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ACTIVITY OF THE ALKALI METALS IN THEIR LEAD BASED BINARY LIQUID ALLOYS

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ABSTRACT
Alkali metals are highly reactive. Within a binary alloy they generally form complexes. Due to formation of such complexes the thermodynamic properties of the alloys often show asymmetry around equi-atomic composition. In the present work we have considered two lead based binary alloys of alkali metals e.g. Li-Pb and Na-Pb. The phase diagrams of these alloys reveal that at their liquid state complexes are formed. We have confined our study in computing the activity of lithium and sodium within these molten alloys. Activity is one of the fortunate thermodynamic functions which can be measured directly by experiment. For the purpose of our theoretical study Flory's model has been employed. It is a statistical mechanical model based on the size factor of the constituent species of a binary liquid alloy. For each alloy we have started with the mathematical expression for the free energy of mixing according to this model and found out the interchange energy between the ingredients from the observed values of the former by the method of successive approximations. Using this value of the interchange energy finally the activity of the concerned alkali metal has been computed for different concentrations. Our calculation indicates that the lithium-lead liquid alloys are structurally disordered at lower concentrations of lithium.

Key words: *Binary liquid alloys, Alkali metals, Lead based alloys, Flory's model, Free energy of mixing, Interchange energy, Activity.*

INTRODUCTION

The concentration dependent thermodynamic and electrical properties of binary liquid alloys, especially the complex forming ones, are interesting in many ways. The properties of mixing are not symmetrical about the equi-atomic composition—deviating maximally from those of the ideal alloys [1–4].

In the present work two lead based alloys of alkali metals have been taken into account at molten state *e.g.* lithium-lead liquid alloy and sodium-lead liquid alloy. The liquidus lines of these alloys reveal that the ingredients form complexes. The thermodynamic properties of them show anomaly around equi-atomic composition. We have considered Flory's model [5] for computation of the activity of lithium and lead in their respective alloys.

For each alloy, first of all, the expression for the free energy of mixing (G_M) has been considered. After knowing the ratio of the atomic volumes of the constituent species of an alloy the prime task

becomes the determination of the interchange energy (ω) between them as comes in the said mathematical expression. For this purpose the experimental values of G_M for different concentrations of the ingredients are collected. From these known values ω has been computed by using this expression for G_M. A suitable value of ω is chosen from within the range of values so obtained. Putting this value of ω the free energy of mixing is calculated for several concentrations and then compared with its observed values. Accordingly, a modified value of ω has been considered and the calculations are repeated. In this way by the method of successive approximations we have ascertained the value of the interchange energy. Thereafter, with the help of standard thermodynamic relation activity has been computed.

In Section 2 the working expression according to this model is furnished. Section 3 deals with the results of computation of the activity of the alkali metals within the present liquid alloys. Section 4 provides a brief conclusion.

MATERIALS AND METHOD

FORMULATION

The activity (a) of an element in a binary liquid alloy is given by

$$K_B T \ln a = -zFE,$$

where 'z' is the valency of carrier ions of the element, F the Faraday's constant, K_B the Boltzmann constant, T the absolute temperature and E the electromotive force which is observed directly from the experiment.

In order to obtain the expression for 'a' let us recall the standard thermodynamic relation:

$$RT \ln a = G_M + (1-c)\frac{\partial G_M}{\partial c}, \qquad (1)$$

where R is the universal gas constant, G_M the free energy of mixing and 'c' the concentration of the concerned metal within a binary liquid alloy.

Flory's expression for the free energy of mixing of a binary mixture consisting of Nc mole of species A and N(1– c) mole of species B is given by [5]

$$G_M = RT\,[c \ln c + (1-c)\ln(1-c) + c\ln(1-\upsilon) - \ln(1-\upsilon c)] + \omega c\frac{1-c}{1-\upsilon c}, \qquad (2)$$

where

$$\upsilon = 1 - \frac{V_A}{V_B}, \qquad (3)$$

V_A and V_B being the atomic volumes of species A and B respectively.

Differentiating equation (2) with respect to 'c',

$$\frac{\partial G_M}{\partial c} = RT\left[\ln c - \ln(1-c) + \ln(1-\upsilon) + \frac{\upsilon}{1-\upsilon c}\right] + \omega\left[\frac{1-2c}{1-\upsilon c} + \frac{\upsilon(1-c)c}{(1-\upsilon c)^2}\right]. \qquad (4)$$

Using equations (2) and (4) in equation (1) we get

$$\ln a = \ln\frac{c(1-\upsilon)}{1-\upsilon c} + \frac{\upsilon(1-c)}{1-\upsilon c} + \frac{\omega}{RT}\frac{(1-c)^2}{(1-\upsilon c)^2}. \qquad (5)$$

RESULT AND DISCUSSION

Lithium-Lead Liquid Alloy

For the purpose of equation (3) considering

$$A \equiv Li \quad \text{and} \quad B \equiv Pb,$$

we have [6]

$$\frac{V_A}{V_B} = 0.7167.$$

After finding

$$\upsilon = 0.2833,$$

the value of interchange energy (ω) has been determined on using equation (2) from the observed data [3] of G_M at 932 K. in the concentration range of lithium from 0.1 to 0.9 by the method of successive approximations. We have considered in the present work

$$\frac{\omega}{RT} = -8.7.$$

Equation (5) has been used to compute ln a_{Li} at 932 K. and tabulate in Table–1.

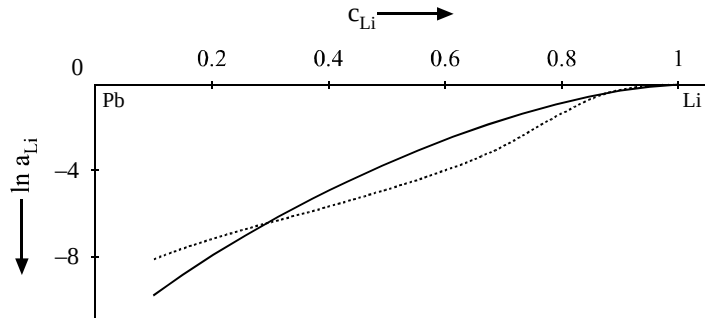
Table–1

ACTIVITY OF LITHIUM Li-Pb liquid alloys at 932 K.

c_{Li}	ln a_{Li}	
	Theoretical	**Experimental***
0.1	–9.8085	–8.1271
0.2	–7.9009	–7.0860
0.3	–6.3232	–6.3859
0.4	–4.9211	–5.6978
0.5	–3.6606	–4.8665
0.6	–2.5416	–3.9899
0.7	–1.5810	–2.9642
0.8	–0.8078	–1.2662
0.9	–0.2628	–0.1926

*Saboungi *et al*, 1978

The theoretical values of the activity of lithium are plotted against c_{Li} in Figure–1 along with the experimental values [3] at 932 K. The computed and observed values are in reasonable agreement. In the concentration range $c_{Li}<0.29$ the computed values of ln a_{Li} are slightly smaller than the observed values but in the concentration range $0.29<c_{Li}<0.88$ the computed values are slightly greater than the experimental ones.



Figure–1: Activity (ln a_{Li}) of lithium in the lithium-lead liquid alloy at 932 K. for different concentrations of Li. The full curve represents the theoretical values. The dotted curve shows the experimental values due to Saboungi *et al* (1978).

Sodium-Lead Liquid Alloy

Considering

$$A \equiv Na \quad \text{and} \quad B \equiv Pb,$$

we get

$$\frac{V_A}{V_B} = 1.3918$$

at 700 K. [2].
Now calculating

$$\upsilon = -0.3918$$

from equation (3), the interchange energy is ascertained on using equation (2) from the observed data [2] of G_M at 700 K. in the concentration range of sodium from 0.1 to 0.9 by successive approximations method. The value of interchange energy used in this case is

$$\frac{\omega}{RT} = -10.$$

The computed values of ln a_{Na} at 700 K. are furnished in Table–2.

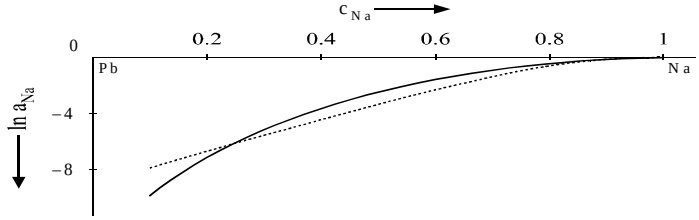
Table–2

ACTIVITY OF SODIUM Na-Pb liquid alloys at 700 K.

c_{Na}	ln a_{Na}	
	Theoretical	**Experimental***
0.1	–9.8505	–7.8753
0.2	–7.1486	–6.6926
0.3	–5.1534	–5.5649
0.4	–3.6215	–4.4228
0.5	–2.4533	–3.3697
0.6	–1.5671	–2.3086
0.7	–0.9150	–1.4188
0.8	–0.4567	–0.5621
0.9	–0.1604	–0.1381

*Hultgren *et al*, 1973

The computed values of ln a_{Na} are plotted in Figure–2 along with its observed values [2] at 700 K. The computed and experimental values of activity are in well agreement. In the concentration range $c_{Na}<0.25$ the computed values of ln a_{Na} are slightly smaller than the observed values but in the concentration range $0.25<c_{Na}<0.88$ the computed values of ln a_{Na} are slightly greater than the observed ones.



Figure–2: Activity (ln a_{Na}) of sodium in the sodium-lead liquid alloy at 700 K. for different concentrations of Na. The full curve represents the theoretical values. The dotted curve shows the experimental values due to Hultgren *et al* (1973).

CONCLUSION

Flory's model has been considered to study the concentration dependence of the activity of the alkali metals in the Li-Pb and Na-Pb liquid alloys. Our theoretical investigation explains the deviation from the ideal values of the activity of lithium and sodium to a great extent for different concentrations of them in these lead based binary alloys in liquid phase. The nature of curves as found experimentally is well corroborated by our theoretical values for different concentrations. However, our computation indicates that the lithium-lead liquid alloys are structurally disordered at lower concentrations of lithium.

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Substance information for UN 1421 - Alkali metal alloys, liquid, n.o.s based on the Hazardous Materials Table (Title 49 CFR 172.101) to assist in preparing a risk assessment for loading, transporting and storing hazardous materials.Â Date of the visual inspection must be stenciled on the tank near the other required markings. Browse special provision B48. N34. Aluminum construction materials are not authorized for any part of a packaging which is normally in contact with the hazardous material. Browse special provision N34. W31. Gibbs-Bogolyubov variational technique is used to study â€˜internal energyâ€™ and â€˜entropyâ€™ of liquid alkali metals as well as â€˜heat of mixingâ€™ and â€˜entropy of mixingâ€™ of their equiatomic alloys. Shaw and Ashcroft forms of model potentials with Vashistha, Singwi and Shaw forms of exchange and correlation functions are used for the calculations of the said properties.Â In course of theoretical treatment the activity of antimony is also computed for different concentrations. Our results indicate that Sb-In alloys are thermodynamically most stable around the equi-atomic composition. Read more. Article.Â It is found that the thermodynamic properties of Na-based liquid binary alloys are sensitive to the forms of the model potential and the local field correction function used in the computation.