Thermodynamic proof of the existence of compounds in the phase diagrams of systems without solid solutions I. Description of the method and its testing on a model system

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Thermodynamic analysis of the course of liquidus curve of substance A in the system A—B makes it in principle possible to determine the existence of a complex compound which occurs in this system. If the behaviour of the system is not very far from ideality, the stoichiometric coefficients of the compound and the degree of its thermal dissociation can be calculated as well.

Термодинамический анализ хода кривых ликвидуса вещества А в системе А—В дает принципиальную возможность определить существование комплексного соединения, образующегося в данной системе. Если поведение системы не слишком отклоняется от идеальности, можно также определить стехиометрические коэффициенты соединения и степень его термической диссоциации.

Experimentally determined phase diagrams often raise the question about their principle correctness. Particularly topical is this question in the case of equilibria at higher temperatures when experimental difficulties are responsible for the loss of accuracy which can result in doubts about the existence of a chemical compound in the studied system [1]. There are many examples which show that the existence of compound escaped from attention of researchers or that a great effort was exerted for unsuccessful seeking of a nonexisting compound.

In the present work we intend to show that the presence of a complex chemical compound $Z = A_r B_s$ in the system A—B can be proved or disproved on the basis of thermodynamical analysis of coordinates of a few, and/or in some cases of only one point on the liquidus curves of basic components A or B.

At the proof of existence of a compound, which is the nearest neighbour of the component A, we assume an ideal behaviour of the system and nonexistence of solid solutions on the base of component A. For the proof we need only experimental data on pure component A (the calorimetric value of its enthalpy of fusion ΔH_A^t (calor) and temperature of fusion T_A^t) and coordinates of one point of liquidus curve of the component A. Let us suppose that we know the eutectic point

which is determined by the mole fraction x_A^E of component A in the system A—B and by the temperature of eutectic crystallization T^E . This is the most common case which we meet in praxis.

We shall also show that knowledge of more figurative points on liquidus curve of component A allows to obtain further quantitative information about the compound Z.

Transformation of coordinates

If we admit the possibility of existence of compound Z in the system (assuming that the conditions mentioned above are fulfilled), then the course of liquidus curve of the compound A is not influenced directly by component B but by the compound Z. Then it is advantageous to investigate the figurative points lying on the liquidus curve of component A which is a part of the subsystem A—Z. This approach requires a transformation of composite coordinates. Rules characterizing this transformation can be used for forecast (or as a proof) that the nearest neighbour of component A in the phase diagram A—B is not the component B but the chemical compound Z.

The transformation of composite coordinates of component A from the system A-B to the system A-Z is based on the following scheme

$$x A + (1-x)B = y A + (1-y) A_{r}B_{s}$$
 (1)

where x is the mole fraction of component A in the untransformed system A—B and y is the mole fraction of the same component A in the transformed system A—Z.

The transformed composition coordinate is given by the expression

$$y = \frac{(r+s)x - r}{(r+s-1)x - r + 1}$$
 (2)

Application of the Le Chatelier—Shreder equation to the analysis of figurative points on the liquidus curve of the component A

The principle of the method described in this paper consists in the application of the Le Chatelier—Shreder equation [2—4] to the analysis of figurative points of liquidus curve of component A. According to this equation it generally holds

$$\ln a_{\rm A} = \frac{\Delta H_{\rm A}^{\rm f}}{R} \left(\frac{1}{T_{\rm A}^{\rm f}} - \frac{1}{T} \right) + f(\Delta C_{\rm PA}^{\rm V/s}) \tag{3}$$

where a_A is the activity of component A and R is the gas constant. If we assume

that the quantity ΔH_A does not depend on temperature, the second term in eqn (3) equals zero.

If we assume an ideal behaviour of the system, the activity can be replaced by the mole fraction of the component in the mixture. Then for an arbitrary point M on the liquidus curve of component A, which is characterized by the composition y_A^M and temperature T^M , we can calculate (rearranging eqn (3)) the value ΔH_A^r (calc)

$$\Delta H_{A}^{t} (calc) = R \frac{T_{A}^{t} T^{M}}{T^{M} - T_{A}^{t}} \ln y_{A}^{M}$$
(4)

and compare it with the calorimetric value $\Delta H'_A$ (calor). If the agreement between both the calculated and calorimetric values of enthalpy of fusion of component A is good, it means that the system A—Z was chosen correctly and that the mole fraction y_A of component A in the system A—Z corresponds to true mole fraction of component A in the system. And oppositely, if there is poor agreement between the calorimetric and calculated value of $\Delta H'_A$, our assumption about composition of the component Z is not correct or even the compound does not exist.

Therefore, the existence of chemical compound influences the expression

$$a_{\rm A}^{\rm M} = y_{\rm A}^{\rm M} = f(x_{\rm A}^{\rm M}) \tag{5}$$

Alternatively eqn (3) can be used for calculation of thermodynamic activity of component A if the calorimetric value is used for enthalpy of fusion and it can be compared with y_{A}^{M} . Provided the assumption about ideality holds, the ratio

$$a_{\rm A}^{\rm M}/y_{\rm A}^{\rm M} = D \tag{6}$$

characterizes correctness of the chosen concentration base. We shall call this ratio the coefficient of adequacy of the choice of concentration base (further only coefficient of adequacy) because its value indicates (similarly as agreement between ΔH_A^r (calc) and ΔH_A^r (calor)) correctness of the choice of the concentration base and, therefore, also correctness of the assumption about the existence of a compound of given composition in the system in question.

Application of the method to the model system A-(Z)-B

Applicability of the described method will be tested on the example of an ideal model system. The necessary thermodynamic data are chosen so as to reflect values in real mixtures of the type MF—AlF₃ because the method will be applied to these systems. We shall show that the method gives more information if we use more figurative points for the analysis. This allows also to evaluate the influence of possible experimental errors if the method is applied to real systems.

Calculation of a model system

Let us assume the existence of an ideal system with components A and B which form a congruently melting compound Z = AB. There are no solid solutions on the base of component A in the system. Let the pure component A be characterized by $T_A^t = 1250$ K and ΔH_A^t (calor) = 25 kJ mol⁻¹. Further we choose an "experimental" point M. It may be chosen arbitrary. However, in our case, we shall choose it so that it is the eutectic point in the ideal system A—Z. Therefore, it can be calculated as an intersection of the liquidus curves of components A and Z. The compound Z is characterized by the following thermodynamic data: $T_z^t = 1600$ K, ΔH_z^t (calor) = 80 kJ mol⁻¹. In this stage we assume that the compound does not dissociate or that the degree of dissociation is negligible.

The calculated coordinates of the eutectic point in the original system A—B are following: $x_A^E (A-B) = 0.8910$, $T^E = 1185.7$ K.

Application of the method to the case of one figurative point on the liquidus curve of component A

Let us suppose that we know experimental data of the eutectic point in the system A—B (x_A^E, T^E) and thermodynamic values ΔH_A^r (calor), T_A^r . We do not know if there is any chemical compound in this system. Then, using the quasi-experimental data given in the former section we can find out if the nearest neighbour of component A is a compound or the pure component B.

First using eqn (3) we calculate the activity of component A in the eutectic point: $a_A^E = 0.8777$. Comparison of the values of a_A^E and x_A^E indicates (D = 0.9843) that a compound may be present in this system. Therefore we shall make a sequence of trials with different combinations of stoichiometric coefficients r and s and make transformations of the concentration coordinate of the eutectic point for each case (see eqns (1) and (2)). Then we can calculate the values of $\Delta H'_A$ (calc) and compare them with $\Delta H'_A$ (calor) or we test how the value of D approaches 1. The best agreement is achieved when the correct compound is found.

If we know only one figurative point on the liquidus curve, the stoichiometric coefficients r and s cannot be calculated directly because we have only one equation with two unknown parameters $y_A^M = f(x_A^M, r, s)$. However, there are not many reasonable combinations of r and s and therefore it is not difficult to find the right compound. Usually it is sufficient to test integers from 1 to 5. This approach was used also in this case and the results for combinations of r and s ranging from 1 to 3 are summarized in Table 1. It readily follows that the compound should have the composition AB.

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System	$y^{E} = f(x_{A}^{E})$	$\Delta H'_{\rm A}$ (calc)/J mol ⁻¹	D
 А—В	x = 0.8910	22118	0.985
A—AB	(2x-1)/x = 0.8777	25008	1.000
A-A ₂ B	(3x-2)/(2x-1) = 0.8606	28768	1.020
A—A ₃ B	(4x-3)/(3x-2) = 0.8380	33863	1.047
$A - A_2 B_2$	(4x-2)/(3x-1) = 0.9348	12912	0.939
$A - A_3 B_2$	(5x-3)/(4x-2) = 0.9303	13845	0.943
A-AB ₂	(3x-1)/2x = 0.9388	12097	0.935
A-AB ₃	(4x-1)/3x = 0.9592	30097	0.915
$A - A_2 B_3$	(5x-2)/(4x-1) = 0.9575	8326	0.917
$A - A_3 B_3$	(6x-3)/(5x-2) = 0.9556	8704	0.918

Calculated values of ΔH_A^r (calc) and D for different systems

Application of the method to the case of two figurative points on the liquidus curve of component A

This task will be solved for the same set of data as in the previous case. Let us further suppose that we know coordinates of another point Q on the liquidus curve of component A: $T^{Q} = 1200$ K, $x_{A}^{Q} = 0.9129$.

In this case it is not necessary to seek the composition of compound by solution of eqns (4) and (6) for all possible combinations of r and s but we can calculate these stoichiometric coefficients directly from the equations

$$a_{\rm A}^{\rm E} = y_{\rm A}^{\rm E} = \mathbf{f}(x^{\rm E}, r, s) \tag{7}$$

$$a_{\rm A}^{\rm Q} = y_{\rm A}^{\rm Q} = \mathbf{f}(x_{\rm A}^{\rm Q}, r, s) \tag{8}$$

For the chosen system we insert in the equations the following values: $a_A^E = 0.8777$, $a_A^Q = 0.9046$, $x_A^E = 0.891$, and $x_A^Q = 0.9129$. We obtain

$$s = 0.9995$$
; $r = 0.9977$

which is in good agreement with the precise values of these coefficients (r = 1, s = 1).

It may be remarked that application of the Le Chatelier—Shreder equation to the coordinates of two points on the liquidus curve of component A can be used also in another way, viz. for the identification of compound in the system A—B in the case if we do not know the quantity T_A .

If we know points M and N on the liquidus curve of component A which fulfil the condition

$$x_A^E \leq x_A^M < x_A^N < 1$$

then application of eqn (3) after elimination of the parameter T_A^t yields

$$\Delta H_{A}^{f} \text{ (calc)} = R \, \frac{T^{M} T^{N}}{T^{N} - T^{M}} \ln \frac{a_{A}^{M}}{a_{A}^{N}} \tag{9}$$

It can be proved that if the system deviates from ideality this procedure gives more reliable information than eqn (4).

Application of the method to the case of three figurative points on the liquidus curve of component A

Until now we have not taken into account a possibility of dissociation of chemical compound Z. Generally, however, the compound can dissociate. The phenomenon of dissociation will influence the expression for activity of component A in the mixture [5].

Let us assume that a pure compound dissociates according to the scheme

$$(1 - b_0) A_r B_s = b_0 r A + b_0 s B$$
(10)

where b_0 is the degree of dissociation of pure compound Z.

For dissociation of compound Z in the mixture with component A it holds

$$(1-y)(1-b) A_r B_s = br(1-y) A + bs(1-y) B$$
 (11)

where b = f(y) is the degree of dissociation of compound Z in the mixture with A. Then the activity of the component A depends also on b

$$a_{\mathsf{A}} = \varphi(\mathbf{y}_{\mathsf{A}}, b) \tag{12}$$

Since the dissociation constants of reactions (10) and (11) are equal we can calculate the value of b for each y_A

$$b = \psi(y_{\mathsf{A}}, b_0) \tag{13}$$

Because according to eqn (2) $y_A = f(x_A, r, s)$, simultaneous solution of eqns (2), (12), and (13) allows to express the activity of component A in each point of the liquidus curve (x_A, T)

$$a_{\rm A} = f\{\phi[\psi(x_{\rm A}, r, s, b_0)]\}$$
(14)

The value of activity a_A can be obtained from eqn (3).

It readily follows that we need to know the coordinates of three points M, N, Q on the liquidus curve of A in order to be able to write a set of three equations

$$a_{A}^{N} = f\{\phi[\psi(x_{A}^{N}, r, s, b_{0})]\}$$

$$a_{A}^{N} = f\{\phi[\psi(x_{A}^{N}, r, s, b_{0})]\}$$

$$a_{A}^{Q} = f\{\phi[\psi(x_{A}^{Q}, r, s, b_{0})]\}$$

(15)

Simultaneous solution of the set of these equations gives three unknown variables: degree of dissociation of pure compound b_0 and its stoichiometric coefficients r and s.

It should be pointed out that eqn (13) is quadratic with respect to the parameter b_0 only in the case of compound of the type AB. For compounds with higher values of stoichiometric coefficients we obtain equations of higher orders. Method of solution of this task will be discussed in a special paper.

It is not without interest to notice that this method revealed a new piece of knowledge useful for thermodynamic analysis of systems with known dissociating compounds. In this case we know the stoichiometric coefficients r and s. Assuming that these systems are close to ideality we can calculate (applying the presented relations) the degree of dissociation of compound knowing only one point on the liquidus curve of component A and further also the degree of dissociation of this pure compound A_rB_s .

Sensitivity of the method

From the data presented in Table 1 it follows that the calculated values of ΔH_A^t differ according to the choice of concentration base with respect to the correct calorimetric value by 11.53% for the system A—B and 15.1% for the system A—A₂B. Even if the numerical results depend on concrete values of ΔH_A^t (calor) and T_A^t , nevertheless they give evidence that the proposed method requires the calorimetric value ΔH_A^t (calor) having precision better than 10%. In opposite case the comparison of calculated and calorimetric value ΔH_A^t indicates uncorrect compound. It is not difficult to fulfil this requirement because the contemporaneous experimental technique yields this quantity with precision approximately $\pm 3\%$.

In praxis we do not know the exact values of ΔH_A^t (calor), T_A^t , T^E , and x^E . Therefore we tested on the model system also the influence of experimental uncertainty on the sensitivity of the proposed method. For this purpose the original model values were intentionally deformed. E.g. instead of ΔH_A^t (calor) = 25 kJ mol⁻¹ the value different by $\pm 1\%$ and $\pm 5\%$ was used and the correct $x^E = 0.891$ was replaced by the value $x^E = 0.901$. Deviation W was evaluated according to the relation

$$W = \frac{V_0 - V}{V_0} \, 100 \tag{16}$$

where V_0 is the correct value of the parameter and V is the deformed value.

From Table 2 it follows that error in any parameter can influence the precision of the method. However, the most important role plays the error in determination of the concentration coordinate of eutectic point.

Τ	a	b	le	2

Deviations $W_{\Delta H}$ and	W_D resulting from the use of the values ΔH_A^f (calor), T_A^f , T^E , and x^E influenced by	
experimental errors. The degree of dissociation b_0 is omitted		

Thermodynamic quantity	Error in experimental determination	Deviation in $W_{\Delta H}$	calculation, % W_{D}
$\Delta H_{\rm A}^{\rm f}$ (calor)	0%	-0.03	0
	-1%	+ 1.03	-0.1
	+1%	-0.97	+ 0.1
	- 5%	+ 5.03	-0.65
	+ 5%	- 5.00	+ 0.65
T_{A}	+ 3 K	+ 4.2	+ 0.6
	-3 K	-4.7	-0.8
$T^{\scriptscriptstyle E}$	+ 3 K	- 5.2	-0.6
	- 3 K	+ 4.7	+ 0.6
x ^E	+ 1 mole %	+ 10.8	+1.4
	-1 mole %	- 11.2	-1.5
b_0	10%	0.3	0.05
	40%	5.5	1.47
	70%	63.0	45.0

The model system A—(Z)—B was used also for estimation of sensitivity of the method of "one point" to the neglecting of dissociation of the compound Z. These calculations are rather extensive and will be not published here. It was found that at a low degree of dissociation the tested method indicates the right compound. It can be estimated that the method using only one figurative point on the liquidus curve fails for the dissociation degree higher than 30-40%.

Discussion

The derived relationships are exactly valid for ideal systems. The extent in which a deviation from ideality influences the precision of the method can be judged from Table 2. As it has been already mentioned, the precision of concentration coordinate of the eutectic point plays a decisive role in this respect. If the activity coefficient does not cause greater shift of the concentration coordinate of the eutectic point than ± 1 mole % and ± 6 K, then the presented relationships can be applied also to real systems.

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