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Calorimetric studies and thermodynamic properties of liquid Ag–Ca alloys

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ABSTRACT

Integral molar enthalpies of mixing were determined by drop calorimetric method for Ag–Ca liquid alloys at temperatures (1254 and 1131) K using a Setaram MHTC 96 Line evo calorimeter. Measurements were conducted for alloys of concentrations between $0.0642 \leqslant X_{\mathrm{Ca}} \leqslant 0.9396$ at $T = 1254$ K and at 1131 K between $0.7564 \leqslant X_{\mathrm{Ca}} \leqslant 0.9647$. The obtained values are negative in the entire range of concentrations and the minimum of the integral enthalpy of mixing equal −24609 J/mol of atoms was observed for 0.4634 mol fraction of calcium at $T = 1254$ K. The analysis of experimental data showed that most probably ΔH_m of Ag–Ca liquid alloys is independent of temperature and that they are almost twice less exothermic than those ones by the partial pressure measurements. Based on the data of this study and that available in the literature, the interaction parameters of Redlich–Kister equation for the liquid Ag–Ca phase were evaluated. The concentration fluctuation structure factor Scc(0) calculated using drawn up in this study equation showed the swallow minimum between Ca concentrations appropriate for Ag_9Ca_2 and AgCa intermetallic phases what can suggest at two kind of associates in liquid solutions.

1. Introduction

In the last twenty years, we have been observing intensive actions aiming at the promotion of ecological technologies, such as the development of the hydrogen power industry in the context of applications in the automotive sector and ecological energy sources. The Ag–Ca based alloys are also used in the construction of starting batteries, which characterize in a prolonged operation time, as well as reliability at low and elevated temperatures. Despite the significant role played by the Ag–Ca alloys in relation to their applications, both the equilibrium system of those alloys and their thermodynamic properties are not experimentally determined. The existing experimental data on the enthalpy of formation published in 1982 by Notin and Hertz [1] were determined only for three out of the six intermetallic phases identified by means of the potentiometric technique. In the case of the partial Gibbs energy there are only experimental data by Delcet and Egan [2], who measured the activity of calcium in liquid Ag–Ca solutions by the electromotive forces (EMF) with the use of a solid electrolyte CaF_2 and the Fischbah's data [3] by the partial pressure measurements of Ca applying the Knudsen effusion technique. The most recent elaboration of the Ag–Ca system by Huang *et al.* [4] from 2008 is based on the sparse data [5–12] concerning the thermodynamics of the Ag–Ca system (figure 1).

The calculated phase diagram presented in figure 1 was compared with the data from [6,7], in which significant discrepancies in the equilibrium temperatures were observed. The Ag_3Ca_5 phase was determined as one which forms as a result of a eutectic reaction and not, following the work of Baar [5], as a consequence of a peritectic reaction, accepted in the thermodynamic elaboration of the Ag–Ca system from "The Landolt–Börnstein Database" [13].

The literature review presented above showed that no calorimetric measurements have been performed in reference to either the liquid phase (change of the enthalpy of mixing ΔH_m) or the enthalpy of formation of intermetallic compounds (phases). Though the heats of mixing of liquid Ag–Ca solutions were calculated by Fischbach [3] based on the partial pressure measurements of Ca, they are much lower than those suggested in [13]. The enthalpy of mixing change (ΔH_m) is the important thermodynamic function for the description of the thermodynamics of Ag–Ca liquid phase so, the main aim of this work was to measure ΔH_m by the drop calorimetric technique and to evaluate the Redlich–Kister equation [14] describing the excess Gibbs energy of Ag–Ca liquid solutions based on experimental data available in the literature.

2. Experimental

To determination integral enthalpy of mixing liquid Ag–Ca alloys, metallic silver (purity 99.9 mass.% INNOVATOR Sp. z o.o.) and calcium (Alfa Aesar purity 99.5 mass.%) were used.

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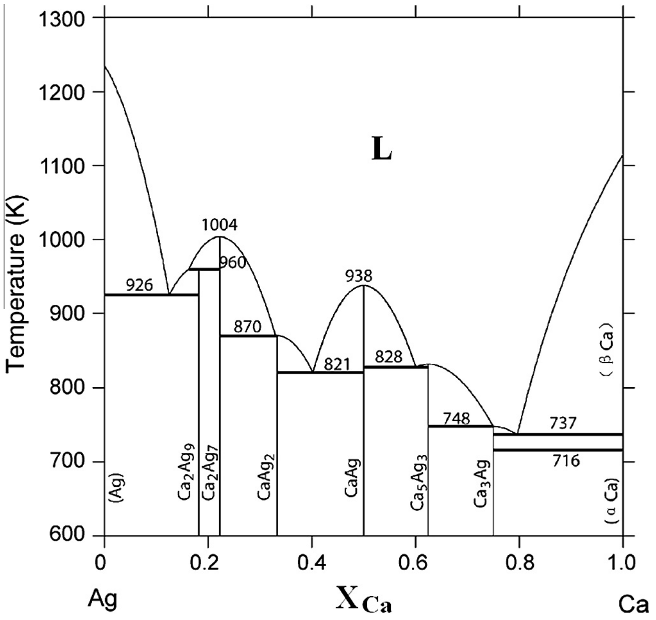

FIGURE 1. Calculated Ag–Ca phase diagram assessed by Huang *et al.* [4].

Calorimetric measurements were done by using the commercial MHTC 96 Line evo calorimeter from Setaram, France. All calorimetric measurement were carried out with the protective atmosphere of high purity argon (Air Products 99.9999 mass.%). To calorimetric study, heat resistant steel crucibles (H25T) with protective alumina tube were used. At the beginning of the all series, the calorimeter was calibrated by using pieces of silver or calcium. In case of calibration by using pieces calcium, the prepared pieces of calcium were closed inside the glove box with high purity argon in a calorimetric antechamber. The antechamber was removed from the glove box, and connected with the calorimeter. Before each experimental run and before dropping the pieces of the sample of Ag or Ca into the calorimeter the apparatus was evacuated with a diffusion pump several times, and then flushed with high purity argon of the same quality as that inside the glove box. The voltage signal from the thermopile was registered in a digital form by the computer with the use of commercial Calisto software. Calorimetric measurements were done at $T = 1254$ K (Series 1 till Series 5) and at $T = 1131$ K (Series 6 and Series 7).

3. Results

The drop calorimetric technique is well established [15,16] and in the case of two component (Ag–Ca system) the measured enthalpy is the integrated heat flow at constant pressure and follows this equations:

$$H_{\text{DISS}-X} = \left(\Delta H_{\text{Signal}} \cdot K\right) - \left(H_X^{T_D \to T_M} \cdot n_X\right), \tag{1}$$

$$\Delta H_{\text{mix}} = \frac{\sum H_{\text{DISS}-X}}{n_{\text{Ag}} + n_{\text{Ca}}}, \tag{2}$$

where ΔH_{Signal} is the heat effect each drop of metal (Ag or Ca) which equaled added drop enthalpy, K is calorimeter constant, T_D and T_M are the drop and calorimetric absolute temperatures of respective measurement in Kelvin, respectively. The $H_X^{T_D \to T_M}$ is the enthalpy of the pure metals (Ag or Ca) which was obtained from Thermo–Calc [17], n_{Ag} and n_{Ca} are the number of moles of silver and calcium respectively. The $H_{\text{DISS}-X}$ is enthalpy of dissolution of pure silver or calcium. Errors in calorimetric measurement were less than 1 kJ/mol.

The mole fraction of pure calcium, drop enthalpy and integral molar enthalpy of mixing of liquid Ag–Ca alloys obtained in six separate series and two temperatures 1254 K (Series 1–5) and 1131 K (Series 6, 7) are given in tables 1 and 2, respectively. All experimental results compared with literature data [2,3,13] are also shown in Figure 2.

Gibbs energy of liquid solution G is expressed of the equation:

$$G = \sum_{i=1}^{n} X_i\left(G_i^0 + \Delta G_i\right) = \sum_{i=1}^{n} X_i\left(G_i^0 + \Delta G_{i(id)} + G_i^E\right), \tag{3}$$

and after introducing to (3) the equations describing the partial functions of components one obtains the relation as follows:

$$\begin{aligned} G &= \sum_{i=1}^{n} X_i[G_i^0 + R \cdot T \cdot \ln(a_i)] \\ &= \sum_{i=1}^{n} X_i[G_i^0 + R \cdot T \cdot \ln(X_i) + R \cdot T \cdot \ln(\gamma_i)], \end{aligned} \tag{4}$$

where: G_i^0, $\Delta G_{i(id)}$ and G_i^E the standard Gibbs energy, partial Gibbs energy change of ideal solution and partial excess Gibbs energy of component i, respectively, R is the universal gas constant, T the absolute temperature, a_i and γ_i the activity and the coefficient of activity and X_i is the concentration of component i in the mole fraction.

G_i^0 is calculated based on the literature data [18]. G_{id} from the alloy composition and the partial excess Gibbs energy based on the experimental data of the partial Gibbs energy change of the component i using the relation below:

$$G_i^E = RT\ln(\gamma_i) = \Delta G_i - \Delta G_{i(id)} = RT\ln(a_i) - RT\ln(X_i). \tag{5}$$

Knowing G_i^E its dependence on temperature and composition can be driven out using different equation. One of these is the Redlich–Kister equation often used to describe the integral excess Gibbs energy (G^E) which in the case of binary Ag–Ca system is as follows:

$$G^E = X_{Ag} \cdot X_{\text{Ca}} \cdot \sum_{i=1}^{n} (A_i + B_i \cdot T) \cdot (X_{\text{Ag}} - X_{\text{Ca}})^{i-1}, \tag{6}$$

and associated with it the partial functions derived based on the Gibbs–Duhem relation are given of the relations:

$$\begin{aligned} G_{\text{Ag}}^E = {} & X_{\text{Ca}} \cdot X_{\text{Ca}} \cdot \sum_{i=1}^{n} (A_i + B_i \cdot T) \cdot (X_{\text{Ag}} - X_{\text{Ca}})^{i-1} \\ & \cdot [(2 \cdot i + 1) \cdot X_{\text{Ag}} - X_{\text{Ca}}], \end{aligned} \tag{7}$$

$$\begin{aligned} G_{\text{Ca}}^E = {} & X_{\text{Ag}} \cdot X_{\text{Ag}} \cdot \sum_{i=1}^{n} (A_i + B_i \cdot T) \cdot (X_{\text{Ag}} - X_{\text{Ca}})^{i-1} \\ & \cdot [X_{\text{Ag}} - (2 \cdot i + 1) \cdot X_{\text{Ca}}]. \end{aligned} \tag{8}$$

Using equation (6) the mixing enthalpy change, excess entropy and mixing entropy change of 1 mol solution are calculated applying following relations:

$$\Delta H_m = X_{\text{Ag}} \cdot X_{\text{Ca}} \cdot \sum_{i=1}^{n} A_i \cdot (X_{\text{Ag}} - X_{\text{Ca}})^{i-1}, \tag{9}$$

$$S_m^E = -X_{\text{Ag}} \cdot X_{\text{Ca}} \cdot \sum_{i=1}^{n} B_i \cdot (X_{\text{Ag}} - X_{\text{Ca}})^{i-1}, \tag{10}$$

$$\Delta S_m = S_m^E + R \cdot T \cdot [\ln(X_{\text{Ag}}) + \ln(X_{\text{Ca}})]. \tag{11}$$

The partial Ag and Ca excess entropy, partial entropy and enthalpy change, activity and activity coefficients could be calculated applying the equations which are written as follow: