

Solubility calculation of poorly soluble components in solid α -phase from thermodynamic parameters of interacting elements

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Parametric expressions are obtained for determining the limiting solubility of poorly soluble components in the solid α -phase by the thermodynamic parameters of interacting elements. In the derivation of the expressions, two approaches are considered. The first approach uses a temperature-independent limiting distribution coefficient for behavior of an ideal system. In the second method, the calculation is carried out taking into account the deviation from ideal behavior through the temperature-dependent partial enthalpy of dissolution of the second component in the solid α -phase. The results of calculations of the solubility of the second component for such systems as Cd–Tl, Zn–Sn, Te–As, Te–Cu using the obtained expressions are presented. It was shown that the solubility of the second component is less than 1 at.% in the investigated systems. Relative deviations of the limiting solubility values obtained by different calculation methods have been determined. The interpretation for the scatter in the calculated data on the solubility of poorly soluble components in the solid α -phase is given.

Keywords: solid α -phase, solubility, interfacial equilibrium, limiting separation coefficient, partial enthalpy of dissolution.

Розрахунок розчинності малорозчинних компонентів у твердій α -фазі за термодинамічними параметрами. *О.П.Щербань, О.А.Даценко.*

Отримано параметричні вирази для визначення граничної розчинності малорозчинних компонентів у твердій α -фазі за термодинамічними параметрами взаємодіючих елементів. При виведенні виразів розглянуто два підходи. Перший підхід використовує граничний коефіцієнт розподілу, що не залежить від температури, для ідеальної поведінки системи. У другому методі розрахунок проводиться з урахуванням відхилення від ідеальної поведінки через залежну від температури парціальну ентальпію розчинення другого компонента у твердій α -фазі. Приведено результати застосування отриманих виразів для розрахунку розчинності другого компонента для таких систем як Cd–Tl, Zn–Sn, Te–As, Te–Cu. Показано, що досліджуються, системах розчинність другого компонента становить < 1 ат.%. Визначено відносні відхилення значень граничної розчинності компонентів, отриманих різними розрахунковими методами. Дана інтерпретація розкиду отриманих розрахункових даних розчинності малорозчинних компонентів у твердій α -фазі.

Получены параметрические выражения для определения предельной растворимости малорастворимых компонентов в твердой α -фазе по термодинамическим параметрам взаимодействующих элементов. При выводе выражений рассмотрены два подхода. Первый подход использует не зависящий от температуры предельный коэффициент распределения для идеального поведения системы. Во втором методе расчет проводится с

учетом отклонения от идеального поведения через зависящую от температуры парциальную энтальпию растворения второго компонента в твердой α -фазе. Приведены результаты применения полученных выражений для расчета растворимости второго компонента для таких систем как Cd-Tl, Zn-Sn, Te-As, Te-Cu. Показано, что в исследуемых системах растворимость второго компонента составляет < 1 ат.%. Определены относительные отклонения значений предельной растворимости компонентов, полученных разными расчетными методами. Дана интерпретация разброса полученных расчетных данных растворимости малорастворимых компонентов в твердой α -фазе.

1. Introduction

Analysis of known state diagrams (SD) of binary metal systems [1, 2] shows that in most cases, the systems are characterized by complete insolubility, limited and unlimited solubility of components in the solid state. The formation of solid solutions occupies an important place in solid state thermodynamics. Both in nature and in technology, we constantly have to deal with solutions, and not with pure components. Pure substances are only a limiting state, which is never actually reached. High-purity metals obtained in modern technology by vacuum distillation and zone melting methods, still contain negligible amounts (10^{-6} %) of impurities and are essentially solutions.

Binary systems with complete insolubility of components are of particular interest. Since the absolute insolubility of the components in each other does not exist, the SD should have a line of limited solubility of the α -phase as a function of temperature and composition. The absence of such lines is due to the fact that in some binary systems, the regions of solid solutions of the α -phase are rather narrow (< 1 at.%), which complicates their exact experimental determination. Many systems belong to this type of SD, such as Cd-Na, Cd-Tl, Te-As, Te-Cu, Te-Ga, Zn-Sn, etc. For these and similar systems, the representation of the region of primary solid solutions is impossible on ordinary scales on SD (assumed solidus lines coincide with the ordinate axis of the pure components). Therefore, for systems with low solubility of the second element in the solid α -phase, calculation methods for determining the components solubility are of practical interest.

Earlier, authors of this work proposed the computational method for determining the solubility [3–5], taking into account the thermodynamics of phase equilibria (equilibrium distribution coefficient k_{0B}) and parameters of liquidus lines of known SD. This work is a sequel of research in this direction. It is of interest to determine the solubility only by thermodynamic values of

components of binary systems. The aim of the work is to develop a computational method for determining the solubility of poorly soluble components in the solid α -phase by the thermodynamic parameters of interacting elements.

2. Calculation method

This paper discusses two different approaches to determining the solubility of components with low solubility in the solid α -phase by the thermodynamic parameters of the components.

The first approach considers the case of ideal solution; the corresponding expression describes the limited concentration x_{SB} of component B using the following parameters: enthalpy change ΔH_{MB} on melting component B ; the melting point T_{MA} of the main component A ; entropy change ΔS_{MB} during melting of component B ; the universal gas constant R ; and temperature-independent limiting distribution coefficient k_{0limB}^A of component B in the base A . It should be noted that reference experimental and calculated data on values k_{0limB}^A for systems with low solubility are very limited. We have developed the method for determining limiting coefficients for such systems, which is described in [6, 7]. The values k_{0limB}^A obtained there were used in the calculations in this work.

The second approach took into account the deviation of the system from ideal behavior. In this case, the expression for x_{SB} includes the same thermodynamic parameters as in the first case, but instead of the parameter k_{0limB}^A , temperature-dependent partial enthalpy $\overline{\Delta H_B^\alpha}$ of dissolution of component B in the solid α -phase is introduced. To determine x_{SB} in the systems under study, the values $\overline{\Delta H_B^\alpha}$ were taken from [8], which describes a method for determining this value. The values of the other thermodynamic parameters were taken from [9]. Analytical expressions for determining the solubility of poorly soluble

components in the solid α -phase are given below. The obtained expressions are based on the fundamental law of distribution, which describes the equilibrium between solid and liquid solutions at a constant temperature, for example, the distribution of impurities between the solid and liquid phases during crystallization. This phenomenon is effectively used for purification of materials by methods of directional crystallization.

The expression for the distribution of the main component A over the liquid-solid interface was obtained from the condition of equality of chemical potentials $\mu_{SA} = \mu_{LA}$ for an ideal solution [9]:

$$\ln\left(\frac{x_{SA}}{x_{LA}}\right) = \frac{\Delta H_{MA}}{R} \left(\frac{1}{T} - \frac{1}{T_{MA}} \right). \quad (1)$$

Assuming that these binaries satisfy the following relationships:

$$x_{SA} = 1 - x_{SB}, \quad (2)$$

$$x_{LA} = 1 - x_{LB} \quad (3)$$

after some transformations and assumptions [9], an expression can be obtained for the concentration of the dissolved component B in the liquid and solid phases as a function of temperature:

$$x_{LB} - x_{SB} = \frac{\Delta H_{MA}}{R} \left(\frac{1}{T} - \frac{1}{T_{MA}} \right). \quad (4)$$

It should be noted that equation (4) is derived under the assumption that the chemical potential of the main component A (μ_A) is the same in the liquid phase and in its pure form for the ideal behavior of the system. In this case, it is assumed that the melting enthalpy ΔH_{MA} is constant in the investigated temperature range.

In [9, 10], the expression is given for the ratio of concentrations of component B in liquid and solid α -phases:

$$\ln \frac{x_{SB}}{x_{LB}} = \frac{T_{MA}}{T} \ln k_{0\text{lim}B}^A - \frac{\Delta S_{MB}}{R} \left(\frac{T_{MA}}{T} - 1 \right), \quad (5)$$

where x_{LB} is the concentration of the component B dissolved in the liquid phase at temperature T ; x_{SB} is the concentration of the limiting solubility of component B in the α -phase at temperature T ; T is the temperature of interfacial equilibrium.

Equation (5) was obtained under the assumption that the chemical potentials $\mu_{LB} = \mu_{SB}$ of component B in the liquid and solid phases at equilibrium are equal.

Using expressions (4) and (5), it is possible to obtain an equation for x_{SB} as a function of temperature, excluding the value of x_{LB} . Solving (4) together with (5) and introducing corresponding parameters, the following parametric expression was found for the solubility of component B in the solid α -phase:

$$x_{SB} = \frac{D(T)e^{C(T)}}{1 - e^{C(T)}}, \quad (6)$$

where,

$$D(T) = \frac{\Delta H_{MA}}{R} \left(\frac{1}{T} - \frac{1}{T_{MA}} \right),$$

$$C(T) = \frac{T_{MA}}{T} \ln k_{0\text{lim}B}^A - \frac{\Delta S_{MB}}{R} \left(\frac{T_{MA}}{T} - 1 \right),$$

The thermodynamic quantities in these expressions are the same as in the expression (5).

The expression (6) includes, in addition to ΔH_{MA} , ΔH_{MB} , ΔS_{MB} , T_{MA} , and R , also the temperature T and the coefficient of the limiting equilibrium T and the limiting distribution coefficient of component B in base A . The limiting distribution coefficient $k_{0\text{lim}B}^A$ characterizes the behavior of the system in the region of low concentrations of the second component and is a constant value that does not depend on temperature and concentration [6, 7, 9]. Since the derivation of Eq. (6) assumed the equality of chemical potentials for an ideal solution (1) $\mu_{SA} = \mu_{LA}$, the values of x_{SB} obtained from (6) characterize the ideal behavior of the system upon dissolution of the second component. To determine the solubility of the second component, taking into account the deviation from ideal behavior, we have considered another approach. One of variables characterizing this deviation is the activity of the second component, which is related to the partial dissolution enthalpy $\Delta \bar{H}_B^\alpha$ of a solid component in the α -phase [8].

Based on the consideration of the thermodynamic properties of component A in the solid α -phase and in the liquid phase, the following expression for the solubility of component B in the liquid phase x_{LB} was given in [11].

$$\ln x_{LA} = \ln(1 - x_{LB}) = \frac{\Delta H_{MA}}{R} \left(\frac{1}{T_{MA}} - \frac{1}{T} \right), \quad (7)$$

where x_{LA} is the concentration of the main component A in the liquid phase at temperature T .

Equation (7) describes the liquidus line for equilibrium with the α -phase.

Also in [11], from the condition of equality of chemical potentials, $\mu_{LB} = \mu_{SB}$, in equilibrium, for the ratio of the concentrations of component B in the liquid and solid phases, the following expression was obtained:

$$\ln \frac{x_{SB}}{x_{LB}} = \frac{\Delta H_{MB} - \overline{\Delta H}_B^\alpha}{RT} - \frac{\Delta S_{MB}}{R}, \quad (8)$$

where $\overline{\Delta H}_B^\alpha$ is partial enthalpy of dissolution of the component in the solid α -phase; other thermodynamic values are the same as in expression (7).

If the x_{LB} value from equation (7) enters into the equation (8), x_{SB} as a function of temperature is obtained. By performing the same procedure, designating the right-hand sides of equations (7) and (8) as parameters $D(T)$ and $C(T)$, we obtain the following expression:

$$x_{SB} = e^{C(T)}(1 - e^{D(T)}) \quad (9)$$

where

$$D(T) = \frac{\Delta H_{MA}}{R} \left(\frac{1}{T_{MA}} - \frac{1}{T} \right),$$

$$C(T) = \frac{\Delta H_{MB} - \overline{\Delta H}_B^\alpha}{RT} - \frac{\Delta S_{MB}}{R}.$$

Thermodynamic quantities in these expressions are the same as in (7) and (8).

3. Results and discussion

Expression (9) contains $\overline{\Delta H}_B^\alpha$ — the value of the partial enthalpy of dissolution of the component in the solid α -phase; the reference data for this value are very limited. The x_{SB}/x_{LB} ratio in equation (8) is the equilibrium distribution coefficient k_{0B} , reference data for which are very extensive, for example, in [12]. Therefore, knowing the k_{0B} value, it is possible to determine the $\overline{\Delta H}_B^\alpha$ value and use it for calculations of x_{SB} in expression (9). In [8, 13], authors developed the calculation method for deter-

mining $\overline{\Delta H}_B^\alpha$ both for systems with low solubility and for systems with limited solubility of component B in the solid α -phase.

Resulting equations (6) and (9) have an exponential form and are parametric expressions for determining the limiting solubility of component B in the solid α -phase. Expression (6) characterizes the ideal behavior of binary systems, since ignores the dependence of the distribution coefficient on the temperature; and the equation (9) takes into account the deviation of interaction of components from ideal through temperature dependence of the enthalpy of partial dissolution of the second component in the solid phase. The applicability interval of equations (6) and (9) extends from the melting point of the pure component to the temperature of the eutectic transformation.

It should be noted that expressions (6) and (9) may be used to assess the solubility of the second component in systems with limited solubility. Such estimations are useful for comparing experimentally obtained data of solubility with calculated values for thermodynamic parameters.

The Table shows the calculated data obtained using expressions (6) and (9) for the solubility of component B in the base A for the binary systems under study. The calculations were performed for given temperatures T , k_{0limB}^A limiting distribution coefficients and $\overline{\Delta H}_B^\alpha$ partial enthalpies of dissolution. The fifth column shows the x_{SB} values previously obtained in [8] using the temperature-dependent equilibrium distribution coefficients k_{0B} and parameters of liquidus lines of phase diagrams.

As can be seen from the Table, the concentrations of limiting solubility for the systems under study and selected parameters obtained by different methods differ from each other. To assess the scatter of the obtained data, the comparative criterion $\delta, \%$ was used:

$$\frac{x_{SB}}{x_{SB}(T)} = 1 \pm \delta, \quad (10)$$

where x_{SB} is the calculated component solubility for the ideal system behavior; $x_{SB}(T)$ is the determined solubility of the component, taking into account the deviation from the ideal behavior of the system.

Thus, the δ values can be considered as the "activity" of the second component when it is dissolved in the solid phase. In

Table. Calculated values of the limiting solubility of components x_{SB} , at.% in Cd-Tl, Zn-Sn, Te-As, Te-Cu systems and their relative deviation δ ,%

System	T , °C	$\overline{\Delta H}_B^\alpha$, J/mol	k_{0limB}^A [5, 7]	x_{SB} , at.%, [8]	x_{SB} , at.% (6)	x_{SB} , at.% (9)	$\delta_1 \times 100$, %	$\delta_2 \times 100$, %
Cd-Tl	295.09	15010	0.05	0.25	0.25	0.23	0	8.7
	256.08	15570		0.90	0.5	0.44	55.5	13.6
	222.55	16050		1.40	0.6	0.51	42.8	17.6
Zn-Sn	403.12	11830	0.07	0.24	0.21	0.25	87.5	16.0
	356.93	14400		1.45	0.61	0.55	42.0	10.9
	229.89	17940		1.09	0.66	0.52	60.5	26.9
Te-As	443.35	32180	0.006	0.013	0.015	0.015	15.3	0.0
	440.21	32280		0.019	0.022	0.021	15.8	4.7
	406.94	33370		0.059	0.071	0.064	20.3	10.9
Te-Cu	440.88	24660	0.05	0.15	0.18	0.17	20.0	5.8
	415.37	25150		0.46	0.62	0.55	34.8	12.7
	351.60	26380		0.69	1.2	0.95	73.9	26.3

the Table, δ_2 is the deviation of the values obtained by formulas (6) and (9). For comparison, the values of the deviations of the solubility δ_1 obtained using the equilibrium distribution coefficients k_{0B} are given. [8]. In [8], the values of the activity of component B in the solid α -phase were obtained as a function of temperature for the systems under study; they correlate with some values of the comparative deviations δ_1 ,%. The estimation of the relative deviation δ_2 ,% of the dissolution concentration shows that the values obtained using the proposed expressions with limiting coefficients k_{0limB}^A and partial enthalpies $\overline{\Delta H}_B^\alpha$ of dissolution of the second component in the solid α -phase, have the range from 0 % to maximum 26.3 % for the Te-Cu system and 26.9 % for the Zn-Sn system. The relative scatter of the values δ_1 ,%, obtained with the limiting k_{0limB}^A and equilibrium k_{0B} [8] distribution coefficients is much larger. The maximum data scatter is, for example, up to 73.9 % for the Te-Cu system and up to 87.5 % for the Zn-Sn system. This is probably due to the large contribution of the temperature dependence of k_{0B} in calculating the limiting concentration of dissolution.

In the formulas for the calculations, concentrations in molar fractions were used, while Table shows the recalculated values of concentrations in at.% for a more practical presentation of the results obtained.

The scatter of the solubility data calculated by different methods is explained by the choice of equilibrium conditions when deriving the expressions, the accuracy of the reference values of thermodynamic quantities, the accuracy of the experimentally constructed curves of liquidus lines in phase diagrams, etc., but the main contribution is made by the temperature-dependent values of k_{0B} and $\overline{\Delta H}_B^\alpha$.

Thus, when choosing a computational method for determining the limiting solubility of components, it is necessary to take into account all sorts of aspects, including those associated with deviations from the ideal behavior of the system, which can lead to errors in the results obtained by computational methods.

4. Conclusions

Parametric expressions for determining the solubility of poorly soluble components in the solid α -phase are obtained by the thermodynamic parameters of interacting elements. When deriving expressions, two approaches were used: the first — for the ideal behavior of the system when the second component dissolves; and the second — taking into account the deviation from the ideal behavior. It was shown that the solubility of the second component in the systems under study is <1 at.%.

The results of applying the obtained expressions for calculating the second component solubility are presented for the sys-

tems Cd–Ti, Zn–Sn, Te–As, Te–Cu. For the systems under study and the selected parameters, the values of the limiting solubility concentrations obtained by different methods differ from each other. The relative deviations of the limiting solubility values calculated by different methods were determined. When investigated by determining the partial enthalpy of dissolution ΔH_B^0 , the relative spread is from 0 % to a maximum of 26.3 % for the Te–Cu system and 26.9 % for the Zn–Sn system. The relative spread of solubility values obtained from equilibrium distribution coefficients k_{0B} is 3...4 times higher. The main reason for the scatter in the solubility values calculated by different methods is the temperature dependence of the equilibrium distribution coefficients k_{0B} and partial enthalpies of dissolution ΔH_B^0 used in the calculations.

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