

Applicability of four parameter formalisms in interpreting thermodynamic properties of binary systems

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Abstract. The four parameter functions are generally considered to be adequate for representation of the thermodynamic properties for the strongly interacting binary systems. The present study involves a critical comparison in terms of applicability of the three well known four-parameter formalisms for the representation of the thermodynamic properties of binary systems. The study indicates that the derived values of the infinite dilution parameters based on the formalisms compare favourably with the computed data available in the literature. The standard deviations in terms of the partial and integral excess functions of all the models lie well within the experimental scatter of the computed data and coincide exactly with each other. The formalisms are useful in representation of the thermodynamic properties of most of the binary systems except for the Mg–Bi and Mg–In systems. In such systems, it appears that the additional compositional terms may be necessary for the formalisms for adequate description of behaviour of the systems. Since the derived values of the thermodynamic properties of all the formalisms match favourably over the entire compositional range for the systems as studied in the present research, any one of them may be used for adequate representation of the properties of the systems.

Keywords. Four-parameter formalism; Redlich–Kister polynomial; Legendre polynomial; asymmetric integral function.

1. Introduction

Various multiparameter analytical equations have extensively been used in interpreting the thermodynamic properties as a function of composition. They are important in describing the equilibrium properties and in determining the phase equilibria of the system. Early representation of the thermodynamic properties has been made using the symmetric form of function with respect to composition or regular solution behaviour (Hilderbrand 1929). Generally, such a behaviour is rarely encountered in practice. It is well established that most of the solutions are characterized by the asymmetric behaviour with unequal infinite dilution parameters. The sub-regular solution model introduced by Hardy (1953) interprets the asymmetric behaviour of integral properties in terms of the linear composition dependent parameters. However, based on the knowledge gained through several decades (Krupkowski 1950; Hardy 1953; Darken 1968; Hajra 1980), it is evident that the two parameter equations, such as sub-regular model, provides adequate description of behaviour for systems showing relatively weak interactions. They are inadequate in interpreting the behaviour of the systems showing large deviations from ideality. In such systems, it is obvious that the higher power compositional terms are also to be considered in order to obtain as

close data fit as possible. Therefore, in the present investigation, efforts have been directed to interpret the asymmetric behaviour of the excess thermodynamic properties in terms of four parameter formalisms. Three well known formalisms which are being used by various researchers (Redlich and Kister 1948; Hajra and Mazumdar 1991) for the evaluation of the thermodynamic properties of the binary systems are: (i) the four-parameter model (Hajra and Mazumdar 1991), (ii) the Redlich–Kister polynomial (Redlich and Kister 1948), and (iii) application of Legendre polynomial (Pelton and Bale 1986).

One of us has proposed the four-parameter function for binary alloys based on the interaction parameter formalism (Hajra and Mazumdar 1991). Integral excess function, ΔG^{xs} , based on the equation may be expressed as

$$\Delta G^{xs} = x_1 x_2 \{a_1 x_1 + a_2 x_2 + x_1 x_2 (a_3 x_1 + a_4 x_2)\}, \quad (1)$$

where a_1 , a_2 , a_3 and a_4 represent the binary constants, and the mole fractions of the components, 1 and 2, are designated as x_1 and x_2 , respectively.

The second type of formalism which is known as the Redlich–Kister polynomial (Redlich and Kister 1948) may be expressed as

$$\Delta G^{xs} = x_1 x_2 \sum_{i=0}^{\infty} L_i (x_1 - x_2)^i. \quad (2)$$

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The integral excess free energy of a system in terms of the four parameter Redlich–Kister polynomial may be represented as

$$\Delta G^{xs} = x_1 x_2 \{ L_0 + L_1(x_1 - x_2) + L_2(x_1 - x_2)^2 + L_3(x_1 - x_2)^3 \}. \quad (3)$$

Recently, representation of the thermodynamic properties has also been made using the Legendre polynomial: a four-parameter formulation based on the latter is expressed (Pelton and Bale 1986) as

$$\Delta G^{xs} = x_1 x_2 \{ p_0 + p_1(2x_2 - 1) + p_2(6x_2^2 - 6x_2 - 1) + p_3(20x_2^3 - 30x_2^2 + 12x_2 - 1) \}. \quad (4)$$

The partial properties of the components as expressed by the formalisms are obtained from the following equations:

$$\ln \gamma_1 = \frac{\Delta G^{xs}}{RT} + (1 - x_1) \frac{1}{RT} \frac{\partial \Delta G^{xs}}{\partial x_1}, \quad (5)$$

$$\ln \gamma_2 = \frac{\Delta G^{xs}}{RT} - x_1 \frac{1}{RT} \frac{\partial \Delta G^{xs}}{\partial x_1}. \quad (6)$$

The constants involved in (1), (3) and (4) are generally evaluated using the regression analysis of the experimental data of various systems. They may be correlated to their respective interaction parameters of the system. These interrelations between the constants and their corresponding interaction parameters may be established using the technique of repeated differentiation of (1), (3) and (4) in conjunction with (5) and (6) with the application of the dilute solution restrictions, $x_1 \rightarrow 0$ and $x_2 \rightarrow 0$, respectively. Based on the procedure one obtains the following relations as

$$\left(\frac{\partial \Delta G^{xs}}{\partial x_2} \right)_{x_2 \rightarrow 0} = RT \ln \gamma_2^0 = a_1, \quad (7)$$

$$\left(\frac{\partial \Delta G^{xs}}{\partial x_1} \right)_{x_1 \rightarrow 0} = RT \ln \gamma_1^0 = a_2, \quad (8)$$

$$\left(\frac{\partial \Delta G^{xs}}{\partial x_2} \right)_{x_2 \rightarrow 0} = RT \ln \gamma_2^0 = L_0 + L_1 + L_2 + L_3, \quad (9)$$

$$\left(\frac{\partial \Delta G^{xs}}{\partial x_1} \right)_{x_1 \rightarrow 0} = RT \ln \gamma_1^0 = L_0 - L_1 + L_2 - L_3, \quad (10)$$

$$\left(\frac{\partial \Delta G^{xs}}{\partial x_2} \right)_{x_2 \rightarrow 0} = RT \ln \gamma_2^0 = p_0 - p_1 - p_2 - p_3, \quad (11)$$

$$\left(\frac{\partial \Delta G^{xs}}{\partial x_1} \right)_{x_1 \rightarrow 0} = RT \ln \gamma_1^0 = p_0 + p_1 - p_2 + p_3, \quad (12)$$

$$\left(\frac{\partial^2 \Delta G^{xs}}{\partial x_2^2} \right)_{x_2 \rightarrow 0} = RT \varepsilon_2^2(1) = -4a_1 + 2a_2 + 2a_3, \quad (13)$$

$$\left(\frac{\partial^2 \Delta G^{xs}}{\partial x_1^2} \right)_{x_1 \rightarrow 0} = RT \varepsilon_1^1(2) = -4a_2 + 2a_1 + 2a_4, \quad (14)$$

$$\left(\frac{\partial^2 \Delta G^{xs}}{\partial x_2^2} \right)_{x_2 \rightarrow 0} = RT \varepsilon_2^2(1) = -2L_0 - 6L_1 - 10L_2 - 14L_3, \quad (15)$$

$$\left(\frac{\partial^2 \Delta G^{xs}}{\partial x_1^2} \right)_{x_1 \rightarrow 0} = RT \varepsilon_1^1(2) = -2L_0 + 6L_1 - 10L_2 + 14L_3, \quad (16)$$

$$\left(\frac{\partial^2 \Delta G^{xs}}{\partial x_2^2} \right)_{x_2 \rightarrow 0} = RT \varepsilon_2^2(1) = -2p_0 + 6p_1 - 10p_2 + 26p_3, \quad (17)$$

$$\left(\frac{\partial^2 \Delta G^{xs}}{\partial x_1^2} \right)_{x_1 \rightarrow 0} = RT \varepsilon_1^1(2) = -2p_0 - 6p_1 - 10p_2 - 26p_3. \quad (18)$$

It is to be noted that the infinite dilution parameters are extrapolated quantities and represent basic and fundamental properties characteristic of the systems. In subsequent stages of the paper, a detailed study comprising of the numerical evaluation of the established relations (7) to (18) is worked out for the formalisms based on the regression analysis of the experimental data of several binary systems. The study also reveals a numerical correlation between the constants involved in these formalisms.

2. Physico-chemical aspects of interaction parameters

The interaction parameter formalism is based on the assumption and existence of the Maclaurin infinite series, which is expressed in terms of the logarithm of activity coefficients of the solute components in a solvent rich multicomponent system (Wagner 1962; Lupis and Elliott 1966). The thermodynamic behaviour of dilute solutions has been expressed in terms of the interaction parameters by Wagner (1962). In a subsequent development, Lupis and Elliott (1966) introduced the central atoms model for interpreting the physico-chemical aspects of the interaction parameters for dilute solutions. However, the concept is considered to be equally applicable to the concentrated solutions as the parameters are extrapolated quantities at infinite dilution. The model takes into account the interaction of a central atom with respect to its nearest neighbours and compares the energy of the

Table 1. Comparison of computed values of a_i , L_i and p_i of (1), (3) and (4) for various systems and their respective standard deviations in J mole^{-1} based on molar integral excess and partial excess.

Systems	Parameters							
	Present eqn (a_i), Redlich–Kister polynomial (L_i), Legendre polynomial (p_i)							
AB	i	0	1	2	3	4	SD (J mole^{-1})	
Zn–Sn at 750 K	a_i	–	1.5264	0.6668	–0.7001	–0.3810	0.767 (integral excess), 8.425 (partial excess)	Moser <i>et al</i> (1985) ± 146.54 (integral excess), ± 209.35 (partial excess)
	L_i	0.9614	0.3898	0.1353	0.04019	–	0.766 (integral excess), 8.577 (partial excess)	
	p_i	1.1877	–0.4143	0.0903	–0.0162		0.7873 (integral excess), 8.664 (partial excess)	
Zn–In at 700 K	a_i	–	2.3934	1.3089	–1.6641	–0.0303	6.011 (integral excess), 108.30 (partial excess)	Dutkiewicz and Zakulski (1984) ± 209.35 (integral excess), ± 209.35 (partial excess)
	L_i	1.6393	0.3379	0.2120	0.20463	–	6.011 (integral excess), 108.62 (partial excess)	
	p_i	1.9938	–0.4613	0.1413	–0.0822		6.0163 (integral excess), 108.663 (partial excess)	
Zn–Bi at 873 K	a_i	–	3.0487	0.9695	–3.4223	–0.8864	9.738 (integral excess), 161.598 (partial excess)	Hultgren <i>et al</i> (1973) ± 209.35 (integral excess), ± 209.35 (partial excess)
	L_i	1.4705	0.7223	0.5388	0.31771	–	9.738 (integral excess), 162.222 (partial excess)	
	p_i	2.3708	–0.9140	0.3597	–0.1276		9.7462 (integral excess), 162.349 (partial excess)	
Sn–In at 700 K	a_i	–	0.3520	–1.0324	–2.6916	0.5865	7.474 (integral excess), 112.493 (partial excess)	Hultgren <i>et al</i> (1973) ± 209.35 (integral excess), ± 209.35 (partial excess)
	L_i	–0.6033	0.2822	0.2630	0.4103	–	7.473 (integral excess), 112.851 (partial excess)	
	p_i	–0.1659	–0.5287	0.1751	–0.1642		7.4801 (integral excess), 114.27 (partial excess)	
Tl–K at 798 K	a_i	–	–4.9417	–1.3524	–4.1866	–0.1286	6.49 (integral excess), 101.497 (partial excess)	Hultgren <i>et al</i> (1973) ± 1046.75 (integral excess), ± 1046.75 (partial excess)
	L_i	–3.6864	–2.301	0.5390	0.50583	–	6.49 (integral excess), 101.151 (partial excess)	
	p_i	–2.7909	1.9998	0.3592	–0.2017		6.5011 (integral excess), 100.85 (partial excess)	
Na–In at 713 K	a_i	–	0.2893	–2.6303	–6.5898	–4.9404	82.21 (integral excess), 304.555 (partial excess)	Hultgren <i>et al</i> (1973) ± 628.05 (integral excess), ± 628.05 (partial excess)
	L_i	–2.611	1.2478	1.4377	0.22385	–	82.19 (integral excess), 284.86 (partial excess)	
	p_i	–0.2158	–1.3835	0.9589	–0.0902		82.254 (integral excess), 282.02 (partial excess)	
Mg–In at 923 K	a_i	–	–4.6532	–3.2486	1.6593	2.8885	8.413 (integral excess), 408.70 (partial excess)	Hultgren <i>et al</i> (1973) ± 209.35 (integral excess), ± 209.35 (partial excess)
	L_i	–3.3824	–0.8559	–0.5690	0.15337	–	8.412 (integral excess), 408.70 (partial excess)	
	p_i	–4.3337	0.7643	–0.3796	–0.0616		8.4194 (integral excess), 405.23 (partial excess)	
Mg–Ga at 923 K	a_i	–	–4.5942	–3.7962	–6.4690	–0.1594	28.312 (integral excess), 493.02 (partial excess)	Hultgren <i>et al</i> (1973) ± 1256.1 (integral excess), ± 1256.1 (partial excess)
	L_i	–5.0237	–1.1875	0.8278	0.7884	–	28.312 (integral excess), 493.34 (partial excess)	
	p_i	–3.6453	0.7148	0.5528	–0.3159		28.3335 (integral excess), 496.93 (partial excess)	

(Contd.)

Table 1. (Continued)

Systems	Parameters							
	Present eqn (a_i), Redlich–Kister polynomial (L_i), Legendre polynomial (p_i)							
AB	i	0	1	2	3	4	SD (J mole ⁻¹)	
Mg–Bi at 975 K	a_i	–	–6.3373	–5.6885	–36.9197	5.8590	377.7 (integral excess), 3419.49 (partial excess)	Hultgren <i>et al</i> (1973) ±1674.8 (integral excess), ±2093.8 (partial excess)
	L_i	–9.8954	–5.6772	3.8826	5.3472	–	377.7 (integral excess), 3412.87 (partial excess)	
	p_i	–3.4299	2.4659	2.5890	–2.1394		378.022 (integral excess), 3417.6 (partial excess)	
Pb–Mg at 973 K	a_i	–	–2.1694	–6.6691	0.2364	0.1850	14.67 (integral excess), 594.63 (partial excess)	Hultgren <i>et al</i> (1973) ±628.05 (integral excess), ±628.05 (partial excess)
	L_i	–4.3665	2.2557	–0.0534	–0.00469	–	14.67 (integral excess), 577.21 (partial excess)	
	p_i	–4.4580	–2.2552	–0.0353	0.0010		14.6865 (integral excess), 576.71 (partial excess)	

Table 2. Numerical correlations between regressional values of parameters, a_i and L_i involved in formalisms (eqs (1) and (3)).

System	Derived relation (20)		Derived relation (21)		Derived relation (22)		Derived relation (23)	
	a_1	$L_0 + L_1 + L_2 + L_3$	a_2	$L_0 - L_1 - L_2 - L_3$	a_3	$-4(L_2 + L_3)$	a_4	$4(L_3 - L_2)$
Zn–Sn at 750 K	1.5264	1.5267	0.6668	0.6667	–0.7001	–0.702	–0.3810	–0.3804
Zn–In at 700 K	2.3934	2.3938	1.3089	1.3088	–1.6641	–1.6664	–0.0303	–0.0296
Zn–Bi at 873 K	3.0487	3.0493	0.9695	0.9693	–3.4223	–3.426	–0.8864	–0.8844
Sn–In at 700 K	0.3520	0.3522	–1.0324	–1.0328	–2.6916	–2.6932	0.5865	0.5892
Tl–K at 798 K	–4.9417	–4.9426	–1.3524	–1.3522	–4.1866	–4.1792	–0.1286	–0.1328
Na–In at 713 K	0.2893	0.2983	–2.6303	–2.6449	–6.5898	–6.646	–4.9404	–4.8556
Mg–In at 923 K	–4.6532	–4.6539	–3.2486	–3.2489	1.6593	1.6624	2.8885	2.8896
Mg–Ga at 923 K	–4.5942	–4.595	–3.7962	–3.7968	–6.469	–6.4648	–0.1594	–0.1576
Mg–Bi at 975 K	–6.3373	–6.3428	–5.6885	–5.6828	–36.919	–36.919	5.859	5.858
Pb–Mg at 973 K	–2.1694	–2.1689	–6.6691	–6.6709	0.2364	0.2324	0.1850	0.1948

Table 3. Numerical correlations between regressional values of parameters, a_i and p_i , involved in formalisms (eqs (1) and (4)).

System	Derived relation (24)		Derived relation (25)		Derived relation (26)		Derived relation (27)	
	a_1	$p_0 - p_1 - p_2 - p_3$	a_2	$p_0 + p_1 - p_2 + p_3$	a_3	$-6p_2 + 10p_3$	a_4	$-6p_2 - 10p_3$
Zn–Sn at 750 K	1.5264	1.5279	0.6668	0.6669	–0.7001	–0.7038	–0.3810	–0.3798
Zn–In at 700 K	2.3934	2.3938	1.3089	1.3088	–1.6641	–1.6698	–0.0303	–0.0258
Zn–Bi at 873 K	3.0487	3.0527	0.9695	0.9695	–3.4223	–3.4342	–0.8864	–0.8822
Sn–In at 700 K	0.3520	0.3519	–1.0324	–1.0339	–2.6916	–2.6926	0.5865	0.5914
Tl–K at 798 K	–4.9417	–4.9482	–1.3524	–1.352	–4.1866	–4.1722	–0.1286	–0.1382
Na–In at 713 K	0.2893	0.299	–2.6303	–2.6484	–6.5898	–6.6554	–4.9404	–4.8514
Mg–In at 923 K	–4.6532	–4.6568	–3.2486	–3.2514	1.6593	1.6616	2.8885	2.8936
Mg–Ga at 923 K	–4.5942	–4.597	–3.7962	–3.7992	–6.469	–6.4758	–0.1594	–0.1578
Mg–Bi at 975 K	–6.3373	–6.3454	–5.6885	–5.6924	–36.919	–36.928	5.859	5.86
Pb–Mg at 973 K	–2.1694	–2.1685	–6.6691	–6.6769	0.2364	0.2218	0.1850	0.2018

Table 4. Values of various infinite dilution constants based on eqs (1), (3), (4) and (7–18).

Zn–Sn at 750 K	$\ln \gamma_{\text{Zn}}^0$	$\ln \gamma_{\text{Sn}}^0$	$\varepsilon_{\text{Zn}}^{\text{Zn}}$	$\varepsilon_{\text{Sn}}^{\text{Sn}}$
Four parameter equation	0.6668	1.5264	–0.3764	–6.1722
Redlich–Kister function	0.66671	1.52669	–0.37434	–6.1772
Legendre polynomial	0.6669	1.5279	–0.3714	–6.1854
Moser <i>et al</i> (1985)	0.6709	1.5213	–	–
Zn–In at 700 K	$\ln \gamma_{\text{Zn}}^0$	$\ln \gamma_{\text{In}}^0$	$\varepsilon_{\text{Zn}}^{\text{Zn}}$	$\varepsilon_{\text{In}}^{\text{In}}$
Four parameter equation	1.3089	2.3934	–0.5094	–10.284
Redlich–Kister function	1.3088	2.3938	–0.5064	–10.2908
Legendre polynomial	1.309	2.396	–0.4956	–10.3056
Dutkiewicz and Zakulski (1984)	1.3658	2.4385	–	–
Zn–Bi at 873 K	$\ln \gamma_{\text{Zn}}^0$	$\ln \gamma_{\text{Bi}}^0$	$\varepsilon_{\text{Zn}}^{\text{Zn}}$	$\varepsilon_{\text{Bi}}^{\text{Bi}}$
Four parameter equation	0.9695	3.0487	0.4466	–17.1004
Redlich–Kister function	0.9693	3.0493	0.4526	–17.1106
Legendre polynomial	0.9695	3.0527	0.463	–17.1402
Hultgren <i>et al</i> (1973)	1.0374	3.4862	–	–
Sn–In at 700 K	$\ln \gamma_{\text{Sn}}^0$	$\ln \gamma_{\text{In}}^0$	$\varepsilon_{\text{Sn}}^{\text{Sn}}$	$\varepsilon_{\text{In}}^{\text{In}}$
Four parameter equation	–1.0324	0.3520	6.0066	–8.856
Redlich–Kister function	–1.0327	0.3523	6.013	–8.8618
Legendre polynomial	–1.0339	0.3519	6.0222	–8.8606
Hultgren <i>et al</i> (1973)	–0.9781	0.2159	–	–
Tl–K at 798 K	$\ln \gamma_{\text{Tl}}^0$	$\ln \gamma_{\text{K}}^0$	$\varepsilon_{\text{Tl}}^{\text{Tl}}$	$\varepsilon_{\text{K}}^{\text{K}}$
Four parameter equation	–1.3524	–4.9417	–4.731	8.6888
Redlich–Kister function	–1.3518	–4.943	–4.7444	8.71
Legendre polynomial	–1.352	–4.9482	–4.7648	8.7444
Hultgren <i>et al</i> (1973)	–1.3056	–5.1160	–	–
Na–In at 713 K	$\ln \gamma_{\text{Na}}^0$	$\ln \gamma_{\text{In}}^0$	$\varepsilon_{\text{Na}}^{\text{Na}}$	$\varepsilon_{\text{In}}^{\text{In}}$
Four parameter equation	–2.6303	0.2893	1.219	–19.5974
Redlich–Kister function	–2.6451	0.2981	1.4654	–19.7746
Legendre polynomial	–2.6484	0.299	1.4888	–19.8036
Hultgren <i>et al</i> (1973)	–2.7646	–0.1473	–	–
Mg–In at 923 K	$\ln \gamma_{\text{Mg}}^0$	$\ln \gamma_{\text{In}}^0$	$\varepsilon_{\text{Mg}}^{\text{Mg}}$	$\varepsilon_{\text{In}}^{\text{In}}$
Four parameter equation	–3.2486	–4.6532	9.465	15.4342
Redlich–Kister function	–3.2489	–4.6539	9.467	15.4426
Legendre polynomial	–3.2514	–4.6568	9.4792	15.4476
Hultgren <i>et al</i> (1973)	–3.4112	–4.7105	–	–
Mg–Ga at 923 K	$\ln \gamma_{\text{Mg}}^0$	$\ln \gamma_{\text{Ga}}^0$	$\varepsilon_{\text{Mg}}^{\text{Mg}}$	$\varepsilon_{\text{Ga}}^{\text{Ga}}$
Four parameter equation	–3.7962	–4.5942	5.6776	–2.1534
Redlich–Kister function	–3.7968	–4.595	5.682	–2.1432
Legendre polynomial	–3.7992	–4.597	5.6872	–2.162
Hultgren <i>et al</i> (1973)	–3.6120	–4.8283	–	–
Mg–Bi at 975 K	$\ln \gamma_{\text{Mg}}^0$	$\ln \gamma_{\text{Bi}}^0$	$\varepsilon_{\text{Mg}}^{\text{Mg}}$	$\varepsilon_{\text{Bi}}^{\text{Bi}}$
Four parameter equation	–5.6885	–6.3373	21.7978	–59.8674
Redlich–Kister function	–5.6884	–6.3372	21.7968	–59.8672
Legendre polynomial	–5.6924	–6.3454	21.7988	–59.8592
Hultgren <i>et al</i> (1973)	–5.1672	–9.2103	–	–
Pb–Mg at 973 K	$\ln \gamma_{\text{Pb}}^0$	$\ln \gamma_{\text{Bi}}^0$	$\varepsilon_{\text{Pb}}^{\text{Pb}}$	$\varepsilon_{\text{Bi}}^{\text{Bi}}$
Four parameter equation	–6.6691	–2.1694	22.7076	–4.1878
Redlich–Kister function	–6.6709	–2.1689	22.7354	–4.2014
Legendre polynomial	–6.6769	–2.1685	22.7742	–4.2362
Hultgren <i>et al</i> (1973)	–6.9077	–2.1203	–	–

configuration of the atom with that of a cluster containing similar atoms. In this simple approach, however, only the short range interactions are considered neglecting the non-nearest neighbour interactions. Although the central atoms model assumes short range effect between atoms, it is permitted to be extended to the non-nearest neighbours. This is particularly so as a nearest neighbour atom of a given cluster may act as a central atom to the adjacent cluster. The zeroth order parameter such as, $\ln \gamma_i^{i,0}(j)$ as mentioned above compares the energy of i atom surrounded by j atoms to the energy of i atom surrounded by Z atoms i . The first-order

parameter, $\varepsilon_i^i(j)$, compares the energy of configuration of i central atom surrounded by $Z - 1$ atoms j and one i atom to that of i surrounded by all i atoms. In the present investigation, apart from the study of the applicability of the two formalisms, the derived values of the interaction parameters which are essentially the extrapolated quantities at infinite dilution are also evaluated based on the two formalisms and interpreted using the concept of the central atoms model in the subsequent sections.

The compositional terms with their corresponding coefficients as devised by Redlich–Kister for a four-parameter

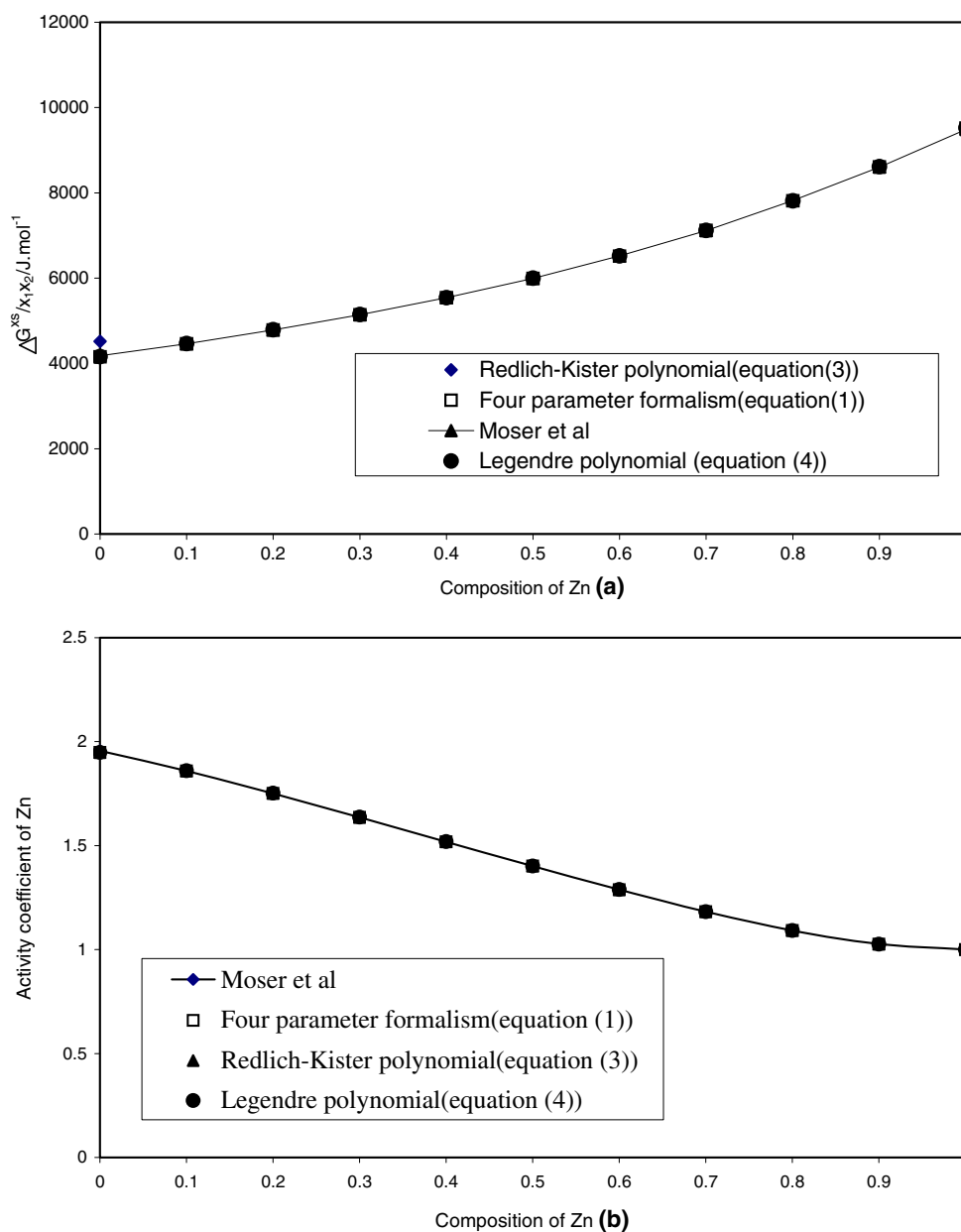


Figure 1. Comparison between calculated and experimental values of (a) integral excess free energy and (b) activity coefficient of Zn in Zn–Sn system at 750 K.

polynomial for representation of the integral excess thermodynamic property of a binary system may be expressed as,

$$\Delta G^{xs} = x_1x_2\{L_0+L_1(x_1-x_2)+L_2(x_1-x_2)^2+L_3(x_1-x_2)^3\}.$$

In order to equate the coefficients of similar compositional terms involved in the two four-parameter formalisms, the Redlich–Kister polynomial (3) is transformed in stages as,

$$\begin{aligned} \Delta G^{xs} = & x_1x_2\{L_0(x_1+x_2)+L_1(x_1-x_2) \\ & + L_2[(x_1+x_2)^2-4x_1x_2] \\ & + L_3(x_1-x_2)[(x_1+x_2)^2-4x_1x_2]\} \end{aligned}$$

$$\begin{aligned} = & x_1x_2\{L_0(x_1+x_2)+L_1(x_1-x_2)+L_2[(x_1+x_2)-4x_1x_2] \\ & + L_3(x_1-x_2)[(x_1+x_2)-4x_1x_2]\} \\ = & x_1x_2\{L_0(x_1+x_2)+L_1(x_1-x_2)+L_2[(x_1+x_2)-4x_1x_2] \\ & + L_3(x_1-x_2)[(1-4x_1x_2)]\} \\ = & x_1x_2\{(L_0+L_1+L_2+L_3)x_1+(L_0-L_1+L_2+L_3) \\ & + 4x_1x_2\{-L_2-L_3(x_1-x_2)\}\} \\ = & x_1x_2\{(L_0+L_1+L_2+L_3)x_1+(L_0-L_1+L_2-L_3)x_2 \\ & + 4x_1x_2\{-L_2(x_1+x_2)-L_3(x_1-x_2)\}\} \\ = & x_1x_2\{(L_0+L_1+L_2+L_3)x_1+(L_0-L_1+L_2-L_3)x_2 \\ & + x_1x_2\{(-4L_2-4L_3)x_1+(-4L_2+4L_3)x_2\}\}. \end{aligned} \quad (19)$$

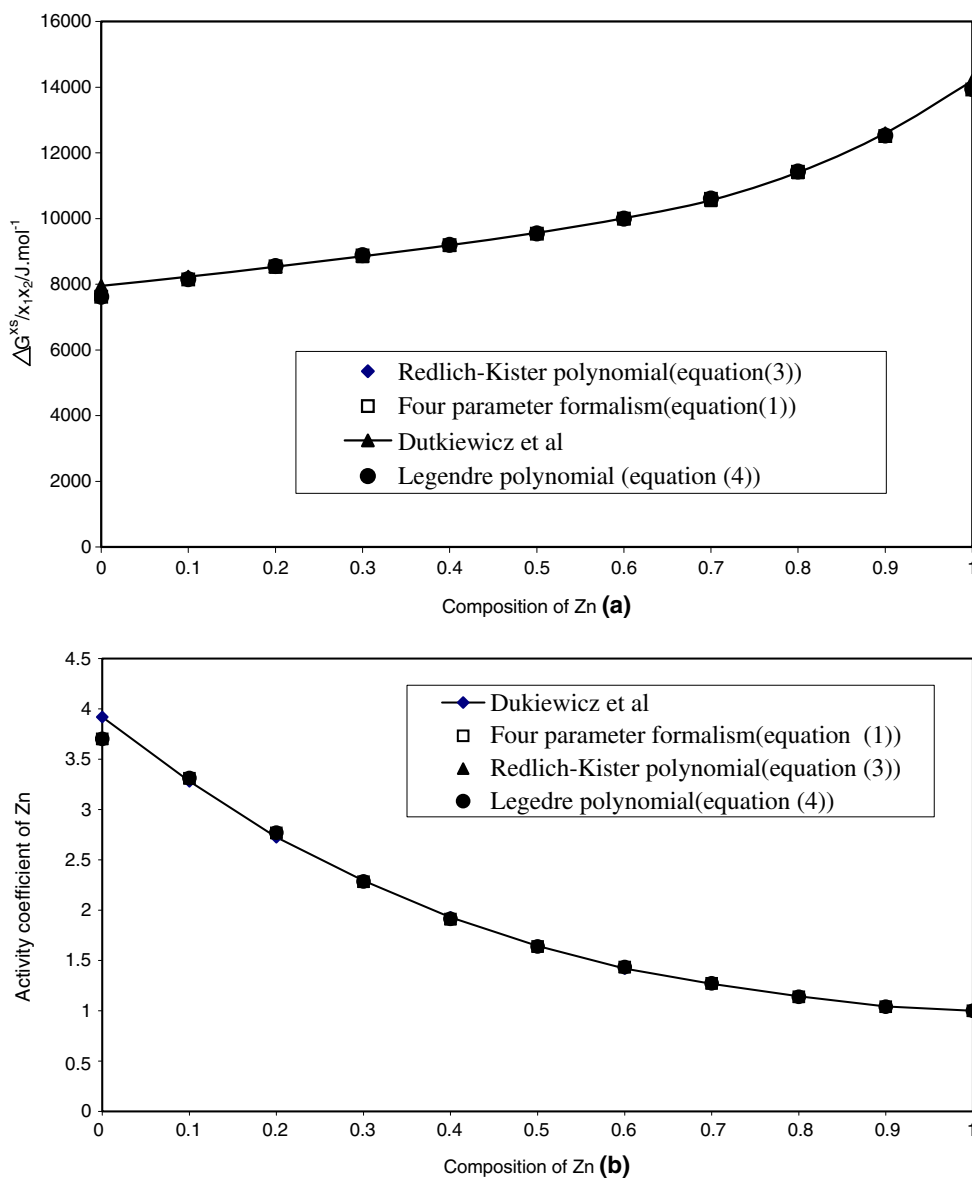


Figure 2. Comparison between calculated and experimental values of (a) integral excess free energy and (b) activity coefficient of Zn in Zn–In system at 700 K.

Since (1) and (19) represent the integral excess function of a system, the following identity may be arrived at,

$$x_1x_2\{a_1x_1 + a_2x_2 + x_1x_2(a_3x_1 + a_4x_2)\} \\ - x_1x_2\{(L_0 + L_1 + L_2 + L_3)x_1 + (L_0 - L_1 + L_2 - L_3)x_2 \\ + x_1x_2\{(-4L_2 - 4L_3)x_1 + (-4L_2 + 4L_3)x_2\}\} = 0,$$

or,

$$x_1x_2\{x_1(a_1 - (L_0 + L_1 + L_2 + L_3 + L_4)) \\ + x_2(a_2 - (L_0 - L_1 + L_2 - L_3 + L_4)) \\ + x_1x_2\{(a_3 - (-4L_2 - 4L_3))x_1 \\ + (a_4 - (-4L_2 + 4L_3))x_2\}\} = 0.$$

In this identity, it is obvious that the relations between the two sets of parameters a_i and L_i pertaining to the two formalisms in the closed brackets tend separately to zero treating their associated compositional terms to be non-zero.

Validity of the relations has been studied based on the regressional values of the constants involved in (1) and (3) for various binary systems in the next section.

The Legendre polynomial may be simplified algebraically as

$$\Delta G^{xs} = x_1x_2\{p_0 + p_1(2x_2 - 1) + p_2(6x_2^2 - 6x_2 - 1) \\ + p_3(20x_2^3 - 30x_2^2 + 12x_2 - 1)\}$$

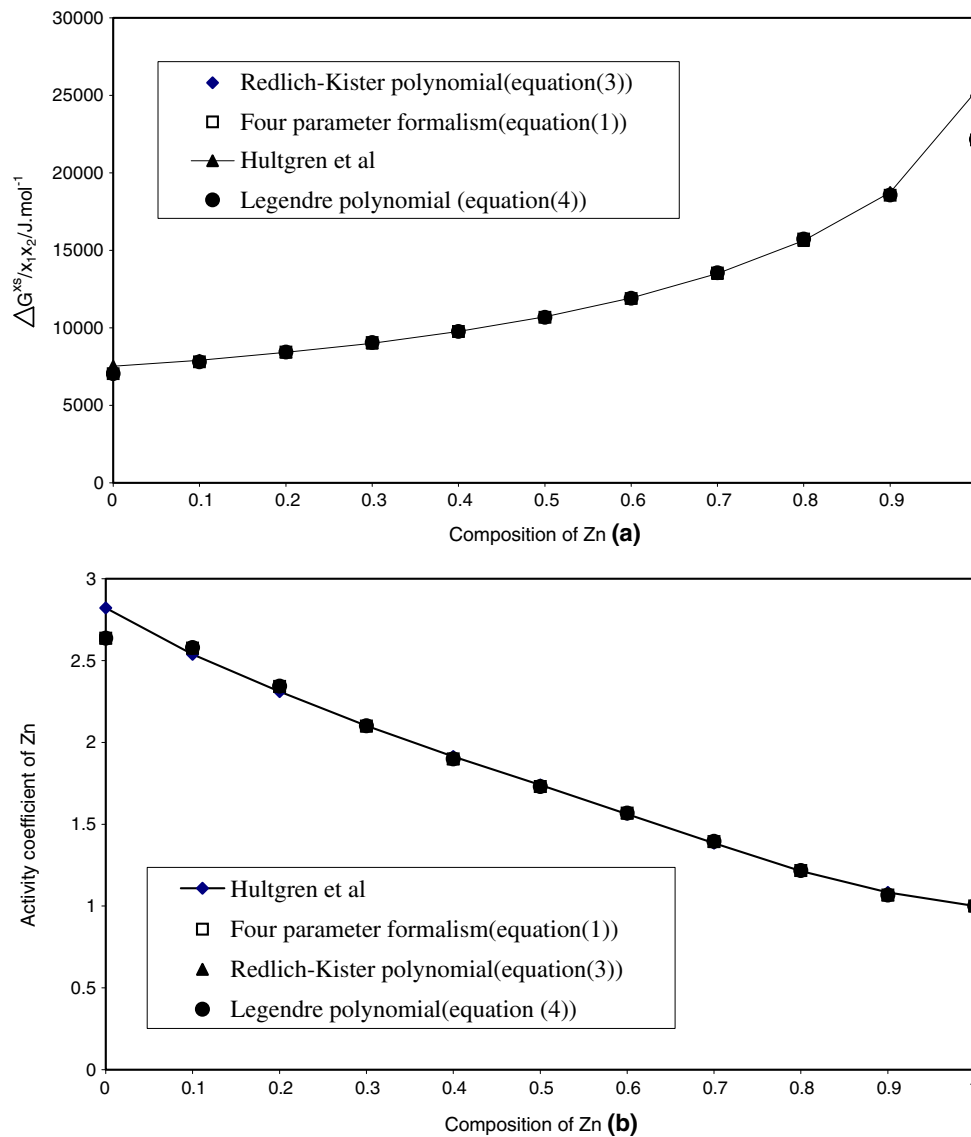


Figure 3. Comparison between calculated and experimental values of (a) integral excess free energy and (b) activity coefficient of Zn in Zn-Bi system at 873 K.

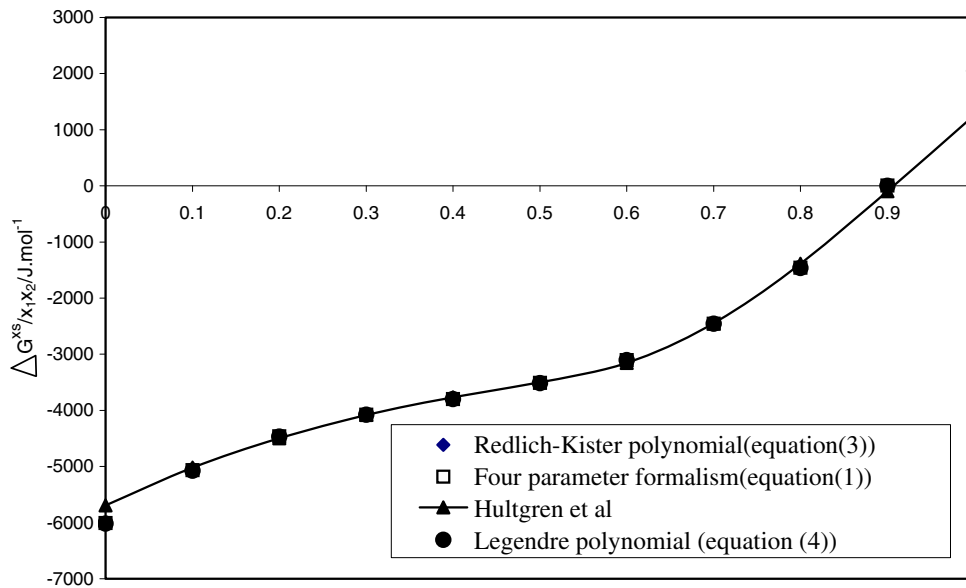
$$\begin{aligned}
 &= x_1x_2\{p_0 + p_1(2x_2 - 1) \\
 &\quad + p_2((2x_2 - 1)^2 + 2x_2^2 - 2x_2 - 2) \\
 &\quad + p_3((2x_2 - 1)^3 + 6x_2(2x_2^2 - 3x_2 + 1))\} \\
 &= x_1x_2\{p_0 + p_1(2x_2 - 1) + p_2(2x_2 - 1)^2 \\
 &\quad + p_3(2x_2 - 1)^3\} + x_1x_2\{2p_2(x_2^2 - x_2 - 1) \\
 &\quad + 6p_3x_2(2x_2^2 - 3x_2 + 1)\}.
 \end{aligned}$$

3. Discussion

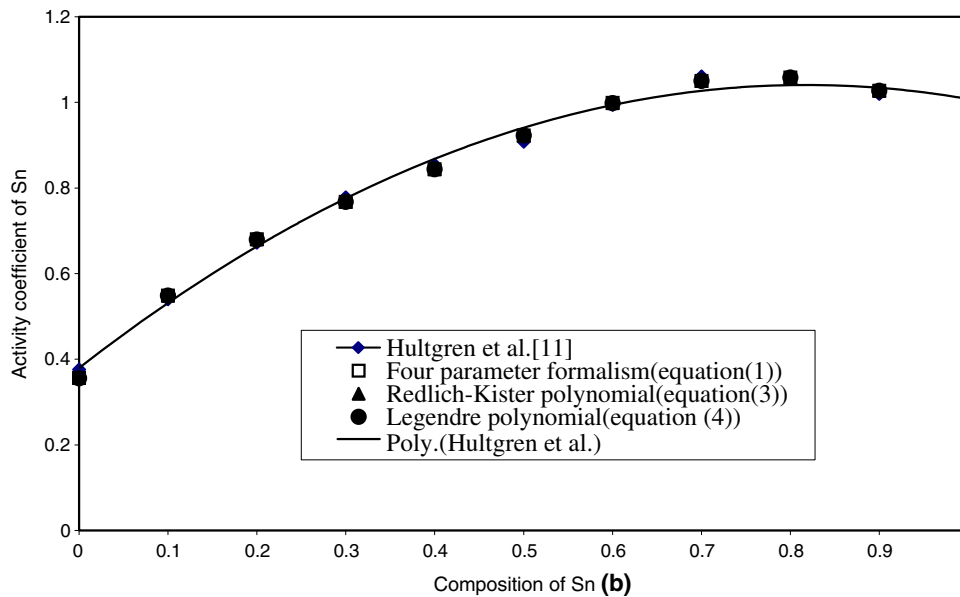
The integral excess free energy for the liquid alloys may be represented by the polynomial form as

$$\Delta G^{xs} = x(1-x) * (\alpha + \beta x + \gamma x^2 + \delta x^3),$$

where, α , β , γ , δ are represented by the coefficient of the polynomial, and x is the mole fraction of the component, where $x = x_2$ and $(1-x) = x_1$. Correlating the coefficients



Composition of Sn (a)



Composition of Sn (b)

Figure 4. Comparison between calculated and experimental values of (a) integral excess free energy and (b) activity coefficient of Sn in Sn–In system at 700 K.

of the above equation with (1), one obtains the following relations,

$$\begin{aligned}\alpha &= a_1, \\ \beta &= a_3 + a_2 - a_1, \\ \gamma &= a_3 - 2a_3, \\ \delta &= a_3 - a_4.\end{aligned}$$

Similarly, comparing the coefficient of (28) with (3) and (4) may be expressed as

$$\begin{aligned}\alpha &= L_0 + L_1 + L_2 + L_3, & \alpha &= p_0 - p_1 - p_2 - p_3, \\ \beta &= -2L_1 - 4L_2 - 6L_3, & \beta &= 2p_1 - 6p_2 + 12p_3,\end{aligned}$$

$$\gamma = 4L_2 + 12L_3, \quad \gamma = 6p_2 - 30p_3,$$

$$\delta = -8L_3, \quad \delta = 20p_3.$$

We obtained the following correlations between the constants of the three formalisms.

The interrelationships between the constants of the Redlich–Kister polynomial with the corresponding coefficients of the four-parameter equation (1) are obtained by equating similar compositional terms of the formalisms. The relation between the a_i and L_i ($a_i \leftrightarrow L_i$) is

$$a_1 = L_0 + L_1 + L_2 + L_3, \quad L_0 = \frac{1}{2}a_1 + \frac{1}{2}a_2 + \frac{1}{8}a_3 + \frac{1}{8}a_4, \quad (20)$$

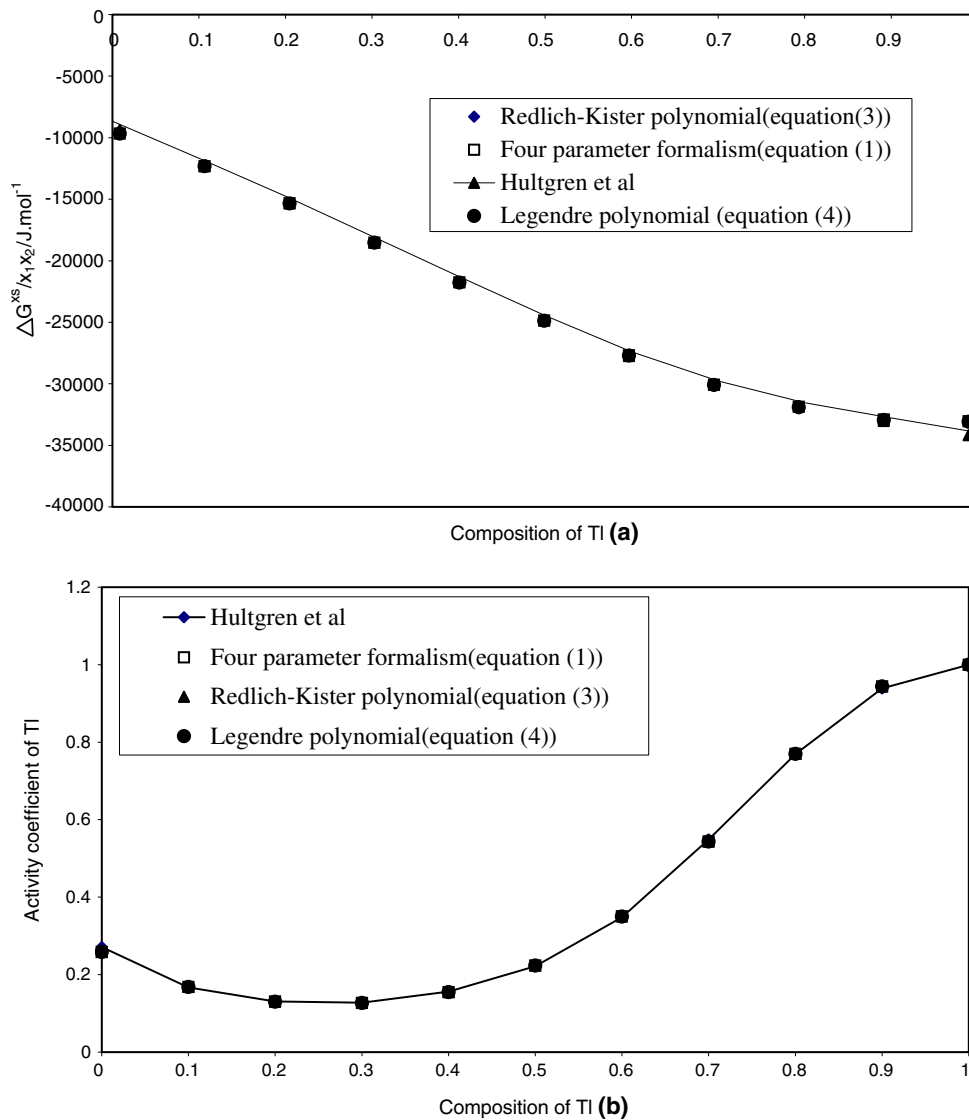


Figure 5. Comparison between calculated and experimental values of (a) integral excess free energy and (b) activity coefficient of Tl in Tl–K system at 798 K.

$$a_2 = L_0 - L_1 + L_2 - L_3, \quad L_1 = \frac{1}{2}a_1 - \frac{1}{2}a_2 + \frac{1}{8}a_3 - \frac{1}{8}a_4, \quad (21) \quad a_3 = -6p_2 + 10p_3, \quad p_2 = -\frac{1}{12}a_3 - \frac{1}{12}a_4, \quad (26)$$

$$a_3 = -4L_2 - 4L_3, \quad L_2 = -\frac{1}{8}a_3 - \frac{1}{8}a_4, \quad (22) \quad a_4 = -6p_2 - 10p_3, \quad p_2 = \frac{1}{20}a_3 - \frac{1}{20}a_4. \quad (27)$$

$$a_3 = -4L_2 + 4L_3, \quad L_2 = -\frac{1}{8}a_3 + \frac{1}{8}a_4. \quad (23) \quad \text{The relation between } p_i \text{ and } L_i (p_i \leftrightarrow L_i) \text{ is given as}$$

$$p_0 = L_0 + \frac{5}{3}L_2, \quad L_0 = p_0 - \frac{5}{2}p_2, \quad (28)$$

The relation between a_i and $p_i (a_i \leftrightarrow p_i)$ is given as

$$a_1 = p_0 - p_1 - p_2 - p_3, \quad p_0 = \frac{1}{2}a_1 + \frac{1}{2}a_2 - \frac{1}{12}a_3 - \frac{1}{12}a_4, \quad (24) \quad p_1 = -L_1 - \frac{3}{5}L_3, \quad L_1 = -p_1 + \frac{3}{2}p_3, \quad (29)$$

$$a_2 = p_0 + p_1 - p_2 + p_3, \quad p_1 = -\frac{1}{2}a_1 + \frac{1}{2}a_2 - \frac{1}{20}a_3 - \frac{1}{20}a_4, \quad (25) \quad p_2 = \frac{2}{3}L_2, \quad L_2 = \frac{3}{2}p_2, \quad (30)$$

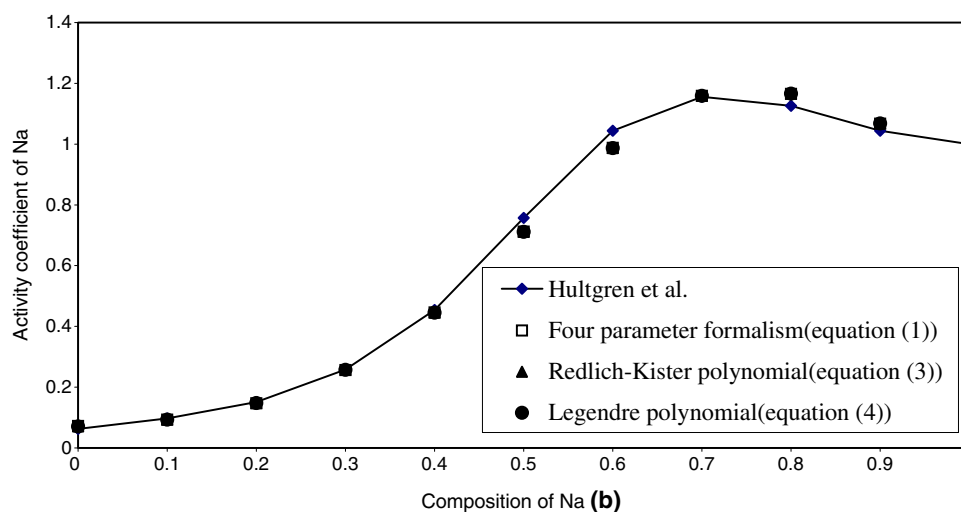
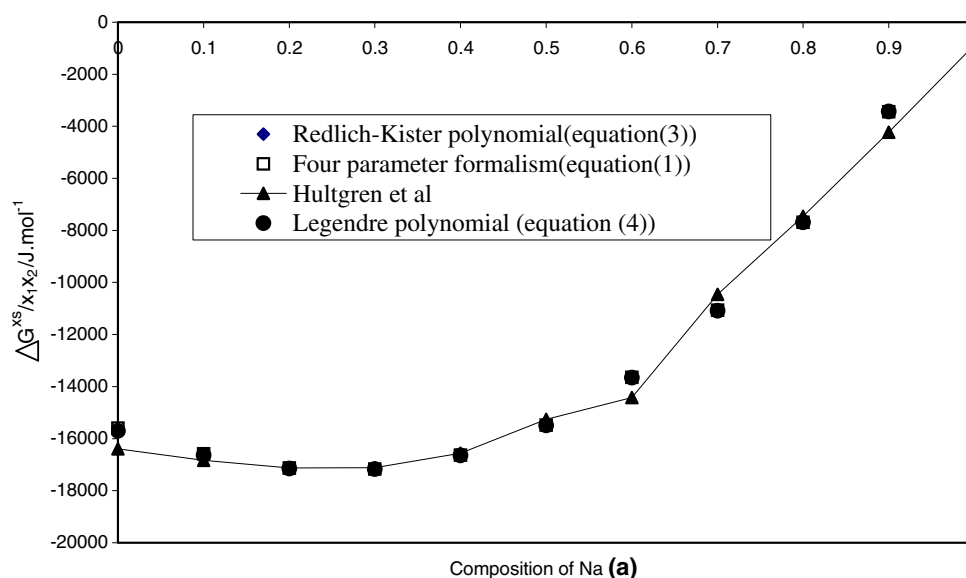


Figure 6. Comparison between calculated and experimental values of (a) integral excess free energy and (b) activity coefficient of Na in Na–In system at 713 K.

$$p_3 = -\frac{2}{5}L_3, \quad L_3 = \frac{5}{2}p_3. \quad (31)$$

The applicability of (1), (3) and (4) has been studied using selected values of the thermodynamic properties of several alloy systems (Hultgren *et al* 1973; Dutkiewicz and Zakulski 1984; Moser *et al* 1985). The systems are so chosen such that they exhibit an increasing order of positive deviation from ideality in the systems, Zn–Sn, Zn–In and Zn–Bi, while the Sn–In system represents both types of deviations from ideality with respect to the composition. In the series of alloys exhibiting positive deviation from ideality, the Zn–Bi system shows liquid–liquid immiscibility

signifying the extreme positive deviation in the series. The other set of selected alloys as adopted in the investigation, Tl–K, Na–In, Mg–In, Mg–Ga, Mg–Bi and Pb–Mg systems exhibit an increasing order of negative deviation from ideality to the extent of formation of an intermetallic compound, such as Mg_3Bi_2 in the Mg–Bi system. In the sequence, the Pb–Mg system is characterized by having a highly asymmetric integral free energy function and exhibits a change over from the negative deviation to the positive deviation for the Pb rich alloys.

The object of present work is to analyse the comparative applicability of the three four-parameter functions

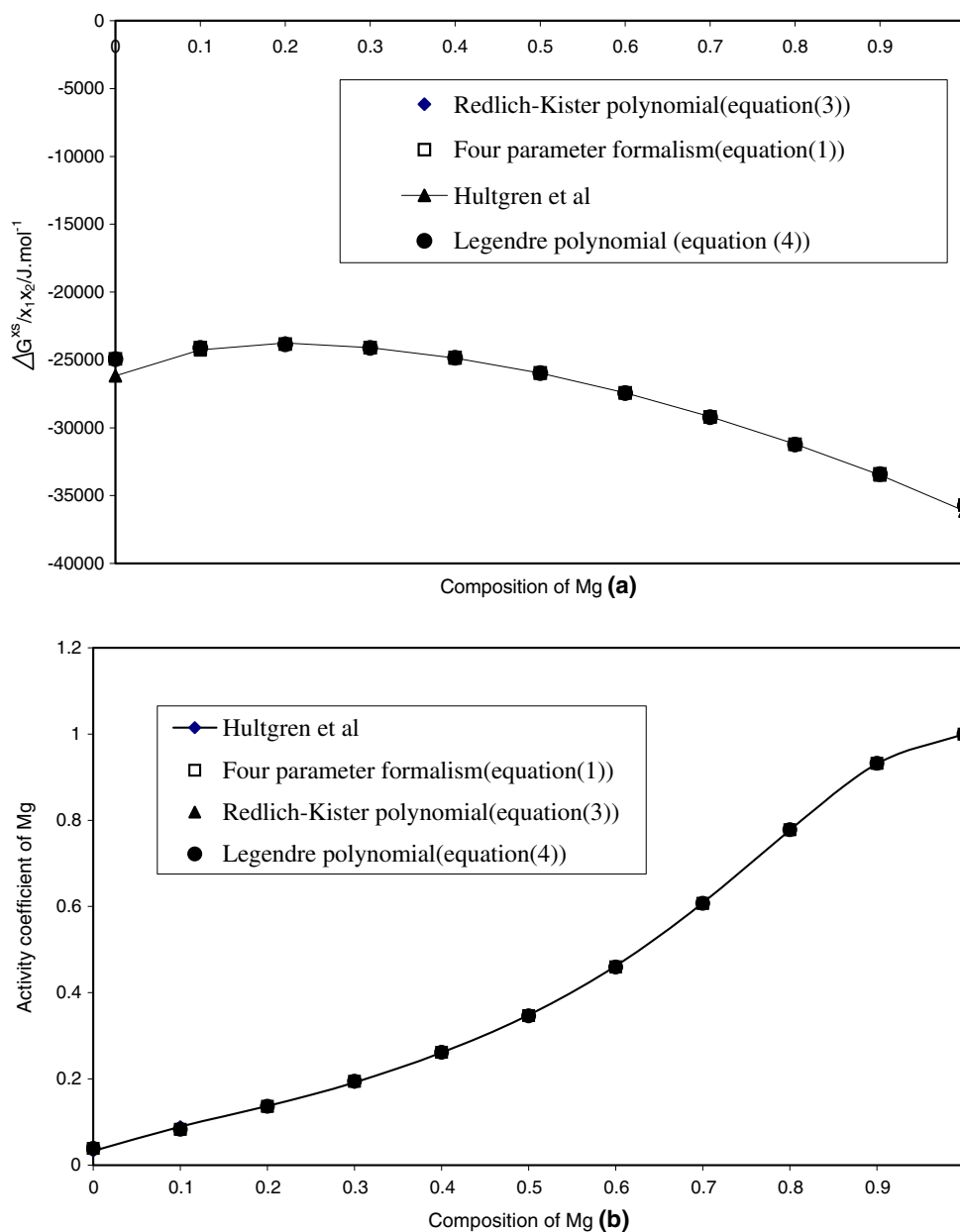


Figure 7. Comparison between calculated and experimental values of (a) integral excess free energy and (b) activity coefficient of Mg in Mg–In system at 923 K.

represented by (1), (3) and (4) with respect to the experimental data (Hultgren *et al* 1973; Dutkiewicz and Zakulski 1984; Moser *et al* 1985) of the systems exhibiting various degrees of asymmetric integral properties. The constants a_i , L_i and p_i involved in (1), (3) and (4) are evaluated by the least squares regression technique of the selected partial and integral excess properties of the alloys and listed along with their respective standard deviations in table 1. However, since the partial properties are generally measured, the standard deviations based on the latter have also been assessed and listed in the table for the quantitative evaluation of the applicability of the formalisms. Tables 2 and 3 depict the numerical

correlations between the regressional values of a_i of (1) with those of L_i of (3) and p_i of (4). The evaluation based on the table clearly validates the derived relations (20) through (27) as described here. The infinite dilution constants involved in (1), (3) and (4) are also evaluated based on (7) through (18) and are computed in table 4. It may be noted that the derived values of the zeroth order parameters based on the three formalisms coincide with each other and are in good agreement with those of the compiled values of Hultgren *et al* (1973), Moser *et al* (1985), and Dutkiewicz and Zakulski (1984). It may further be mentioned that the derived values of first-order parameter based on the formalisms match exactly in

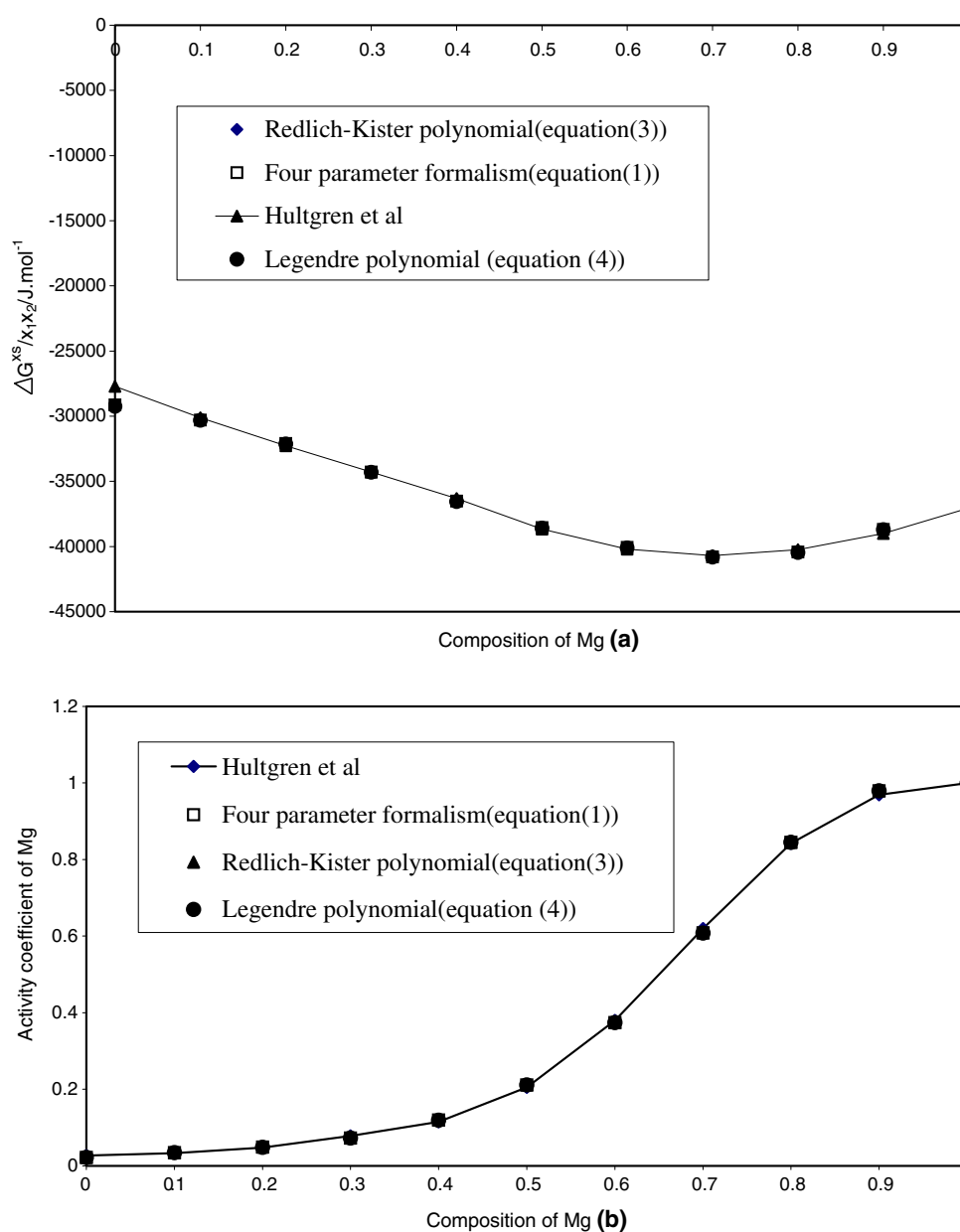


Figure 8. Comparison between calculated and experimental values of (a) integral excess free energy and (b) activity coefficient of Mg in Mg-Ga system at 923 K.

terms of sign and magnitude for all the systems studied in the present investigation.

The positive $\ln \gamma_i^0$ values as computed in table 3 for the systems such as Zn–Sn, Zn–In and Zn–Bi, indicate the repulsive interactions between the central atom with respect to its nearest dissimilar atoms. It automatically follows then that the zeroth-order configuration is considerably less stable relative to its cluster surrounded by similar atoms. It may be noted that the derived values of the first-order interaction parameters invariably exhibit negative values for most of the systems due to the substitution of a similar bonding in the cluster as shown in the table. The observation is, therefore, considered to be consistent with the physico-chemical interpretation based on the central atoms model. The analysis establishes an interesting observation that thermodynamics of the concentrated solutions of several binary

systems, as investigated in the present article, is basically governed by the zeroth order and first order interactions between atoms. However, the dilute solution behaviour of the systems exhibiting limited solubilities of the solutes, such as, S, O, C, N, Si, Ti etc in liquid Fe (Hajra and Divakar 1999; Divakar and Hajra 2001; Hajra *et al* 2003a, b), is generally considered to be much more complex than that of the concentrated solutions of the binary systems. The higher order interactions are expected to play an important role along with the zeroth and first order interactions in interpreting the dilute solution behaviour of the systems consisting of the sparingly soluble solutes (Hajra and Divakar 1999; Divakar and Hajra 2001; Hajra *et al* 2003a, b) in the solvent rich systems.

For the purpose of comparison, the derived values of the properties based on the models have also been shown in

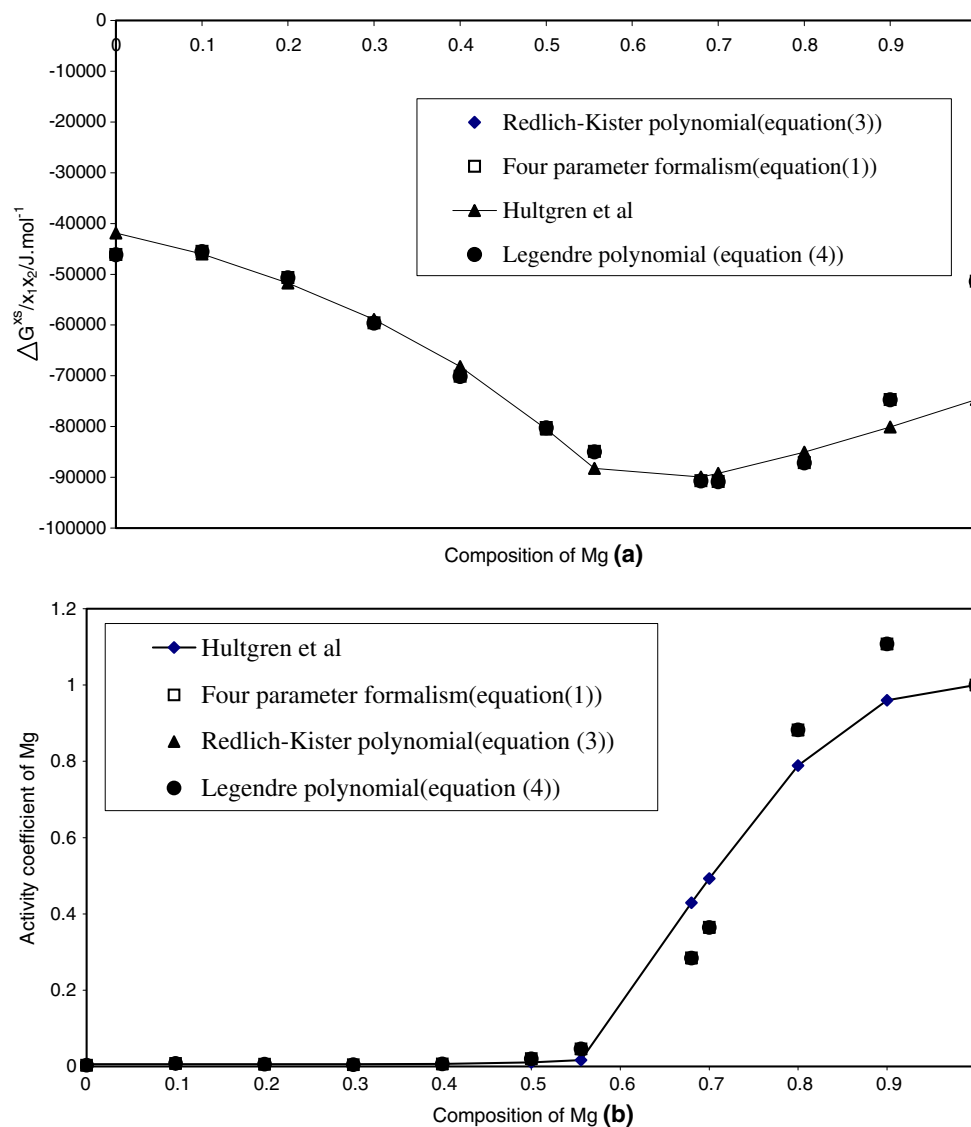


Figure 9. Comparison between calculated and experimental values of (a) integral excess free energy and (b) activity coefficient of Mg in Mg–Bi system at 975 K.

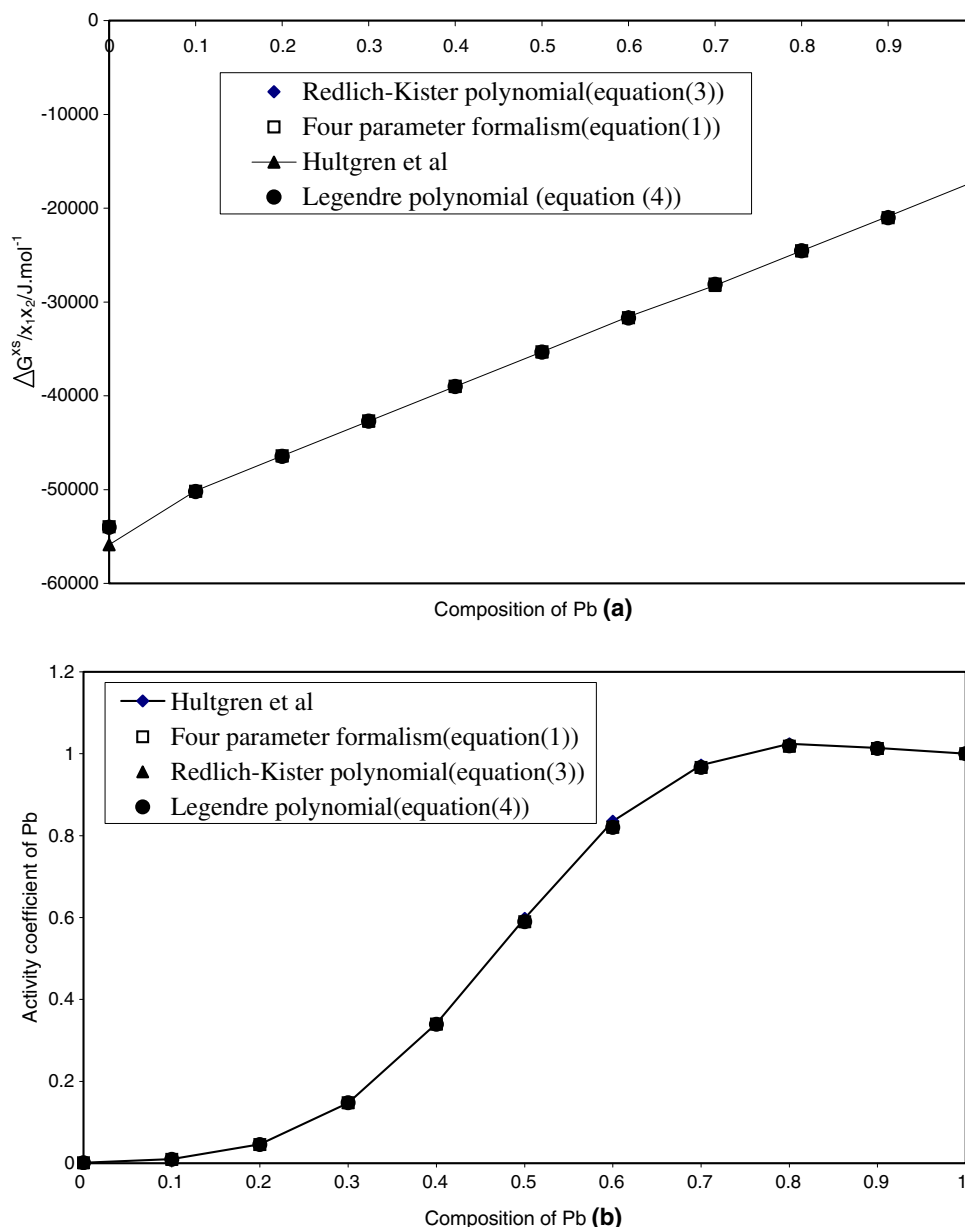


Figure 10. Comparison between calculated and experimental values of (a) integral excess free energy and (b) activity coefficient of Pb in Pb–Mg system at 973 K.

figures 1–10. They give a comprehensive view of capability in interpreting the partial and integral thermodynamic properties of the systems as a function of composition. The derived data based on the formalisms clearly indicate that they match favourably well with each other and those of the experimental data of the systems. Their capability are adequately substantiated by the low computed values of standard deviations in terms of the integral and partial properties of the systems. Although the formalisms are capable of interpreting most of the systems, they, however, are found to exceed the experimental scatter in terms of the partial properties of the Mg–Bi and Mg–In systems. In view of this deviation, it appears that in such

systems higher order compositional terms may be necessary in the formalisms in order to get as close a data fit as possible.

4. Conclusions

The present investigation indicates that the three four-parameter formalisms are equally capable of interpreting the dilute and concentrated solution behaviour of several relatively strongly interacting binary systems. The analysis indicates that the constants involved in the equations essentially consist of the zeroth- and first-order interaction parameters;

the derived values of which are susceptible to the physico-chemical description based on the central atoms model. Perceptible deviation in the standard deviation based on the partial properties has been found in a few systems such as, the Mg–Bi and Mg–In, where additional compositional terms may be inducted for adequate representation of thermodynamic behaviour. In view of the similar behaviour of the three formalisms with respect to the several experimental data of binary systems, the use of one formalism over the other is considered to be dependent on the discretion of the investigator.

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