ACTIVITY OF MERCURY IN ITS AMALGAMS AT MOLTEN STAGE

S. K. Chakrabarti*, **B. K. Jha*** and **I. S. Jha***

*Department of Physics, M. M. A. M. Campus, Tribhuvan University, Biratnagar, Nepal.

Abstract: In the present work we have considered two molten amalgams e.g. sodium amalgam and potassium amalgam. Efforts are made to compute the activity of mercury therein by applying Flory's model. This statistical mechanical model is based on the size factor of the ingredients of a binary liquid alloy. In case of each of the amalgams we have started with the expression for the free energy of mixing (G_M) according to this model. After knowing the ratio of the atomic volumes of the constituent species of an amalgam the prime task becomes the determination of the interchange energy (ω) between them. For this purpose the experimental values of G_M for different concentrations of the ingredients of the amalgam are collected. From these known values ω has been computed by using the expression for G_M. A suitable value of ω is chosen from the set 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. The results explain the observed anomaly of the activity of mercury in the present molten amalgams.

Keywords: Binary liquid alloys; Flory's model; Amalgams; Activity of mercury.

INTRODUCTION

Mercury, the only liquid metal at normal temperature, is usually reluctant to mix up homogeneously with other materials due to high cohesive force between its molecules. However, it dissolves many metals at their molten stage in order to form amalgams of them. The thermodynamic properties of these molten amalgams deviate considerably from the ideal values. The alloying behaviour of liquid amalgams can be studied by the help of electronic theory of mixing and also by the statistical mechanical theory of mixing. According to the first theory a liquid amalgam is assumed to consist of a system of ions and electrons. The problem, usually, in this approach is tackled through pseudopotential theory and hard sphere model. The approach cannot be used to obtain information regarding the concentration fluctuations in the long wave-length limit [$S_{cc}(0)$], an important thermodynamic function which determines the stability of alloys. The other theory can be successfully used to obtain the analytical expressions for various thermodynamic functions that are not possible otherwise.

As regards mixing of two metals it is widely known that most metals dissolve in one another readily once they are in liquid phase but the same is not true for the solid alloys. The solubility of a homogeneous solid phase is governed predominantly by the size factor, electrochemical effect and electron concentration. Experiences show that these factors cannot be used effectively to explain the alloying behaviour of liquid alloys to a great deal. Thus liquid alloys generate manifold interests for the experimentalists[1–3] as well as theoreticians[4–8].

In the present work the deviation from the ideal values of the activity of mercury has been considered for the purpose of study in case of two molten amalgams e.g. Hg-Na and Hg-K. Flory's model is used to explain such anomaly. The model is based on the statistical mechanical theory of mixing in which the size factor of the constituent species of the alloy is considered.

Working expressions are summarised in Section 2. Section 3 deals with the results. A brief conclusion is provided in Section 4.

FORMULATION

Activity is one of the fortunate thermodynamic functions which are obtained directly from experiment. 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 :

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

where R is the universal gas constant, G_M the free energy of mixing and 'c' the concentration of the element within the 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[9]

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

where $\upsilon = 1 - $ \qquad\qquad (3)

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

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

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

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

(5)

RESULTS AND DISCUSSION

3.1 Sodium amalgam at molten stage

For the purpose of equation (3) considering $A \equiv Hg$ and $B \equiv Na$ we have $V_B/V_A = 1.698$ at[10] 673 K. After finding υ the value of interchange energy has been determined on using equation (2) from the observed data[1] of G_M in the concentration range of mercury from 0.1 to 0.9 by the method of successive approximations. The value of ω/RT used in the present work is –7.5. Equation (5) has been used to compute ln a_{Hg} at 673 K. and then tabulate in Table 1.

Table 1: Activity of Hg in Hg-Na liquid alloys at 673 K.

*Hultgren *et al*, 1973

ln a_{Hg} is plotted against c_{Hg} in Figure 1 along with its experimental values[1] at 673 K. The computed and observed

values are in well agreement. It is observed that the activity of Hg in the sodium amalgam remains quite small for most of the concentrations i.e. c_{Hg} 0.6 and then it rises very fast in the region $c_{Hg} > 0.7$. Slight disagreement between the theoretical and experimental values of ln a_{Hg} is noticed for concentrations of Hg in between 20% and 50%. This may be due to the formation of complexes within the alloy[1].

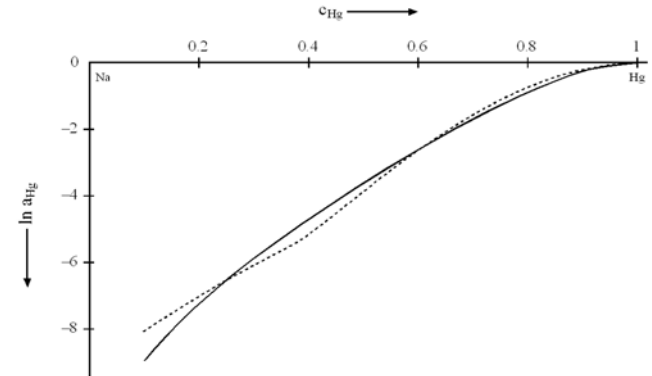**Figure 1.** Activity (ln a_{Hg}) of mercury in the molten sodium amalgam at 673 K. for different concentrations of Hg. The full curve represents the theoretical values. The dotted curve shows the experimental values due to Hultgren *et al* (1973).

3.2 Potassium amalgam at molten stage

Here, considering AHg and BK we have $V_B/V_A = 3.3$ at[10] 600 K. Calculating υ the value of interchange energy is then determined from the observed data[1] of G_M in the concentration range of mercury from 0.1 to 0.9. The value of ω/RT has been found out to be –5.51 by the method of successive approximations. The computed values of ln a_{Hg} at 600 K. are shown in Table 2.

Table 2: Activity of Hg in Hg-K liquid alloys at 600 K.

*Hultgren *et al*, 1973

These computed values of ln a_{Hg} are plotted against the concentrations of mercury in Figure 2 along with the experimental values[1] at 600 K. The computed and observed values of activity are in considerable agreement. It is found that the activity of mercury in the potassium amalgam remains quite a small value for most of the concentrations i.e. $c_{Hg} \leq 0.7$ and then it rises sharply. There is slight disagreement between the theoretical and experimental values of ln a_{Hg} for concentrations of mercury below 60%. This may be due to the formation of complexes within the alloy[1].

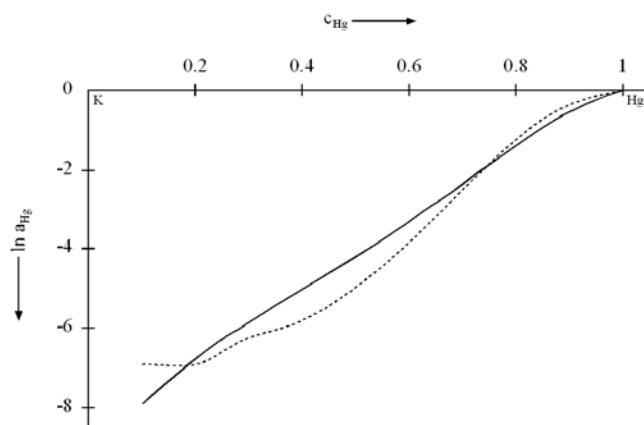**Figure 2.** Activity (ln a$_{Hg}$) of mercury in the molten potassium amalgam at 600 K. for different concentrations of Hg. The full curve represents the theoretical values. The dotted curve shows the experimental values due to Hultgren *et al* (1973).

SUMMARY AND CONCLUSION

Flory's model has been considered to study the concentration dependence of the activity of mercury in the Hg-Na and Hg-K liquid alloys. Our theoretical investigation explains the deviation from the ideal values of the activity of Hg in these molten amalgams to a great extent. The nature of curves as found experimentally is well corroborated by our theoretical values for different concentrations.

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