

REGULAR ASSOCIATED SOLUTION MODEL FOR THE ESTIMATION OF FREE ENERGY OF MIXING OF BINARY LIQUID ALLOYS

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Abstract: We have found the equilibrium constants and pairwise interaction energies between the species and the complexes of liquid CuSn, AgAl, FeSi, CdNa and HgNa alloys on the basis of regular associated solution model. These parameters are then used to estimate the free energies of mixing of each alloy. The observed asymmetry in the free energy of mixing of each alloy with respect to concentration is well explained.

Key Words: Free energy of mixing; Asymmetry; Binary alloys; Interaction energy.

1. INTRODUCTION

To solve the difficulties and complexities of obtaining thermodynamic parameters, researchers have suggested many models to correlate thermodynamic parameters and concentrations. One of the models successfully used for accounts of the thermodynamic characteristics of binary liquid alloy systems, is the model of regular associated solution model. In regular associated solution model, it is assumed that strong associations among the constituent species exist in the liquid phase close to the melting temperature. These associations are given different names such as 'complexes', 'pseudomolecules', 'clusters', 'associations' etc. This assumption has been used by several researchers^{1,12} to explain the asymmetry of the properties of mixing for binary alloys. Thus binary alloys in a liquid phase can be considered as a ternary mixture of unassociated atoms of components and complexes, all in chemical equilibrium. Jordan³ proposed that activity of unassociated atoms and the complexes can be estimated by treating the mixture as a ternary system and termed this mixture as regular associated solution. Jordan³ applied this idea in the congruently melting semiconductors Zn-Te and Cd-Te and determined thermodynamic equations for liquidus curve (the melting temperature against concentration curve) of these alloys. This model is further extended and applied by other researchers^{4,5,12} for the determination of thermodynamics and microscopic parameters of different alloy systems in molten state. In present paper, we intend to apply regular associated solution model to obtain the free energy of mixing of liquid CuSn, AgAl, FeSi, CdNa and HgNa alloys. For this, we have

assumed Cu₃Sn, Ag₃Al, Fe₂Si, Cd₂Na and Hg₄Na complexes in liquid CuSn, AgAl, FeSi, CdNa and HgNa alloys respectively by studying their corresponding phase diagram in solid state¹³.

Theoretical formalism is given in section 2, section 3 deals with the numerical result and discussion. Conclusion is provided in section 4.

2. THEORY: MODEL BASIS

Suppose there be three species in equilibrium in the liquid alloy, namely, monomers A, B and A_pB molecules in the respective concentrations n_A, n_B, and n_{ApB} moles.

Considering a solution of n₁ atoms of A and n₂ atoms of B,

the formation of n_{ApB} complex requires n₁ = n_A + pn_{ApB} and n₂ = n_B + n_{ApB} for conservation of mass in the partially associated solution. 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 x₁ and x₂, where

$$x_1 = n_1 / (n_1 + n_2) \text{ etc. and } x_A = n_A / (n_A + n_B + n_{ApB}) \text{ etc.}$$

Using above relations, the two sets of mole fractions are related to each other by the relations

$$x_A = x_1 - px_2 x_{ApB}, \quad x_B = x_2 - (1 - px_2) x_{ApB} \quad (1)$$

In regular associated solution solutions, the gross chemical

potentials of components 1 and 2 are equal to the chemical potentials of the monomeric species A and B¹⁴. The activity coefficients γ_A , γ_B and γ_{ApB} of monomers and complex can be expressed in terms of pairwise interaction energies through³

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

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

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

where ω_{12} , ω_{13} and ω_{23} are interaction energies for the species A, B; A, A_pB and B, A_pB respectively, T the temperature and R stands for the universal gas constant. The equilibrium constant in a regular associated can be obtained⁶ as

$$\ln k = \ln \left(\frac{x_A^p x_B}{x_{ApB}} \right) + \frac{\omega_{12}}{RT} [px_B(1-x_B) + x_A] + \frac{\omega_{13}}{RT} [px_{ApB}(1-x_A) - x_A] + \frac{\omega_{23}}{RT} [x_{ApB}(1-px_B) - x_B] \quad (3)$$

Now using the equations listed above the integral excess free energy ΔG^{xs} is given by

$$\Delta G^{xs} = \frac{1}{(1+px_{ApB})} (x_A x_B \omega_{12} + x_A x_{ApB} \omega_{13} + x_B x_{ApB} \omega_{23}) + \frac{RT}{(1+px_{ApB})} \times (x_A \ln x_A + x_B \ln x_B + x_{ApB} \ln x_{ApB}) - RT(x_1 \ln x_1 + x_2 \ln x_2) + \frac{x_{ApB}}{(1+px_{ApB})} RT \ln k \quad (4)$$

Once the expressions for ΔG [= $\Delta G^{xs} + RT(x_1 \ln x_1 + x_2 \ln x_2)$] is obtained, other thermodynamic and microscopic functions follow readily.

The pairwise interaction energies and equilibrium constant are determined by the following method:

In a regular associated solution $x_1 \gamma_1 = x_A \gamma_A$ and $x_2 \gamma_2 = x_B \gamma_B$, where γ_1 and γ_2 are respective gross activity coefficients of components 1 and 2. Thus

$$\ln \gamma_1 = \ln \gamma_A + \ln \frac{x_A}{x_1} \quad (5a)$$

$$\text{and } \ln \gamma_2 = \ln \gamma_B + \ln \frac{x_B}{x_2} \quad (5b)$$

the pairwise interaction energies, the equilibrium constants and the activity coefficients at infinite dilution can be written as⁹

$$\ln \gamma_1^0 = \frac{\omega_{12}}{RT} \quad (6a)$$

$$k \exp(\omega_{13} / RT) = \frac{\gamma_1^0 \gamma_2^0}{\gamma_1^0 - \gamma_2^0} \quad (6b)$$

where γ_1^0 and γ_2^0 are activity coefficients of component A and that of B at zero concentrations.

Solving equations (2a) and (2b) we obtain

$$\frac{\omega_{13}}{RT} = \frac{x_B \ln \left(\frac{a_2}{x_B} \right) + (1-x_B) \ln \left(\frac{a_1}{x_A} \right) - x_B(1-x_B) \frac{\omega_{12}}{RT}}{x_{ApB}^2} \quad (7)$$

$$\frac{\omega_{23}}{RT} = \frac{x_A \ln \left(\frac{a_1}{x_A} \right) + (1-x_A) \ln \left(\frac{a_2}{x_B} \right) - x_A(1-x_A) \frac{\omega_{12}}{RT}}{x_{ApB}^2} \quad (8)$$

Using equations (6), (16) and (17), we can derive

$$\ln k + \frac{\omega_{13}}{RT} = \left(\frac{1+x_A}{x_{ApB}} \right) \ln \left(\frac{a_1}{x_A} \right) + \frac{x_B}{x_{ApB}} \left[\ln \left(\frac{a_2}{x_B} \right) - \frac{\omega_{12}}{RT} \right] + \ln \left(\frac{a_1^p a_2}{x_{ApB}} \right) \quad (9)$$

3. RESULTS AND DISCUSSION

To find free energy of mixing of binary alloys, we have found the complex concentration in a regular associated solution of respective alloys by using equations (6), (9) and observed data of corresponding activities¹³. The complex concentration of liquid alloys in molten state are presented in table 1. We have found the equilibrium constants and the pairwise interaction energies between the species and the complexes using equations (3), (4), (6), (7), (8), and observed data of corresponding integral excess free energies of mixing. The equilibrium constants and pairwise interaction energies of different binary alloys are listed in table 2.

3.1 Liquid CuSn alloys at 1400K

All the pairwise interaction energies in liquid CuSn alloys at 1400K are found to be negative. This clearly indicates that Cu and Sn atoms are attracted to each other and to the complex.

Theoretical calculation of free energy of mixing for CuSn liquid alloy shows that CuSn alloy in liquid state is not as strongly interacting system as other Sn-based alloys¹³. Our theoretical investigations explain the asymmetry observed in the free energy of mixing of CuSn alloys in liquid state. The calculated value of free energy of mixing of CuSn alloy at 1400K is found to be -1.182 RT at $x_{Cu} = 0.6$ which exactly matches with the experimental value. Figure 1 shows an excellent agreement between the experimental and calculated free energies of mixing.

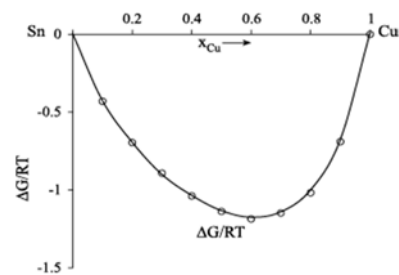


Figure-1: Free energy of mixing ($\Delta G/RT$) versus x_{Cu} of liquid CuSn solution (1400K); (—) theory, (ooo) experimental¹

3.2 Liquid AgAl alloys at 1273K

All the interaction energies in liquid AgAl alloys at 1273K are found to be negative. This means Ag and Al atoms are attracted to each other and to the complex.

Theoretical calculation of free energy of mixing for AgAl liquid alloy shows that the minimum value of free energy of mixing for AgAl is about $-1.22RT$ where as it is $-3.35RT$ for HgK and $-3.13RT$ for HgNa¹³. This suggests that AgAl alloy in liquid state is not as strongly interacting system as liquid amalgams. Our theoretical investigations explain the asymmetry observed in the free energy of mixing of AgAl alloys in liquid state. Figure 2 shows that the agreement between the experimental and calculated free energies is very good.

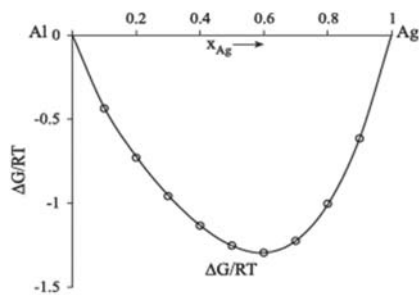


Figure-2: Free energy of mixing ($\Delta G/RT$) versus x_{Ag} of liquid AgAl solution (1273K); (—) theory, (ooo) experiment [1]

3.3 Liquid FeSi alloys at 1873K

All the interaction energies in liquid FeSi alloys at 1873K are found to be large negative value. This shows that Fe and Si atoms are attracted to each other and to the complex.

Theoretical calculation of free energy of mixing for FeSi liquid alloy shows that FeSi alloy in liquid state is strongly interacting system. The free energy of mixing is minimum ($= -2.29RT$) at $x_{Fe} = 0.6$. Figure 3 shows excellent agreement between calculated and experimental free energy of mixing and explains the observed asymmetry in the free energy of mixing of FeSi alloy in molten state at 1873K.

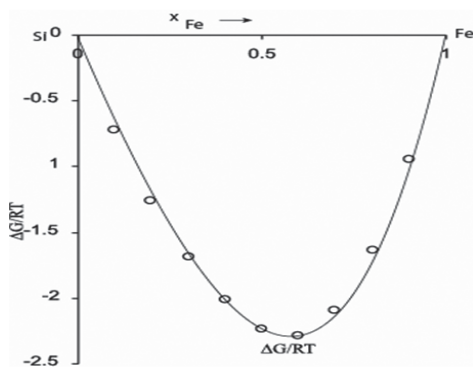


Figure-3: Free energy of mixing ($\Delta G/RT$) versus x_{Fe} of liquid FeSi solution (1873K); (—) theory, (ooo) experiment¹

3.4 Liquid CdNa alloys at 673K

Positive values of ω_{12} and ω_{23} show that there is repulsion between (i) Cd and Na atoms and (ii) Na atoms and the complexes Cd_2Na in the liquid in liquid CdNa alloys. But the value of ω_{13} is found to be negative which shows that Cd atoms and Cd_2Na complexes are attracted with each other.

The experimental and calculated value of free energy of mixing of CdNa alloys at 673K is compared in figure 3. There is a very good agreement between the calculated and experimental values. The experimental value of free energy of mixing is minimum at $x_{Cd} = 0.7$. The calculated value of free energy of mixing is also found to be minimum ($= -5.02kJ$) at $x_{Cd} = 0.7$.

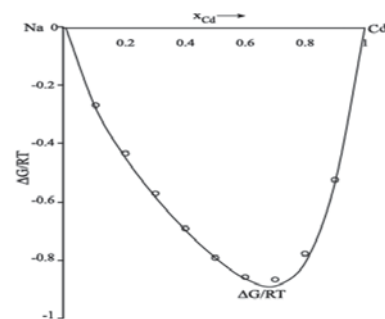


Figure-4: Free energy of mixing ($\Delta G/RT$) versus x_{Cd} of liquid Cd-Na solution (673K); (—) theory, (ooo) experiment¹

3.5 Liquid HgNa alloys at 673K

All the interaction energies in liquid HgNa alloys at 673K are found to be negative showing that Hg and Na atoms are attracted to each other and to the complex.

The calculated value of the free energy of mixing is found to be minimum ($-3.260RT$) at $x_{Hg} = 0.6$. The experimental value of free energy of mixing is also minimum at $= 0.6$. Figure 5 shows a good agreement between the experimental and calculated free energies and explains the observed asymmetry in the free energy of mixing of HgNa alloy in molten state at 673K.

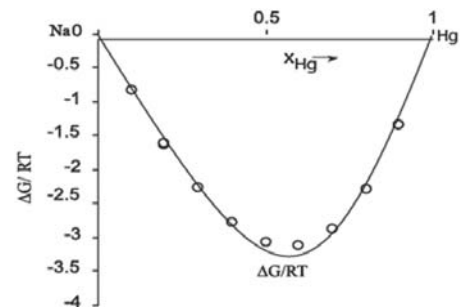


Figure-5: Free energy of mixing ($\Delta G/RT$) versus x_{Hg} of liquid HgNa solution (673K); (—) theory, (ooo) experiment¹

Table 1

$x_{Cu}/x_{Ag}/x_{Fe}/x_{Cd}/x_{Hg}$	x_{Cu_3Sn}	x_{Ag_3Al}	x_{Fe_2Si}	x_{Cd_2Na}	x_{Hg_4Na}
0.1	0.001095	0.008257	0.01635	0.01563	0.01192
0.2	0.008378	0.03075	0.05294	0.04992	0.04263
0.3	0.02658	0.0656	0.1086	0.09436	0.07812
0.4	0.05146	0.1138	0.1869	0.1474	0.1317
0.5	0.08541	0.1803	0.2903	0.2017	0.1877
0.6	0.1240	0.2517	0.3337	0.2428	0.2561
0.7	0.1525	0.3075	0.3720	0.2509	0.3161
0.8	0.1650	0.2355	0.2968	0.2125	0.3252
0.9	0.1192	0.1056	0.1098	0.1036	0.1382

Table 2

Parameter	Liquid alloy Systems				
	CuSn at 1400K	AgAl at 1273K	FeSi at 1873K	CdNa at 673K	HgNa at 673K
k	0.1652	0.0494	0.004139	0.236	0.00095
ω_{12} (Jmol ⁻¹)	-13500	-11382	-64170	4590	-34750
ω_{13} (Jmol ⁻¹)	-24900	-617	-14720	-6030	-14780
ω_{23} (Jmol ⁻¹)	-16500	-28064	-45500	7850	-120240

4. CONCLUSION

The regular associated solution model is found to be suitable to estimate the free energy of mixing for both weakly and strongly interacting binary liquid alloys. The observed asymmetries in the free energies of mixing of binary liquid alloys with respect to the concentrations are well explained on the basis of regular associated solution models.

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