FREE ENERGY OF MIXING AND ACTIVITY OF HgK LIQUID ALLOY

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Abstract

The large asymmetry observed in free energy of mixing of HgK liquid alloy is discussed on basis of Flory's model. The concentration dependence of the free energy of mixing and activity of mercury has got special attention in the discussion.

Key words: liquid alloy, Flory's model, Free energy of mixing, activity.

1. Introduction

The free energy of mixing and activity of HgK liquid alloy show large deviation from the ideal values [1,5]. The observed values of free energy of mixing (G_M) are quite asymmetrical around the equi-atomic composition (c=0.5) and they show large minima near 60% of Hg [1].

In the present work, Flory's expression for the free energy of mixing has been used to explain the alloying behaviour of HgK liquid alloys.

Working expressions and the results for free energy of mixing and activity are given in Section 2 and 3 receptively. Conclusion of the work is given in section 4.

2. General Formalism

Flory's expression for the free energy of mixing of a binary mixture consisting of Nc mole of species A(=Hg) and N(1-c) mole of species B(=K) is given by [2].

$$G_M = RT[c\ln c + (1-c)\,\mathrm{In}\,(1-c) + c\ln(1-\beta) - \mathrm{In}(1-\beta c)] + \omega c\frac{1-c}{1-\beta c}, \;.............(i)$$

where

$$\beta = 1 - \frac{V_A{}^0}{V_B}$$

$V_A{}^0$ and $V_B{}^0$ being the atomic volumes of species A and B respectively $\left[V_B{}^0 / V_A{}^0 = 3.3 \text{ at } 600\,\text{K.(Simoji 1977)}\right]$. [4]

Activity is a very important thermodynamic function because it is one of the fortunate functions which are obtained directly from experiment. The activity (a) of an element in a binary liquid is given by

$$K_B T\,\mathrm{Ina} = -ZFE$$

Where

Z = valency of carrier ions of the element

F = Faraday's constant

K_B = Boltzmann constant

E = Electromotive force which is observed directly from the experiment

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

$$RT\ \text{In}\ a = G_M + (1-c)\frac{\partial G_M}{\partial c}. \qquad \text{................(ii)}$$

Differentiating equation (i) partially with respect to 'c'

$$\frac{\partial G_M}{\partial c} = RT\left[\text{In}\ c - \ln(1-c) + \text{In}\,(1-\beta) + \frac{\beta}{\beta c}\right] + \omega\left[\frac{1-2c}{1-\beta c} + \frac{\beta(1-c)c}{(1-\beta c)^2}\right] \qquad \text{...........(iii)}$$

Using equations (i) and (iii) in equation (ii), we get

$$\text{In}\ a = \ln\frac{c(1-\beta)}{1-\beta c} + \frac{\beta(1-c)}{1-\beta c} + \frac{\omega}{RT}\frac{(1-c)^2}{(1-\beta c)^2} \qquad \text{............(iv)}$$

3. Result and Discussion

The value of interchange energy is determined form the observed data of G_M in the concentration range from 0.1 to 0.9 [1]. The value of ω / RT used in the present work is -5.51. The computed values of G_M / RT from equation (i) are furnished in Table -1 and plotted in Fig. – 1 with its observed values at 600 K. as a function of c_{Hg}. The computed and observed values of the free energy of mixing are in well agreement. It may be noted that the free energy of mixing of HgK liquid alloys exhibits asymmetry around equi-atomic composition. Our computed values of G_M do not differ from the experimental values by more than 7.6% at any concentration.

Equation (iv) has been used to compute In a_{Hg}, which is tabulated in Table-2 and plotted in Fig.-2 along with the experimental values of ln a_{Hg} at 600K, [3]. The computed and observed values of activity are in reasonable agreement/ it is observed that the activity of Hg in the HgK liquid alloys remains quite a small value for most of the concentrations i.e. $c_{Hg} \leq 0.7$ and then it rises very fast. There is slightly disagreement between the theoretical and experimental values of ln a_{Hg} for small concentrations of mercury but this disagreement reduces considerably at the Hg-rich end.

4. Conclusion

Flory's, model has been considered to study the concentration dependence of free energy of mixing and activity of HgK liquid alloy. Our theoretical investigation explains the asymmetry in the free energy of mixing to a great extent. The activity has been successfully explained.

References

1. T.E Faber, Introduction to the theory of Liquid Metals, Cambridge University Pres, U.K. (1972).
2. P.J. Flory, J. Chem. Phys. 10, (1942) 51.
3. R. Hultgren, O.D Desai,, D.T. Hawkins, M. Gleiser, and K.K., Kelley, Selected Values of the Thermodynamics Properties of Binary Alloys, A.S.M., U.S.A. (1973).
4. M. Simoji, Liquid Metals, London Acad., U.K. (1977).
5. R.N. Singh, and A.B. Bhatia, J. Phys., F14, (1984) 2309.

TABLES & GRAPHS

Table – 1

Free energy of mixing of HgK liquid at 600 K

c_{Hg}	GM/RT	
	Theoretical	Experimental*
0.1	-0.9053	-0.8181
0.2	-1.6135	-1.4835
0.3	-2.1975	-2.0927
0.4	-2.6573	-2.6491
0.5	-2.9759	-3.0963
0.6	-3.1206	-3.3464
0.7	-3.0368	-3.2809
0.8	-2.6327	-2.7800
0.9	-1.7432	-1.7218

- Hultgen et al, 1973

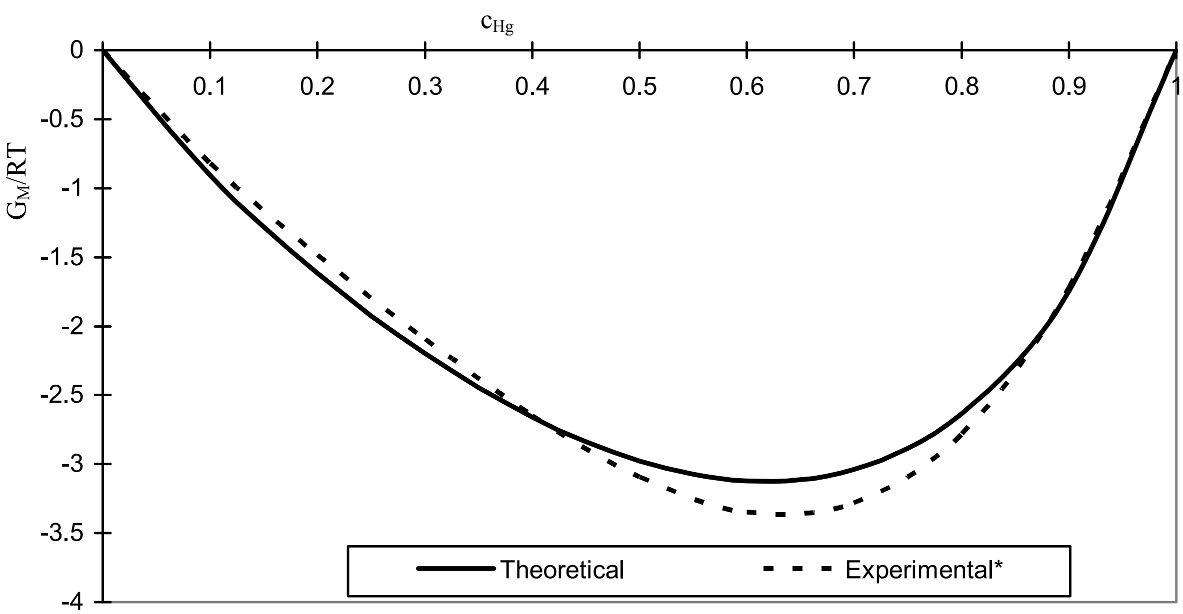

Fig.-1. G_M/RT – c_{Hg} curve for HgK liquid alloy at 600 K

Table – 2

Activity of Hg in liquid alloys at 600 K

c_{Hg}	In a_{Hg}	
	Theoretical	Experimental*
0.1	-7.9069	-6.9078
0.2	-6.7666	-6.9078
0.3	-5.8626	-6.2146
0.4	-5.0171	-5.8091
0.5	-4.1689	-4.9618
0.6	-3.2883	-3.8167
0.7	-2.3639	-2.4889
0.8	-1.4125	-1.2483
0.9	-0.5220	-0.3538

*Hultgren et al, 1973

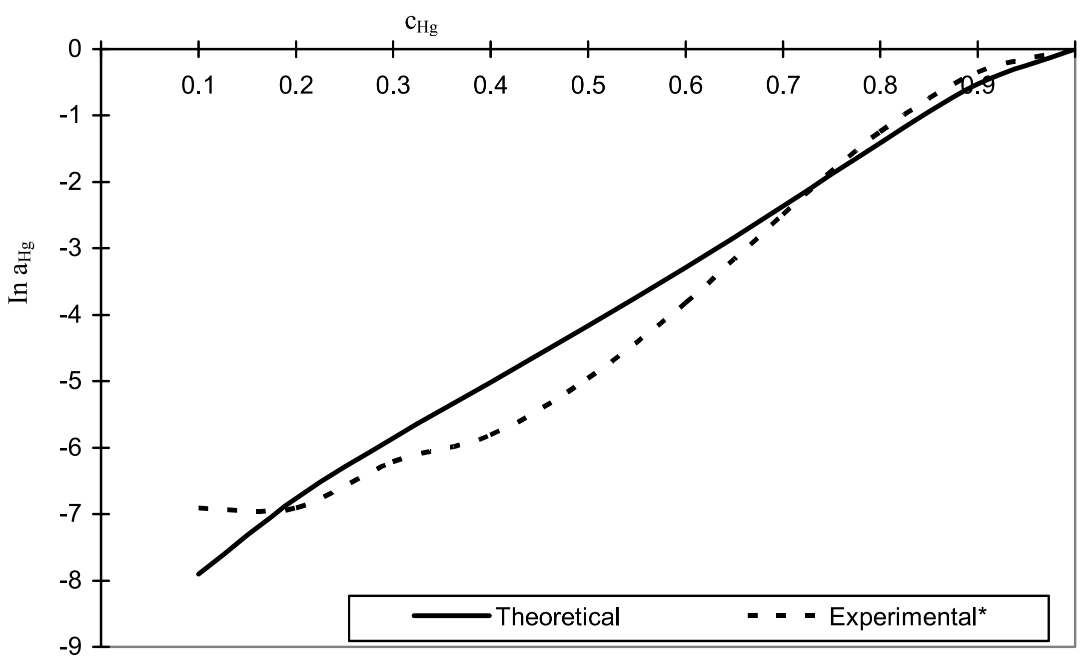

Fig.-2. In a_{Hg}-c_{Hg} curve for liquid alloy at 600 K.