

Thermodynamic investigations of liquid gallium–cadmium alloys

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Abstract

The activity of Cd in liquid Ga–Cd alloys in the 723–851 K range was determined by an electrochemical technique using LiCl–KCl+5 wt.% CdCl₂ as molten salt electrolyte. The system exhibits a strong positive deviation from Raoult's law. From the activity values computed at different temperatures, the partial, integral, and excess molar thermodynamic quantities have been calculated. The composition dependence of the α -function confirms that the system does not follow a regular solution model. The analysis of Darken's stability function reiterates that though the stability is positive for all compositions, it is poor in the $0.25 \leq x_{\text{Cd}} \leq 0.45$ composition range. This shows a tendency for immiscibility in this composition range. © 1998 Elsevier Science B.V.

Keywords: Activity; Ga–Cd system; Immiscibility; Thermodynamic properties

1. Introduction

Thermodynamic investigations of metallic solutions are important for several reasons. In the first place, thermodynamic data are needed in order to formulate the conditions of equilibrium between liquid (and solid) alloys and a gas phase or a slag, especially for reactions used in process metallurgy and heat treatment. Secondly, thermodynamic data form the basis for a better understanding of the peculiarities of phase diagrams. Thirdly, by combining the results of thermodynamic studies with electrical, magnetic, and X-ray investigations, one may obtain a deeper insight into the 'constitution' of metallic phases.

The equilibrium phase diagram of the Ga–Cd system as compiled by Hansen and Anderko [1] shows a wide ranging miscibility gap in the liquid state. The

monotectic reaction according to this diagram occurs at 531 K. However, the phase diagram reported by Hultgren et al. [2], based on the data published by Heumann and Predel [3], shows the monotectic reaction at 555 K. It depicts only a small miscibility gap in the liquid state, the maximum of which occurs at 568 K. Further, Predel [4] has also reported a strong positive deviation from ideality in the 699–868 K range.

In view of the large discrepancy in the two phase diagrams reported in the literature [1,2], it was considered worthwhile to carry out detailed thermodynamic measurements on this system. In the present investigation, the activity of Cd in liquid Ga–Cd alloys has been determined by an electrochemical technique using molten salt electrolyte. Various partial, integral and excess thermodynamic quantities have been calculated from activity values. The results have been discussed in light of these

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quantities and Darken's stability and excess stability parameters.

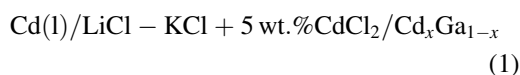
2. Experimental

2.1. Materials

High purity (99.999%, Johnson Matthey, U.K.) cadmium and gallium were used. The following analytical reagent grade salts were used for preparation of the electrolyte: lithium chloride (Sisco, India), potassium chloride (Qualigens, India), and cadmium chloride (Thomas Baker, UK).

2.2. Electrochemical measurements

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



A eutectic mixture of LiCl–KCl containing 5 wt.% CdCl₂ was used as the electrolyte. A cell assembly made of BOROSIL glass containing three lower limbs (6 mm i.d. each) below a tubular electrolyte compartment (55 mm i.d.) 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. [5].

The experiment was performed by forming the proper electrodes in different limbs. In one limb, ca. 4 g of pure cadmium was melted and frozen under dried and pure nitrogen. In the other two limbs, the electrodes of appropriate alloys (Cd_xGa_{1-x}) were formed by heating pieces of cadmium and gallium (frozen prior to weighing) in suitable proportions in an atmosphere of pure nitrogen. 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 heated to 400 K) and heating commenced after flushing nitrogen for 1 h.

The temperature of the cell was controlled to an accuracy of ± 0.5 K by a digital temperature con-

troller. Both, the temperature and cell emf were measured by a digital electrometer at an input impedance of $>2 \times 10^{12} \Omega$. The cell attained equilibrium after 20 h, and thereafter, the emf values remained constant for over 30 h. The general criteria for reversibility, namely

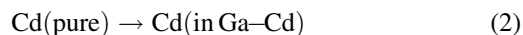
- the time independent emf at a constant temperature,
- the reproducibility of emf values whether approaching from higher or lower temperature side, and
- recoverability of the same emf after passage of a small amount of impressed current through the cell in either direction,

were applied to ensure the correct reversible cell emf. Reversibility of the galvanic cell indicates the absence of any side or exchange reaction within the cell. After attaining a constant emf at one temperature, the temperature was changed and sufficient time was allowed for reestablishment of equilibrium. The emf values were measured in both heating and cooling cycles. The measurements for each composition were conducted twice to check the reproducibility of the results.

3. Results and discussion

3.1. Activity of components

The virtual cell reaction in the galvanic cell (1) may be represented as follows:



The activity of Cd (a_{Cd}) in the Ga–Cd system was calculated from the relation

$$\ln a_{\text{Cd}} = - \frac{nFE}{RT} \quad (3)$$

where n is the number of electrons (two in the present case) transferred during reaction (2), E the open circuit emf of the galvanic cell (1), F the Faraday constant, and R the universal gas constant. The reversible cell emf values measured in the 723–851 K range are listed in Table 1. The variation of emf with temperature for nine compositions was calculated by the least-squares method and summarized in Table 1 in the form of a linear equation ($E=A+BT$). The error limits shown in

Table 1
Emf in mV at different temperatures

x_{Cd}	Temperature/K				$E=A+BT$	
	723	751	801	851	-A	B
0.1	16.55±0.39	19.03±0.43	23.52±0.72	27.15±0.72	43.57	0.0833
0.2	10.97±0.27	12.42±0.28	15.25±0.44	17.85±0.57	26.15	50.0514
0.3	8.99±0.08	10.02±0.16	11.84±0.37	13.84±0.67	18.35	0.0378
0.4	8.60±0.30	9.40±0.60	10.60±0.60	12.25±0.60	11.71	0.0281
0.5	7.45±0.15	8.50±0.25	9.80±0.20	10.94±0.10	11.78	0.0268
0.6	5.01±0.20	5.43±0.20	6.44±0.15	7.80±0.30	10.91	0.0219
0.7	4.44±0.04	4.85±0.07	5.22±0.18	5.44±0.66	1.46	0.0083
0.8	2.95±0.06	3.09±0.06	3.40±0.15	3.80±0.30	1.89	0.0066
0.9	2.04±0.05	2.23±0.06	2.50±0.10	2.72±0.14	1.75	0.0053

Table 1 are the maximum deviations from the average values of cell emfs from two independent runs.

From the emf values measured at different temperatures, activities of Cd in Ga–Cd liquid alloys were calculated and are listed in Table 2. The corresponding values of activity coefficient of Cd (γ_{Cd}) as calculated by using the equation

$$\gamma_{\text{Cd}} = \frac{a_{\text{Cd}}}{x_{\text{Cd}}} \quad (4)$$

are also presented in Table 2 at different temperatures and also in the form of a linear equation ($\ln \gamma_{\text{Cd}}=A/T+B$). The activity as well as the activity coefficient decrease with increase of temperature. Fig. 1 shows the variation of activity and activity coefficient of cadmium as a function of composition (x_{Cd}) at 851 K. The plots exhibit positive deviation from Raoult's law. This indicates the tendency of clustering of cadmium and gallium. The continuous variation of activity with composition (Fig. 1) shows that the Ga–Cd system consists of a single-phase field throughout the entire range of composition in this temperature range.

The activity of gallium in the system has been calculated using the following form of Gibbs–Duhem integration [6]

$$\ln \gamma_{\text{Ga}} = -\alpha_{\text{Cd}}x_{\text{Cd}}x_{\text{Ga}} - \int_{x_{\text{Ga}}=1}^{x_{\text{Ga}}=x_{\text{Ga}}} \alpha_{\text{Cd}}dx \quad (5)$$

where

$$\alpha_{\text{Cd}} = \frac{\ln \gamma_{\text{Cd}}}{(1-x_{\text{Cd}})^2} \quad (6)$$

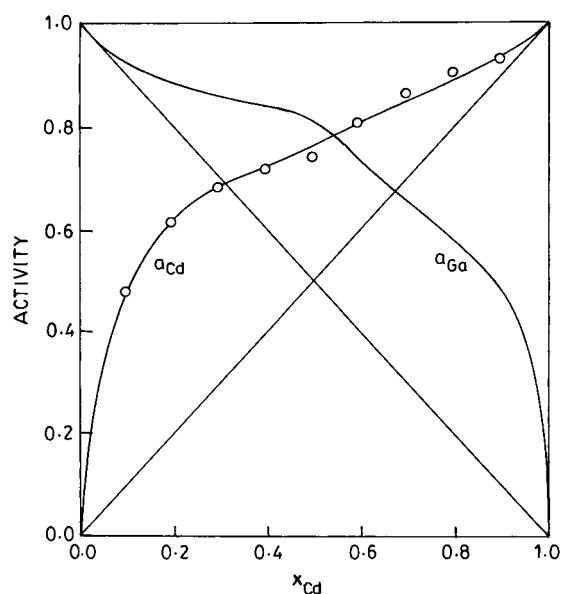


Fig. 1. Activity–composition relations in liquid Ga–Cd alloys at 851 K.

The values of activity and activity coefficient of Ga in Ga–Cd liquid alloys, thus computed have been incorporated in Table 3. The values of a_{Ga} at 851 K are plotted in Fig. 1. The curve also shows positive deviation from Raoult's law.

3.2. Partial, integral and excess molar thermodynamic properties

From the emf values measured at different temperatures (Table 1), the partial molar free energy of

Table 2
Activity and activity coefficient of Cd in Ga–Cd alloys

x_{Cd}	a_{Cd}									γ_{Cd}									$\ln \gamma_{\text{Cd}}=A/T+B$	
	723 K	751 K	801 K	851 K	723 K	751 K	801 K	851 K	723 K	751 K	801 K	851 K	A	B						
0.1	0.5878±0.0073	0.5553±0.0074	0.5057±0.0107	0.4768±0.0093	5.878±0.073	5.553±0.074	5.057±0.107	4.768±0.093	1022	0.354										
0.2	0.7030±0.0060	0.6812±0.0059	0.6428±0.0082	0.6145±0.0095	3.515±0.030	3.406±0.030	3.214±0.041	3.072±0.048	591	0.437										
0.3	0.7492±0.0019	0.7336±0.0036	0.7095±0.0076	0.6855±0.0127	2.497±0.006	2.445±0.013	2.365±0.025	2.285±0.040	427	0.325										
0.4	0.7587±0.0073	0.7478±0.0137	0.7355±0.0121	0.7159±0.0118	1.897±0.018	1.869±0.034	1.839±0.032	1.790±0.029	270	0.267										
0.5	0.7872±0.0038	0.7689±0.0059	0.7527±0.0040	0.7420±0.0021	1.574±0.008	1.538±0.012	1.505±0.009	1.484±0.004	277	0.066										
0.6	0.8514±0.0055	0.8455±0.0052	0.8297±0.0036	0.8083±0.0066	1.419±0.009	1.409±0.009	1.383±0.006	1.347±0.011	252	0.005										
0.7	0.8671±0.0011	0.8608±0.0019	0.8596±0.0045	0.8597±0.0014	1.239±0.002	1.230±0.003	1.228±0.005	1.228±0.002	39	0.158										
0.8	0.9096±0.0017	0.9089±0.0017	0.9062±0.0040	0.9015±0.0074	1.137±0.002	1.136±0.002	1.133±0.005	1.127±0.009	39	0.075										
0.9	0.9367±0.0018	0.9335±0.0015	0.9302±0.0025	0.9285±0.0035	1.048±0.002	1.037±0.002	1.034±0.003	1.032±0.005	41	0.018										

Table 3
Activity and activity coefficient of Ga in Ga–Cd alloys

a_{Ga}	x_{Ga}	γ_{Ga}				$\ln \gamma_{\text{Ga}}=A/T+B$				
		723 K	751 K	801 K	851 K	723 K	751 K	801 K	851 K	A
0.1	0.5476	0.5281	0.5028	0.4817	5.476	5.281	5.028	4.817	780	0.643
0.2	0.6564	0.6238	0.5966	0.5704	3.282	3.119	2.983	2.852	635	0.298
0.3	0.7544	0.7316	0.6981	0.6581	2.515	2.439	2.327	2.194	595	0.093
0.4	0.7800	0.7572	0.7447	0.7361	1.950	1.893	1.862	1.840	270	0.287
0.5	0.8567	0.8490	0.8368	0.8162	1.713	1.698	1.674	1.632	215	0.242
0.6	0.8825	0.8685	0.8527	0.8404	1.471	1.448	1.421	1.401	230	0.066
0.7	0.8880	0.8770	0.8688	0.8596	1.269	1.253	1.241	1.228	135	0.051
0.8	0.9067	0.8988	0.8943	0.8875	1.133	1.123	1.118	1.109	96	-0.010
0.9	0.9314	0.9279	0.9264	0.9255	1.035	1.031	1.029	1.028	27	-0.004

mixing of cadmium, $\Delta\bar{G}_{\text{Cd}}^{\text{M}}$, is calculated using the relation

$$\Delta\bar{G}_{\text{Cd}}^{\text{M}} \equiv RT \ln a_{\text{Cd}} = -nFE \quad (7)$$

The values of partial molar enthalpy ($\Delta\bar{H}_{\text{Cd}}^{\text{M}}$) and entropy ($\Delta\bar{S}_{\text{Cd}}^{\text{M}}$) of cadmium in Ga–Cd liquid solutions were obtained, respectively, from the intercept and slope of $\Delta\bar{G}_{\text{Cd}}^{\text{M}}$ vs. T plots. In the estimation of $\Delta\bar{H}_{\text{Cd}}^{\text{M}}$ and $\Delta\bar{S}_{\text{Cd}}^{\text{M}}$, the heat capacity contribution to the formation of alloys in the narrow 723–851 K range has been neglected. The excess partial molar thermodynamic quantities were calculated as follows

$$\Delta\bar{G}_{\text{Cd}}^{\text{XS}} \equiv \Delta\bar{G}_{\text{Cd}}^{\text{M}} - \Delta\bar{G}_{\text{Cd}}^{\text{M}} = RT \ln \gamma_{\text{Cd}} \quad (8)$$

$$\Delta\bar{H}_{\text{Cd}}^{\text{XS}} \equiv \Delta\bar{H}_{\text{Cd}}^{\text{M}} \text{ as } \Delta\bar{H}_{\text{Cd}}^{\text{M}} = 0 \quad (9)$$

$$\Delta\bar{S}_{\text{Cd}}^{\text{XS}} \equiv \Delta\bar{S}_{\text{Cd}}^{\text{M}} - \Delta\bar{S}_{\text{Cd}}^{\text{M}} = -\frac{\partial(\Delta\bar{G}_{\text{Cd}}^{\text{XS}})}{\partial T} \quad (10)$$

Various partial molar thermodynamic quantities, viz. $\Delta\bar{G}_{\text{Cd}}^{\text{M}}$, $\Delta\bar{G}_{\text{Cd}}^{\text{XS}}$, $\Delta\bar{H}_{\text{Cd}}^{\text{M}}$, $\Delta\bar{S}_{\text{Cd}}^{\text{M}}$, $\Delta\bar{S}_{\text{Cd}}^{\text{XS}}$, are summarised in Table 4.

The analogous thermodynamic parameters for the component Ga, viz., $\Delta\bar{G}_{\text{Ga}}^{\text{M}}$, $\Delta\bar{G}_{\text{Ga}}^{\text{XS}}$, $\Delta\bar{H}_{\text{Ga}}^{\text{M}}$, $\Delta\bar{S}_{\text{Ga}}^{\text{M}}$ and $\Delta\bar{S}_{\text{Ga}}^{\text{XS}}$ have also been calculated from the estimated values of a_{Ga} and γ_{Ga} (based on Gibbs–Duhem integration) and are listed in Table 5. The integral molar quantities (ΔQ : ΔG^{M} , ΔG^{XS} , ΔH^{M} , ΔS^{M} and ΔS^{XS}) of the system were obtained from the partial molar quantities of the components:

$$\Delta Q_{\text{Cd}_x\text{Ga}_{1-x}} = x_{\text{Cd}}\Delta\bar{Q}_{\text{Cd}} + x_{\text{Ga}}\Delta\bar{Q}_{\text{Ga}} \quad (11)$$

The integral molar quantities, so obtained (at different temperatures), are summarized in Table 6 and pre-

sented in Fig. 2 in a suitable form as a function of composition at 851 K. The quantities vary roughly parabolically. For comparison, values of $\Delta\bar{G}_{\text{Cd}}^{\text{M}}$ and $T\Delta\bar{S}_{\text{Cd}}^{\text{M}}$ are also included in the figure. Our estimated values of integral molar enthalpy of mixing in the 723–851 K range are comparable with those of Moser et al. [7,8] based on the calorimetric measurements at 694 K (incorporated in Fig. 2). The negative values of integral molar free energy of formation of Ga–Cd

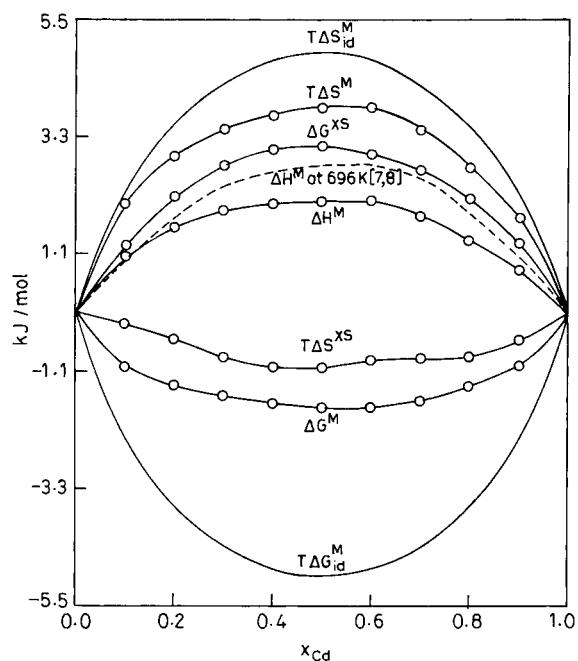


Fig. 2. Integral and excess molar thermodynamic quantities of liquid Ga–Cd alloys at 851 K.

Table 4
 Partial and excess molar thermodynamic quantities of Cd in liquid Ga–Cd alloys

x_{Cd}	$-\Delta\bar{G}_{\text{Cd}}^{\text{M}}/(\text{kJ/mol})$					$\Delta\bar{G}_{\text{Cd}}^{\text{XS}}/(\text{kJ/mol})$					$\Delta\bar{H}_{\text{Cd}}^{\text{M}}/(\text{kJ/mol})$	$\Delta\bar{S}_{\text{Cd}}^{\text{M}}/(\text{J/K mol})$	$-\Delta\bar{S}_{\text{Cd}}^{\text{XS}}/(\text{J/K mol})$
	723 K	751 K	801 K	851 K	723 K	751 K	801 K	851 K	723 K	751 K			
0.1	3.194±0.075	3.673±0.083	4.539±0.138	5.240±0.138	10.642±0.074	10.699±0.082	10.788±0.140	11.046±0.136	8.408	16.083	3.052		
0.2	2.115±0.050	2.392±0.055	2.938±0.085	3.440±0.109	7.534±0.051	7.640±0.054	7.761±0.085	7.928±0.109	5.425	12.558	2.960		
0.3	1.735±0.016	1.934±0.031	2.285±0.071	2.671±0.129	5.498±0.014	5.580±0.033	5.730±0.070	5.844±0.123	3.540	7.289	2.726		
0.4	1.660±0.058	1.814±0.116	2.046±0.116	2.364±0.116	3.847±0.057	3.903±0.113	4.055±0.115	4.117±0.114	2.259	5.412	2.208		
0.5	1.438±0.029	1.641±0.048	1.891±0.039	2.111±0.019	2.725±0.031	2.687±0.048	2.721±0.040	2.792±0.019	2.268	5.167	0.599		
0.6	0.967±0.039	1.048±0.039	1.243±0.029	1.505±0.058	2.103±0.038	2.140±0.040	2.158±0.029	2.107±0.057	2.103	4.214	0.023		
0.7	0.857±0.008	0.936±0.013	1.007±0.035	1.069±0.012	1.288±0.009	1.292±0.115	1.367±0.027	1.452±0.012	0.279	1.595	1.340		
0.8	0.569±0.012	0.596±0.012	0.656±0.035	0.733±0.058	0.771±0.011	0.796±0.011	0.831±0.029	0.846±0.056	0.364	1.283	0.588		
0.9	0.392±0.010	0.429±0.010	0.481±0.018	0.524±0.027	0.241±0.011	0.226±0.012	0.222±0.019	0.230±0.027	0.343	1.023	0.000		

Table 5
Partial and excess molar thermodynamic quantities of Ga in liquid Ga–Cd alloys

x_{Ga}	$-\Delta G_{\text{Ga}}^{\text{M}} / (\text{kJ/mol})$				$-\Delta G_{\text{XS}}^{\text{M}} / (\text{kJ/mol})$				$-\Delta \bar{H}_{\text{Ga}}^{\text{M}} / (\text{kJ/mol})$	$\Delta \bar{S}_{\text{Ga}}^{\text{M}} / (\text{J/K mol})$	$-\Delta \bar{S}_{\text{Ga}}^{\text{XS}} / (\text{J/K mol})$
	723 K	751 K	801 K	851 K	723 K	751 K	801 K	851 K			
0.1	3.614	3.980	4.571	5.159	10.204	10.372	10.737	11.105	5.057	12.013	7.099
0.2	2.526	2.942	3.434	3.965	7.132	7.090	7.266	7.405	5.366	10.983	2.391
0.3	1.691	1.948	2.389	2.955	5.534	5.558	5.615	5.550	5.406	9.792	0.205
0.4	1.491	1.734	1.960	2.164	4.008	3.978	4.133	4.307	2.127	5.072	2.524
0.5	0.928	1.020	1.185	1.434	3.230	3.300	3.425	3.460	1.912	3.908	1.846
0.6	0.750	0.879	1.059	1.228	2.316	2.307	2.336	2.382	1.907	3.693	0.549
0.7	0.713	0.818	0.935	1.069	1.430	1.406	1.435	1.451	1.230	2.705	0.239
0.8	0.588	0.665	0.743	0.843	0.749	0.723	0.724	0.730	0.794	1.924	0.069
0.9	0.426	0.466	0.508	0.547	0.206	0.190	0.192	0.197	0.231	0.919	0.043

liquid alloys (Table 4) increase with temperature at each composition. This indicates that the feasibility of formation of solutions in the system increases with increase of temperature.

3.3. Solution model

The variation of α_{Cd} with composition (x_{Cd}) at different temperatures is shown in Fig. 3 and it is clearly evident that α_{Cd} is dependent on composition as well as temperature. This means the Ga–Cd system

does not follow a regular solution model. Further, the system does not satisfy Darken's quadratic formalism [9] as the data cannot be presented according to the equation

$$\ln(\gamma_{\text{Cd}}/\gamma_{\text{Cd}}^{(0)}) = \alpha_{\text{Ga}}(x_{\text{Cd}}^2 - 2x_{\text{Cd}}) \quad (12)$$

Hence, thermodynamic behaviour of the Ga–Cd system has been analysed in the light of Darken's stability and excess stability functions [9] which are defined for a binary solution as the second derivative of its molar free energy and excess free energy, respectively, with respect to the mole fraction of either constituent:

$$\text{Stability} \equiv \frac{\partial^2 \Delta G^{\text{M}}}{\partial x_{\text{Cd}}^2} = -2RT \frac{\partial \ln a_{\text{Cd}}}{\partial (1-x_{\text{Cd}})^2} \quad (13)$$

$$\text{Excess stability} \equiv \frac{\partial^2 \Delta G^{\text{XS}}}{\partial x_{\text{Cd}}^2} = -2RT \frac{\partial \ln \gamma_{\text{Cd}}}{\partial (1-x_{\text{Cd}})^2} \quad (14)$$

Thus, these values may be calculated by multiplying the slopes of $\ln a_{\text{Cd}}$ vs. $(1-x_{\text{Cd}})^2$ and $\ln \gamma_{\text{Cd}}$ vs. $(1-x_{\text{Cd}})^2$ plots with $-2RT$. The plot of $\ln \gamma_{\text{Cd}}$ vs. $(1-x_{\text{Cd}})^2$ is shown in Fig. 4 at a typical temperature of 851 K. The best polynomial equation of the curve generated is given below:

$$\begin{aligned} \ln \gamma_{\text{Cd}} = & 3.68(1-x_{\text{Cd}})^2 - 21.44(1-x_{\text{Cd}})^4 \\ & + 81.99(1-x_{\text{Cd}})^6 - 146.84(1-x_{\text{Cd}})^8 \\ & + 126.17(1-x_{\text{Cd}})^{10} - 41.47(1-x_{\text{Cd}})^{12} \end{aligned} \quad (15)$$

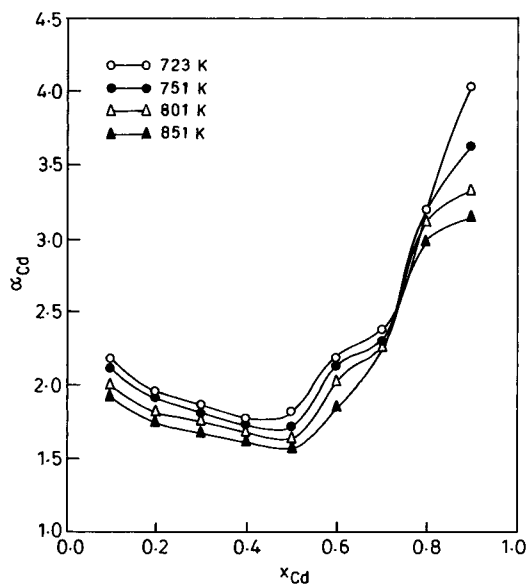


Fig. 3. α_{Cd} vs. x_{Cd} in liquid Ga–Cd alloys at different temperatures.

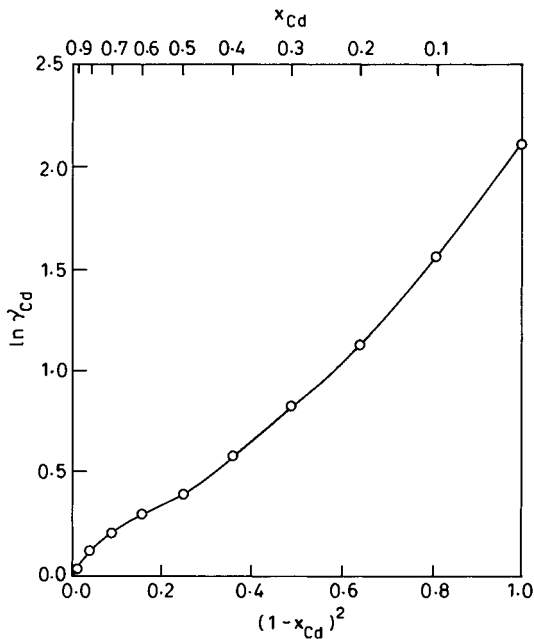


Fig. 4. Plot of $\ln \gamma_{\text{Cd}}$ vs. $(1-x_{\text{Cd}})^2$ plot at 851 K.

The slope of the curve shown in Fig. 4 as obtained by differentiating the above equation with respect to $(1-x_{\text{Cd}})^2$ was used to calculate the excess stability of the Ga–Cd system. The value of Darken's stability has been calculated by adding the value of excess stability to the ideal stability defined as

$$\text{Ideal stability} \equiv \frac{RT}{x_{\text{Cd}}(1-x_{\text{Cd}})} \quad (16)$$

Calculations show that stability of Ga–Cd alloys is always positive. The variation of stability and excess

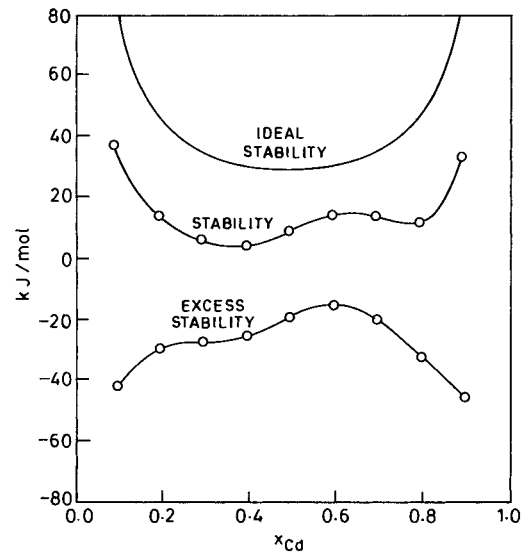


Fig. 5. Stability and excess stability functions of the Ga–Cd system at 851 K.

stability with composition at 851 K is depicted in Fig. 5. It can be seen that the value of stability is slightly positive in the $0.25 \leq x_{\text{Cd}} \leq 0.45$ composition range, which is indicative of the poor stability of the solution. In other words, there is a tendency for immiscibility or separation in this range of composition.

4. Conclusions

Activities of Cd and Ga in liquid Ga–Cd alloys in the 723–851 K range exhibit strong positive deviation

Table 6
Integral and excess molar thermodynamic quantities of liquid Ga–Cd alloys

x_{Cd}	$-\Delta G^{\text{M}}/(\text{kJ/mol})$				$\Delta G^{\text{XS}}/(\text{kJ/mol})$				$\Delta H/(\text{kJ/mol})$	$\Delta S^{\text{M}}/(\text{J/K mol})$	$-\Delta S^{\text{XS}}/(\text{J/K mol})$
	723 K	751 K	801 K	851 K	723 K	751 K	801 K	851 K			
0.1	0.703	0.787	0.911	1.016	1.250	1.241	1.252	1.282	1.046	2.431	0.265
0.2	0.898	1.014	1.173	1.362	2.108	2.106	2.146	2.169	1.608	3.476	0.580
0.3	1.020	1.153	1.340	1.550	2.650	2.658	2.724	2.770	1.923	4.080	0.997
0.4	1.114	1.253	1.454	1.682	2.928	2.945	3.024	3.076	2.046	4.378	1.217
0.5	1.183	1.331	1.538	1.769	2.978	2.994	3.073	3.126	2.086	4.532	1.218
0.6	1.177	1.322	1.530	1.769	2.865	2.875	2.948	2.987	2.114	4.560	1.024
0.7	1.107	1.240	1.422	1.635	2.561	2.572	2.641	2.681	1.818	4.055	1.000
0.8	0.960	1.065	1.212	1.379	2.043	2.005	2.118	2.158	1.366	3.224	0.950
0.9	0.714	0.784	0.890	0.990	1.237	1.241	1.274	1.310	0.815	2.126	0.593

from Raoult's law. The partial, integral, and excess molar thermodynamic quantities derived from electrochemical measurements include $\Delta\bar{G}_{\text{Cd}}^{\text{M}}$, $\Delta\bar{G}_{\text{Ga}}^{\text{M}}$, ΔG^{M} , $\Delta\bar{G}_{\text{Cd}}^{\text{XS}}$, $\Delta\bar{G}_{\text{Ga}}^{\text{XS}}$, ΔG^{XS} , $\Delta\bar{H}_{\text{Cd}}^{\text{M}}$, $\Delta\bar{H}_{\text{Ga}}^{\text{M}}$, ΔH^{M} , $\Delta\bar{S}_{\text{Cd}}^{\text{M}}$, $\Delta\bar{S}_{\text{Ga}}^{\text{M}}$, ΔS^{M} , $\Delta\bar{S}_{\text{Cd}}^{\text{XS}}$, $\Delta\bar{S}_{\text{Ga}}^{\text{XS}}$, and ΔS^{XS} .

The Ga–Cd system does not follow the regular solution model. The thermodynamic data cannot be interpreted according to the Darken's quadratic formalism. The analysis of Darken's stability shows poor stability in the $0.25 \leq x_{\text{Cd}} \leq 0.45$ composition range. This presents a possibility of immiscibility in the said composition range. Nevertheless the stability has been found to be positive.

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