CALCULATION OF ACTIVITIES IN Ga−Cd AND Cu−Pb BINARY SYSTEMS

D. Manasijević, D. Živković and Ž. Živković

University of Belgrade, Technical Faculty, VJ 12, 19210 Bor, Yugoslavia

Abstract

Calculations of activities in Ga-Cd and Cu-Pb binary systems were done based on their known phase diagrams, using different calculation methods. First, activities of cadmium at 700 K and copper at 1263 K in Ca - Cd and Cu - Pb systems, respevtively, were calculated by melting point depression method and Zhang-Chou method for binary systems with phase diagrams involving two liquid or solid coexisting phases. In order to obtain activity values in the entire composition range, these methods were applied in the definite parts of composition range in both investigating systems. The same procedure was done, using modified Rao-Belton method by Chou, who used Richardson assumption. Activities of the second component in both investigating systems were calculated by use of Gibbs-Duhem equation. All calculated results were compared with literature data and mutual comparison between applied methods was done.

1. Introduction

There is an important connection between thermodynamic properties and phase diagrams. From that point of view, due to the great efforts of CALPHAD (CALculation of PHAse Diagrams) group [1] this scientific area has been developed to a very high level.

Calculation of activities from binary phase diagrams, which has progressed during the past several decades [2], is one among the methods for activity data obtaining. This is very important from the scientific and technological point of view, because correct determination of thermodynamic properties for binary systems presents a starting point for calculation of phase diagrams of more complex, multi-component systems.

In this work, three methods have been used for thermodynamic investigation of Ga-Cd and Cu-Pb systems. First is melting point depression method [2] used for simple eutectic systems and is based on following two approximations:

-regular solution model and
-melting enthalpy of component is temperature independent quantity.

In many cases approximation dealing with regular behavior of components can cause a great errors in calculated activity values. For that reason, Chou [3] developed new method based on Rao-Belton method [4] and Richardson assumption [5]. This semi-empirical equation was shown for the first time in Lupis and Elliot work [6], in the same year when Kubashewski published a similar concept [7].

Third method, developed by Zhang and Chou [8], is based on the same assumption and it is used for systems with two liquid or solid coexisting phases.

The aim of this work was to investigate mutually compatibility and accuracy of mentioned methods. For that purpose, Ga-Cd and Cu-Pb binary systems, with appropriate phase diagrams and literature experimental data were selected for calculation process.

2. Theoretical fundamentals

The representative phase diagram for calculations done in this work is shown in Fig. 1.

Determination of activities of component A in the whole composition range is possible with application of different analytical methods [2,3,8].

In the composition intervals from $x_B=0$ to $x_B = x_B^E$ and from $x_B = x_B^G$ to $x_B= 1$, activities of component A at the fixed temperature T_0 can be calculated by any of the following equations (1) and (2)[2,3]:

$$\ln \gamma_{A(x_A,T_0)} = \frac{\Delta H_f^0(A)T}{RT_0}\left(\frac{1}{T_f(A)} - \frac{1}{T}\right) - \frac{T}{T_0}\ln x_A \qquad (1)$$

Fig. 1. The representative phase diagram A-B

where $\gamma_A (x_A, T_O)$: activity coefficient of component A at temperature T_0 and x_A mole fraction; $\Delta H^O_f (A)$: melting molar enthalpy of component A; T: temperature at the liquids line for x_A mole fraction and $T_f (A)$: melting temperature of component A.

where $\gamma_A (x_A, T_O)$: activity coefficient of component A at temperature T_0 and x_A mole

$$\ln \gamma_{A(x_{A,T_0})} = -\frac{\sigma}{\sigma_0}\left(\frac{\Delta G_f^0(A)}{RT} + \ln x_A \right) \tag{2}$$

fraction; $\Delta G^O_f (A)$: melting molar Gibbs energy of component A at temperature T; T: temperature at the liquids line for x_A mole fraction and:

$$\sigma = \frac{T}{1 - \dfrac{T}{\theta}} \tag{3}$$

$$\sigma_0 = \frac{T_0}{1 - \dfrac{T_0}{\theta}} \tag{4}$$

$$\theta = \frac{H_i}{S_i^E} = 3000K \quad \text{(Richardson assumption [5])} \tag{5}$$

In the composition interval involving two coexisting liquid phases (L_1+L_2), activities of component A can be obtained through the following equations[8]:

From $x_B = x_B^E$ to $x_B = x_B^F$ the formula for calculation of activity coefficient for component A is given as:

$$\ln \gamma_{A\left(x_A^{L_1},T_0\right)} = \ln \gamma_{A\left(x_A^E,T_0\right)} + \int_{\frac{\sigma_E}{\sigma_0}}^{\frac{\sigma}{\sigma_0}} \delta_A d\left(\frac{\sigma}{\sigma_0}\right) - \left(\frac{\sigma}{\sigma_0}\ln x_A^{L_1} - \frac{\sigma_E}{\sigma_0}\ln x_A^E\right) \qquad (6)$$

and in the composition interval from $x_B = x_B^F$ to $x_B = x_B^G$:

$$\ln \gamma_{A(x_A^{L_2},T_0)} = \ln \gamma_{A\left(x_A^{L_1},T_0\right)} - \frac{\sigma}{\sigma_0}\ln\frac{x_A^{L_2}}{x_A^{L_1}} \qquad (7)$$

where $\gamma_{A(x_A^{L_1},T_0)}$: activity coefficient of component A at temperature T_0 and $x_A^{L_1}$ mole fraction; $\gamma_{A(x_A^E,T_0)}$: activity coefficient of component A at temperature T_0 and x_A^E mole fraction; $\gamma_{A(x_A^{L_2},T_0)}$: activity coefficient of component A at temperature T_0 and $x_A^{L_2}$ mole fraction and:

$$\delta_A = \frac{1}{x_B^{L_1} - x_B^{L_2}}\left[x_B^{L_1}\Sigma^{L_2} - x_B^{L_2}\Sigma^{L_1}\right] \qquad (8)$$

$$\Sigma^{L_1} = x_A^{L_1}\ln x_A^{L_1} + x_B^{L_1}\ln x_B^{L_1} \qquad (9)$$

$$\Sigma^{L_2} = x_A^{L_2}\ln x_A^{L_2} + x_B^{L_2}\ln x_B^{L_2} \qquad (10)$$

Equation (6) can be solved if phase diagram of investigating system and activity coefficient of component A in the investigating temperature T_0 for x_A^E mole fraction

are known. Very often, depending on phase diagram shape in region near to point E, it is possible to calculate this value with application of some other calculation method (eqs.1 and 2 in this work). In some cases it can be approximately used as equal to unit (if $x^E_A \cong 1$).

After the determination of activities for component A in the entire composition interval, activities of component B can be derived from following equation, using Gibbs-Duhem equation and α-function:

$$\ln a_B = \ln x_B - x_A x_B \alpha_A + \int_0^{x_A} \alpha_A dx_A \tag{11}$$

$$\alpha_A = \frac{\ln \gamma_A}{(1 - x_A)^2} \tag{12}$$

where γ is the activity coefficient and *x* is the mole fraction.

3. Results and discussion

3.1. Ga-Cd system

Phase diagram of Ga-Cd system [9], used for calculation, is shown in Fig. 2. Two extreme end points E and G on the bottom of two coexisting liquid phases region at temperature 555 K are x^E_{Ga} = 0,227 and x^G_{Ga} =0,725, respectively. The critical point F is at 568 K.

Thermodynamic data [10] used for calculation are:

$$T_f(Cd) = 594K$$

$$\Delta H^0_f(Cd) = 6192\,(J\,/mol\,)$$

$$c^0_P \langle Cd \rangle = 22,228 + 12,307 \cdot 10^{-3}\,T \quad (J\,/mol^0\,)$$
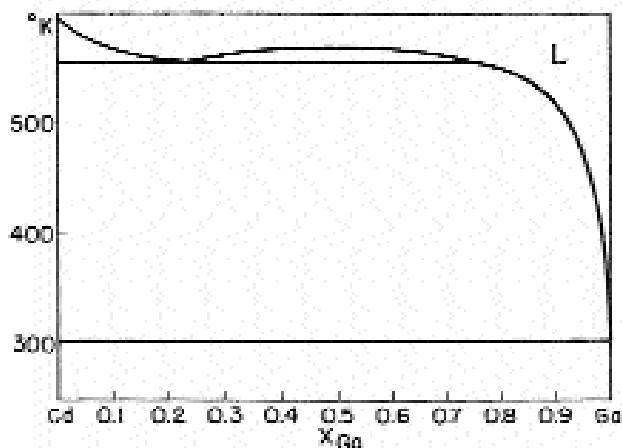
$$c^0_P \{Cd\} = 29,721 (J\,/mol^0\,)$$

Fig. 2. Ga-Cd phase diagram

In the composition range from $x_{Ga} = 0$ to $x_{Ga}^E = 0{,}227$ and from $x_{Ga}^G = 0{,}725$ to $x_{Ga} = 1$, activities of cadmium at 700 K were calculated by eq.(1) and also by eq.(2) and listed in the Tab.1.

Table 1. Starting data and activities of cadmium   obtained by eq.(1) and eq.(2)
for chosen alloys at 700 K.

x_{Cd}	$T(K)$	$\Delta G_f^0(Cd)(J/mol)$	a_{Cd} (calculated by eq.1)	a_{Cd} (calculated by eq.2)
0,95	578	167	0,963	0,962
0,9	569	261	0,938	0,935
0,85	563	323	0,916	0,913
0,8	558	375	0,896	0,890
0,773	555	406	0,884	0,877
0,2	550	458	0,655	0,609
0,15	537	593	0,580	0,531
0,1	518	790	0,480	0,428
0,05	474	1241	0,307	0,261

Based on the above values activities of cadmium in the composition range from $x_{Ga} = 0{,}227$ to $x_{Ga} = 0{,}725$ were calculated by eqs. (6-7). All calculated results and starting data are listed in Tab. 2.

278

Table 2. Starting data and activity values of cadmium obtained by eqs.(6-7) for chosen alloys at 700 K.

$x_{Ga}^{L_1}$	$x_{Cd}^{L_1}$	$x_{Ga}^{L_2}$	$x_{Cd}^{L_2}$	T(K)	$a_{Cd}^{L_1}$ (using data obtained by eq.1)	$a_{Cd}^{L_1}$ (using data obtained by eq.2)	$a_{Cd}^{L_2}$ (using data obtained by eq.1)	$a_{Cd}^{L_2}$ (using data obtained by eq.2)
0,227	0,773	0,725	0,275	555	0.884	0,877	0,680	0,675
0,25	0,75	0,72	0,28	558	0,877	0,869	0,685	0,680
0,3	0,7	0,68	0,32	561	0,860	0,854	0,711	0,705
0,35	0,65	0,63	0,37	563	0,845	0,838	0,737	0,731
0,4	0,6	0,6	0,4	565	0,828	0,821	0,752	0,746
0,45	0,55	0,56	0,44	567	0,811	0,804	0,770	0,763

Activities of gallium were derived from eq.(11) and the obtained values are shown in Table 3.

Table 3. Activities of gallium in Ga-Cd system at 700 K.

x_{Ga}	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9
a_{Ga} (using data obtained by eqs. 1,6,7)	0,468	0,614	0,697	0,749	0,791	0,825	0,852	0,878	0,924
a_{Ga} (using data obtained by eqs. 2,6,7)	0,443	0,594	0,678	0,731	0,761	0,799	0,831	0,870	0,921

The activities of cadmium and gallium obtained in this work are compared with experimental data [11] in Fig. 3.

After comparing calculated results with experimental data taken from Predel EMF measurements [11], it could be concluded that both calculated curves are very close to experimental points. Also, it is clear that activity curve for cadmium obtained by eqs. (2, 6 and 7) has more proper shape than activity curve obtained by eqs. (1, 6 and 7) which has smooth breakage, indicating smaller compatibility of applied methods in this case. It is obvious that methods represented by eqs.(2, 6 and 7), derived on the same theoretical basics, are more compatible than methods represented by eqs.(1, 6 and 7) and give more proper shape of activity curve.
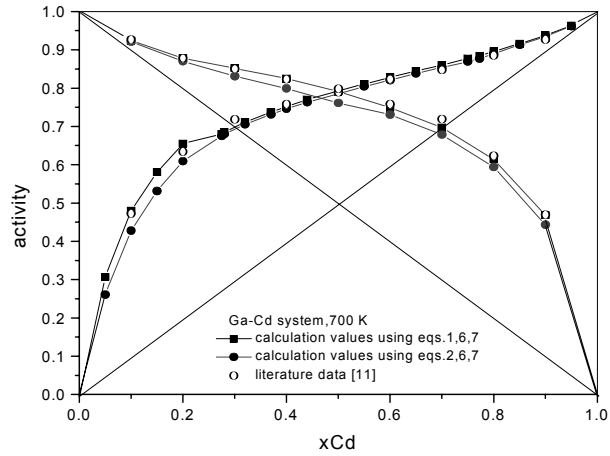
Fig. 3. Activities of cadmium and gallium at 700 K.

3.2. Cu-Pb system

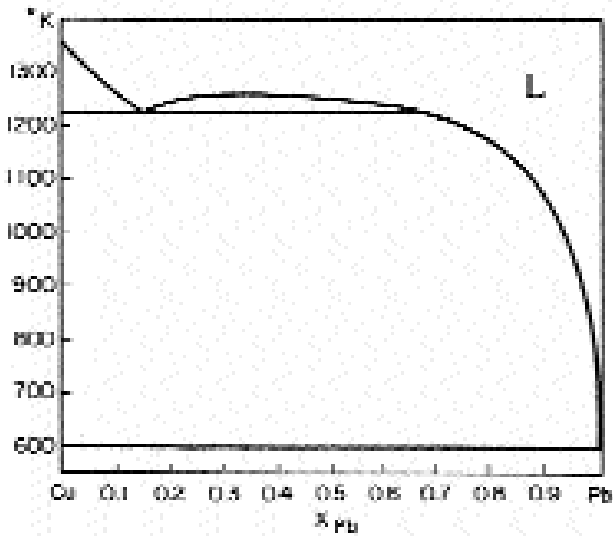Phase diagram of Cu−Pb system [9] is shown in Fig. 4.

Fig.4. Cu-Pb phase diagram

For the Cu-Pb binary system, critical temperature is 1263 K, and the composition of two extreme terminates on the bottom of two coexisting phases region are x_{Pb}^{E} = 0,147 and x_{Pb}^{G} = 0,67, respectively. Thermodynamic data [10] used for calculation are:

$$T_f(Cu) = 1357K$$
$$\Delta H_f^0(Cu) = 13260\,(J/mol)$$
$$c_P^0\langle Cu\rangle = 24,853 + 3,787 \cdot 10^{-3}T - 1,389 \cdot 10^{5}T^{-2}\,(J/mol^0)$$
$$c_P^0\{Cu\} = 31,38\,(J/mol^0)$$

After the same procedure used in the example of Ga-Cd, activities of copper and lead at 1263 K are calculated, and the obtained results are listed in Tables. 4., 5. and 6.

Table 4. Starting data and activities of copper obtained by eq.(1) and eq.(2) for chosen alloys at 1263 K.

x_{Cu}	T(K)	$\Delta G_f^0(Cu)(J/mol)$	a_{Cu} (calculated by eq.1)	a_{Cu} (calculated by eq.2)
0,95	1300	547	0,950	0,951
0,9	1260	934	0,913	0,915
0,853	1228	1242	0,883	0,884
0,3	1220	1319	0,845	0,826
0,2	1175	1749	0,755	0,710
0,1	1070	2737	0,538	0,458

Table 5. Starting data and activity values of Cu obtained by eqs.(6-7) for chosen alloys at 1263 K.

$x_{Pb}^{L_1}$	$x_{Cu}^{L_1}$	$x_{Pb}^{L_2}$	$x_{Cu}^{L_2}$	T(K)	$a_{Cu}^{L_1}$ (using data obtained by eq.1)	$a_{Cu}^{L_1}$ (using data obtained by eq.1)	$a_{Cu}^{L_2}$ (using data obtained by eq.1)	$a_{Cu}^{L_2}$ (using data obtained by eq.1)
0,147	0,853	0,67	0,33	1228	0,883	0,884	0,845	0,845
0,2	0,8	0,555	0,445	1240	0,874	0,879	0,862	0,863
0,25	0,75	0,46	0,54	1255	0,874	0,875	0,871	0,872
0,3	0,7	0,4	0,6	1260	0,873	0,874	0,873	0,874

Table 6. Activities of lead in Cu-Pb system at 1263 K

x_{Pb}	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9
a_{Pb} (using data obtained by eqs. 1,6,7)	0,610	0,799	0,815	0,815	0,821	0,830	0,837	0,866	0,915
a_{Pb} (using data obtained by eqs. 2,6,7)	0,584	0,765	0,782	0,783	0,785	0,796	0,811	0,851	0,915

The activities of copper and lead obtained in this work are compared with literature data [9] in Fig. 5.
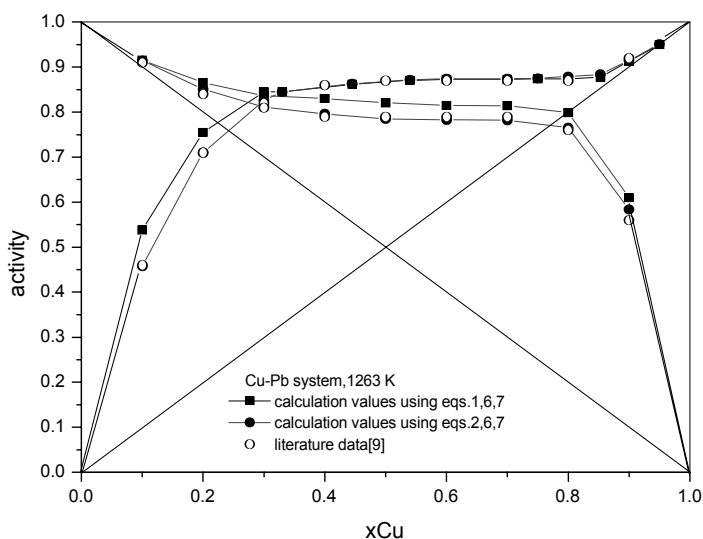

Fig.5. Activities of copper and lead at 1263 K.

Using obtained activities for copper and lead integral Gibbs energy of mixing curves were calculated and compared with literature [9] in Fig. 6.

From Figs.5 and 6 it can be concluded that there exist very good agreement between calculated curves and experimental data. Also, it can be seen that results obtained by melting point depression method (eq.1) show considerable deviation from the experimental results in the composition range with low copper content. In this composition range, temperatures at the liquids line are much lower than melting temperature of copper and approximation that melting enthalpy of copper is temperature independent quantity leads to a certain deviation between calculated results by eq. 1 and experimental data.
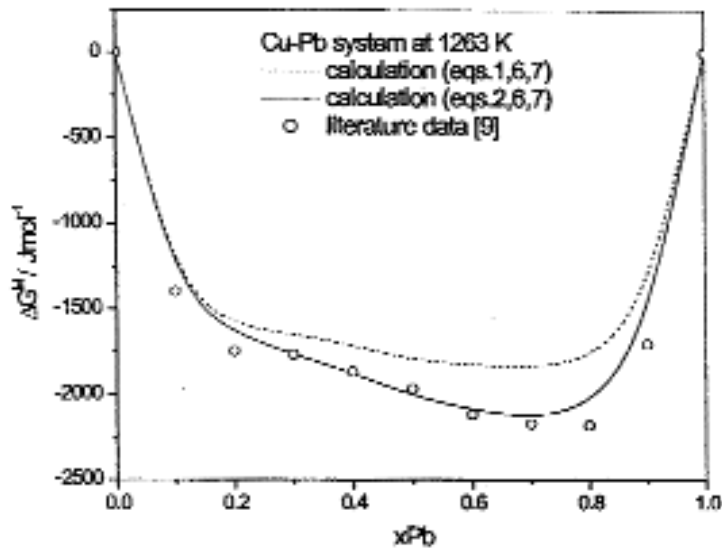
Fig. 6. Integral Gibbs energies of mixing at 1263 K

4. Conclusion

Two methods for calculating activities of components in simple eutectic systems and one method for calculation of activities in systems with phase diagrams containing a miscibility gap were used and the activities of components in Ga-Cd and Cu-Pb binary systems were calculated. In all cases obtained values show positive deviation from ideality. There is very good agreement between the calculated results and literature data for both investigating systems. It may be concluded that formula (2) for simple eutectic systems, based on Richardson assumption, in combination with method for systems having miscibility gap, based on the same assumption, represented by formulae (6) and (7), gives more accurate results then combination of melting point depression method (1) and method for systems with a miscibility gap. All applied methods, however, showed high accuracy for thermodynamic calculations in this kind of binary systems.

References

1. http: //www.calphad.org
2. K. C. Chou, J. J.Wang, *Metall. Trans*., 18A (1987) 323
3. K. C. Chou, *Calphad*, 14(3) (1990) 275.

4. Y. K.Rao, G. R. Belton, in Chemical Metallurgy-A Tribute to Carl
   Wagner, edited by N. A. Gocken, pp.75-96, Metall. Soc. of AIME,
   Warrendale, Pa., 1981.
5. F. D. Richardson, Physical Chemistry of Melts in Metallurgy, Vol.1
   Academic Press, 1974, PP.135.
6. C.H.Lupis, J.F. Elliot, *Acta Metallurgica*,15 (1967) 265.
7. O. Kubaschewski, Phase Stability of Metals and Alloys, McGraw-Hill,
   1967.
8. F. Zhang, K. C. Chou , *Calphad*, 14 (4) (1990) 349.
9. R. Hultgren et al., Selected Values of the Thermodynamic Properties of
   Binary Alloys, *ASM International*, Metals Park OH, 1973.
10. O. Kubaschewski, C.B. Alcock , Metallurgical Thermochemistry, 5th
    Ed.,Pergamon Press, Oxford, 1979.
11. B. Predel, *Z. Metallkd.* , 49 (1958) 226-31.