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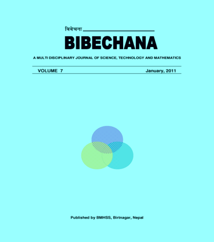

Complex formation in liquid potassium-lead alloy

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Abstract

Regular associated solution model has been used to study the mixing properties of KPb liquid alloy at 848 K. The values of different thermodynamic parameters obtained from this model are compared with corresponding experimental values. Most of the computed values are in good agreement with the observed values.

Keywords: Compound forming alloy; Pairwise interaction energy; Equilibrium constant

1. Introduction

Liquid alloys, which are disordered systems in the sense of having no long-range atomic or magnetic order, display a remarkable variety of local chemical order. The free energy of mixing, heat of mixing and entropy of mixing of several liquid alloys are asymmetric with respect to concentration. The knowledge of thermodynamic and microscopic properties of binary liquid alloys is necessary for the design and development of reliable materials for high temperature application. The purpose of present investigation is to study energetic and structural properties of potassium lead alloy in molten state.

Potassium lead alloy in molten state is strongly compound forming alloy [1]. The phase diagram of KPb [2] lists KPb and KPb_2 intermediate compounds in solid state. The formation of compound in solid state led many theoreticians to believe the existence of strong associations present in the alloy in molten state near melting temperature [4-13].

In this paper, we have calculated the equilibrium concentration of complex assuming KPb_2 complex present in liquid state of KPb alloy at 848 K on the basis of regular associated solution model. We have then used these concentrations to calculate free energy of mixing (ΔG), heat of mixing (ΔH), entropy of mixing (ΔS) and activities of pure species in liquid KPb alloy.

2. Model Basis

Suppose type A (=Pb) and type B (=K) metals are mixed in the melt to form alloy AB (=PbK). According to regular associated solution model, the melt consists of three species namely unassociated A-atoms, unassociated B-atoms and complex AB. Considering a solution of n_1

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atoms of A and n_2 atoms of B, the formation of n_{ApB} complex requires $n_1 = n_A + pn_{ApB}$ and $n_2 = n_B + n_{ApB}$ for conservation of mass in the partially associated solution, where n_A, n_B, and n_{ApB} are concentration of unassociated A-atoms, B- atoms and complex respectively where p is small integer. When there is association, the thermodynamic behaviour of complexes A and B components is governed by their true mole fractions x_A, x_B and x_{ApB} rather than their gross mole fraction x_1 and x_2, where $x_1 = \frac{n_1}{n_1 + n_2}$, $x_2 = \frac{n_2}{n_1 + n_2}$ $x_A = \frac{n_A}{n_A + n_B + n_{ApB}}$,

$$x_B = \frac{n_B}{n_A + n_B + n_{ApB}} \text{ and } x_{ApB} = \frac{n_{ApB}}{n_A + n_B + n_{ApB}} \tag{1}$$

The free energy of mixing in regular associated solution model of given by [14]

$$\Delta G = \frac{1}{(1 + 2x_{A_2B})}[(x_A x_B \omega_{12} + x_A x_{A_2B} \omega_{13} + x_B x_{A_2B} \omega_{23}) + RT\ (x_A \ln x_A + x_B \ln x_B + x_{A_2B} \ln x_{A_2B}) + RT\, x_{A_2B} \ln k] \tag{2}$$

where ω_{12}, ω_{13} and ω_{23} are pairwise interaction energies for the species A, B ; A, A_2B and B, A_2B respectively, k is equilibrium constant, T the temperature and R stands for the universal gas constant. The pairwise interaction energies and equilibrium constant are determined using the methods employed by Lele and Ramchandrarao [14].

Once the expressions for ΔG is obtained, other thermodynamic and microscopic functions follow readily. Heat of mixing and entropy of mixing are related to ΔG through standard thermodynamic relations

$$\Delta H = \Delta G \ - T\left(\frac{\partial \Delta G}{\partial T}\right)_{T,P} \tag{3}$$

$$\Delta S \ = \frac{\Delta H - \Delta G}{T} \tag{4}$$

Following Jordan [15] the activity coefficients γ_A, γ_B and γ_{A_2B} of monomers and complex can be expressed in terms of pairwise interaction energies through

$$RT \ln \gamma_A = x_B^2 \omega_{12} + x_{A_2B}^2 \omega_{13} + x_B x_{A_2B}(\omega_{12} - \omega_{23} + \omega_{13}) \tag{5a}$$

$$RT \ln \gamma_B = x_{A_2B}^2 \omega_{23} + x_A^2 \omega_{12} + x_A x_{A_2B}(\omega_{23} - \omega_{13} + \omega_{12}) \tag{5b}$$

$$RT \ln \gamma_{A_2B} = x_A^2 \omega_{13} + x_B^2 \omega_{23} + x_B x_{A_2B}(\omega_{13} - \omega_{12} + \omega_{23}) \tag{5c}$$

And

$$\ln k = \ln\left(\frac{x_A^2\, x_B}{x_{A_2B}}\right) + \frac{\omega_{12}}{RT}[2x_B(1 - x_B) + x_A] + \frac{\omega_{13}}{RT}[2x_{A_2B}(1 - x_A) - x_A] + \frac{\omega_{23}}{RT}[x_{A_2B}\ (1 - 2x_B) - x_B] \tag{6}$$

3. Results and Discussion

The compositional dependence of various species (figure 1) shows that the maximum association occurs at 60 at. pct. of Pb. At this composition and 848 K, about 52 mol pct. of the liquid alloy is associated.

The equilibrium constant and interaction energies for the alloy PbK in liquid state are found to be

$k = 0.009$, $\omega_{12} = -32523 \text{ J mol}^{-1}$, $\omega_{13} = -14110 \text{ J mol}^{-1}$ and $\omega_{23} = -50596 \text{ J mol}^{-1}$

All the interaction energies are found to be negative and show that left over Pb and K atoms are attracted to each other and to the complex.

Theoretical calculation of free energy of mixing for PbK liquid alloy shows that the minimum value of free energy of mixing for PbK is -18.0 kJmol^{-1} at $x_{Ag} = 0.5$.

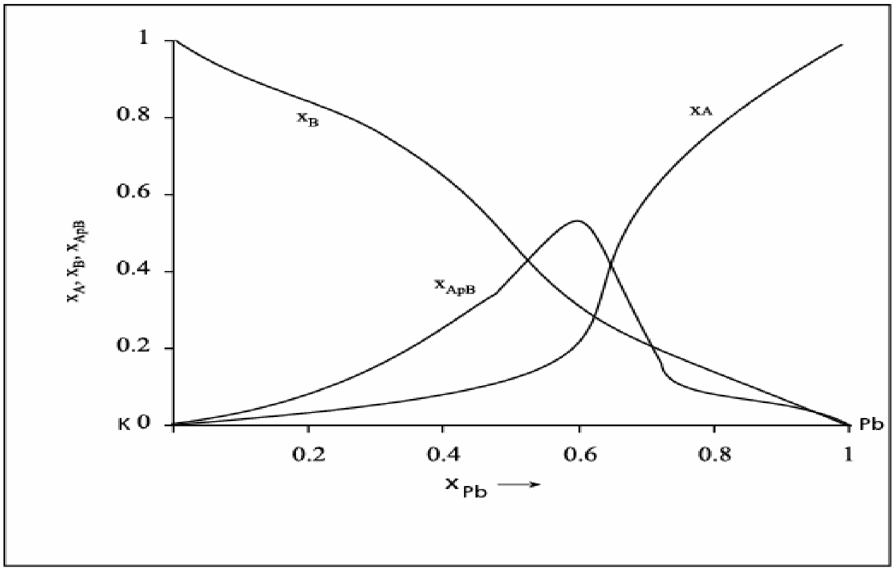

Figure 1 : Compositional dependence of mole fractions x_A (A=Pb), x_B (B=K) and x_{ApB} (AB= Pb_2K) versus x_{Pb} (concentration of Pb in the liquid PbK solution (848K)

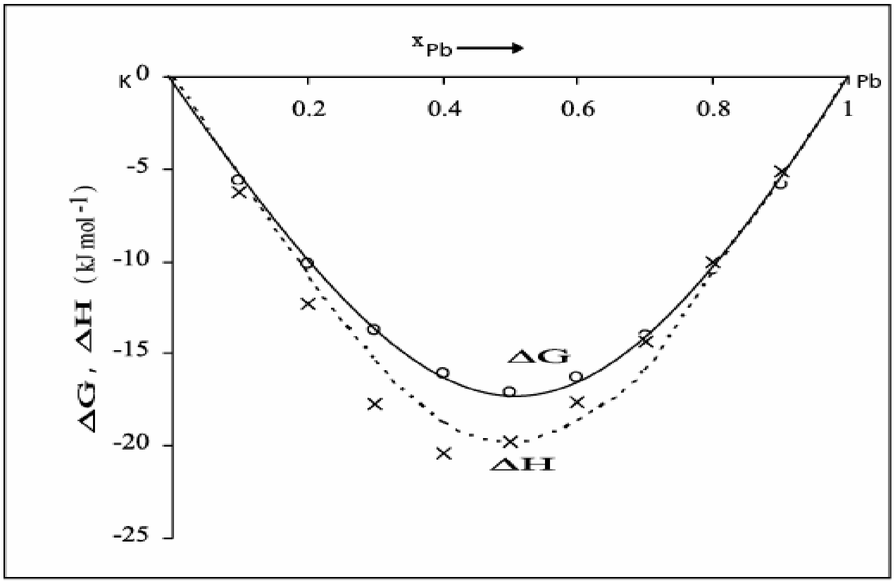

Figure 2 : Free energy of mixing (ΔG) versus x_{Pb} (concentration of Pb) in the liquid PbK solution (848 K); (——) theory, (000) experiment [2] and Heat of mixing (ΔH) versus x_{Pb} (concentration of Pb) in the liquid PbK solution (848 K) (………) theory, (×××) experiment [2].

This minimum value of free energy of mixing of this alloy shows that PbK alloy in molten state is strongly interacting system. The agreement between calculated and observed value of free energy of mixing is good.

It is found from the analysis that the interaction energy parameters are temperature dependent. The best fit values of temperature dependent interaction energy parameters and heat of dissociation are found to be

$$\frac{\partial \omega_{12}}{\partial T} = +20\,\mathrm{Jmol^{-1}K^{-1}}, \frac{\partial \omega_{13}}{\partial T} = +40\,\mathrm{Jmol^{-1}K^{-1}}, \quad \frac{\partial \omega_{23}}{\partial T} = +45\,\mathrm{Jmol^{-1}K^{-1}} \quad \text{and} \quad R\,T^2 \frac{\partial \ln k}{\partial T} = 35500 \pm 1500\ \mathrm{J\ mol^{-1}}$$

It is found from the analysis that the heat of mixing is negative at all concentration which is in agreement with experimental result. There is reasonable agreement between calculated and observed value of heat of mixing of PbK alloy in molten state. Figure 2 shows the comparison between the experimental and calculated values of free energy of mixing and heat of mixing. The calculated value and observed value of entropy of mixing are furnished in figure 3. The calculated values of entropy of mixing do not always match in sign with experimental values. The deviation of calculated value of entropy of mixing is more below the concentration x_{Pb} = 0.6. The discrepancy could be due to errors in enthalpy data or neglect of vibrational and electronic contributions on entropy. The deviations in entropy are, however, not significant enough to influence the agreement between other calculated and observed thermodynamic functions as shown in figure 2.

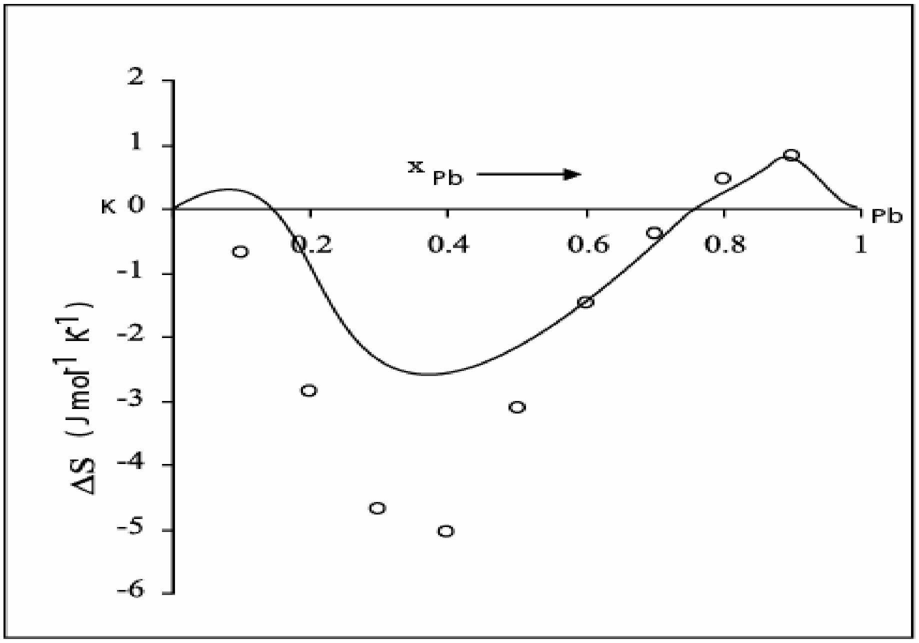

Figure 3 : Entropy of mixing (S_M) versus x_{Pb}(concentration of Pb) in the liquid PbK solution (848K); (——) theory, (000) experiment [2].

The deviations from ideal behaviour of the alloy can be incorporated into activities. The calculated and experimental activities are compared in figure 4. There is a good agreement between the calculated and experimental values.

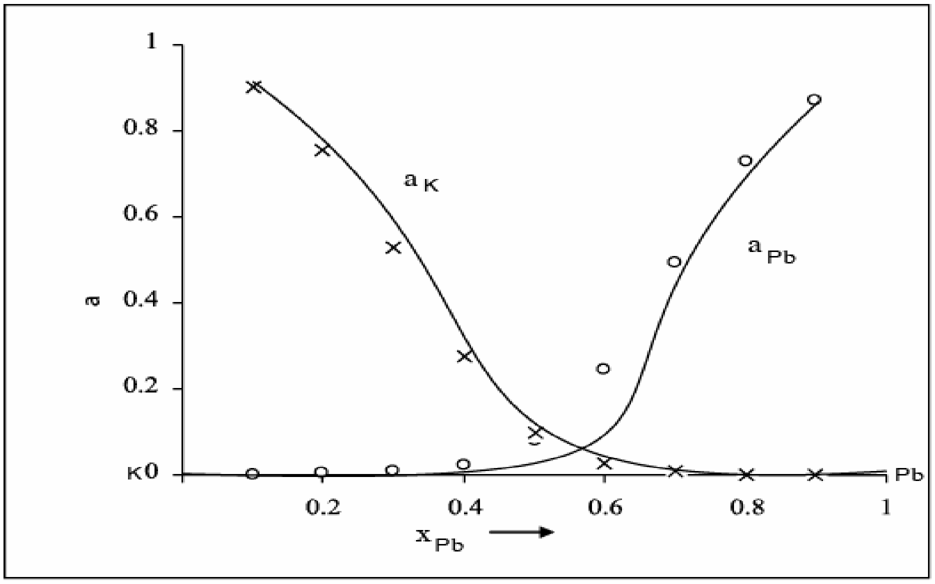

Figure 4: Activity (a) of Pb and K in liquid KPb solution (848 K) versus x_{Mg} ; (——) theory, (○○○) and (xxxx) experiment [2].

4. Conclusion

The analysis based on regular associated solution model shows that the KPb system is strongly interacting heterocoordination system and the pairwise interaction energies of this system depend strongly on temperature. Our theoretical analysis also shows that there exist complexes Pb_2K in PbK alloy in molten state.

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