

Systems with transformed composition coordinates

I. Fundamental relationships

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Phase diagrams of the systems with transformed composition coordinates are discussed. A fundamental law of the transformation is derived. It holds

$$\frac{\Delta H_i^{t,*}}{\Delta H_i^t} = \frac{\ln x_i^*}{\ln x_i}$$

The reciprocal principle for direct transformation is formulated. It is pointed out that there is a connection between a special case of direct transformation and the Temkin expression for activity of component in a binary system.

Разбираются вопросы диаграмм состояния с трансформированными композиционными координатами. Приводится вывод основного закона трансформирования

$$\frac{\Delta H_i^{t,*}}{\Delta H_i^t} = \frac{\ln x_i^*}{\ln x_i}$$

Сформулировался так называемый взаимный принцип прямого трансформирования. Указывается на связь между одним специальным случаем прямого трансформирования и выражением активности компонента бинарной системы по Темкину.

One can often find in literature diagrams (especially phase diagrams) the components of which are multiples of components of the original system. For example the systems NaCl—CaCl₂ or NaF—AlF₃ are often presented in coordinates (NaCl)₂—CaF₂ and (NaF)₆—(AlF₃)₂, respectively. The reason for such a presentation is a requirement of equality of sum of charges, which is especially useful in the case of reciprocal systems [1]. In another case it is desired to enlarge geometrically a region of primary crystallization of one or more components of the system. This can be also achieved by a suitable choice of multiples of the relative molecular mass of components [2]. Also combination of two systems according to the scheme A—M + M—B = A—(M)—B (A and B are the basic components and M is a compound) results in the so-called additive transformation of composition

coordinates. General result of a transformation is a shift of figures inside the diagram of the system, connected with deformation of lines, *e.g.* with deformation of liquidus curves in the case of solidus—liquidus equilibrium.

*Fundamental law of the transformation of composition
coordinates*

Let us consider a binary condensed system. Then on the curve of monovariant phase equilibrium (it need not be only a liquidus curve)

$$T_i = f(a_i, \Delta H_i^f) \quad (1)$$

T_i is the equilibrium temperature corresponding to the activity a_i and ΔH_i^f is the enthalpy of phase transition of the i -th component. For simplicity, it is assumed that the correction corresponding to ΔC_p connected with the phase transition is negligible.

The transformation of composition coordinates causes a shift in the mole fraction of components from x_i to x_i^* . (The asterisk denotes the quantities in the transformed system.) If we require that the functional relationship between the activity and composition should not change, then it holds also for the activity that $a_i \rightarrow a_i^*$; then $a_i = f(x_i)$ and $a_i^* = f(x_i^*)$. (Dependence of the activity on temperature is not explicitly taken into account.) Since the temperature of equilibrium coexistence T_i does not change under the transformation it follows that ΔH_i^f must formally change into ΔH_i^{f*} when the functional relationship (1) is to be preserved. Therefore it holds

$$T_i = f(a_i, \Delta H_i^f) = f(a_i^*, \Delta H_i^{f*}) \quad (2)$$

The rule (2) will be further applied to a simple eutectic system. For the temperature coordinate T_i of a point on liquidus curve it holds that

$$T_i = \frac{\Delta H_i^f}{\Delta H_i^f/T_i^f - R \ln a_i} \quad (3)$$

ΔH_i^f is the molar change in enthalpy of fusion of the i -th component, T_i^f is its temperature of fusion, and a_i is the activity of the substance in liquid solution which is saturated with this substance.

For temperature coordinate T_i of the same point in a transformed system we can write

$$T_i = \frac{\Delta H_i^{f*}}{\Delta H_i^{f*}/T_i^f - R \ln a_i^*} \quad (4)$$

It is evident that $a_i = f(x_i) \neq a_i^* = f(x_i^*)$. The functional dependence between activity and composition is according to our assumptions the same. Since the quantities T_i and T_i^* in eqns (3) and (4) are the same and $a_i \neq a_i^*$, the value of ΔH_i^f must change to $\Delta H_i^{f,*}$. Generally it holds that $\Delta H_i^{f,*} = f(a_i^*)$.

After elimination of T_i from eqns (3) and (4) and rearrangement we obtain the basic law for transformation of composition coordinates

$$\frac{\Delta H_i^{f,*}}{\Delta H_i^f} = \frac{\ln a_i^*}{\ln a_i} \quad (5)$$

This relationship holds if $a_i \neq 1$, $a_i^* \neq 1$. When $x_i \rightarrow 1$, $a_i \rightarrow 1$ but also $x_i^* \rightarrow 1$ and $a_i^* \rightarrow 1$. In this case

$$\lim_{x_i \rightarrow 1} \frac{\Delta H_i^{f,*}}{\Delta H_i^f} = \lim_{x_i \rightarrow 1} \frac{\ln a_i^*}{\ln a_i} \quad (6)$$

As on the right side of eqn (6) is an uncertain expression of the type 0/0, we have to use the l'Hospital's rule

$$\lim_{x_i \rightarrow 1} \frac{\ln a_i^*}{\ln a_i} = \lim_{x_i \rightarrow 1} \frac{(1/a_i^*) da_i^*}{(1/a_i) da_i} = \lim_{x_i \rightarrow 1} \frac{da_i^*}{da_i} \quad (7)$$

We have taken into account that for $x_i \rightarrow 1$ $\lim a_i^* = \lim a_i = 1$.

For a demonstration of the derived relationships let us consider a system A—B ($x_1 + x_2 = 1$). We shall transform it to another system A_p—B_q ($x_1^* + x_2^* = 1$). This type of transformation will be denoted as a "direct" one. The task is to find the functional dependence $x_i^* = f(x_i)$.

It obviously holds

$$x_1 A + x_2 B \rightarrow \frac{x_1}{p} A_p + \frac{x_2}{q} B_q$$

$$\left(\frac{x_1}{p} + \frac{x_2}{q} \neq 1, \text{ provided } p \neq 1 \wedge q \neq 1. \right)$$

$$x_1^* = \frac{x_1/p}{x_1/p + x_2/q} = \frac{qx_1}{p - x_1(p - q)} \quad (8)$$

$$x_2^* = \frac{px_2}{q + x_2(p - q)} \quad (9)$$

From the relationships (8) and (9) it follows that for $p = q$ $x_1 = x_1^*$, $x_2 = x_2^*$ regardless of value of the coefficients p and q . For $x_i = 0$ and $x_i = 1$ it holds that $x_i = x_i^*$. For $0 < x_i < 1$ it holds that $0 < x_i^* < 1$ but also that $x_i \neq x_i^*$.

Let us assume that the system A—B (and therefore also the system A_p — B_q) are classically ideal. Then it holds

$$a^\dagger = x^\dagger = \frac{qx_1}{p - x_1(p - q)}$$

$$\frac{dx^\dagger}{dx_1} = \frac{pq}{[p - x_1(p - q)]^2}$$

and

$$\lim_{x_1 \rightarrow 1} \frac{dx^\dagger}{dx_1} = \frac{p}{q} \quad (10)$$

Because $a_1 = x_1$, $da_1/dx_1 = 1$ it follows that

$$\lim_{x_1 \rightarrow 1} \frac{\Delta H_1^{f,*}}{\Delta H_1^f} = \frac{p}{q} \quad (11)$$

For the second component we can write similarly

$$\lim_{x_2 \rightarrow 1} \frac{\Delta H_2^{f,*}}{\Delta H_2^f} = \frac{q}{p} \quad (12)$$

We shall denote the relationships (11) and (12) as *the reciprocal principle of the transformation of composition coordinates*. The principle says: Let p/q be denoted as k . Then the ratio of enthalpy of fusion in transformed and untransformed system in the limit $x_1 \rightarrow 1$ equals k . Simultaneously for the second component it holds in the limit $x_2 \rightarrow 1$ that this ratio equals $1/k$.

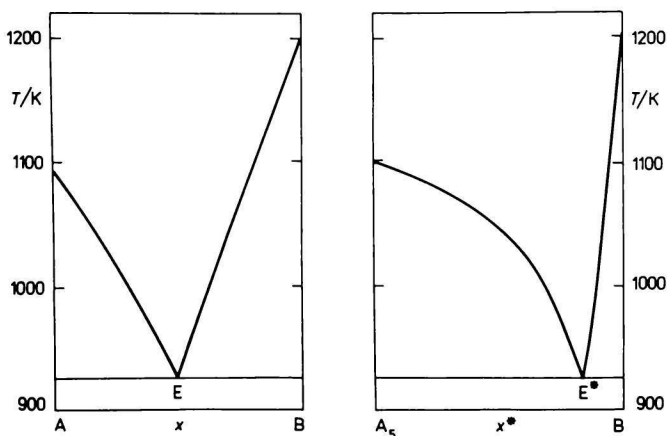


Fig. 1. Phase diagram of a simple eutectic system presented both for the system A—B and for the system A_5 —B with transformed coordinates.

An illustration of the transformation is presented in Fig. 1. In this case a system A—B is transformed into a system A_s—B. For temperature and enthalpy of fusion the following data were chosen:

Substance A: $T_1^f = 1100$ K, $\Delta H_1^f = 33\,000$ J mol⁻¹.

Substance B: $T_2^f = 1200$ K, $\Delta H_2^f = 24\,000$ J mol⁻¹.

The dependence of ratio $\Delta H_i^{f*}/\Delta H_i^f$ on x_i is presented in Table 1.

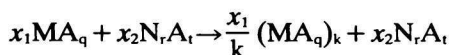
Table 1

Ratio of a formal enthalpy of fusion $\Delta H_i^{f*}(i)$ and the real enthalpy of fusion $\Delta H_i^f(i)$ of components A and B for the case of transformation of the system A—B into the system A_s—B

$x(i)$	$x^*(A)$	$x^*(B)$	$\frac{\Delta H_i^{f*}(A)}{\Delta H_i^f(A)}$	$\frac{\Delta H_i^{f*}(B)}{\Delta H_i^f(B)}$
1.000	1.00000	1.00000	5.00000	0.20000
0.999	0.99502	0.99980	4.99002	0.20008
0.995	0.97549	0.99900	4.95062	0.20040
0.990	0.95192	0.99798	4.90243	0.20081
0.980	0.90741	0.99593	4.80944	0.20162
0.970	0.86607	0.99385	4.72067	0.20245
0.950	0.79167	0.98958	4.55449	0.20415
0.900	0.64286	0.97826	4.19353	0.20861

Relation between a classical activity of the first component in the system MA_q—N_rA_t and Temkin's activity in the special case of transformation

Let a binary ionic system MA_q—N_rA_t having common anion undergo the following direct transformation



Obviously

$$x_1^* = \frac{x_1/k}{x_1/k + x_2} = \frac{x_1}{k - x_1(k-1)} \quad (13)$$

$$x_2^* = \frac{x_2}{x_1/k + x_2} = \frac{kx_2}{1 + x_2(k-1)} \quad (14)$$

Now we shall derive the expression for activity of the component MA_q in the original system MA_q—N_rA_t according to the Temkin model [3]

$$a_{1,\text{Tem}} = \frac{x_1}{x_1 + rx_2} \cdot 1 = \frac{x_1}{r - x_1(r-1)} \quad (15)$$

From a comparison of eqns (13) and (15) it follows that for $k=r$ both relationships are identical. It means that the Temkin activity of the first component in the untransformed system equals the classical activity of this component (it means to its mole fraction) in the transformed system $(MA_q)_k - N_r A_r$.

References

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2. Malinovský, M. and Matiašovský, K., *Chem. Zvesti* 28, 468 (1974).
3. Temkin, M., *Acta Physicochim. URSS* 20, 411 (1945).

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