ENTROPY OF MIXING OF TWO COMPLEXES OF Cu-Sn AND Cd-Mg FORMING BINARY LIQUID ALLOYS

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Abstract : In the present work two binary molten alloys are considered *e.g.* Cu-Sn and Cd-Mg in which complexes are formed as revealed from their liquidus lines. There are a large number of binary liquid alloys which exhibit interesting behaviour as a function of concentration as regards the thermodynamic properties. The former alloy shows anomaly in its thermodynamic properties of mixing. On the other hand, the alloying behaviour of the latter one is symmetric around the equi-atomic composition. But so far as entropy of mixing (S_M) is concerned copper-tin liquid alloy also shows symmetry about equi-atomic composition. Here the quasi-lattice chemical model has been used for computation of the values of SM of these alloys for different concentrations of the ingredients. For each alloy calculations are started with the expression for excess free energy of mixing (G_M^{xs}) according to this model and the values of different interaction parameters (ω_{ij}) are primarily found out from the experimental data of for several concentrations of the constituent species. Putting these values of ω_{ij} the free energy of mixing (G_M) is calculated for various concentrations and then compared with its observed values both numerically and graphically. Accordingly, a modified set of values of ω_{ij} has been considered and the calculations are repeated. In this way by the method of successive approximation the values of the interaction parameters have been ascertained and thereby the set of values of G_M. Similarly, the expression for heat of mixing (H_M) is taken into account and the temperature derivatives of the said interaction parameters are ascertained from the observed values of H_M for different concentrations by such successive approximation method. Finally, S_M has been computed on using the standard thermodynamic relation from the sets of values of G_M and H_M thus obtained. The results explain the observed symmetry in the entropy of mixing of the present alloys.

Index Terms **- Entropy of mixing, Binary liquid alloys, Quasi-lattice chemical model.**

I. INTRODUCTION

It is well known that most of the metals dissolve in one another readily when 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 say that these factors cannot be used effectively to explain the alloying behaviour of liquid alloys in details. So, liquid alloys generate manifold interest for both the experimentalists (Hultgren *et al* 1973, Saboungi *et al* 1978, Lamparter *et al* 1984, Harada *et al* 1988) and the theoreticians (Flory 1942, Harrison 1966, Hoshino and Young 1981, Kanth and Chakrabarti 2009). A good understanding of the properties of liquid alloys is really a matter of interest because most of the binary solid alloys are formed by cooling from the liquid state.

A large number of binary liquid alloys, especially the complex forming ones, show anomaly in their thermodynamic and electrical properties. The properties of mixing are not generally symmetrical about the equi-atomic composition—deviating maximally from those of the ideal alloys. Some of these alloys also depict metal-nonmetal transition across a narrow band of concentrations. The liquidus lines are usually S-shaped and the heat of mixing and excess free energy of mixing are large negative quantities at one or other concentrations (Shimoji 1977). The anomalous behaviour of these liquid alloys is least understood and demands extensive theoretical investigation.

In the present work two weak interacting systems are dealt—Cu-Sn and Cd-Mg alloys. The liquidus lines of these alloys reveal that the constituent species form complexes. So, the quasi-lattice chemical model (Bhatia and Singh 1982) has been considered for computation of their entropy of mixing. It is a statistical mechanical model in which grand partition function is used with the assumption that the energy of a given nearest neighbour bond is different if it belongs to the complex than if it does not.

In Section 2 the general theory of quasi-lattice chemical model is briefly narrated and working expressions are furnished. Section 3 deals with the results of computation of the entropy of mixing of these complex forming binary liquid alloys. Section 4 provides a brief conclusion.

II. BASIC FORMALISM

The quasi-lattice chemical model for the binary liquid alloys, in essence, assumes the existence of chemical complexes $A_\mu B_\nu$, where μ & ν are small integers and A & B the constituent species of the alloy :

$$\mu A + \nu B \rightleftharpoons A_\mu B_\nu$$

According to this model, the expression for excess free energy of mixing :

$$G_M^{xs} = N\left[c(1-c)\omega + \Phi_{AB}\Delta\omega_{AB} + \Phi_{AA}\Delta\omega_{AA} + \Phi_{BB}\Delta\omega_{BB}\right] \quad \text{..... (1)}$$

where N is the total number of atoms of A and B in the alloy, 'c' the concentration of A-atoms, ω's the ordering energies and Φ's some constants given by

$$K_B T\Phi_{\mu,\nu} = \Delta\omega_{AB}\left[2\beta(\mu+1,\nu)-2\beta(\mu,\nu+1)+\beta(2\mu-1,2\nu)-\beta(2\mu-2\nu-1)\right]+$$
$$\Delta\omega_{AA}\left[\beta(2\mu-2,2\nu+1)-2\beta(\mu,\nu+1)\right]+\Delta\omega_{BB}\left[2\beta(\mu+1,\nu)-\beta(2\mu+1,2\nu-2)\right] \quad \text{..... (2)}$$

K_B being the Boltzmann constant and T the absolute temperature.

Hence, the free energy of mixing of a complex forming binary liquid alloy,

$$G_M = G_M^{xs} + RT\left[c\ln c+(1-c)\ln(1-c)\right] \quad \text{..... (3)}$$

where R is the universal gas constant.

The heat of mixing is given by

$$H_M = N\left[\Phi\left(\omega - T\frac{d\omega}{dT}\right)+\Phi_{AB}\left\{\Delta\Phi_{AB}-T\frac{t}{dT}(\Delta\omega_{AB})\right\}\right.$$
$$\left.\Phi_{AA}\left\{\Delta\Phi_{AA}-T\frac{d}{dT}(\Delta\omega_{AA})\right\}+\Phi_{BB}\left\{\Delta\Phi_{BB}-T\frac{d}{dT}(\Delta\omega_{BB})\right\}\right] \quad \text{..... (4)}$$

where $\Phi(c)=c(1-c)$.

Now, the entropy of mixing can be found out by using (iii) and (iv) :

$$S_M = \frac{H_M - G_M}{T} \quad \text{..... (5)}$$

III. Results and Discussion

Copper-tin liquid alloy

In this case the phase diagram reveals that the complex Cu_4Sn is most likely to be formed within the liquid alloy. So, for this alloy

A ≡ Cu, B ≡ Sn, μ = 4, ν = 1.

Finding the values of the β-functions in (ii), (i) becomes

$$G_M^{xs} = N\left[\omega c(1-c)+\Delta\Phi_{AB}\left(\frac{27}{140}c+\frac{1}{2}c^4-\frac{4}{5}c^5\frac{1}{6}c^6+\frac{2}{7}c^7-\frac{1}{8}c^8\right)\right.$$
$$\left.\Delta\Phi_{AA}\left(-\frac{79}{840}c+\frac{1}{2}c^4-\frac{2}{5}c^5\frac{1}{6}c^6+\frac{2}{7}c^7-\frac{1}{8}c^8\right)\right]$$

[∵ coeff $(\Delta\omega_{BB}) = 0$ for ν<2]

The value of the above interaction parameters has been determined from the experimental values of free energy of mixing at 1400 K. in the concentration range of copper from 0.1 to 0.9 (Hultgren *et al* 1973) by the method of successive approximation :

$$\frac{\omega}{K_B T} = 0.1 \qquad \frac{\Delta\Phi_{AA}}{K_B T} = -4.2 \qquad \Delta\Phi_{AA} \approx 0$$

The observed values of heat of mixing at 1400 K. in the concentration range of copper from 0.1 to 0.9 (Hultgren *et al* 1973) are used to find out the temperature derivative of interaction parameters in (iv) by successive approximation method :

$$\frac{1}{K_B}\frac{d\omega}{dT} = 9.2, \qquad \frac{1}{K_B}\frac{d}{dT}(\Delta\Phi_{AB}) = -4.5 \qquad \frac{d}{dT}(\Delta\Phi_{AA}) \approx 0$$

$$\frac{d}{dT}(\Delta\Phi_{BB}) \approx 0$$

Finally, the entropy of mixing of Cu-Sn liquid alloys has been computed at 1400 K. as a function of concentration from (v) on taking the corresponding values of free energy of mixing and heat of mixing. The computed values of the entropy of mixing of copper-tin liquid alloys are furnished in Table–1 along with its observed values at 1400 K. in the concentration range of copper from 0.1 to 0.9 (Hultgren *et al* 1973).

Table–1
Entropy of mixing

of Cu-Sn liquid alloys at 1400 K.

c_{Cu}	SM/R	
	Theoretical	Experimental*
0.1	0.4161	0.4480
0.2	0.7956	0.6990
0.3	1.0516	0.8570
0.4	1.1678	0.9420
0.5	1.1457	0.9660
0.6	1.0017	0.9280
0.7	0.7668	0.8110
0.8	0.4815	0.6660
0.9	0.1947	0.4500

*Hultgren *et al*, 1973

The plots of S_M/R versus c_{Cu} are depicted in Fig.–1 for both the theoretical and experimental values, which show good agreement. The theoretical value of S_M is maximum at c_{Cu}=0.45 while experimentally it is found to be maximum at c_{Cu}=0.5.

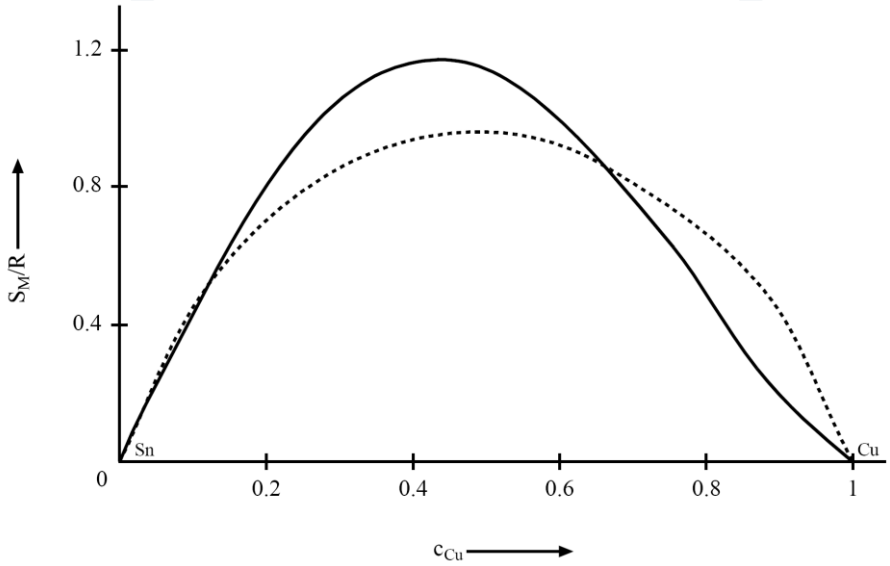

Fig.–1. Entropy of mixing (S_M/R) of Cu-Sn liquid alloys at 1400 K. for different concentrations of copper. The full curve represents the theoretical values. The dotted curve shows the experimental values due to Hultgren *et al* (1973).

Cadmium-magnesium liquid alloy

The phase diagram of Cd-Mg alloy suggests that the complex Cd_3Mg is formed within the alloy (Hultgren *et al* 1973). So, for the cadmium-magnesium liquid alloy

A ≡ Cd, B ≡ Mg, μ = 3, ν = 1.

Finding the values of the β-functions in (ii), we have from (i)

$$G_M^{xs} = N\left[\omega c(1-c) + \Delta\omega_{AB}\left(\frac{1}{5}c + \frac{2}{3}c^3 - c^4 - \frac{1}{5}c^5 + \frac{1}{3}c^6\right) + .\right.$$
$$\left.\Delta\omega_{AA}\left(-\frac{2}{20}c + \frac{2}{3}c^3 - \frac{3}{4}c^4 + \frac{2}{5}c^5 - \frac{1}{6}c^6\right)\right]$$

Like before the value of interaction parameters is determined from the observed values of free energy of mixing at 923 K. (Hultgren *et al* 1973) in the concentration range of cadmium from 0.1 to 0.9 by successive approximation method :

$$\frac{\omega}{K_B T} = -2.21 \qquad \frac{\Delta\omega_{AB}}{K_B T} = -0.35 \qquad \Delta\omega_{AA} \approx 0$$

The experimental values of heat of mixing at 923 K. (Hultgren *et al* 1973) in the concentration range of cadmium from 0.1 to 0.9 have been used, as in the case of Cu-Sn alloy, to find out the temperature derivative of interaction parameters in (iv) by the method of successive approximation :

$$\frac{1}{K_B}\frac{d\omega}{dT} = -4.2 \qquad \frac{1}{K_B}\frac{d}{dT}(\Delta\omega_{AB}) = -2.3 \qquad \frac{d}{dT}(\Delta\omega_{AA}) \approx 0$$

$$\frac{d}{dT}(\Delta\omega_{BB}) \approx 0$$

The computed values of the entropy of mixing, by using (v), of Cd-Mg liquid alloys at 923 K. are furnished in Table–2 along with its observed values in the concentration range of cadmium from 0.1 to 0.9 (Hultgren *et al* 1973).

Table–2
Entropy of mixing
of Cd-Mg liquid alloys at 923 K.

c_{Cd}	S_M/R	
	Theoretical	Experimental*
0.1	0.1001	0.2559
0.2	0.2718	0.4000
0.3	0.4312	0.4972
0.4	0.5564	0.5510
0.5	0.6323	0.5666
0.6	0.6441	0.5515
0.7	0.5796	0.5048
0.8	0.4326	0.4193
0.9	0.2114	0.2795

*Hultgren *et al*, 1973

The plots of S_M/R versus c_{Cd} at 923 K. are shown in Fig.–2 for both the computed and observed values. They are in fine agreement. SM is maximum at c_{Cd}=0.58 theoretically whereas experimentally the same is at c_{Cd}=0.5.

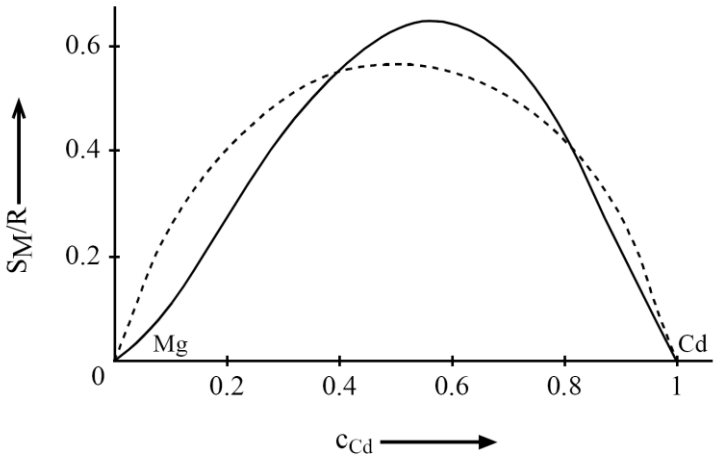

Fig.–2. Entropy of mixing (S_M/R) of Cd-Mg liquid alloys at 923 K. for different concentrations of cadmium. The full curve represents the theoretical values. The dotted curve shows the experimental values due to Hultgren *et al* (1973).

IV. SUMMARY AND CONCLUSION

Quasi-lattice chemical model has been applied to study the symmetry in the entropy of mixing (S_M) of Cu-Sn and Cd-Mg molten alloys. The symmetric nature of the entropy of mixing of copper-tin liquid alloys is well explained by the present theoretical model. The symmetry in S_M around equi-atomic composition in case of cadmium-magnesium molten alloys is also explained nicely by this model. The nature of curves as found experimentally is corroborated to a great extent by the computed values of entropy of mixing of these complex forming binary liquid alloys for different concentrations of the ingredients.

REFERENCES

[1] Bhatia, A. B. and Singh, R. N., *'Thermodynamic Properties of Compound Forming Molten Alloys in a Weak Interaction Approximation'* : Phys. Chem. Liq., **11** (1982) 343

[2] Flory, P. J., *'Thermodynamics of High Polymer Solutions'* : J. Chem. Phys., **10** (1942) 51

[3] Harada, S., Takahashi, S., Takeda, S., Tamaki, S., Grey, P. and Cusack, N. E., *'Thermodynamic Properties of Liquid Na-Cd and Na-In'* : J. Phys., **F18** (1988) 2559

[4] Harrison, W. A., *Pseudopotential in the Theory of Metals* (1966) Benjamin, New York Hoshino, K. and Young, W. H., *'On the Entropy of Mixing of the Liquid Na-Pb Alloy'* : J. Phys., **F11** (1981) L7

[5] Hultgren, R., Desai, P. D., Hawkins, D. T., Gleiser, M. and Kelley, K. K., *Selected Values of the Thermodynamic Properties of Binary Alloys* (1973) A. S. M., Ohio Kanth, B. K. and Chakrabarti, S. K., *'Heat of Mixing of Some Binary Liquid Alloys'* : Sc. World, **7** (2009) 96

[6] Lamparter, P., Martin, W., Steeb, S. and Freyland, W., *'Local Order in Liquid Potassium-Antimony Alloys Studied by Neutron Diffraction'* : J. Non-Cryst. Solids, **61-62** (1984) 279

[7] Saboungi, M. L., Marr, J. and Blander, M., *'Thermodynamic Properties of a Quasi-ionic Alloy from Electromotive Force Measurements : the Li-Pb System'* : J. Chem. Phys., **68** (1978) 1375

[8] Shimoji, M., *Liquid Metals* (1977) London Acad., London