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Thermodynamic analysis of the quasi-binary section A–Pb in the ternary system Pb–Bi–Mg. Part 2. Predicting the thermodynamic properties of the quasi-binary section A–Pb in the ternary system Pb–Bi–Mg

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Abstract

The *R*-function method for predicting ternary thermodynamic properties from those of its binaries was applied to the quasi-binary section A–Pb in the ternary system Pb–Bi–Mg. The results of the ternary partial thermodynamic properties of Pb, Bi and Mg, calculated by means of the *R*-function method are given in this paper.

INTRODUCTION

There have been many formulas reported for predicting ternary thermodynamic properties from binary parameters, for example those of Kohler and Muggianu (see ref. 1), Colinet (see ref. 2), Toop (see ref. 3), Hillert (see ref. 4) and Chou (see refs. 5–7). In this paper, the *R*-function method proposed by Chou was chosen for its simplicity as compared with the other graphical methods.

According to refs. 5–7, the ternary molar excess free energy ΔG^{E} can be expressed by the equation

$$\Delta G^{E} = x_2 \Delta G^{E}_{12}/(1 - x_1) + x_3 \Delta G^{E}_{23}/(1 - x_2) + x_1 \Delta G^{E}_{31}/(1 - x_3) \quad (1)$$

where $\Delta G^{E}_{12}, \Delta G^{E}_{23}, \Delta G^{E}_{31}$ indicate the binary molar excess free energies for the 1–2, 2–3, 3–1 binary systems, respectively. The geometric representation of the *R*-function method is shown in Fig. 1.

Equation (1) can be rewritten in the following form in terms of an α function

$$\Delta G^{E} = x_1 x_2 \alpha_{12} + x_2 x_3 \alpha_{23} + x_3 x_1 \alpha_{31} \quad (2)$$

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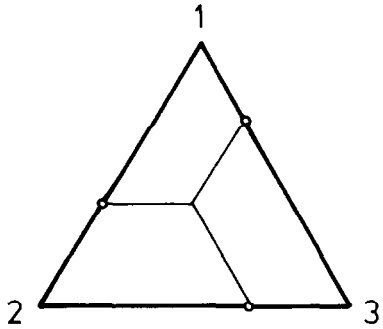

Fig. 1. A geometric representation of the R-function method.

where

$$\alpha_{12} = \Delta G^{E}_{12}/x_1(1-x_1)$$
$$\alpha_{23} = \Delta G^{E}_{23}/(x_2(1-x_2) \quad (3)$$
$$\alpha_{31} = \Delta G^{E}_{31}/x_3(1-x_3)$$

The R-function is defined as

$$R = \Delta G^{E}/(1-x_1)$$
$$= x_1(1-y)\alpha_{12} + (1-x_1)y(1-y)\alpha_{23} + x_1 y\alpha_{31} \quad (4)$$

where

$$y = x_3/(1-x_1) \quad (5)$$

Substituting the α function expressions fitted by a third-degree polynomial

$$\alpha = a_0 + a_1 x + a_2 x^2 + a_3 x^2 \quad (6)$$

into eqn. (4) yields the value of the R-function. The excess partial molar free energies G^{E}_1, G^{E}_2, G^{E}_3 can then be calculated

$$G^{E}_1 = (1-x_1)(\sigma R/\sigma x_1)_y$$
$$G^{E}_2 = [\sigma(R/y)/\sigma(1/y)]_{x_1} - x_1 G^{E}_1/(1-x_1) \quad (7)$$
$$G^{E}_3 = \{\sigma[R/(1-y)]/\sigma[1/(1-y)]\}_{x_1} - x_1 G^{E}_1/(1-x_1)$$

RESULTS AND DISCUSSION

The excess free energies of the three binary systems Pb–Bi, Bi–Mg, Mg–Pb are taken from Hultgren et al. [8]. The plots of the α function of the three binary systems versus mole fraction x at 973 K are shown in Fig. 2. The α function were fitted by a third-degree polynomial and the fitting coefficients are listed in Table 1.

The results of the activities, activity coefficients and other ternary partial thermodynamic properties for Pb, Bi and Mg, calculated by means of the R-function method, are given in Table 2.

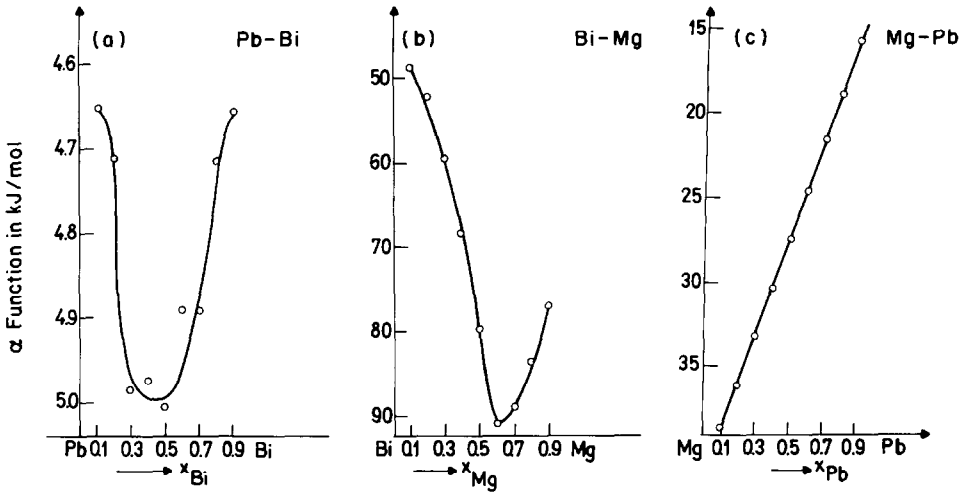

Fig. 2. Plots of the α function vs. mole fraction at 973 K for the systems: (a) Pb–Bi; (b) Bi–Mg; (c) Mg–Pb.

TABLE 1

Polynomial coefficients of the α function for Pb–Bi, Bi–Mg and Mg–Pb binary systems at 973 K (J mol^{-1})

System	a_0	a_1	a_2	a_3
Pb–Bi	−4330	−3278	4838	−1742
Bi–Mg	−50604	58166	−401304	340639
Mb–Pb	−41789	29147	0	0

Activity curves for Pb and Mg in the investigated quasi-binary section A–Pb in the ternary system Pb–Bi–Mg are given in Fig. 3. A comparison of the activity of Pb between the calculated and experimental values obtained by Oelsen calorimetry [9], are shown in the same figure.

The ternary molar excess free energy and ternary molar free energy of mixing versus mole fraction x at 973 K are also presented (Fig. 4).

It can be concluded that the R-function method can be used to calculate the ternary partial thermodynamic properties for all three components in the ternary system. This method is very simple and useful in an analytic calculation, especially in cases where it is quite difficult to obtain these data experimentally. Also, the results obtained by the R-function method are in good agreement, which indicates that the calculated values are consistent with the experimental ones.

TABLE 2

Ternary thermodynamic properties for Pb, Bi and Mg in the investigated quasi-binary section A–Pb in the ternary system Pb–Bi–Mg, calculated by the R-function method

x_{Pb}	a_{Pb}	γ_{Pb}	E^{E}_{Pb}/ (J mol^{-1})	G^{M}_{Pb}/ (J mol^{-1})	x_{Bi}	a_{Bi}	γ_{Bi}	G^{E}_{Bi}/ (J mol^{-1})	G^{M}_{Bi}/ (J mol^{-1})	x_{Mg}	a_{Mg}	γ_{Mg}	G^{E}_{Mg}/ (J mol^{-1})	G^{M}_{Mg}/ (J mol^{-1})	ΔG^{E}/ (J mol^{-1})	ΔG^{M}/ (J mol^{-1})
0.919	0.806	0.877	−1065	−1745	0.009	0.004	0.446	−6525	−44666	0.072	0.014	0.197	−13152	−34532	−1985	−4492
0.787	0.491	0.624	−3816	−5754	0.008	0.002	0.254	−11098	−50273	0.205	0.046	0.224	−12090	24909	−5570	−10036
0.566	0.157	0.278	−10365	−14978	0.013	0.0005	0.037	−26660	−61488	0.421	0.142	0.338	−8779	−15790	−9910	−15925
0.437	0.083	0.240	−11540	−20134	0.022	8.8×10^{-6}	0.0004	−64220	−94168	0.631	0.367	0.581	−4397	−8109	−8192	−14175
0.246	0.027	0.111	−17812	−29219	0.021	1.2×10^{-5}	5.8×10^{-4}	−60301	−91659	0.733	0.523	0.714	−2720	−5243	−7642	−12956
0.188	0.013	0.069	−21610	−35131	0.024	8.7×10^{-6}	3.6×10^{-4}	−64069	−94260	0.788	0.628	0.797	−1840	−3763	−7051	−11832
0.087	0.002	0.023	−30429	−50273	0.028	8.2×10^{-5}	2.9×10^{-3}	−47216	−76113	0.885	0.831	0.939	−507	−1498	−4418	−7831
0.012	1.2×10^{-4}	9.6×10^{-3}	−37599	−73032	0.029	1.7×10^{-5}	5.7×10^{-4}	−60455	−88842	0.959	0.954	0.995	−40	−381	−2242	−3817
0.004	3.5×10^{-5}	8.8×10^{-3}	−38283	−82999	0.031	1.9×10^{-5}	6.2×10^{-4}	−59761	−87942	0.965	0.963	0.998	−13	−305	−2018	−3352
0			–	–	0.030	2×10^{-5}	6.8×10^{-4}	−59052	−87527	0.970	≈1	1	0	0	0	0

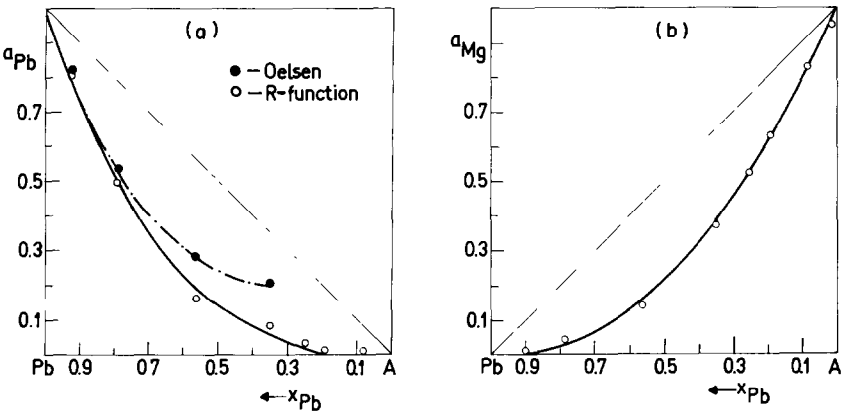

Fig. 3. Activities for Pb and Mg vs. mole fraction at 973 K: (a) Pb; (b) Mg.

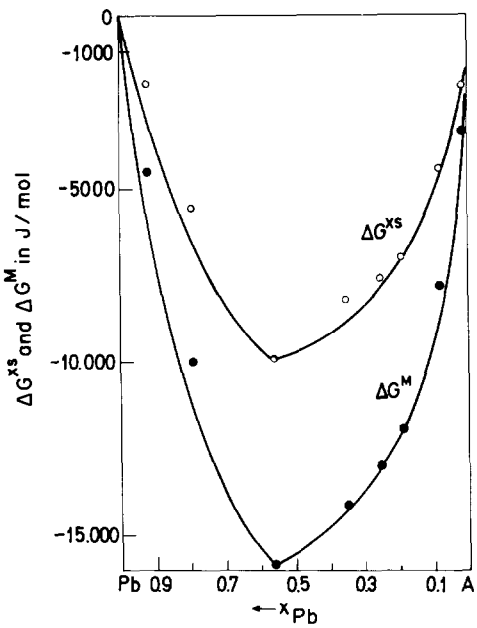

Fig. 4. ΔG^{E} and ΔG^{M} vs. mole fraction at 973 K.

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