

Method of evaluation of the phase diagram of a system with formation of a compound

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Received 11 June 1981

The method for evaluation of phase diagrams of the systems with complete miscibility in liquid phase and forming a compound is proposed. A true equilibrium constant of the reaction leading to the formation of the compound is assumed. Further we assume a hypothetical phase diagram of a ternary system which arises from the both original components and the new formed compound. Section of such a ternary phase diagram presents the known binary phase diagram which can be determined experimentally. The values of the equilibrium constant and of the interaction parameters for excess Gibbs energy of the ternary system are optimized using a computer. The proposed method is illustrated on examples of experimental data published in literature for the following systems: sodium fluoride—sodium sulfate, potassium fluoride—potassium sulfate, calcium chloride—potassium chloride, and calcium bromide—rubidium bromide.

Предложен метод оценки фазовых диаграмм неограничено смешивающихся систем в жидкой фазе и образующих соединение. Предполагается настоящая константа равновесия реакции, ведущей к образованию соединения а также гипотетическая фазовая диаграмма тернарной системы обеих исходных и новообразующегося компонентов. Разрезом такой фазовой диаграммы образуется известная бинарная фазовая диаграмма, которая определяется экспериментально. С помощью счетчика находятся оптимальные значения констант равновесий и параметры взаимодействия для добавочной свободной энтальпии тернарной системы. Применение метода иллюстрируется с помощью экспериментальных данных заимствованных из литературы для систем: флюорид натрия—сульфат натрия, флюорид калия—сульфат калия, хлорид кальция—хлорид калия и бромид кальция—бромид рубидия.

Phase diagrams of the type solidus—liquidus of the systems forming compounds are in praxis well known and phenomenologically well described. The first attempt for quantitative description of such a phase diagram has been done by *Glasstone* [1]. Later the problem was discussed by *Brynstad* [2] and recently by *Gálová et al.*

[3], who studied the influence of dissociation of the compound on the shape of maximum in the phase diagram. However, none of the mentioned authors have taken into account the deviation from an ideal behaviour of the system and also the fact that experimental data used for evaluation are always loaded with experimental errors. The exact solution of this problem is a complicated task involving phase and chemical equilibria and, moreover, complicated with the necessity of statistical approach.

In the beginning it is necessary to make clear how many components are in the system. Let us assume that we have a system containing two components A and B which react with formation of a compound C and which are with this compound in equilibrium $A + B \rightleftharpoons C$. From the practical point of view it is a binary system containing two original components A, B. In this paper, however, we shall treat the system as a ternary one. We suppose that this approach is not in disagreement with any principle of classical thermodynamics. According to these principles each system must fulfil a requirement of economy, which means that it has to be described by a least possible number of chemical individuals. When chemical reactions occur in the system, the number of components is calculated as the number of all components taking part in the system diminished by the number of chemical reactions which can proceed in the system.

Therefore if we treat our system as ternary one we do it intentionally and with knowledge that its components are bound by a chemical reaction. If we consider the system A—B—C to be ternary one we add the adjective hypothetical because the assumption on existence of pure compound C which arises from the chemical reaction is hypothetical. Nevertheless, if we knew the hypothetical temperature and enthalpy of fusion of the pure component C and also the interaction parameters for ΔG^E of this ternary system we would be able to construct the hypothetical phase diagram of this system (Fig. 1a). Let us assume that we know the values of interaction parameters and of the true equilibrium constant. Then we can calculate composition of such system as a function of composition of the original binary system as it is illustrated in Fig. 1b. Section of the phase diagram of the ternary system along the curve corresponding to the change in composition (it is illustrated by overlapping Figs. 1a and 1b; see Fig. 1c) and following projection to the plane A—B—T gives the well-known shape of phase diagram as it is determined experimentally (Fig. 1d). The presented figures illustrate also the influence of the magnitude of the equilibrium constant. If value of the constant K approaches zero then the curve corresponding to composition of ternary system merges with the base A—B of the triangle. On the other hand, if K is large, the curve corresponding to composition merges with the broken line A—C—B, which results in discontinuity of derivation in maximum of the resulting phase diagram.

It is of interest to point out that up to certain value of the equilibrium constant it can happen that the compound need not to appear in the phase diagram.

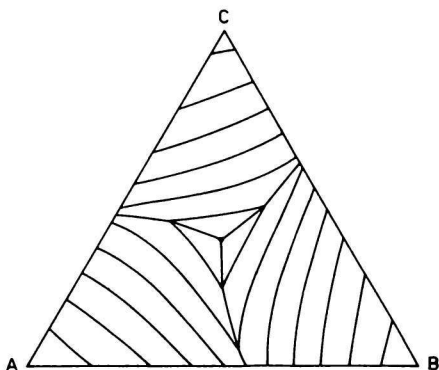


Fig. 1a. Hypothetical phase diagram of a ternary system A—B—C.

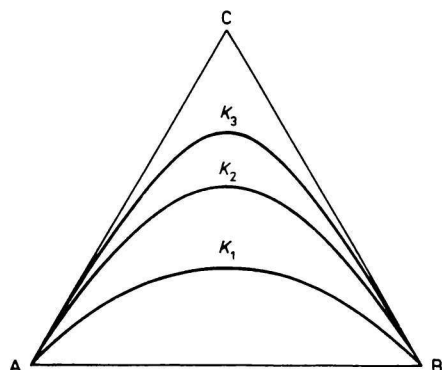


Fig. 1b. Curves corresponding to composition of the ternary system plotted as a function of composition of the original binary system A—B for different values of the equilibrium constant K .

$$K_1 = 3; \quad K_2 = 15; \quad K_3 = 50.$$

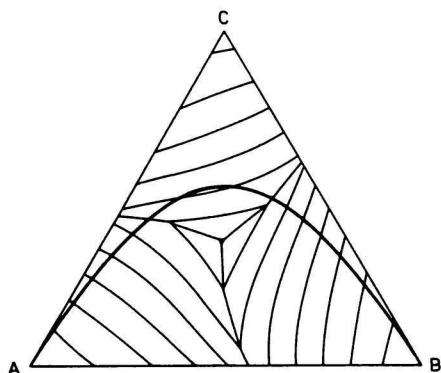


Fig. 1c. Section through the hypothetical phase diagram of a ternary system along the curve corresponding to composition of the ternary system ($K = 15$).

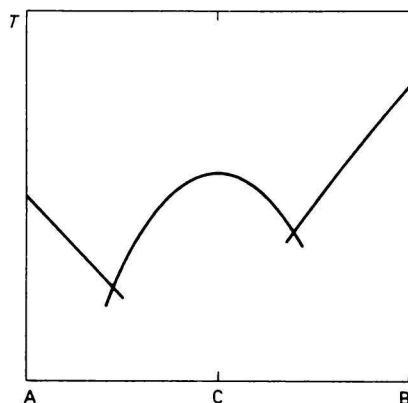


Fig. 1d. Projection of the section of the phase diagram into the plane A—B—T.

Nonideality of the system

If we choose the simplest way for description of the excess Gibbs energy in a binary system

$$\Delta G^E/RT = \alpha x_1 x_2 \quad (1)$$

then for the activity coefficients the following relationships can be written

$$\ln \gamma_1 = \alpha x_2^2 \quad (2a)$$

$$\ln \gamma_2 = \alpha x_1^2 \quad (2b)$$

In a similar way we can express these quantities in ternary system

$$\Delta G^E/RT = \alpha x_1 x_2 + \beta x_1 x_3 + \delta x_2 x_3 \quad (3)$$

$$\ln \gamma_1 = \alpha(1 - x_1)x_2 + \beta(1 - x_1)x_3 - \delta x_2 x_3 \quad (4a)$$

$$\ln \gamma_2 = \alpha x_1(1 - x_2) - \beta x_1 x_3 + \delta(1 - x_2)x_3 \quad (4b)$$

$$\ln \gamma_3 = -\alpha x_1 x_2 + \beta x_1(1 - x_3) + \delta x_2(1 - x_3) \quad (4c)$$

where x_1 , x_2 , and x_3 are the mole fractions of corresponding components and α , β , δ are the interaction parameters.

The chemical equilibrium reaction

The equilibrium composition of a system in which a chemical reaction $A + B \rightleftharpoons C$ takes place can be described by the true equilibrium constant which is defined as

$$K = a_c / (a_A \cdot a_B) \quad (5)$$

where a_i are the activities of components. The activities are generally expressed by the product $a_i = a_i^* \cdot \gamma_i$, where a_i^* are the activities of components in an ideal mixture and γ_i are the corresponding activity coefficients. In ionic systems with one common ion (we apply the method for this class of systems) the activity of components in ideal mixture calculated according to Temkin's model equals mole fraction of the component. Therefore we can write $a_i = x_i \cdot \gamma_i$. Mole fractions of components in the ternary system denoted as x_i can be expressed through the mole fraction x which determines stoichiometric composition of the binary system

$$x_A = 1 - x - x \cdot y; \quad x_B = x - y + x \cdot y; \quad x_C = y \quad (6a-c)$$

After transformation of the relation (5) into logarithmic form and replacing $\ln \gamma_i$ by expressions (4a-c) it is possible to determine the equilibrium composition for known values of the equilibrium constant K and of the interaction parameters. The change of concentration of the compound y as a function of composition of the original binary system is illustrated in the triangle of ternary system in Fig. 1b.

Phase equilibrium

It is assumed that the phase equilibrium solidus—liquidus can be described by the LeChatelier—Shreder equation in its simplest form (for $\Delta H_i = \text{const}$)

$$\ln a = \Delta H_i / R(1/T_i - 1/T) \quad (7)$$

or in a more precise form ($\Delta H_f = f(T)$, $\Delta C_p = \text{const}$)

$$\ln a = \Delta H_f / R(1/T_f - 1/T) + \Delta C_p / R(T_f/T - 1 - \ln(T_f/T)) \quad (8)$$

where ΔH_f and ΔC_p are the change in enthalpy, respectively change in heat capacity at melting, T_f is temperature of fusion of pure component and R is the gas constant. For condition of constant temperature these equations yield the course of isotherms which are essentially isoactivity curves.

If we know T_f and ΔH_f (respectively also ΔC_p) for pure substances and the interaction parameters from the relationships (1) and (3), eqns (7) or (8) allow us to construct the liquidus curves of the binary system or liquidus surfaces of the ternary system. Since plotting of ternary phase diagrams would require a three-dimensional space, only projection of isothermal curves of the ternary diagram is usually presented. If we choose hypothetical values of ΔH_{fC} and T_{fC} we can plot the hypothetical ternary phase diagram of the system A—B—C (Fig. 1).

Phase and chemical equilibria

A combination of phase and chemical equilibria which leads to the formation of phase diagram with chemical compound can be illustrated by means of Figs. 1a—c. When we do a section through the hypothetical ternary system (see Fig. 1c which results from overlapping of Figs. 1a and 1b) and when we project this section into the plane A—B—T (Fig. 1d) we obtain shape of the binary phase diagram in which a compound is formed as it can be determined experimentally. Using this step we have reduced the number of components from 3 to 2 (only one being independent), which is in accord with requirements of classical thermodynamics. Advantage of this procedure is in that we know which influences can here have an effect and we can imagine their consequences on the final shape of the phase diagram. *E.g.* if the equilibrium constant is too small, *i.e.* when the section goes under the ternary eutectic point, formation of a compound in the resulting phase diagram will not appear.

This method is very illustrative but it is based on a simplified assumption that the equilibrium constant does not depend on temperature. If we wished to consider also this dependence the situation would be remarkably more complicated.

Optimization of adjustable parameters

As we know in advance neither the value of the equilibrium constant of the chemical reaction leading to formation of the compound nor the values of interaction parameters in expression for the excess Gibbs energy, nor the temperature and enthalpy of fusion of pure compound we need to consider these quantities

to be adjustable parameters and we have to look for such their values that would give the best agreement with an experiment. In praxis we have usually more experimental data than is the number of the adjustable parameters. However, one should take into account that these data are loaded with a certain experimental error. Therefore it is not possible to use any method for a direct calculation of these adjustable parameters and furthermore, in most cases, it is not possible to employ classical regression methods. The only possibility which remains is the necessity to use a fast computer for optimization of adjustable parameters. As a criterion of agreement with experiment we chose the sum of squares of differences between the experimental and calculated temperatures. This choice is in agreement with a principle of polythermal method of determination of phase diagram. (The method based on measurement of solubility at constant temperature would require rather to choose as criterion a sum of squares of deviations of concentrations.)

Results and discussion

The proposed method was used firstly at the evaluation of phase diagrams of the systems NaF—Na₂SO₄ and KF—K₂SO₄. In both systems, which have a common cation, a congruently melting compound is formed. Mole ratio of components in the compound is 1 : 1, their formulas being Na₃SO₄F and K₃SO₄F. Experimental data on these systems have been obtained by Wolters (1910) and Karandeev (1909) and they were taken from Ref. [4].

For the calculation we used the following values of enthalpies of fusion of pure components [5]

$$\begin{array}{ll} \text{NaF: } \Delta H_f/R = 8030/1.9872; & \text{KF: } \Delta H_f/R = 6750/1.9872 \\ \text{Na}_2\text{SO}_4: \Delta H_f/R = 5670/1.9872; & \text{K}_2\text{SO}_4: \Delta H_f/R = 8760/1.9872 \end{array}$$

The change in heat capacity was omitted (they were considered to equal zero). Values of the optimized parameters α , β , δ and of ΔH_{TC} and T_{TC} are summarized in Table 1 together with criteria of fitness between the calculated liquidus curves and the experimental points of phase diagram. Beside a total sum of squares of deviations of temperature, which was minimized, also the corresponding standard deviations as well as the standard deviations for each liquidus curve are presented. The absolute values of interaction parameters are relatively small, which is in agreement with experience obtained for other systems having common cation. The phase diagrams of both systems calculated with optimal parameters are plotted together with experimental data in Figs. 2 and 3.

The further systems which were used for checking of the proposed method are: CaCl₂—KCl and CaBr₂—RbBr. As in the former case also here one congruently

Table 1

Values of optimized parameters and of the corresponding statistical characteristics given for phase diagrams of the systems A—B

Components		Optimized parameters						Statistical characteristics			
A	B	$\ln K$	α	β	δ	T_{ic}	$\Delta H_{ic}/R$	S_0	s_A	s_B	s_C
Na ₂ SO ₄	NaF	-0.03	- 65	1350	- 165	1282	5367	192.1	6.15	1.75	3.08
K ₂ SO ₄	KF	-1.48	- 160	780	-1610	1603	9291	47.2	1.30	3.06	1.83
CaCl ₂	KCl	2.86	-3420	2040	- 680	861	6164	451.2	5.35	6.24	3.19
RbBr	CaBr ₂	-0.61	-2795	-3551	- 911	2062	6460	117.0	2.25	2.94	2.20

S_0 is the sum of squares of deviations ; s_A , s_B , and s_C are the standard deviations for the liquidus curves of components A, B, and C, respectively.

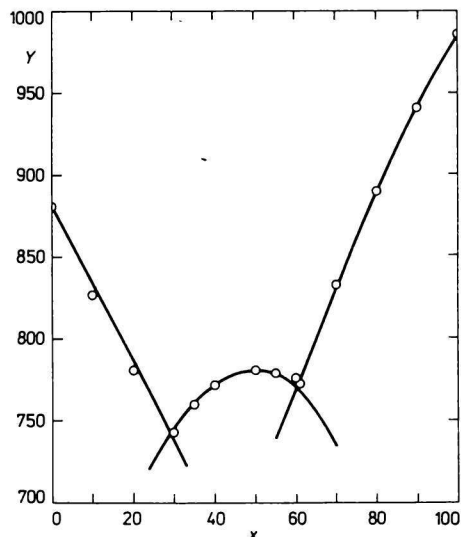


Fig. 2. Calculated curves of liquidus and the experimental points [4] of the phase diagram of the system NaF—Na₂SO₄.

(*x* denotes mole % NaF, *y* is the temperature in °C.)

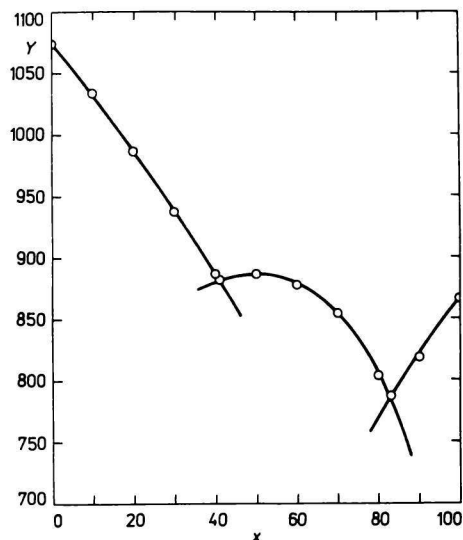


Fig. 3. Calculated curves of liquidus and the experimental points [4] of the phase diagram of the system KF—K₂SO₄.

(*x* denotes mole % KF, *y* is the temperature in °C.)

melting compound with mole ratio of original components 1 : 1 is formed, formulas of the compounds being KCaCl₃ and RbCaBr₃, respectively. The phase diagram CaCl₂—KCl has been measured by Menge (1911) and we quote the data according to Ref. [4]. Phase diagram of the system CaBr₂—RbBr has been measured recently by Emons *et al.* [6]. The values of ΔC_p were neglected again and the values of ΔH_f were taken from [5]

$$\text{CaCl}_2: \Delta H_f/R = 6780/1.9872; \quad \text{CaBr}_2: \Delta H_f/R = 6950/1.9872$$

$$\text{KCl}: \Delta H_f/R = 6340/1.9872; \quad \text{RbBr}: \Delta H_f/R = 5570/1.9872$$

The values of optimized parameters and of statistical characteristics are presented in Table 1. It is interesting to point out that the absolute values of the interaction parameters are higher in comparison with the systems with common cation. Phase diagram of the system CaCl₂—KCl is plotted in Fig. 4.

In the case of the system CaBr₂—RbBr we can substantially improve the fitness between experimental and calculated data if we assume that the value of enthalpy

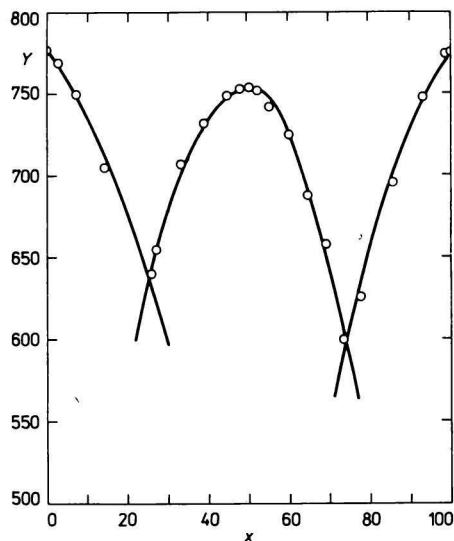


Fig. 4. Calculated curves of liquidus and the experimental points [4] of the phase diagram of the system $\text{CaCl}_2\text{—KCl}$.

(x denotes mole % KCl , y is the temperature in $^\circ\text{C}$.)

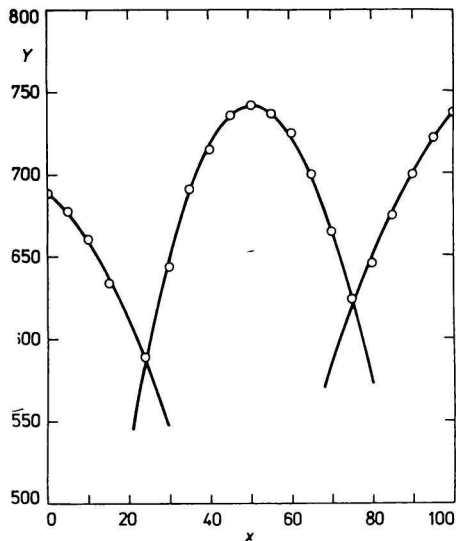


Fig. 5. Calculated curves of liquidus and the experimental points [6] of the phase diagram of the system $\text{CaBr}_2\text{—RbBr}$.

(x denotes mole % CaBr_2 , y is the temperature in $^\circ\text{C}$.)

of fusion of RbBr is unreliable and we allow to optimize it as a further adjustable parameter. The optimized value for enthalpy of fusion of RbBr is $\Delta H_f/R = 4430$. The phase diagram plotted in Fig. 5 corresponds to the latter value.

Conclusion

It follows that it can be advantageous to optimize the values of enthalpy of fusion or eventually also of temperature of fusion of any of the original components in that case if these data are not available or if they are unreliable and also if the compound transforms in another modification. The proposed method can be used also for evaluation of the systems having incongruently melting compound and theoretically also for systems forming more compounds. In the latter case, however, it would be necessary to consider the corresponding number of equilibrium reactions and the number of parameters which should be taken into account would be rather high. Evaluation of the phase diagrams of such systems would require not only reliable experimental data on the phase diagram but also on the enthalpies of fusion of pure components, eventually also on the change of heat capacity under melting.

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Translated by P. Fellner