **…**) are the interaction parameters(binary) of the binary systems.

Table 3.5 Binary interaction parameters as a function of temperature(T).

Interaction parameter	Order(ν)	(J/mol)
L_{Ga-Sn}^{v}	*0*	14.40T-5653
	1	0.12T^2-167.45T+58125
	2	-86.90T+62076
	3	96.93T-67943
L_{Ga-In}^{v}	*0*	-8.84T+11736
	1	13.21T-10519
	2	-0.33T^2+470.04T-164828
	3	1.06T^2-1542.22T+559523
L_{In-Sn}^{v}	*0*	-731
	1	-305
	2	-813
	3	-657

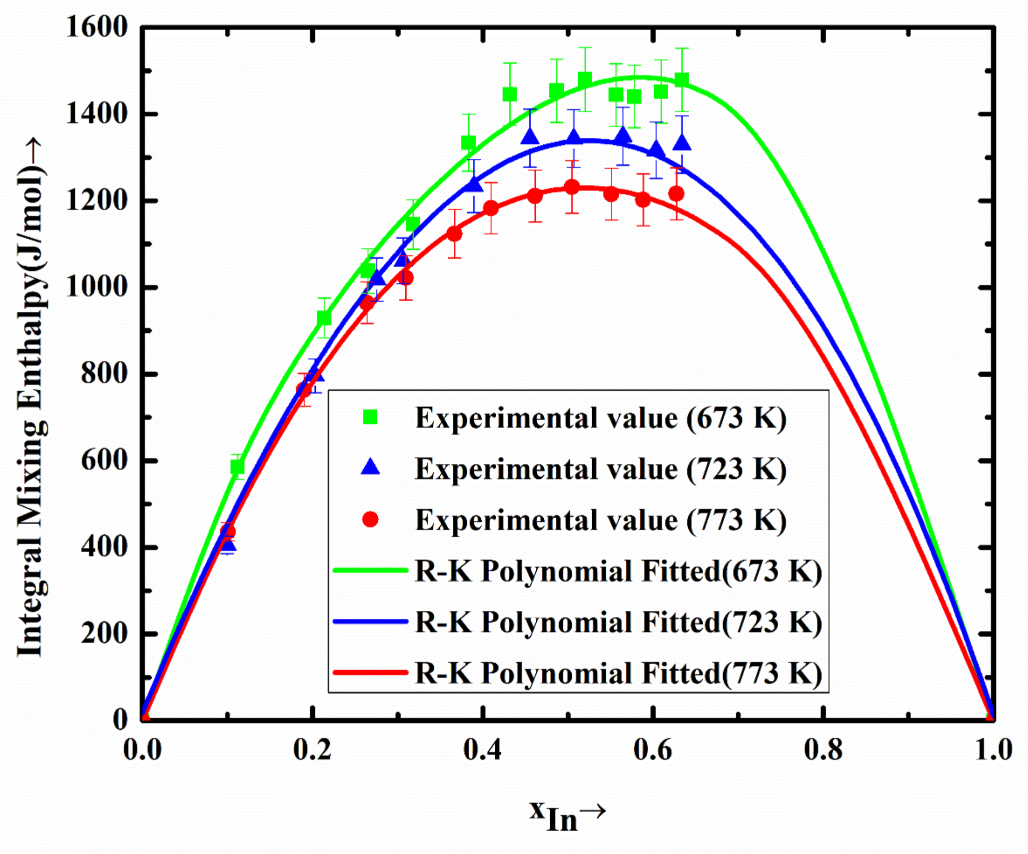

Fig.3.1 The enthalpies of mixing of Ga-In binary system with RK polynomial fitted curves at 673 K,723 K & 773 K.

Ga and In atoms interact in the Ga-In binary system and the nature of mixing enthalpies as a function of composition of indium is shown in **Figure 3.1**. It is quite obvious that mixing enthalpy is endothermic in nature for the given system. Endothermic mixing enthalpy suggests limited solubility or immiscibility between the components. The system tends to resist mixing due to unfavorable interactions or differences in intermolecular forces between the components. As a result, the two components may form separate phases or exhibit a miscibility gap, where they cannot form a homogeneous mixture over a certain composition range. It's important to note that the presence of an endothermic mixing enthalpy alone does not guarantee immiscibility or phase separation. Other factors, such as entropy effects, molecular size, polarity, and specific interactions, can also influence the miscibility behavior in a binary system. The curve representing enthalpy of mixing as function of composition at 673 K is asymmetric in nature however it is symmetric at 723 K and 773 K. This may be due to the presence of chemical short-range order in this liquid binary system. The enthalpy of mixing is temperature dependent as it decreases with increase of temperature. Redlich-Kister (R-K) polynomial is fitted to the experimental data and gives a good agreement with the experimental results.

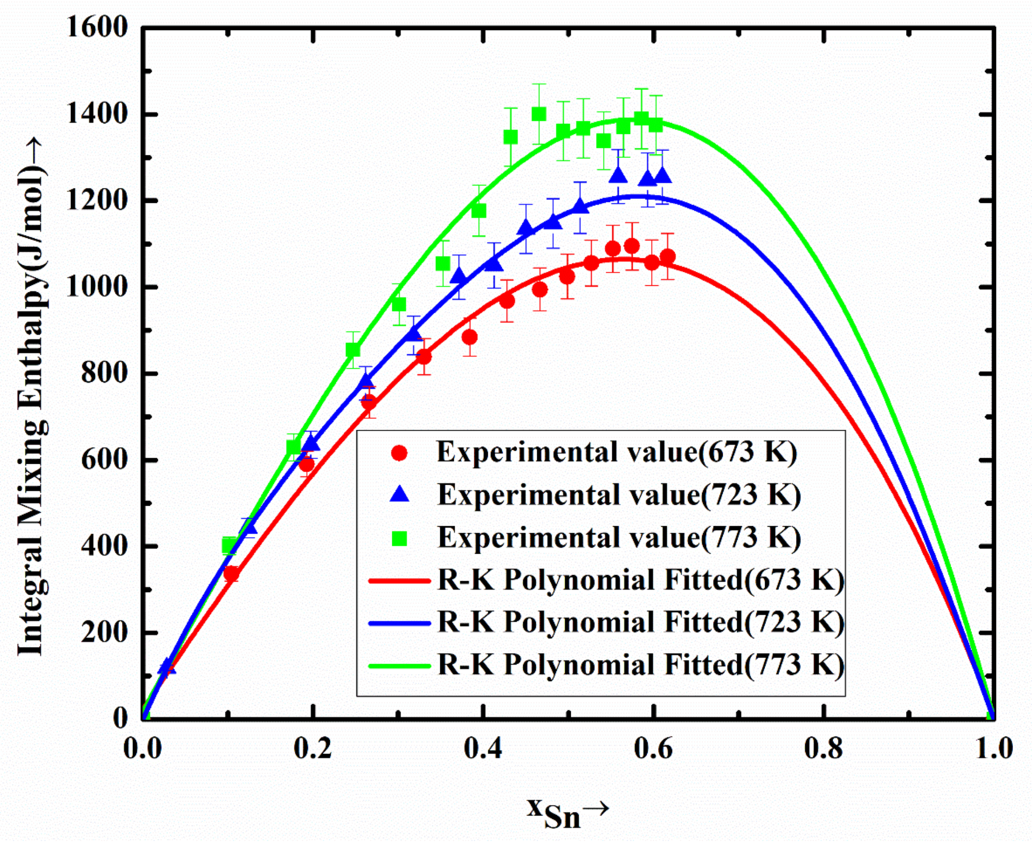

Fig.3.2 The enthalpies of mixing of Ga-Sn binary system with RK polynomial fitted curves at 673 K,723 K & 773K.

Thermodynamic behavior similar to the Ga-In system is also observed for the Ga-Sn System in the temperature range of 673 K-773 K as shown in **Figure 3.2**. The enthalpy of mixing is endothermic in nature and is almost symmetric at all temperature and dependent on temperature. This may be due to the presence of long-range ordering in liquid phase in this system. The atomic interaction is similar to the Ga-In system. The interatomic interaction is neither very strong nor very weak. Mild repulsive behavior between Ga and Sn atoms could be seen in this system. The enthalpy of mixing increases with increase of temperature for the Ga-Sn system. R-K polynomial fits well to the experimental results for the Ga-Sn system.

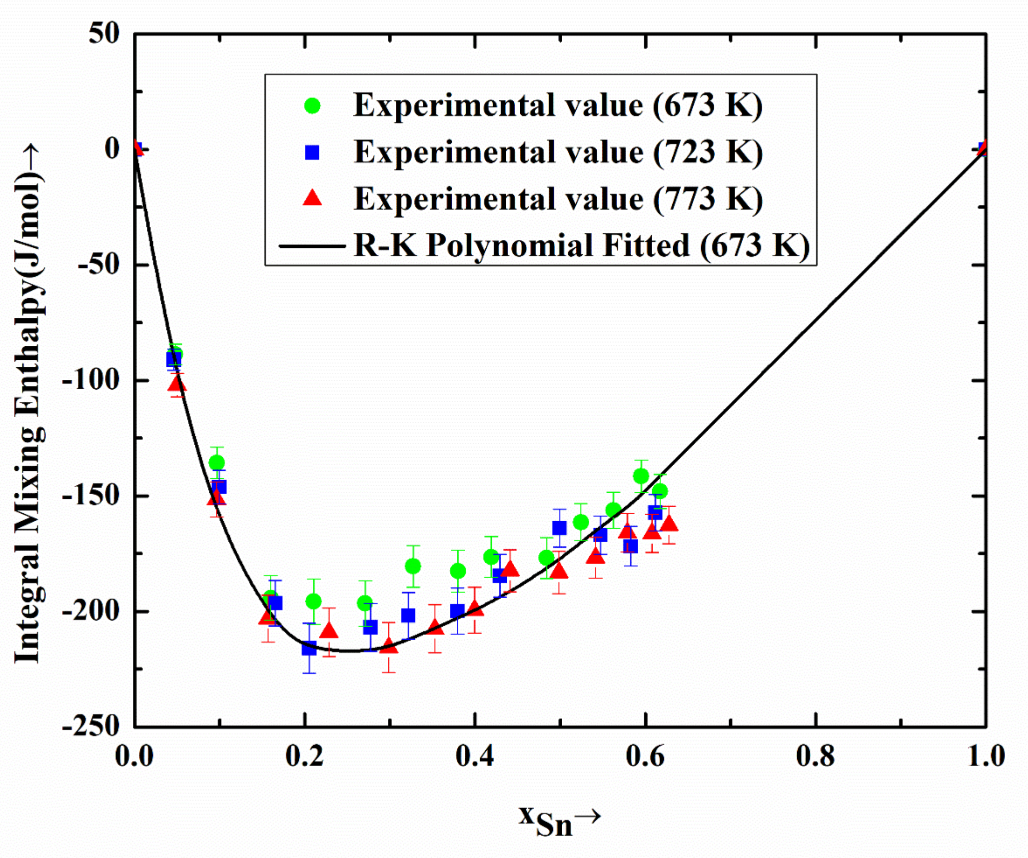

Fig.3.3 The enthalpies of mixing of the In-Sn binary system at 673 K,723 K & 773 K along with RK polynomial fitted curve.

The nature of enthalpies of mixing in In-Sn system as a function of composition of tin is represented in the **Figure 3.3**. Mixing enthalpy is exothermic in nature for the given system. Exothermic mixing enthalpy suggests complete miscibility between the components like In and Sn. The components can mix in any proportion without any significant energy barrier, resulting in a fully homogeneous mixture over the entire composition range. It's important to note that the presence of an exothermic mixing enthalpy alone does not guarantee miscibility. The solubility of both the components in a binary system will also depend on entropy of mixing, molecular size, polarity, and specific interactions. The enthalpy of mixing curve is becoming asymmetric with composition of tin which indicates the presence of chemical short-range order in this liquid binary system. The system is showing temperature independency with respect to mixing enthalpy.

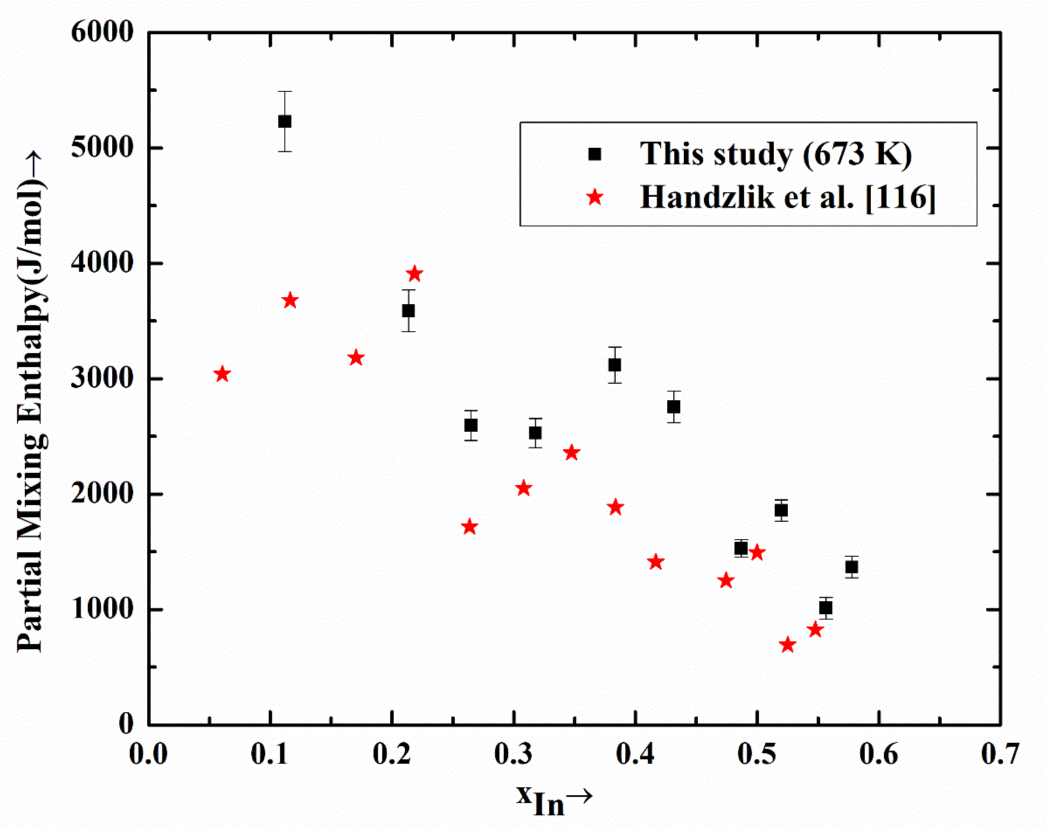

Fig.3.4 The comparison of experimental partial mixing enthalpy data of the Ga-In binary system at 673 K with the data available in literature [116].

Figure 3.4 shows the comparison between experimental data representing partial enthalpy of mixing of Ga-In system at 673 K with the data available in the literature [116]. It can be inferred from the above data points that there is slight difference between the present data and literature data. This variation may be due to difference in temperature and different techniques used by the different researchers. Further, some of the researchers have provided extrapolated data as they have measured up to limited compositions of x_{In}. Therefore, that may be the cause of some deviation. Also decreasing trend of partial enthalpy can be seen easily for this system. As the system moves towards the composition with a lower partial enthalpy of mixing, the components are more likely to form a homogeneous mixture over a wider range of compositions.

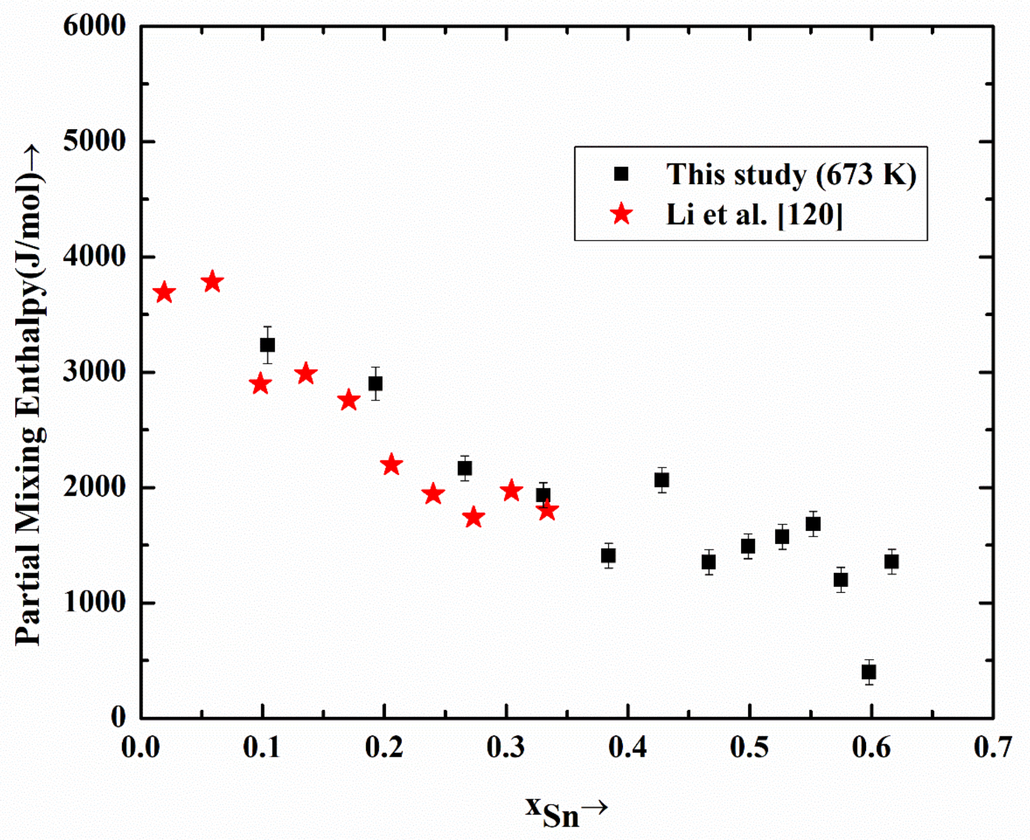

Fig.3.5 The comparison of experimental partial mixing enthalpy data of the Ga-Sn binary system at 673 K with the data available in literature [120].

Figure 3.5 shows the comparison between experimental data representing partial enthalpy of mixing of Ga-Sn system at 673 K with the data available in the literature [120]. It can be inferred from the above data points that there is slight difference between the present data and literature data. Li et al. [120] employed a calvet type calorimeter to measure partial and integral mixing enthalpies of the Ga-Sn system at a specific temperature of 803 K, but only for compositions where $x_{Sn} < 0.35$. This variation may be due to difference in temperature and different techniques used by the different researchers. Further, some of the researchers have provided extrapolated data as they have measured up to limited compositions of x_{Sn}.

Therefore, that may be the cause of some deviation. Also decreasing trend of partial enthalpy can be seen easily which suggests that the energy required to mix the components decreases as the system moves towards a certain composition. The decreasing trend in the partial enthalpy of mixing indicates that the mixing process becomes more favorable as the composition approaches a certain point. This suggests that the components are becoming more compatible and exhibit improved mixing behavior. The decreasing trend in the partial enthalpy of mixing suggests a reduced tendency for phase separation or the formation of distinct phases. It implies that the components have better compatibility, resulting in a more stable and homogenous mixture.

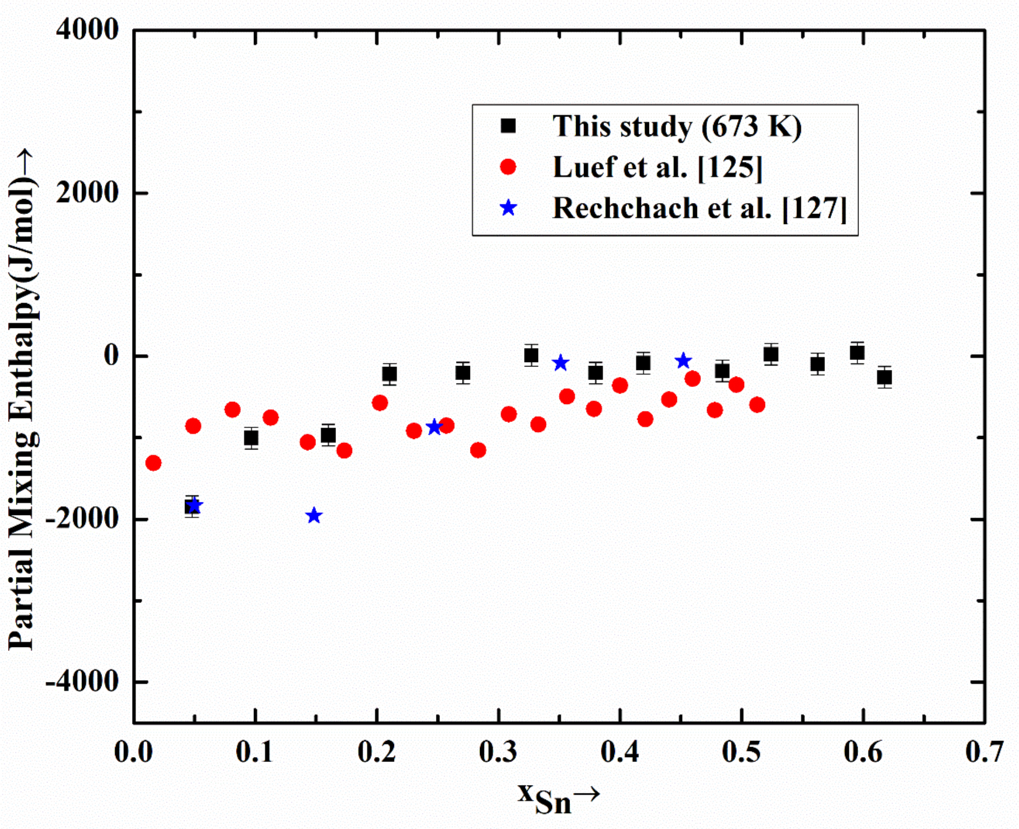

Fig.3.6 The comparison of experimental partial mixing enthalpy data of the In-Sn binary system at 673 K with the data available in literature [125], [127].

Figure 3.6 shows the comparison between experimental data representing partial enthalpy of mixing of In-Sn system at 673 K with the data available in the literature. It can be inferred from the above figure that there is slight difference between the present data and literature data[125], [127] as far as the increasing trend is concerned. This variation may be due to difference in temperature and different techniques used by the different researchers. Further, some of the researchers have provided extrapolated data as they have measured up to limited compositions of $x_{\mathrm{Sn\ and}}$ x_{In}. Therefore, that may be the cause of some deviation.

Partial mixing enthalpy is tending to zero value which indicates that the energy required to mix the components approaches a negligible or minimal value as the system moves towards a certain composition. A partial enthalpy of mixing approaching zero indicates that the components mix nearly ideally. In an ideal mixing scenario, there are no significant energy changes associated with the mixing process, and the components exhibit perfect compatibility and uniform distribution throughout the mixture. The near-zero partial enthalpy of mixing implies a smooth transition between the phases or regions within the system. There are no sharp changes or distinct boundaries associated with phase separation, indicating a continuous variation in properties as the composition changes. It's important to note that the trend in the partial enthalpy of mixing alone provides insights into the mixing behavior but doesn't necessarily indicate complete miscibility or absence of phase separation. Other factors, such as entropy effects, intermolecular interactions, and the presence of miscibility gaps, should be considered to comprehensively analyze the phase and mixing behavior of the binary system.

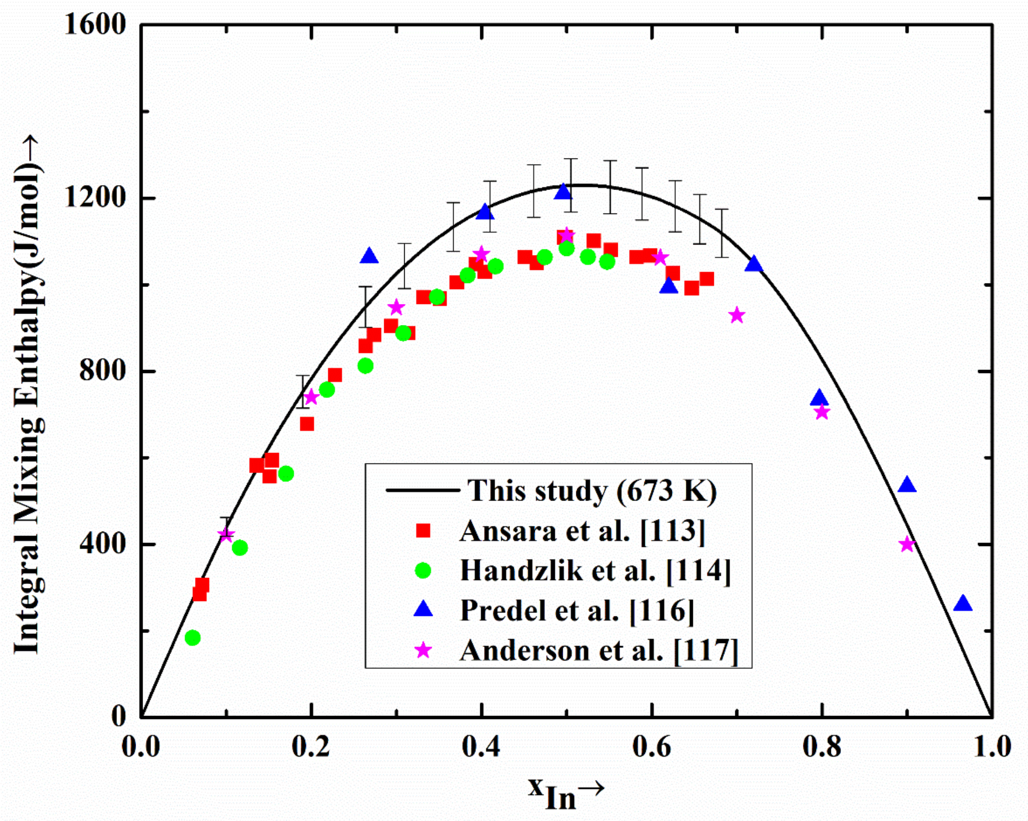

Fig.3.7 Comparison of RK Polynomial fitted results of this study with data available in literature for the Ga–In system at 673 K [113], [114], [116], [117].

Figure 3.7 shows the fitted data of the integral molar enthalpy of mixing for the Ga–In system at 673 K which was derived by fitting the experimental data using standard Redlich–Kister polynomials. All measured enthalpies of mixing are endothermic. The experimental data of this study deviates slightly more from literature [113], [114], [116], [117] near equiatomic composition and shows better agreement at terminal compositions. This variation may be due to difference in temperature and different techniques used by the different researchers. Further, some of the researchers have provided extrapolated data as they have measured up to limited compositions of x_{Sn} and x_{In}. Therefore, that may be the cause of some deviation.

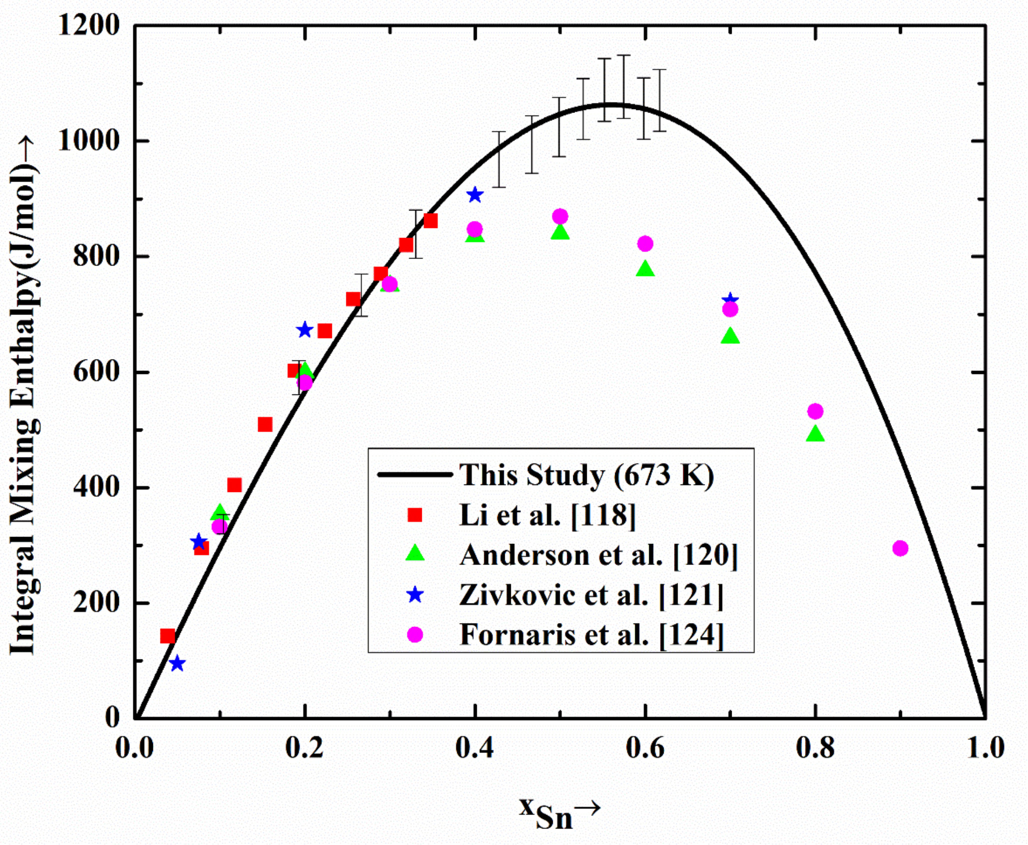

Fig.3.8 Comparison of RK Polynomial Fitted results of this study with data available in literature[118], [120], [121], [124] for the Ga-Sn system.

Figure 3.8 shows experimental data of this study along with the literature data for the Ga-Sn system at 673 K. The experiments were carried out in the liquid region of this alloy. The enthalpies of mixing are found to be endothermic in nature. The data available in the literature [118], [120], [121], [124]show better agreement with our results up to x_{Sn} ~ 0.4 and after that there is slight variation from data available in literature. This variation may be due to difference in temperature and different techniques used by the different researchers. Further, some of the researchers have provided extrapolated data as they have measured up to limited compositions of x_{Sn} and x_{In}. Therefore, that may be the cause of some deviation. This variation may be because there is better miscibility at this temperature as system is getting more symmetric.

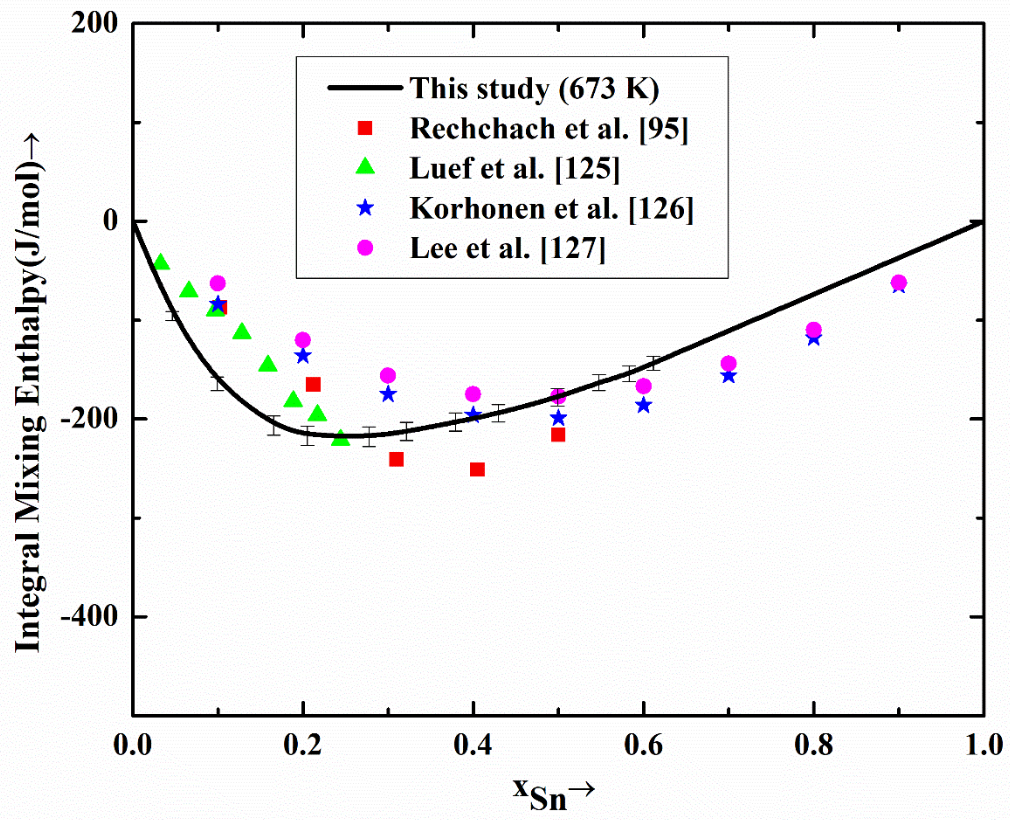

Fig.3.9 Comparison of RK Polynomial fitted results of this study with data available in literature [95], [125]–[127] for the In–Sn system.

Figure 3.9 shows the fitted data of the integral molar enthalpy of mixing for the In–Sn system at 673 K which was derived by fitting the experimental data using standard Redlich–Kister polynomials. This experimental temperature was high enough to obtain fully liquid alloys over the complete concentration range. All measured enthalpies of mixing are slightly exothermic. The data available in the literature [95], [125]–[127] show slight variation with our results irrespective of different temperature of measurements. This variation may be due to difference in temperature and different techniques used by the different researchers.

Table 3.5 lists the interaction parameters for the given binary systems. It is observed that the values for the mixing enthalpies of all systems were in good agreement except for a few compositions. Therefore, the R-K Polynomial Fitting is very well followed by this system in the temperature range of 673 K-773 K. 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%.

3.4 Conclusions

Integral and partial mixing enthalpies of Ga-In, Ga-Sn and In-Sn binary systems were investigated using drop calorimeter (MHTC 96 LINE EVO) in the temperature range of 673 K-773 K. Pieces of pure Indium were dropped into molten Gallium which is kept in crucible; Tin into molten Gallium and Tin into molten Indium. It has been found that the enthalpies of mixing shows temperature-dependency for two binaries Ga-In & Ga-Sn and is independent of temperature for In-Sn System. Enthalpies of mixing was found to be endothermic for Ga-In and Ga-Sn where it was exothermic for In-Sn system. Binary interaction parameters were determined by using R-K Polynomial Fitting, followed by least square optimization. The agreement between the experimental results and theoretical model was very good.