



## Thermodynamic investigations of Sn–Zn–Ga liquid solutions

C.K. Behera, M. Shamsuddin\*

Centre of Advanced Study, Department of Metallurgical Engineering, Institute of Technology, Banaras Hindu University, Varanasi 221005, Uttar Pradesh, India

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### ABSTRACT

Activity of zinc in liquid Sn–Zn–Ga alloys has been measured by electrochemical technique based on molten salt electrolyte galvanic cell in the temperature range 723–823 K along three pseudo-binary lines of  $Zn_x(Sn_yGa_{1-y})_{1-x}$  where  $y = 0.75, 0.50$  and  $0.25$ . The excess molar free energy, enthalpy and entropy have been computed by the Darken's treatment of the ternary solutions using published data of the relevant binary solutions and ternary system investigated. Slope–intercept method has been used to compute the partial molar quantities. The activities of tin and gallium are computed from the partial molar excess free energies of three components at 750 K. The activities of all the three components show positive deviation from the Raoult's law. Thermodynamic properties of Sn–Ga binary system have been predicted at 750 K from the ternary data and compared with those published in the literature.

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### 1. Introduction

Zn–Sn eutectic system is one of the most promising lead free solders among various alloy systems. However, tendency towards oxidation, poor wetting ability and higher melting point of this alloy system confines its applications. Addition of the third element viz. Ag, Bi, Sb, Ga, etc. [1,2] may reduce the fusion temperature and improve other properties of Zn–Sn alloy. Phase diagram and thermodynamic properties of alloy systems are helpful in understanding and predicting the possible interfacial reactions between solder and substrate materials. Recently, ternary phase diagram of Sn–Zn–Ga system based on piecing binary phase diagram method has been presented by Zhang et al. [3]. The eutectic temperature of the Sn–Zn–Ga alloy has been found to be 283 K by the above method. Since thermodynamic properties of ternary Sn–Zn–Ga alloys and low temperature data of Sn–Ga alloys have not been reported in the literature, the present studies have been devoted to determine the activity of zinc in these alloys. Our experimental data together with the published thermodynamic data on Zn–Ga and Zn–Sn alloys have been employed to estimate the thermodynamic properties of Sn–Ga alloys.

The paper highlights activity measurement of zinc in liquid Sn–Zn–Ga alloys by electrochemical technique based on fused salt electrolyte: LiCl–KCl + 5 wt.%  $ZnCl_2$  in the temperature range: 723–823 K along three pseudo-binary lines of  $Zn_x(Sn_yGa_{1-y})_{1-x}$

where  $y = 0.75, 0.50, 0.25$ . The excess molar free energy, enthalpy and entropy were computed by the Darken's treatment of the ternary solutions using the published data of the relevant binary solutions and the ternary systems investigated. Various excess and partial molar thermodynamic quantities and activities of the constituent elements, Sn and Ga have been computed at 750 K.

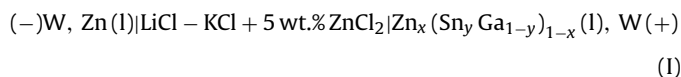
### 2. Experimental

#### 2.1. Materials

High purity (99.999%) zinc, tin and gallium obtained from Johnson Matthey, U. K were used. The following analytical reagent grade salts were used for the preparation of the electrolyte: lithium chloride (Qualigens, India, 99% purity), potassium chloride (Qualigens, India, 99.8% purity) and zinc chloride (MERCK, Germany, 96% purity).

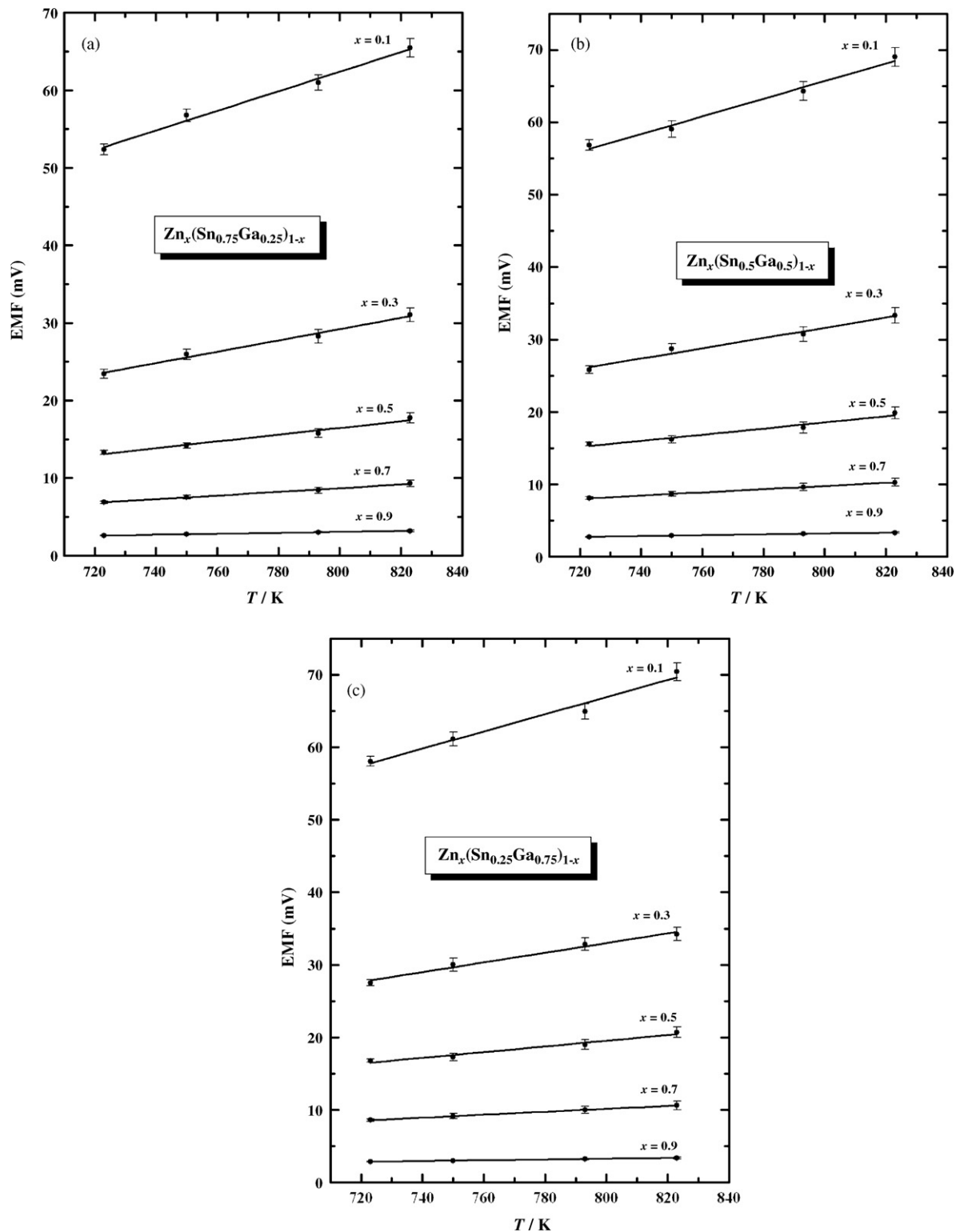
#### 2.2. Electrochemical measurements

The activity of Zn in the liquid Sn–Zn–Ga system was determined by measuring the reversible open circuit electromotive force (emf) of the following electrochemical cell:



The compositions of the ternary alloys along the chosen pseudo-binary lines of  $Zn_x(Sn_yGa_{1-y})_{1-x}$ , where  $y = 0.25, 0.50$  and  $0.75$  were represented as:  $x = 0.1, 0.3, 0.5, 0.7$  and  $0.9$ . A eutectic mixture of

\* Corresponding author. Tel.: +91 542 2369346; fax: +91 542 2369478.  
E-mail address: [shams@bhu.ac.in](mailto:shams@bhu.ac.in) (M. Shamsuddin).



**Fig. 1.** (a) Emf vs. temperature plot of the galvanic cell: (–) W, Zn (l) |LiCl–KCl + 5 wt.% ZnCl<sub>2</sub> |Zn<sub>x</sub>(Sn<sub>0.75</sub>Ga<sub>0.25</sub>)<sub>1–x</sub> (l), W (+); (b) (–) W, Zn (l) |LiCl–KCl + 5 wt.% ZnCl<sub>2</sub> |Zn<sub>x</sub>(Sn<sub>0.5</sub>Ga<sub>0.5</sub>)<sub>1–x</sub> (l), W (+); and (c) (–) W, Zn (l) |LiCl–KCl + 5 wt.% ZnCl<sub>2</sub> |Zn<sub>x</sub>(Sn<sub>0.25</sub>Ga<sub>0.75</sub>)<sub>1–x</sub> (l), W (+) (error bar shows the maximum deviation from the average value of cell emf based on two independent runs and on heating and cooling cycles).

LiCl–KCl containing 5 wt.% ZnCl<sub>2</sub> was used as the electrolyte. A cell assembly made of BOROSIL glass containing six lower limbs (6 mm internal diameter each) below a tubular electrolyte compartment (60 mm internal diameter) was used in this investigation. At the bottom of each limb, an electrode contact wire of tungsten (0.4 mm diameter and 20 cm length) was sealed. The design of the

cell assembly and experimental techniques were similar to those described by Shamsuddin et al. [4].

The experiment was performed by charging pieces of zinc, tin and gallium (frozen prior to weighing) in suitable proportion to form the appropriate alloy electrode [Zn<sub>x</sub>(Sn<sub>y</sub>Ga<sub>1–y</sub>)<sub>1–x</sub>] in the five of the six limbs and the most electropositive metal (Zn) in the alloys,

**Table 1**  
Emf (mV) of the galvanic cell [I] at different temperatures.

$x_{Zn}$	$y/(1-y)$	Temperature (K)				$E = A + BT$	
		723	750	793	823	A	B
0.1	0.75/0.25	52.34(±0.71)	56.76(±0.82)	60.99(±1.00)	65.48(±1.19)	39.19	0.12702
0.3		23.42(±0.57)	25.94(±0.7)	28.27(±0.87)	31.05(±0.89)	29.58	0.0735
0.5		13.31(±0.28)	14.19(±0.35)	15.77(±0.55)	17.76(±0.67)	16.28	0.04082
0.7		6.89(±0.15)	7.52(±0.24)	8.42(±0.39)	9.32(±0.41)	10.10	0.0235
0.9		2.58(±0.07)	2.74(±0.07)	3.01(±0.10)	3.19(±0.11)	1.85	0.00613
0.1	0.50/0.50	56.88(±0.73)	59.07(±1.14)	64.35(±1.29)	69.04(±1.32)	28.60	0.11787
0.3		25.82(±0.54)	28.71(±0.67)	30.74(±0.99)	33.35(±1.08)	26.87	0.07326
0.5		15.55(±0.25)	16.2(±0.50)	17.82(±0.77)	19.87(±0.83)	12.41	0.03858
0.7		8.06(±0.19)	8.65(±0.30)	9.60(±0.49)	10.26(±0.55)	7.84	0.02199
0.9		2.73(±0.06)	2.88(±0.05)	3.13(±0.10)	3.30(±0.11)	1.40	0.00571
0.1	0.25/0.75	58.07(±0.67)	61.17(±0.95)	64.97(±1.08)	70.43(±1.25)	25.15	0.11499
0.3		27.52(±0.40)	30.01(±0.90)	32.85(±0.88)	34.23(±0.93)	23.11	0.07017
0.5		16.78(±0.24)	17.28(±0.50)	18.97(±0.67)	20.7(±0.72)	9.18	0.03581
0.7		8.57(±0.17)	9.12(±0.34)	9.99(±0.52)	10.6(±0.59)	6.10	0.0203
0.9		2.82(±0.05)	2.97(±0.08)	3.2(±0.10)	3.36(±0.12)	1.09	0.00541

was charged in the sixth limb. After charging the reaction compartment with electrolyte, the cell assembly was lowered into the constant temperature zone of a vertical tube furnace (which was already pre-heated to 400 K) and heating commenced after flushing argon for 1 h.

The temperature of the cell was controlled to an accuracy of better than  $\pm 0.5$  K by a digital temperature controller. Both the temperature and cell emf were measured by digital electrometer at an input impedance of greater than  $2 \times 10^{12} \Omega$ . The cell attained equilibrium after 20 h, and thereafter, the emf values remained constant for over 30 h. After attaining the constant emf at one temperature, the temperature was changed and sufficient time was allowed for the reestablishment of the equilibrium. The emf values were measured during heating as well as in cooling cycles. Each composition was repeated twice to check the reproducibility of the results. Chemical analysis of the alloy electrodes removed from the cell after completion of the experiment indicated no change in composition of the alloy charged in the cell while starting the experiment.

### 3. Results and discussion

#### 3.1. Activity of zinc

The virtual cell reaction in the galvanic cell [I] may be represented as follows:

**Table 2**  
Activity and partial molar free energy of Zn in  $\text{Zn}_x(\text{Sn}_y\text{Ga}_{1-y})_{1-x}$  alloys.

$x_{Zn}$	$y/(1-y)$	$a_{Zn}$				$\Delta_{mix} \bar{G}_{Zn}^{\circ} (kJ mol^{-1})$			
		723 K	750 K	793 K	823 K	723 K	750 K	793 K	823 K
0.1	0.75/0.25	0.186(±0.004)	0.172(±0.004)	0.167(±0.005)	0.157(±0.005)	3.739(±0.137)	3.403(±0.157)	3.41(±0.193)	3.118(±0.230)
0.3		0.471(±0.009)	0.448(±0.01)	0.437(±0.011)	0.416(±0.01)	2.717(±0.055)	2.501(±0.135)	2.482(±0.168)	2.245(±0.172)
0.5		0.652(±0.006)	0.644(±0.007)	0.630(±0.01)	0.605(±0.011)	1.598(±0.054)	1.583(±0.068)	1.526(±0.106)	1.315(±0.129)
0.7		0.801(±0.004)	0.792(±0.006)	0.781(±0.009)	0.768(±0.009)	0.814(±0.029)	0.773(±0.046)	0.726(±0.075)	0.642(±0.079)
0.9		0.920(±0.002)	0.918(±0.002)	0.915(±0.003)	0.913(±0.003)	0.135(±0.014)	0.128(±0.014)	0.114(±0.019)	0.105(±0.023)
0.1	0.50/0.50	0.161(±0.004)	0.160(±0.006)	0.152(±0.006)	0.142(±0.005)	2.863(±0.140)	2.957(±0.221)	2.761(±0.124)	2.431(±0.127)
0.3		0.436(±0.008)	0.411(±0.009)	0.406(±0.012)	0.390(±0.012)	2.254(±0.104)	1.966(±0.129)	2.005(±0.191)	1.802(±0.209)
0.5		0.606(±0.005)	0.605(±0.009)	0.593(±0.013)	0.570(±0.013)	1.165(±0.049)	1.196(±0.096)	1.131(±0.149)	0.908(±0.161)
0.7		0.771(±0.005)	0.765(±0.007)	0.755(±0.011)	0.748(±0.012)	0.588(±0.037)	0.555(±0.058)	0.499(±0.094)	0.46(±0.106)
0.9		0.916(±0.002)	0.914(±0.001)	0.912(±0.003)	0.911(±0.003)	0.106(±0.011)	0.101(±0.01)	0.091(±0.019)	0.084(±0.021)
0.1	0.25/0.75	0.154(±0.003)	0.150(±0.004)	0.149(±0.005)	0.137(±0.005)	2.633(±0.128)	2.552(±0.184)	2.642(±0.173)	2.162(±0.242)
0.3		0.413(±0.005)	0.395(±0.011)	0.382(±0.01)	0.380(±0.01)	1.926(±0.077)	1.715(±0.174)	1.598(±0.170)	1.632(±0.180)
0.5		0.583(±0.004)	0.585(±0.009)	0.573(±0.011)	0.557(±0.011)	0.928(±0.046)	0.987(±0.096)	0.909(±0.130)	0.748(±0.139)
0.7		0.759(±0.004)	0.754(±0.008)	0.746(±0.011)	0.741(±0.012)	0.490(±0.033)	0.464(±0.065)	0.423(±0.100)	0.395(±0.114)
0.9		0.913(±0.001)	0.912(±0.002)	0.910(±0.003)	0.909(±0.003)	0.089(±0.010)	0.084(±0.015)	0.077(±0.019)	0.072(±0.023)

The activity of zinc in the Sn–Zn–Ga solution was calculated from the relation:

$$\ln a_{Zn} = -\frac{nFE}{RT} \quad (2)$$

where  $n$  is the number of electrons (two in the present case) transferred during reaction (1),  $E$  the open circuit emf of the galvanic cell [I],  $F$  the Faraday constant and  $R$  the universal gas constant. The variation of emf with temperature shown in Fig. 1a–c for 15 different compositions was calculated by least square method in the form of a linear equation ( $E = A + BT$ ) as shown in Fig. 1a–c and listed in Table 1. The error limit marked in the figures are the maximum deviation from the average value of the cell emf from two independent runs during heating and cooling cycles. From the emf values measured at different temperatures, activities of zinc in Sn–Zn–Ga liquid alloys were calculated and are listed in Table 2. Fig. 2 represents the typical variation of activity with composition at a selected temperature of 750 K. The plot exhibits positive deviations from Raoult's law up to  $\sim 93$  mol% Zn, which indicates the tendency of clustering of Sn and Ga in the second nearest neighborhood (in the electronegative sublattice). The activity decreases with increase of temperature which indicates that the system tends towards ideality with temperature.

#### 3.2. Activity of tin and gallium

As the activity of only one component of the ternary solutions (zinc in the present case) can be determined experimentally by

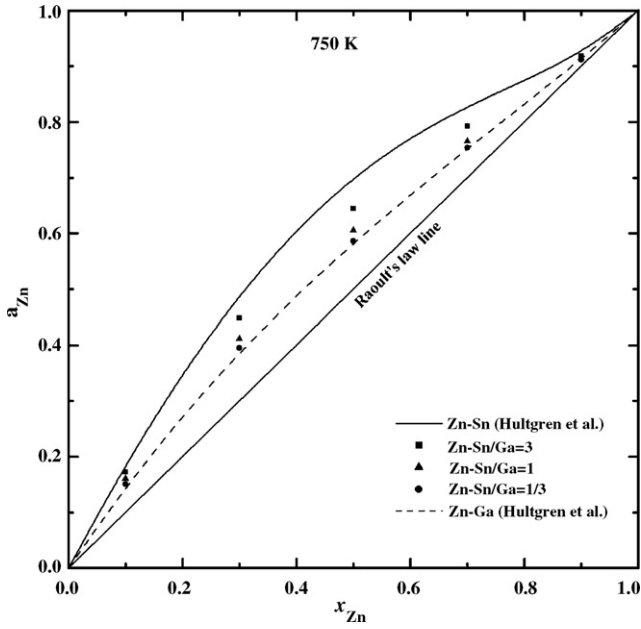


Fig. 2. Activity of zinc in Zn-Sn, Zn-Ga and  $Zn_x(Sn_yGa_{1-y})_{1-x}$  alloys at 750 K.

the use of the cell [1], the activity of other components has been estimated by Gibbs–Duhem equation. Darken [5] has suggested a method for the computation of activities of other two components (at the base of the triangle) provided partial molar property of one component (at the apex) is known over the ternary field. Making use of the following Darken's equations, excess molar free energy,  $\Delta_{mix} \bar{G}_{Zn}^{\circ,E}$  can be derived by two methods: (i) base binary data of gallium–tin and the ternary data along the pseudo-binary system of  $(Sn_yGa_{1-y})-Zn$  [Eq. (3)] or (ii) employing two binary data of zinc–tin and zinc–gallium and the same ternary data [Eq. (4)]:

$$\Delta_{mix} \bar{G}_{Zn}^{\circ,E} = (1 - x_{Zn}) \left[ \int_0^{x_{Zn}} \frac{\Delta_{mix} \bar{G}_{Zn}^{\circ,E}}{(1 - x_{Zn})^2} dx_{Zn} + \Delta_{mix} \bar{G}_{Sn-Ga}^{\circ,E} \right]_{x_{Sn}/x_{Ga}} \quad (3)$$

or

$$\Delta_{mix} \bar{G}_{Zn}^{\circ,E} = (1 - x_{Zn}) \left[ \int_1^{x_{Zn}} \frac{\Delta_{mix} \bar{G}_{Zn}^{\circ,E}}{(1 - x_{Zn})^2} dx_{Zn} \right]_{x_{Sn}/x_{Ga}} + x_{Sn} [\Delta_{mix} \bar{G}_{Sn}^{\circ,E}]_{x_{Zn}=1} + x_{Ga} [\Delta_{mix} \bar{G}_{Ga}^{\circ,E}]_{x_{Zn}=1} \quad (4)$$

The last two terms refer to the infinitely dilute binary solutions of Sn and Ga, respectively in Zn. The values of  $[\Delta_{mix} \bar{G}_{Sn}^{\circ,E}]_{x_{Zn}=1}$  and  $[\Delta_{mix} \bar{G}_{Ga}^{\circ,E}]_{x_{Zn}=1}$  are found from the respective binaries as the integral:

$$\int_0^1 \frac{\Delta_{mix} \bar{G}_{Zn}^{\circ,E}}{(1 - x_{Zn})^2} dx_{Zn}$$

On comparison Eqs. (3) and (4) yield:

$$\Delta_{mix} \bar{G}_{Binary Sn-Ga}^{\circ,E} = - \left[ \int_0^1 \frac{\Delta_{mix} \bar{G}_{Zn}^{\circ,E}}{(1 - x_{Zn})^2} dx_{Zn} \right]_{x_{Sn}/x_{Ga}} + x_{Sn} [\Delta_{mix} \bar{G}_{Sn}^{\circ,E}]_{x_{Zn}=1} + x_{Ga} [\Delta_{mix} \bar{G}_{Ga}^{\circ,E}]_{x_{Zn}=1} \quad (5)$$

The integral molar properties of the binary Sn–Ga can be computed along each pseudo-binary line by Eq. (5) from the ternary data.

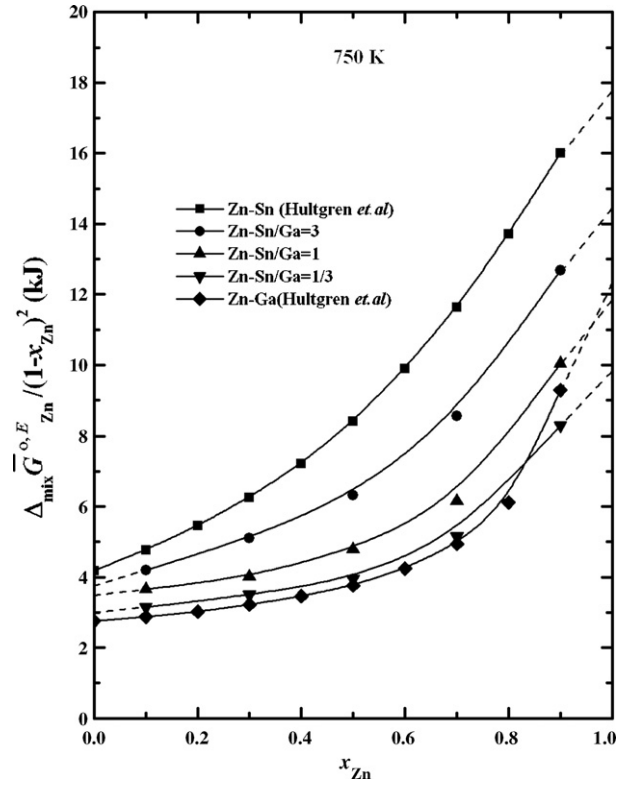


Fig. 3. Free energy function of zinc in Sn-Zn-Ga liquid alloys at 750 K.

The excess partial molar free energy and enthalpy of zinc at 750 K are computed by the following equations:

$$\Delta_{mix} \bar{G}_{Zn}^{\circ,E} = RT \ln \gamma_{Zn} \quad (6)$$

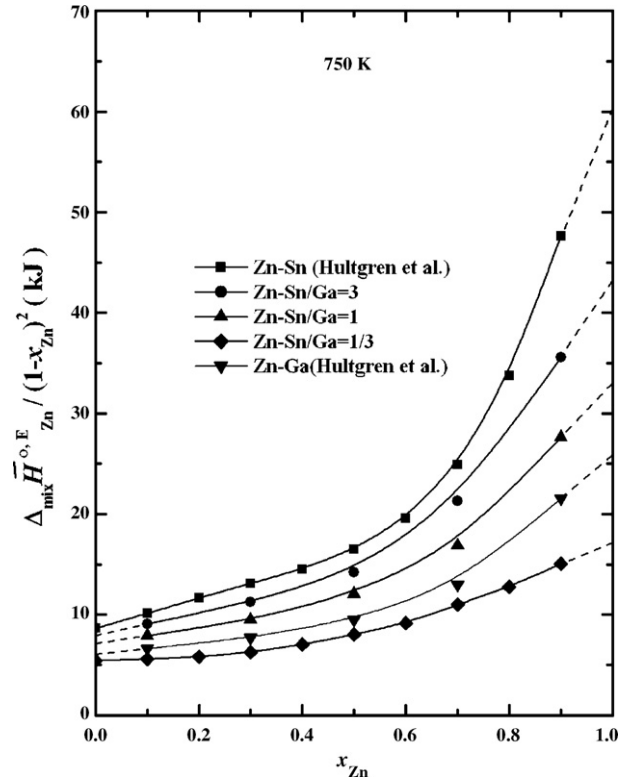


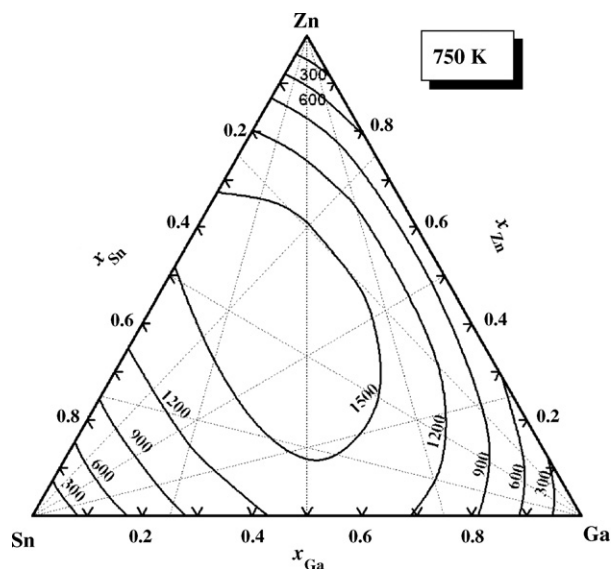
Fig. 4. Heat of solution function of zinc in Sn-Zn-Ga liquid alloys at 750 K.

**Table 3**  
Properties of tin–gallium liquid alloys at 750 K at  $x_{\text{Sn}}/x_{\text{Ga}} = 3, 1$  and  $1/3$ .

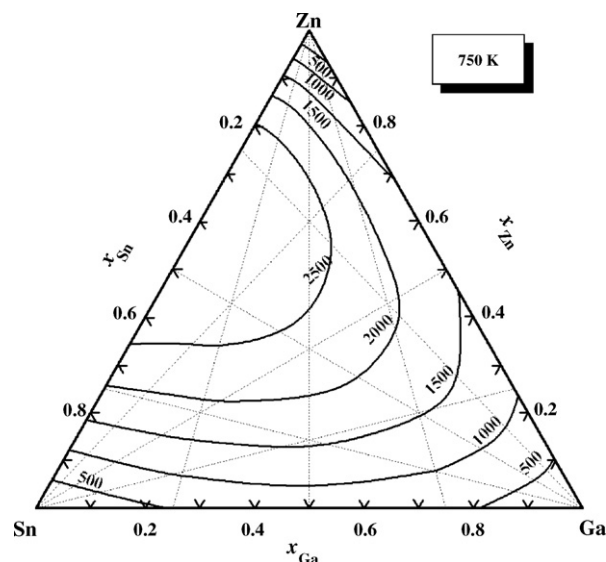
References	$\Delta_{\text{mix}}H^{\circ,E} \text{ (J mol}^{-1}\text{)}$			$\Delta_{\text{mix}}G^{\circ,E} \text{ (J mol}^{-1}\text{)}$		
	3	1	1/3	3	1	1/3
Hultgren et al. [6]	616	829	625	–	–	–
Zivkovic et al. [7]	557	758	572	–	–	–
Zivkovic et al. [8]	626	928	748	–	–	–
Bros and Laffite [9]	638	856	650	–	–	–
Katayama et al. [10] (at 1000 K)	–	–	–	681	1189	1080
Predicted (at 750 K)	510	790	600	820	1310	1090

$$\Delta_{\text{mix}}\bar{H}_{\text{Zn}}^{\circ,E} = -2F \left[ E - T \left( \frac{\partial E}{\partial T} \right)_{x,P} \right] \quad (7)$$

For the graphical calculation of the ternary excess molar free energy and enthalpy at 750 K by Eq. (4), it is essential to plot  $\Delta_{\text{mix}}\bar{G}_{\text{Zn}}^{\circ,E}/(1-x_2)^2$  and  $\Delta_{\text{mix}}\bar{H}_{\text{Zn}}^{\circ,E}/(1-x_2)^2$  as a function of  $x_{\text{Zn}}$ . The experimental data plotted in Figs. 3 and 4 show these two functions for zinc in each of the five binary/pseudo-binary solutions: (A) Zn–Sn, (B) Zn–Sn/Ga = 3, (C) Zn–Sn/Ga = 1, (D) Zn–Sn/Ga = 1/3, and (E) Zn–Ga. The  $\Delta_{\text{mix}}G^{\circ,E}$  and  $\Delta_{\text{mix}}H^{\circ,E}$  values for the 3, 1 and 1/3 pseudo-binary lines crossing ternary field are computed by Eq. (4). The integral on the right hand side of Eq. (4) is the area from  $x_{\text{Zn}} = 1$  to  $x_{\text{Zn}} = x_{\text{Zn}}$  under the appropriate curve in Figs. 3 and 4 and the integration constants  $[\Delta_{\text{mix}}\bar{G}_{\text{Sn}}^{\circ,E}]_{x_{\text{Zn}}=1}$  and  $[\Delta_{\text{mix}}\bar{G}_{\text{Ga}}^{\circ,E}]_{x_{\text{Zn}}=1}$  are obtained from the literature [6]. The excess molar free energy and enthalpy values for the Zn–Sn and Zn–Ga binary systems have also been adapted from the literature [6]. The excess molar thermodynamic properties of Sn–Ga system at 750 K as estimated by Eq. (5) are listed in Table 3 and compared with the values reported in literature.  $\Delta_{\text{mix}}G^{\circ,E}$  and  $\Delta_{\text{mix}}H^{\circ,E}$  values for three pseudo-binary lines as function of  $x_{\text{Sn}}$  were computed by drawing three lines from Sn corner as apex to Zn–Ga binary side at  $x_{\text{Zn}}/x_{\text{Ga}}$  ratio of 1/3, 1 and 3. These lines intersect the pseudo-binary lines drawn from Zn corners to Sn–Ga binary. The corresponding compositions of Zn for the point of intersection were calculated. This composition was used as the upper limit of the integration in Eq. (4).  $\Delta_{\text{mix}}G^{\circ,E}$  and  $\Delta_{\text{mix}}H^{\circ,E}$  curves for the pseudo-binary lines ( $x_{\text{Zn}}/x_{\text{Ga}} = 1/3, 1, 3$ ) were computed by making use of the binary data of Zn–Sn [6], Sn–Ga systems (predicted) by Eq. (5). Similar procedure was followed to com-



**Fig. 5.** Integral excess molar free energy surface ( $\Delta_{\text{mix}}\bar{G}_i^{\circ,E}$ ) of Sn–Zn–Ga liquid alloys at 750 K in 300 J steps.



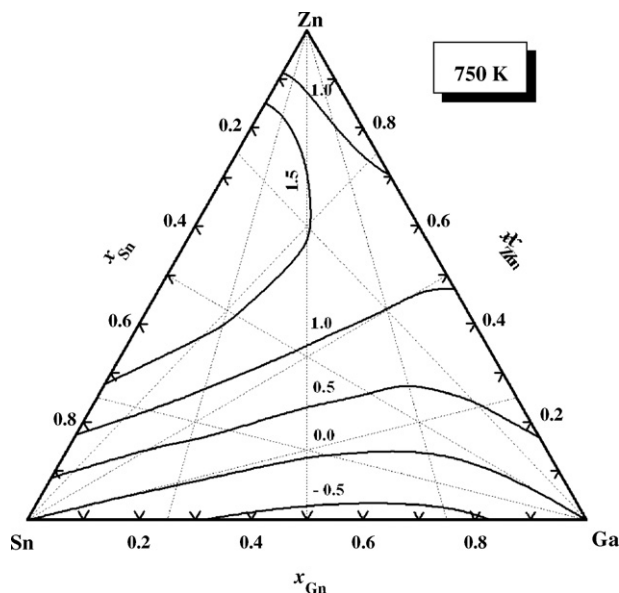
**Fig. 6.** Integral molar enthalpy ( $\Delta_{\text{mix}}\bar{H}_i^{\circ,E}$ ) of Sn–Zn–Ga liquid alloys at 750 K in 500 J steps.

pute  $\Delta_{\text{mix}}G^{\circ,E}$  and  $\Delta_{\text{mix}}H^{\circ,E}$  curves for three pseudo-binary lines ( $x_{\text{Zn}}/x_{\text{Sn}} = 1/3, 1, 3$ ) as function of composition of Ga. From the  $\Delta_{\text{mix}}G^{\circ,E}$  and  $\Delta_{\text{mix}}H^{\circ,E}$  curves for three binary and nine pseudo-binary lines, iso-free energy and isoenthalpic surfaces have been constructed and shown in Figs. 5 and 6, respectively. The excess molar entropy ( $\Delta_{\text{mix}}S^{\circ,E}$ ) of the ternary solution shown in Fig. 7 is derived from Figs. 5 and 6 by the following relation:

$$\Delta_{\text{mix}}S^{\circ,E} = \frac{\Delta_{\text{mix}}H^{\circ,E} - \Delta_{\text{mix}}G^{\circ,E}}{T} \quad (8)$$

The computed excess molar thermodynamic properties of Sn–Zn–Ga ternary system are listed in Tables 4A–4C.

The excess partial molar free energy ( $\Delta_{\text{mix}}\bar{G}_i^{\circ,E}$ ) plots of the three components for the binary and pseudo-binary lines of the ternary system are shown in Fig. 8. The curves for Zn in the pseudo-binary lines are obtained directly from the curves in Figs. 3 and 4 by multiplying each point on the curves by  $(1-x_{\text{Zn}})^2$ . The curves for the Sn



**Fig. 7.** Integral excess molar entropy surface ( $\Delta_{\text{mix}}\bar{S}_i^{\circ,E}$ ) for the Sn–Zn–Ga liquid alloys at 750 K in 0.5 J steps.

**Table 4A**Integral excess molar thermodynamic quantities of the Sn–Zn–Ga liquid alloys at 750 K along constant  $x_{\text{Sn}}/x_{\text{Ga}}$  isopleth.

$x_{\text{Zn}}$	$\Delta_{\text{mix}}G^{\circ,E} \text{ (kJ mol}^{-1}\text{)}$					$\Delta_{\text{mix}}H^{\circ,E} \text{ (kJ mol}^{-1}\text{)}$					$\Delta_{\text{mix}}S^{\circ,E} \text{ (J mol}^{-1}\text{ K}^{-1}\text{)}$				
	$\infty$	3	1	1/3	0	$\infty$	3	1	1/3	0	$\infty$	3	1	1/3	0
0.0	0	0.82	1.30	1.09	0	0	0.51	0.78	0.59	0	0	-0.412	-0.69	-0.657	0
0.1	0.40	1.10	1.49	1.25	0.25	0.84	1.22	1.38	1.10	0.49	0.591	0.172	-0.146	-0.199	0.323
0.2	0.76	1.33	1.62	1.37	0.45	1.62	1.86	1.89	1.53	0.89	1.143	0.705	0.356	0.211	0.58
0.3	1.07	1.50	1.70	1.44	0.62	2.28	2.38	2.29	1.86	1.20	1.611	1.164	0.797	0.563	0.775
0.4	1.32	1.61	1.71	1.45	0.73	2.78	2.76	2.58	2.09	1.42	1.945	1.529	1.161	0.85	0.931
0.5	1.49	1.65	1.65	1.40	0.79	3.09	2.99	2.73	2.20	1.56	2.129	1.788	1.43	1.06	1.037
0.6	1.56	1.60	1.53	1.29	0.79	3.18	3.04	2.72	2.18	1.59	2.162	1.931	1.585	1.179	1.07
0.7	1.49	1.44	1.33	1.12	0.73	3.05	2.89	2.52	2.01	1.50	2.079	1.926	1.594	1.185	1.025
0.8	1.24	1.15	1.03	0.87	0.59	2.61	2.43	2.08	1.65	1.23	1.817	1.701	1.401	1.041	0.847
0.9	0.77	0.69	0.60	0.51	0.37	1.70	1.53	1.29	1.02	0.75	1.248	1.123	0.913	0.679	0.513
1.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

**Table 4B**Integral excess molar thermodynamic quantities of the Sn–Zn–Ga liquid alloys at 750 K along constant  $x_{\text{Zn}}/x_{\text{Ga}}$  isopleth.

$x_{\text{Sn}}$	$\Delta_{\text{mix}}G^{\circ,E} \text{ (kJ mol}^{-1}\text{)}$					$\Delta_{\text{mix}}H^{\circ,E} \text{ (kJ mol}^{-1}\text{)}$					$\Delta_{\text{mix}}S^{\circ,E} \text{ (J mol}^{-1}\text{ K}^{-1}\text{)}$				
	0	1/3	1	3	$\infty$	0	1/3	1	3	$\infty$	0	1/3	1	3	$\infty$
0.0	0	0.55	0.79	0.67	0	0	1.04	1.59	1.36	0	0	0.658	1.063	0.912	0
0.1	0.57	1.04	1.32	1.25	0.77	0.31	1.36	2.03	2.21	1.71	-0.346	0.427	0.946	1.275	1.248
0.2	0.96	1.38	1.6	1.55	1.25	0.53	1.56	2.29	2.72	2.61	-0.573	0.234	0.919	1.558	1.817
0.3	1.2	1.56	1.72	1.66	1.49	0.68	1.64	2.38	2.93	3.05	-0.698	0.103	0.886	1.696	2.079
0.4	1.31	1.57	1.66	1.64	1.56	0.75	1.62	2.33	2.90	3.19	-0.737	0.063	0.899	1.678	2.162
0.5	1.29	1.45	1.52	1.52	1.50	0.76	1.51	2.16	2.66	3.09	-0.704	0.076	0.849	1.522	2.129
0.6	1.17	1.25	1.33	1.32	1.33	0.71	1.32	1.87	2.27	2.79	-0.615	0.090	0.720	1.260	1.945
0.7	0.97	1.02	1.12	1.08	1.08	0.60	1.06	1.49	1.76	2.29	-0.486	0.055	0.497	0.901	1.611
0.8	0.69	0.74	0.83	0.78	0.76	0.44	0.75	1.04	1.18	1.62	-0.330	0.010	0.284	0.531	1.143
0.9	0.36	0.41	0.48	0.42	0.40	0.24	0.39	0.54	0.58	0.84	-0.164	-0.027	0.078	0.211	0.591
1.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

**Table 4C**Integral excess molar thermodynamic quantities of the Sn–Zn–Ga liquid alloys at 750 K along constant  $x_{\text{Zn}}/x_{\text{Sn}}$  isopleth.

$x_{\text{Ga}}$	$\Delta_{\text{mix}}G^{\circ,E} \text{ (kJ mol}^{-1}\text{)}$					$\Delta_{\text{mix}}H^{\circ,E} \text{ (kJ mol}^{-1}\text{)}$					$\Delta_{\text{mix}}S^{\circ,E} \text{ (J mol}^{-1}\text{ K}^{-1}\text{)}$				
	0	1/3	1	3	$\infty$	0	1/3	1	3	$\infty$	0	1/3	1	3	$\infty$
0.0	0	0.92	1.49	1.39	0	0	1.94	3.09	2.81	0	0	1.351	2.137	1.901	0
0.1	0.36	1.16	1.62	1.48	0.37	0.24	1.93	2.92	2.81	0.76	-0.164	1.022	1.743	1.763	0.513
0.2	0.69	1.35	1.69	1.53	0.60	0.44	1.88	2.71	2.67	1.23	-0.330	0.703	1.359	1.519	0.847
0.3	0.97	1.48	1.70	1.53	0.73	0.60	1.78	2.46	2.49	1.50	-0.486	0.406	1.015	1.283	1.025
0.4	1.17	1.54	1.66	1.47	0.79	0.71	1.64	2.19	2.27	1.60	-0.615	0.145	0.712	1.057	1.070
0.5	1.29	1.52	1.55	1.37	0.79	0.76	1.46	1.90	2.00	1.57	-0.704	-0.069	0.455	0.841	1.037
0.6	1.31	1.41	1.38	1.21	0.73	0.75	1.25	1.57	1.69	1.43	-0.737	-0.224	0.248	0.638	0.931
0.7	1.20	1.22	1.15	0.99	0.62	0.68	0.99	1.22	1.33	1.20	-0.698	-0.307	0.094	0.449	0.775
0.8	0.96	0.92	0.84	0.72	0.46	0.53	0.69	0.84	0.93	0.89	-0.573	-0.305	-0.003	0.277	0.580
0.9	0.57	0.52	0.46	0.39	0.25	0.31	0.36	0.43	0.48	0.49	-0.346	-0.207	-0.039	0.123	0.323
1.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

and Ga in the pseudo-binary ( $x_{\text{Zn}}/x_{\text{Sn}} = 1/3, 1, 3$  and  $x_{\text{Zn}}/x_{\text{Ga}} = 1/3, 1, 3$ ) are obtained by the slope–intercept method along various pseudo-binary lines as given below:

$$\Delta_{\text{mix}}\bar{G}_i^{\circ,E} = \Delta_{\text{mix}}G^{\circ,E} + (1 - x_i) \left( \frac{\partial \Delta_{\text{mix}}G^{\circ,E}}{\partial x_i} \right) \quad (9)$$

The ternary excess molar free energy as function of composition of Sn was plotted for various pseudo-binary lines ( $x_{\text{Zn}}/x_{\text{Ga}} = 1/3, 1, 3$ ). The tangents were drawn at various compositions of tin from  $x_{\text{Sn}} = 0.1$  to 0.9 at interval of 0.1. From the slope and intercept of the tangent [Eq. (9)], the partial excess molar properties ( $\Delta_{\text{mix}}\bar{G}_i^{\circ,E}$  and  $\Delta_{\text{mix}}\bar{H}_i^{\circ,E}$ ) were obtained as function of composition of Sn. Similar procedure was followed for obtaining the partial molar properties of gallium as a function of composition. Those for the limiting binary Zn–Sn and Zn–Ga were adapted from the literature [6]. The partial molar properties of Sn–Ga alloys have been obtained from the predicted excess molar thermodynamic properties.

Activity of zinc, tin and gallium as a function of composition in nine pseudo-binaries were computed from  $\Delta_{\text{mix}}\bar{G}_i^{\circ,E}$  curves in Fig. 8

by the following relation:

$$\Delta_{\text{mix}}\bar{G}_i^{\circ,E} = RT \ln \left( \frac{a_i}{x_i} \right) \quad (10)$$

The activity of the components in the limiting binaries: Sn–Zn and Zn–Ga have been adopted from the literature [6] and those for Sn–Ga is based on the predicted results by Eq. (5). The activity surfaces of the three components in the solutions are depicted by isoactivity lines in Fig. 9. The isoactivity lines are interpolated from the resulting activity curves. The activities of all the three components show positive deviation from the Raoult's law.

As shown in Fig. 10, excess molar enthalpies of Sn–Ga alloys estimated by Darken's treatment using excess molar thermodynamic properties of the ternary system Sn–Zn–Ga and binaries Sn–Zn and Zn–Ga, are in good agreement with the values reported in the literature [6–9]. This establishes the usefulness of the Darken's method. The values of  $\Delta_{\text{mix}}G_{\text{Sn-Ga}}^{\circ,E}$  and  $\Delta_{\text{mix}}H_{\text{Sn-Ga}}^{\circ,E}$  predicted from the ternary data have been used to calculate the partial molar free energy and enthalpy by slope–intercept method. From the partial molar free energy values, activities of Sn and Ga in Sn–Ga system

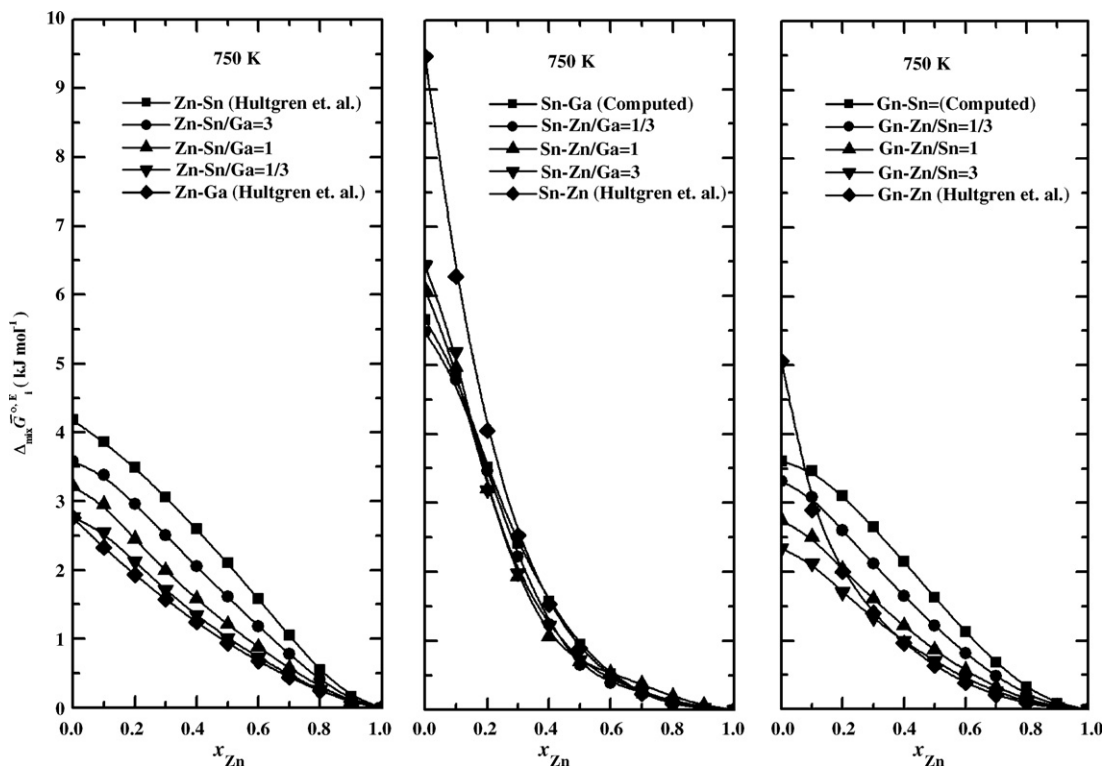


Fig. 8. Excess partial molar free energy curves in Sn–Zn–Ga liquid alloys at 750 K.

have been computed at 750 K. The activities so calculated exhibit stronger positive deviation from Raoult's law compared to those reported by Zivkovic et al. [7,8], Katayama et al. [10] and Predel [11] as evident from Fig. 11. This may be due to difference in temperature of investigations and the technique employed.

The positive values of excess molar free energy and enthalpy of the ternary solutions at 750 K indicate that there is no interaction between constituent atoms. The positive values of excess entropy of solution may be due increase in excess molar volume of the solution. The maximum value of excess molar free energy has been found to be  $1.72 \text{ kJ mol}^{-1}$  ( $x_{\text{Sn}} = 0.3$ ,  $x_{\text{Zn}} = 0.35$  and

$x_{\text{Ga}} = 0.35$ ). The excess molar free energy surface is oriented towards the Zn–Sn binary system and conforms substantially to what one would expect from the knowledge of the corresponding curves of the component binary systems. The excess partial molar free energy curves are more sensitive indicator of the behaviour of

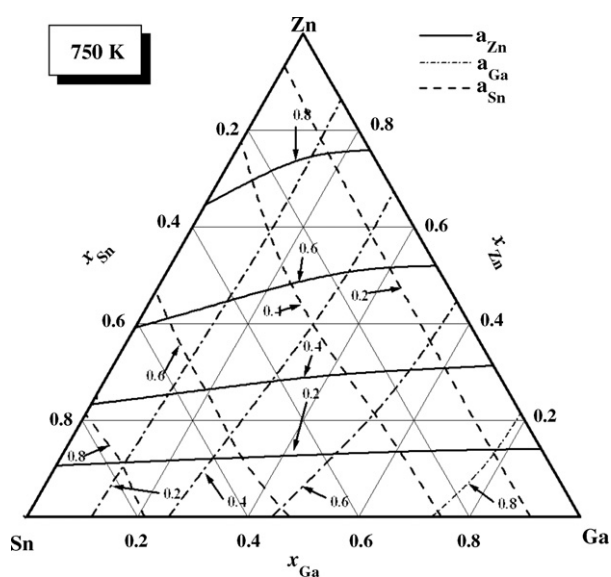


Fig. 9. Isoactivity lines in the Sn–Zn–Ga liquid alloys at 750 K.

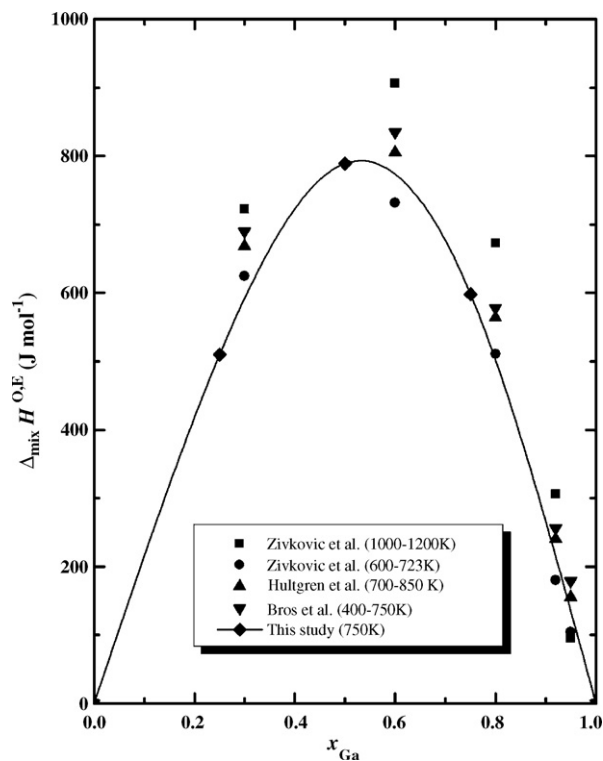
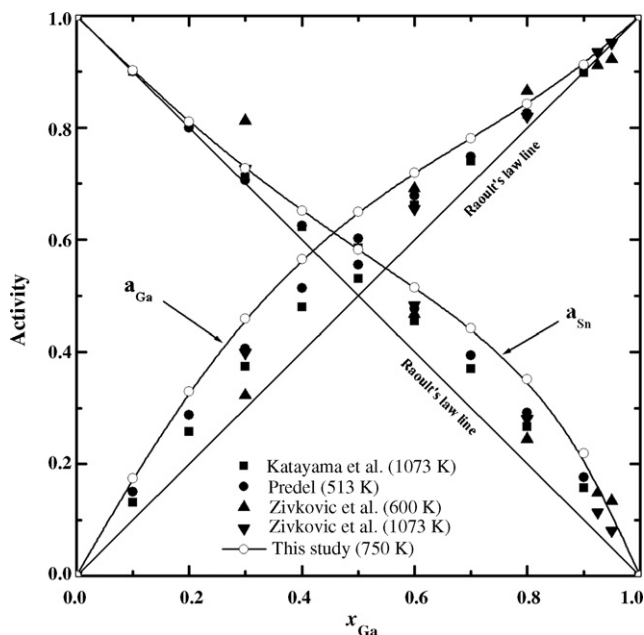


Fig. 10. Comparative review of excess molar enthalpy values obtained from Eq. (5) and the literature of Sn–Ga liquid alloys at 750 K.



**Fig. 11.** Comparison of thermodynamic data obtained by Eq. (5) and the literature for Sn–Ga liquid alloys at 750 K.

the solutions. They vary smoothly from one side of the ternary field to the other. The excess molar enthalpy of solution has been found to be tilted towards the Zn–Sn side. The maximum values of molar excess enthalpy of solution obtained in this case is  $3.18 \text{ kJ mol}^{-1}$  ( $x_{\text{Ga}} = 0.0$ ,  $x_{\text{Zn}} = 0.6$  and  $x_{\text{Sn}} = 0.4$ ). The excess molar entropy surfaces have the maxima in the Zn–Sn side and minima in the Sn–Ga side. The activity and activity coefficients of the components in the Sn–Zn–Ga system vary continuously with composition and exhibit positive deviation from Raoult's law ruling out the formation of any compound in the system at 750 K.

#### 4. Conclusions

Activity of zinc in liquid Sn–Zn–Ga alloys has been measured in the temperature range 723–823 K by electrochemical technique based on fused electrolyte galvanic cell. The Darken's treatment has been found to be very useful in determining the integral and partial molar properties of the ternary system. The excess molar free energy surfaces have the maxima in the Sn–Zn side and have been termed as a crown of hill well. The molar heat of solution curves has been found to be tilted towards the Zn–Sn side. Molar thermodynamic properties of Sn–Ga alloys have been predicted at 750 K. The excess molar enthalpy of the solution of Sn–Ga is compared with the literature data. The excess molar entropy surfaces have the maxima in the Zn–Sn side and minima in the Sn–Ga side. The activities of three components computed from the partial molar excess free energy at 750 K show positive deviations from Raoult's law. The activity of tin and gallium predicted from the ternary data has been compared with the literature values.

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