

Modeling of Thermodynamic Behavior of Systems with Low Departure to Ideality: Application to Au-Pb

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Abstract: A novel regular solution model has been developed to explain the thermodynamic behavior of systems presenting a low departure to ideality. The model is an extension of the regular solution model that discriminates between two forms of one component of binary alloy. The change of enthalpy of formation versus temperature is due to the transformation of one form into another when the temperature varies. The application of the model to the system Au-Pb allows us to explain its thermodynamic behavior by the existence of two forms of lead.

Keywords: Low departure to ideality, thermodynamic modeling, Au-Pb alloy.

1. Introduction

Several thermodynamic models have been developed to try to formulate and explain the variation of thermodynamic function versus temperature and composition. Each of these models is specific for a class of systems. If the enthalpy of formation shows a very strong negative departure to ideality, the regular associated model developed elsewhere [1-16] can be applied. The thermodynamics behaviors of these systems are explained by a short-range order due to the presence of clusters in the liquid state. The variation of enthalpy of formation as a function of temperature is due to the destruction of clusters when the temperature increases. For systems with low positive or negative deviation from ideality, Colinet et al. [17] proposed a model considering that each element of the alloy exists in two forms in equilibrium in the liquid. Mouloudj [18] extended the structure model proposed by Tsuchiya [19-20], explaining the thermodynamic behavior of Se-Te. He related the thermodynamics behaviors to structure of Te in liquid whose coordination number varying between 2 to 3 when the temperature increases. The same assumption was taken by Amzil et al. [21] but with different treatment, to explain the variation of the enthalpy of formation versus temperature and composition of the same system.

In this work, an approach to the thermodynamic modelling of the system presenting a low departure to ideality has been developed to establish a relationship between the atomic structure and thermodynamic quantities of mixing. We assume that one element of the alloy presents two forms in liquid melt. The change of enthalpy of formation versus temperature is due to the transformation of one form into another when the temperature varies. This model was applied to Au-Pb system.

2. Model description

The basic idea underlying this model is to consider that the changes of the thermodynamic properties of the molten are due to coexistence of two forms of one element of the alloy. The main assumption is to treat the binary A-B system as a ternary one, by discriminating between two forms of A atoms, A_1 and A_2 , in equilibrium in pure element and alloy liquid.

In this model, the pure component A can be treated as a binary consisting of species A_1 and A_2 . The molar enthalpy of formation of pseudo binary is given by:

$$h_p = \rho \Delta H^\circ + \omega_{A_1 A_2} \rho (1 - \rho)$$

ρ , $\omega_{A_1 A_2}$ and ΔH° , are respectively the molar fraction of A_2 in pseudo binary, the interaction parameter between A_1 and A_2 and the enthalpy of transformation of A_1 to A_2 .

The molar entropy of pseudo binary system is:

$$S_p = \rho \Delta S^\circ - R(\rho \ln(\rho) + (1 - \rho) \ln(1 - \rho))$$

ΔS° is the entropy of transformation of A_1 to A_2 . The second term of S_p is the entropy of distribution of species corresponding to a random distribution of the atomic species in liquid. The binary system A-B is treated as a ternary ($A_1 - A_2 - B$). In the enthalpy and entropy of pseudo ternary, there is a contribution due to the transformation of A_1 to A_2 ($X_{A_2} \Delta H^\circ$ and $X_{A_2} \Delta S^\circ$) and another due respectively to the interaction between species and the distribution of species in liquid. They are given by:

$$h_B = X_{A_2} \Delta H^\circ + \omega_{A_1 A_2} X_{A_1} X_{A_2} + \omega_{A_1 B} X_{A_1} X_B + \omega_{A_2 B} X_{A_2} X_B$$

$$S_B = X_{A_2} \Delta S^\circ - R(X_{A_1} \text{Log}(X_{A_1}) + X_{A_2} \text{Log}(X_{A_2}) + X_B \text{Ln}(X_B))$$

X_{A_1} , X_{A_2} and X_B are the molar fraction in pseudo ternary system respectively of A_1 , A_2 and B .

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$\omega_{A_1A_2}$, ω_{A_1B} , and ω_{A_2B} are the interaction parameters, supposed to be independent of temperature and composition.

To establish the expression of enthalpy and the entropy formation of the binary system referred to both components A and B , we have to subtract the corresponding quantities in the pure component A . The enthalpy and the entropy of formation referred to pure elements can be written according to the composition x as follows:

$$h^f = (X_{A_2} - x\rho)\Delta H^\circ + \omega_{A_1A_2}X_{A_1}X_{A_2} + \omega_{A_1B}X_{A_1}X_B + \omega_{A_2B}X_{A_2}X_B - x\omega_{A_1A_2}\rho(1 - \rho) \quad (1)$$

$$s^f = (X_{A_2} - x\rho)\Delta S^\circ - R(X_{A_1} \text{Log}(X_{A_1}) + X_{A_2} \text{Log}(X_{A_2}) + X_B \text{Ln}(X_B)) + xR(\rho \text{Ln}(\rho) + (1 - \rho)\text{Ln}(1 - \rho)) \quad (2)$$

Both species A_1 and A_2 are in equilibrium in the liquid mixture. Their numbers must minimize the energy of the system (free enthalpy). Determining the equilibrium equation is equivalent to minimizing the free enthalpy, $g_B = h_B - TS_B$, compared to N_{A_1} or N_{A_2} since the two numbers are related by ($N_{A_1} + N_{A_2} = x$). The equilibrium equation is given by the following equation:

$$\Delta G^\circ + \omega_{A_1A_2}(N_{A_1} - N_{A_2}) + X_B(\omega_{A_2B} - \omega_{A_1B}) + RT \text{Ln}\left(\frac{X_{A_2}}{X_{A_1}}\right) = 0 \quad (3)$$

When X_B tends towards zero, we obtain the equilibrium equation in the pure component A :

$$\Delta G^\circ + \omega_{A_1A_2}(1 - 2\rho) + RT \text{Ln}\left(\frac{\rho}{1-\rho}\right) = 0 \quad (4)$$

The application of this model involves solving the equations of (1), (2), (3) and (4). For N compositions for which we know the enthalpy and free enthalpy of formation at a temperature T , we have $3N$ equations (1), (2), (3). We have also equation (4) from which we calculate ρ . In total we have $3N + 1$ equations and $N + 6$ unknowns parameters; the N values of N_{A_2} , the enthalpy and entropy of transformation (ΔH° and ΔS°), the three parameters interaction and ρ . The system is solved by an iterative method.

3. Application to Au-Pb system

3.1. Bibliographic review

The enthalpy of formation, h^f , of the Au-Pb liquid has been determined Kleppa [22] at 723 and 873 K, by Beja [23] at 823 and 923 K, by Hager [24] at 1200 K, by Kameda [25] at 1223 K and by Michel [26] at 695, 871 and 1123 K. Although these measures are in disagreement, they show that the enthalpy of formation presents low departure to ideality and varies greatly versus temperature. The values selected for this work are those of Michel et al. [26], because whether they are the latest and were

performed at three temperatures. h^f of Au-Pb liquid is negative at low temperatures and becomes positive in the Au rich side with increasing temperature. The free enthalpy of investigated system has been determined by Hager [24] and Rebouillon [27]. There values show a good agreement. The expressions of h^f and g^{xs} versus composition and temperature are given by the following equations:

$$h^f = x_{Au}(1 - x_{Au}) \sum_i (a_i - c_iT - d_iT^2) x^i$$

$$g^{xs} = x_{Au}(1 - x_{Au}) \sum_i \left(\frac{a_i + b_iT + c_iT \text{Ln}(T) + d_iT^2}{i} \right) x^i$$

a_i, b_i, c_i and d_i are consigned in table 1.

Table 1: Coefficient a_i, b_i, c_i and d_i

i	a_i kJ/mol	b_i kJ/mol K	c_i kJ/mol K	d_i kJ/mol K ²
0	-75.56	0.94	-0.136	$6.5 \cdot 10^{-5}$
1	76.57	-1.065	0.156	-8.310^{-5}
2	0	-0.006	0	0

3.2. Application of model

3.2.1. Application at 871 K

The change of enthalpy of formation versus temperature is explained by the presence of two forms of one component, in equilibrium in pure element and alloy liquid. The temperature dependence of the enthalpy of formation is due to the transformation of one form into another when the temperature varies. For the investigated system, we assumed the presence of two forms of lead in liquid. Indeed, the electronic structure of lead is ($4s^24p^2$) and the electrons of the s orbital become, may be, activated at high temperature. Thus lead will divalent at low temperature and tetravalent at high temperature. We applied this model taking into account three parameters of interaction and using the thermodynamic data at 871 K. The results of calculation illustrated by Figure 1 and consigned in table 2 show good agreement between measured and calculated values. The values of enthalpy and entropy of transformation and those of the interaction parameters are consigned in Table 3.

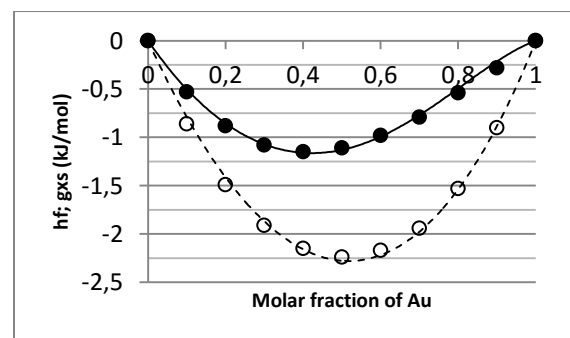


Figure 1: Enthalpy and excess free enthalpy of Au-Pb at 871 K

● h^f measured — : h^f calculated
 ○ g^{xs} measured - - - : g^{xs} calculated

3.2.2. Variation versus temperature

Starting From the enthalpy and entropy of transformation and interaction parameters we calculated h^f and g^{xs} for this system at two other temperatures (695 and 1123 K). The calculation results are shown in Figures 2 and 3 and consigned in Tables 4 and 5. There is a good agreement between measured and calculated values at 1123 K. The model predicts the positive values of h^f in the Au rich side for h^f . At 695 K the agreement is observed only for the excess Gibbs energy and in the Au rich side for h^f . The disagreement is due, may be, to the inaccurate values of h^f in the Pb rich side. Indeed, according to the phase diagram of Au-Pb system, at 695 K, the enthalpy of formation cannot be measured but extrapolated starting from its values in the Au rich side. However, the agreement is qualitative for h^f ; the model predicts the decrease of enthalpy of formation with temperature.

Table 2: Enthalpy and excess free enthalpy measured and calculated of Au-Pb at 871 K

x_{Au}	871 K			
	h_m^f	h_c^f	g_m^{xs}	g_c^{xs}
0.1	-0.53	-0.5	-0.86	-0.79
0.2	-0.88	-0.86	-1.49	-1.41
0.3	-1.08	-1.07	-1.91	-1.87
0.4	-1.15	-1.16	-2.15	2.16
0.5	-1.11	-1.13	-2.24	-2.28
0.6	-0.98	-0.99	-2.17	-2.22
0.7	-0.79	-0.77	-1.94	-1.97
0.8	-0.54	-0.5	-1.53	-1.53
0.9	-0.28	-0.21	-0.9	-0.9

Table 3: Valeurs d'enthalpie et d'entropie standards de transformation et paramètres d'interaction.

$\Delta H^\circ_{Pb_1 \rightarrow Pb_2}$ kJ/mol	72.1
$\Delta S^\circ_{Pb_1 \rightarrow Pb_2}$ J/molK	26.2
ω_{Pb_1, Pb_2} kJ/mol	-25.9
$\omega_{Pb_1, Au}$ kJ/mol	-50.5
$\omega_{Pb_2, Au}$ kJ/mol	-8.2

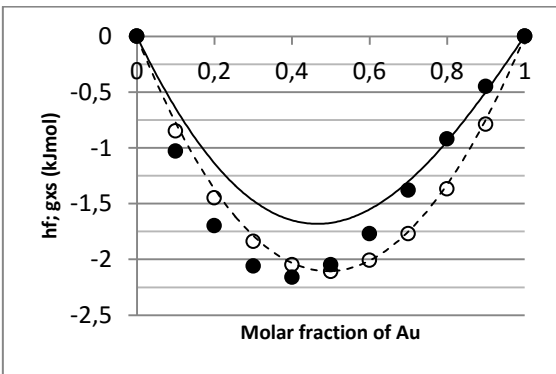


Figure 2: Enthalpy and excess free enthalpy of Au-Pb at 695 K

● h^f measured — : h^f calculated
 ○ g^{xs} measured - - - : g^{xs} calculated

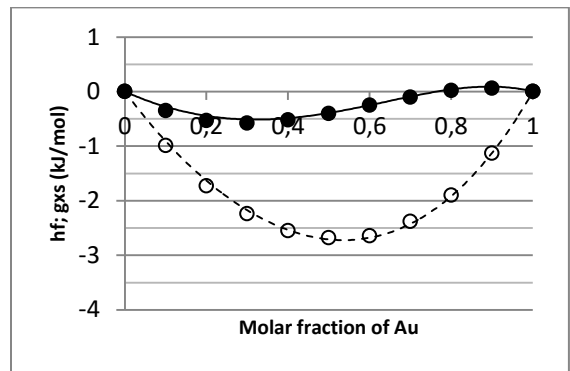


Figure 3: Enthalpy and excess free enthalpy of Au-Pb at 1123 K

● h^f measured — : h^f calculated
 ○ g^{xs} measured - - - : g^{xs} calculated

Table 4: Enthalpy and excess free enthalpy measured and calculated of Au-Pb at 695 K

x_{Au}	695 K			
	h_m^f	h_c^f	g_m^{xs}	g_c^{xs}
0.1	-1.03	-0.65	-0.85	-0.78
0.2	-1.70	-1.14	-1.45	-1.37
0.3	-2.06	-1.47	-1.84	-1.79
0.4	-2.16	-1.65	-2.05	-2.03
0.5	-2.05	-1.67	-2.11	-2.10
0.6	-1.77	-1.55	-2.01	-2.01
0.7	-1.38	-1.31	-1.77	-1.75
0.8	-0.92	-0.94	-1.37	-1.33
0.9	-0.45	-0.49	-0.79	-0.75

Table 5: Enthalpy and excess free enthalpy measured and calculated of Au-Pb at 1123 K

x_{Au}	1123 K			
	h_m^f	h_c^f	g_m^{xs}	g_c^{xs}
0.1	-0.35	-0.28	-0.99	-0.9
0.2	-0.53	-0.44	-1.73	-1.63
0.3	-0.58	-0.51	-2.24	-2.18
0.4	-0.52	-0.49	-2.55	-2.54
0.5	-0.4	-0.39	-2.68	-2.71
0.6	-0.25	-0.25	-2.64	-2.67
0.7	-0.1	-0.09	-2.38	-2.42
0.8	0.02	0.04	-1.9	-1.92
0.9	0.06	0.09	-1.13	-1.13

3.2.3. Influence of temperature and composition on the equilibrium $Pb_1 \rightleftharpoons Pb_2$

Figure 4 illustrated the change of the number of Pb_2 in the pure lead versus temperature. One lead form is observed at low temperatures, from 700 K, the number of Pb_2 increases rapidly and slows down at high temperatures. To examine the influence of temperature and composition on the $Pb_1 \rightleftharpoons Pb_2$ equilibrium in pseudo ternary $Pb_1 - Pb_2 - Au$, we have shown in Figure 5, the relative mole fraction of Pb_2 defined as $\frac{N_{Pb_2}}{N_{Pb_1} + N_{Pb_2}}$ versus temperature and composition. The curves show the same effect of temperature and composition on the equilibrium $Pb_1 \rightleftharpoons Pb_2$. The Pb_2 relative mole fraction increases with temperature and composition.

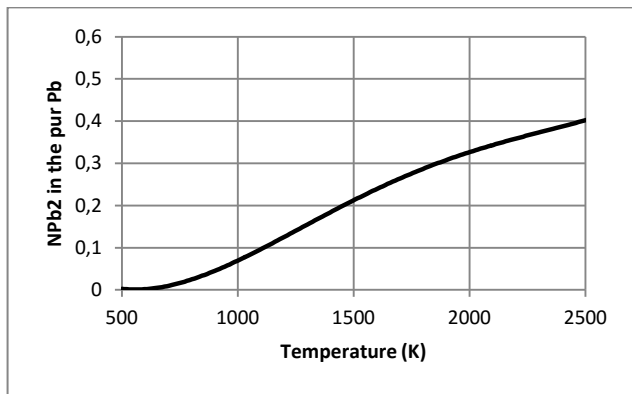


Figure 4: Number of Pb_2 in the pure lead

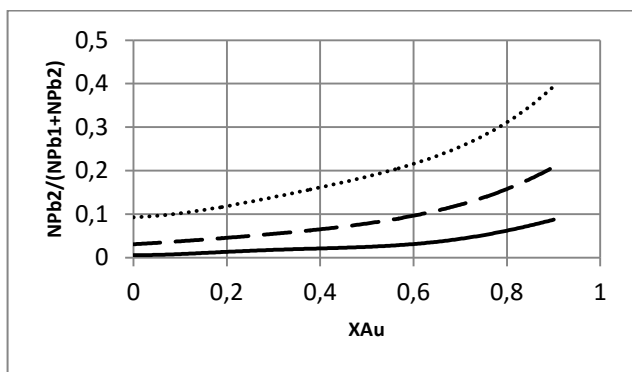


Figure 5: mole fraction of Pb_2 versus temperature and composition
 — : 695 K, - - - : 871 K, : 1123 K

4. Conclusion

The model developed in this work allows us to explain the thermodynamic behavior of systems presenting a low departure to ideality. The application of this model to Au-Pb system shows that the change of enthalpy of formation versus temperature is explained by the presence of two forms of Pb in the liquid. The computed values of thermodynamics properties show a good agreement. The disagreement observed in Pb rich-side for h^f is explained by the inaccurate values in this composition range.

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