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ASSESSMENT OF BINARY BISMUTH — CADMIUM SYSTEM; DATA FITTING PROBLEMS

**KRYTYCZNE OPRACOWANIE UKŁADU RÓWNOWAGI BIZMUT-KADM;
PROBLEMY DOPASOWANIA DANYCH**

On the basis of the earlier evaluation Bi-Cd system was critically assessed by means of CALPHAD method and using the most current thermochemical data for the constituent elements. The influence of various factors on the quality of data fitting was shown on the example of this systems.

Na bazie poprzedniej ewaluacji, układ Bi-Cd został opracowany krytycznie za pomocą metody CALPHAD, przy zastosowaniu najbardziej aktualnych danych termochemicznych dla pierwiastków składowych. Na przykładzie tego układu pokazano wpływ różnych czynników na jakość dopasowania danych do obliczonych krzywych.

1. Introduction

The cadmium-bismuth system was critically evaluated by Moser, Dutkiewicz, Zabdyr and Salawa [1] as a contribution to Massalski's monograph, and liquidus curves were calculated from the thermodynamic description of the liquid phase using the simple polynomial formulas, and thermochemical data for the elements were taken from Hultgren [2] and Kubaschewski [3]; Gibbs energy of the liquid was described by as many as twelve coefficients.

Although no further experimental informations about the system is available, the reassessment is necessary using the new thermochemical data [4] and following the CALPHAD technique, and as for further use in the assessments of higher-order systems.

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2. Modeling

The Gibbs energy function $G_i^{0,\phi}(T) = G_i^\phi(T) - H_i^{SER}$ for element i ($i = \text{Bi}, \text{Cd}$) in the ϕ phase ($\phi = \text{rhombohedral, hcp or liquid}$) is described by well known equation:

$$G_i^{0,\phi}(T) = a + bT + cT \ln T + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9}, \quad (1)$$

where: H_i^{SER} is the molar enthalpy of the stable element reference, SER, at 298.15 K and 1 bar, and T is absolute temperature. Parameters of the equation (1) for bismuth and cadmium are taken from the most recent compilation of Dinsdale [4].

The liquid is treated as disordered substitutional solution and its Gibbs energy is described by the following expression with Redlich-Kister excess term:

$$G^{liq} = (1 - X) G_{Bi}^{liq} + X G_{Cd}^{liq} + RT [X \ln X + (1 - X) \ln (1 - X)] \\ + X(1 - X) [{}^0 L_{Bi,Cd}^{liq} + (1 - 2X)^1 L_{Bi,Cd}^{liq} + (1 - 2X)^2 {}^2 L_{Bi,Cd}^{liq} + \dots], \quad (2)$$

where: R is the gas constant and X is molar fraction of Cd; interaction parameters ${}^i L_{Bi,Cd}^{liq}$ are temperature dependent like first six terms of equation (1) and are to be optimized.

In view of the negligible mutual solid solubility both terminal solid solutions (Bi) and (Cd) are treated as pure elements.

3. Optimisation

All the available experimental data, both from phase equilibria and thermodynamics, were critically evaluated and selected by [1]. The structural data were also listed in the same paper, so there is no need to repeat it here and no solid solubility was assumed on both sides of the system under interest. Carefull analysis of all available thermodynamic data for the liquid showed almost ideal behaviour, displaying both positive and negative, very slight deviations; comparable in magnitude to the uncertainty of emf method. Therefore activity data were not taken into account in optimisation, which was based on the selected values of calorimetric measurements along with constitutional data. Optimisation was performed by PARROT module of ThermoCalc software and various coefficients combinations were tried to fit both thermodynamic and constitutional data.

Since the system under interest is the simple eutectic with almost ideal liquid, it was expected to be easy for optimisation, and four parameters were used in the preliminary optimisation runs. The Bi-rich branch of the liquidus was very well fitted, but Cd-rich part was not correct, and enthalpy of mixing of the liquid was also wrongly reproduced, as can be seen on figures 1 and 2, respectively.

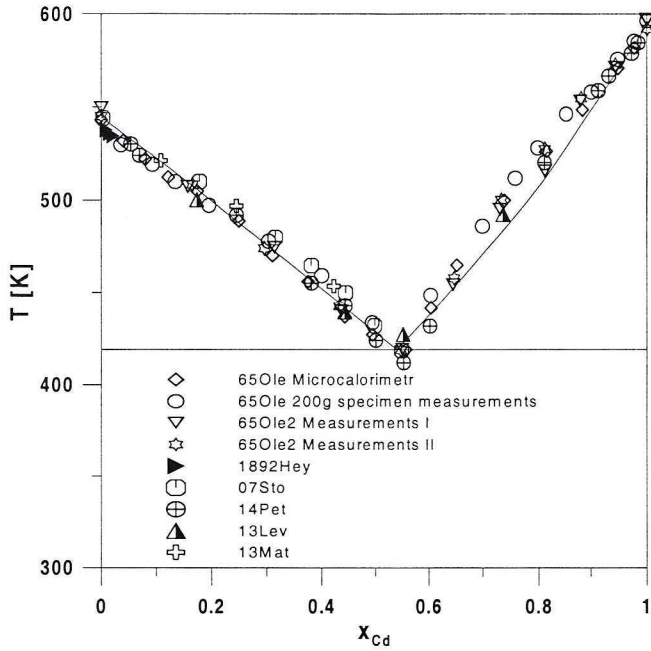
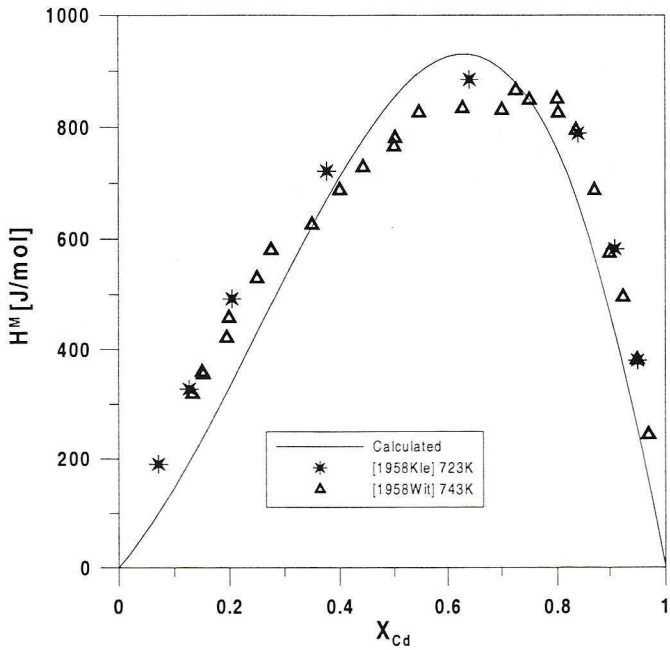


Fig. 1. Four parameter fitting of the liquidus line

Fig. 2. Four parameter fitting of the ΔH curve

When one more parameter was added, enthalpy fit was slightly improved, the fit of the Cd branch was better, but Bi branch appeared to go too high, Fig.3 and 4 respectively.

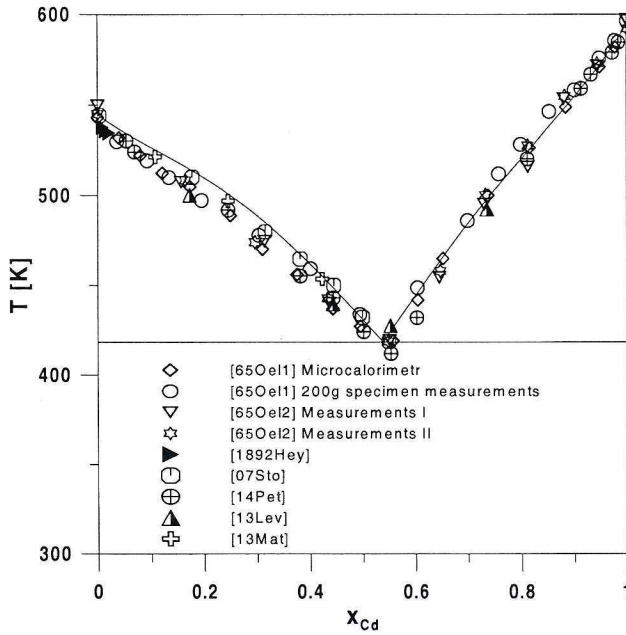


Fig. 3. Six parametr fitting of the liquidus line

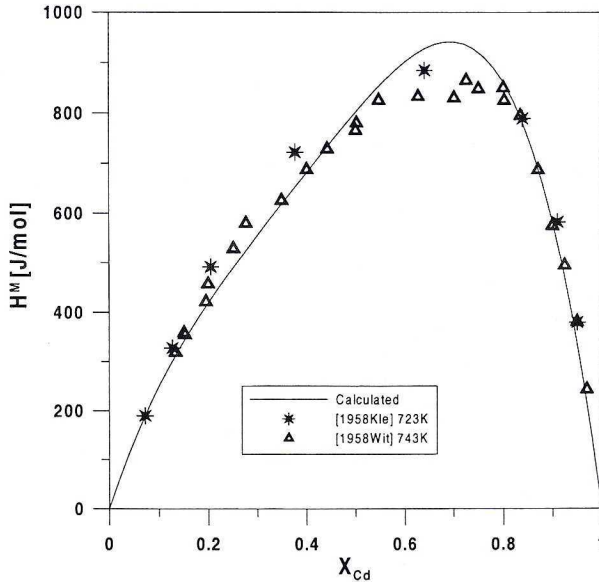


Fig. 4. Six parameter fitting of the ΔH curve

Finally, seven parameters were used for the liquid phase description resulting in considerably good fit on both thermodynamic and constitutional data, although some discrepancies on the near-eutectic part of the Bi branch still occurred, as can be seen on the Fig. 5, 6 and 7; the last representing the fit of cadmium activity in the liquid calculated at 673 K with experimental data.

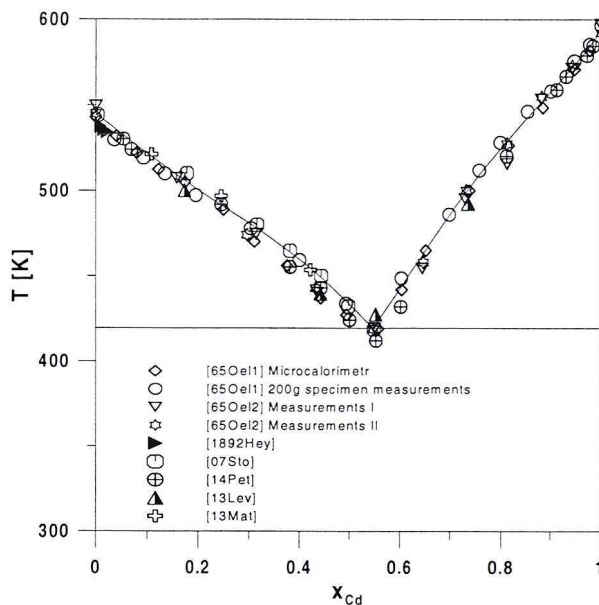


Fig. 5. Seven parametr final fitting of the liquidus line

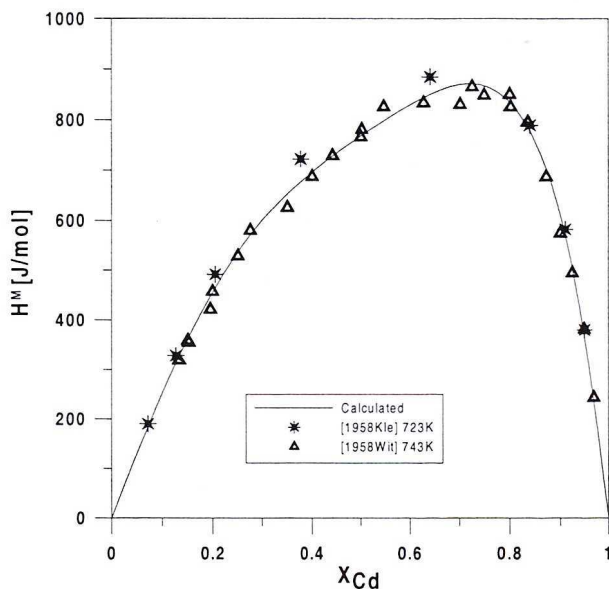


Fig. 6. Seven parametr final fitting of the ΔH curve

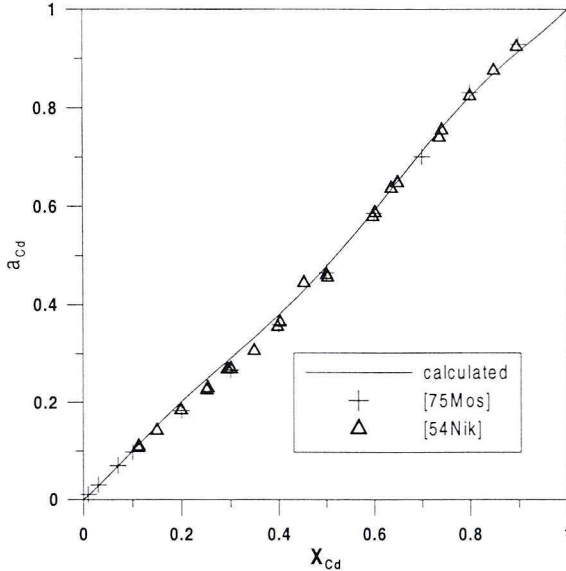


Fig. 7. Seven parametr final fitting of activity data

Experimental data on figures are originally referenced to work [1].

4. Results

Calculated eutectic coordinates: 54.7 at.% Cd and 419.3 K agree excellently with those estimated by [1]: 55% and 419 K, respectively.

The thermochemical data for pure elements along with optimized excess term parameters for the liquid phase are listed below:

$$G_{Bi}^{0,rho}(T) = -7817.776 + 128.418925T - 28.4096529T \ln T + 12.338888 \cdot 10^{-3}T^2 - 8.381598 \cdot 10^{-6}T^3 \quad (298.15 - 544.55K)$$

$$30208.022 - 393.650351T + 51.8556592T \ln T - 75.311163 \cdot 10^{-3}T^2 + 13.499885 \cdot 10^{-6}T^3 - 3616168T^{-1} + 1.661 \cdot 10^{25}T^{-9} \quad (544.55 - 800K)$$

$$G_{Cd}^{0,hcp}(T) = -7083.469 + 99.506198T - 22.0442408T \ln T - 6.273908 \cdot 10^{-3}T^2 - 6966T^{-1} \quad (298.15 - 594.219K)$$

$$-20064.971 + 256.812233T - 45.1611543T \ln T + 8.832011 \cdot 10^{-3}T^2 - 0.899604 \cdot 10^{-6}T^3 + 1241290T^{-1} \quad (594.219 - 1500K)$$

$$G_{Bi}^{0,liq} = 11246.067 - 20.63651T - 5.955 \cdot 10^{-19}T^7 \quad (298.15 - 544.55K)$$

$$11336.259 - 20.810418T - 1.661 \cdot 10^{25}T^{-9} \quad (544.55 - 3000K)$$

$$G_{Cd}^{0,liq} =$$

$$6128.444 - 10.296916T \quad (298.15 - 400K)$$

$$28800.352 - 470.553067T + 75.1756306T \ln T - 108.886009 \cdot 10^{-3}T^2 + 28.899781 \cdot 10^{-6}T^3 -$$

$$-1264849T^{-1} \quad (400 - 594.219K)$$

$$16812.668 - 118.561126T + 15.4547543T \ln T - 8.832011 \cdot 10^{-3}T^2 + 0.899604 \cdot 10^{-6}T^3 -$$

$$-1241290T^{-1} \quad (594.219 - 1500K)$$

$${}^0 L_{Bi,Cd}^{liq} = 3070.43 - 5.09586 \cdot T$$

$${}^1 L_{Bi,Cd}^{liq} = -1313.9 + 2.89966 \cdot T$$

$${}^2 L_{Bi,Cd}^{liq} = 2686.86 - 2.70814 \cdot T$$

$${}^3 L_{Bi,Cd}^{liq} = -1823.33$$

All the calculations, as mentioned above, were referenced to Standard Element Reference, SER: rhombohedral bismuth and hexagonal cadmium, both at 298.15 K and 1 bar.

5. Conclusions

The main influence on the fitting problems described above seems to have unusual features of the liquid phase: considerable asymmetry of ΔH curve and changes of the sign of departure from ideal behaviour. Therefore it was impossible to find out the simple mathematical formula (a few coefficient's number) to match both simple eutectic nature of the system with its quite complex thermodynamic behaviour. Moreover, the optimisation in this work was based on the calorimetric measurements along with phase diagram data, contrary to that carried out in [1], when only emf values were taken into account, and enthalpy data were rejected. The reason to do that was assumption, that calorimetric data are more reliable than uncertain emf values, as explained at the beginning of the Optimisation chapter.

The phenomenon noticed above is of more general meaning. The rule, strongly recommended in optimisation procedure is to limit the number of optimised parameters to as few as possible; the reason of it is explained below. Therefore the assessor's experience is of significance when finding out the compromise between the low number of optimised parameters and the quality of data fit.

One can fit any line or curve to any, even heavily scattered points, by means of the more and more complicated formulas with many adjustable parameters. But it creates at least two problems in thermodynamic assessment practice: one is known as "zig-zag" behaviour, causing the curve strictly fitted to the "cloud" of scattered points by a plenty of parameters following "from point to point" direction, resulting in "zig-zag" shape. It obviously does not reflect the trend of the property, represented by scattered points and may in some cases create false image of the property itself or the phenomenon, as well.

Another problem of "overparametering" the thermodynamic functions is, when extrapolating their values to high temperatures, and multiparameter ΔG formulas for phases

of the system considered may cause the unusual behaviour. The example of this is shown below on the phase diagram of Co-Si system, calculated by Choi [5], using “only” eight parameter relation for the excess term of the Gibbs energy of liquid phase. As can be seen on Fig. 8, the precipitation of the solid phases, known as “artifacts”, occurs over the liquid phase existence range, and their Gibbs energy curves calculated at 1900 K, Fig. 9, confirm this phenomenon.

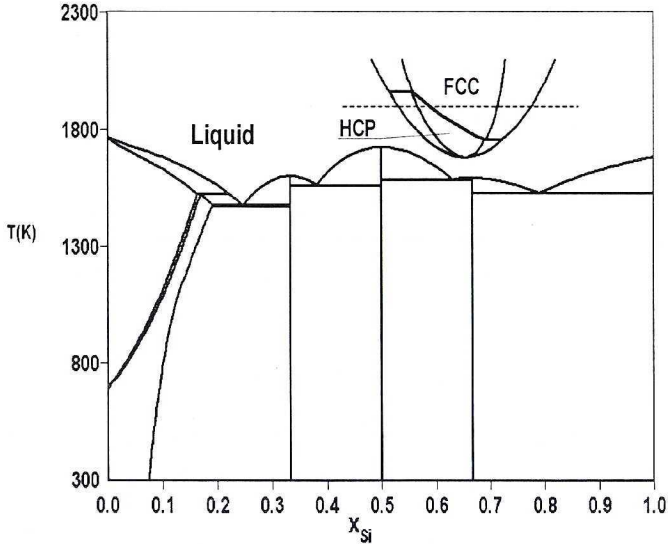


Fig. 8. Precipitation of “artifacts” in the Co-Si system

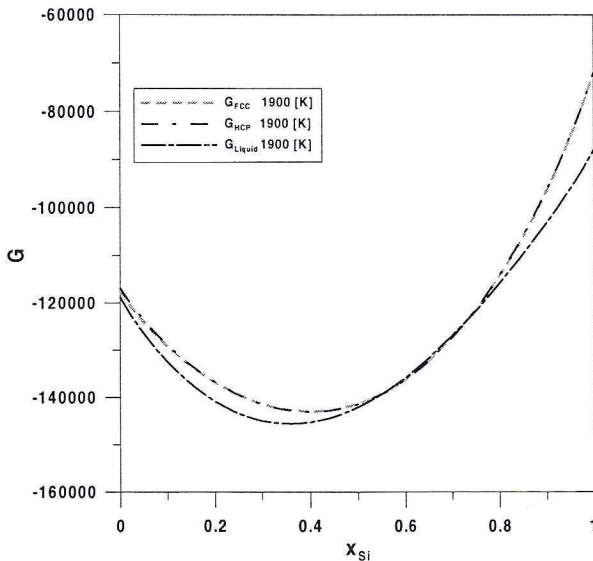


Fig. 9. Gibbs energy curves for “artifacts”

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