

Composition coordinate of the transition point in phase diagrams with polymorphous transformation of one component

I. KOŠTENSKÁ

*Department of Inorganic Technology, Slovak Technical University,
880 37 Bratislava*

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The rule of constancy of the product of the transition point coordinate and the Stortebeker correction factor was theoretically derived for binary systems without solid solutions, but with a component showing a polymorphous transformation. This rule holds with a satisfactory accuracy in the interval $0.9 \leq x_i < 1$ (x_i being the composition coordinate of the transition point). For experimental verification, the liquidus curve of BaCl_2 was measured using the TA method in the systems $\text{BaCl}_2\text{—NaCl}$, $\text{BaCl}_2\text{—NaF}$, and $\text{BaCl}_2\text{—Na}_2\text{SO}_4$ in the vicinity of the transition point. The rule of constancy was obeyed very satisfactorily with all three systems investigated. The course of the liquidus curve of BaCl_2 was analyzed thermodynamically applying CTC I and CTC III (criterion of thermodynamic consistency I and III). The calculated and the measured values showed a very good agreement.

Был сделан теоретический вывод правила о постоянстве произведения координаты точки превращения и корректирующего фактора Стортенбекера в двойных системах без твердого раствора компоненты, которая претерпевает полиморфное превращение. Правило удовлетворительно соблюдается для $0,9 \leq x_i < 1$ (x_i — концентрационная координата точки превращения). С целью экспериментальной проверки этого правила была методом ТА измерена линия ликвидуса BaCl_2 в системах $\text{BaCl}_2\text{—NaCl}$, $\text{BaCl}_2\text{—NaF}$, $\text{BaCl}_2\text{—Na}_2\text{SO}_4$ в области точки превращения. Было доказано, что правило о постоянстве произведения концентрационной координаты и корректирующего фактора Стортенбекера соблюдается в этих случаях весьма удовлетворительно. Форма линии ликвидуса BaCl_2 была подвержена термодинамическому анализу с применением КТК I и КТК III. Было найдено очень хорошее согласие рассчитанных и измеренных значений.

Until present no attention has been paid in the literature to the regularities for the composition coordinate of the transition point on the liquidus curves of a component with polymorphous transformation in binary systems. This problem, which is significant from the technical point of view as well as with respect to the systematic theoretical research of the solidus—liquidus equilibrium, is dealt with in the present paper.

Theoretical

Let us consider the binary condensed system A—B without solid solutions, where the component B exists in two polymorphous enantiotropic modifications: the high-temperature α -modification and the low-temperature β -modification. Let us assume that one molecule of substance A introduces into the system consisting of pure substance B the total number of elementary particles equal to $k_{A/B}^{St}$. Should the transition point Q appear on the liquidus curve of the component B, then the temperature of transformation, T^{tr} , is to be between the melting temperature of the high-temperature modification of the component B, $T_{B,\alpha}^f$, and the eutectic temperature of the system A—B, T_E (Fig. 1). The temperature of transformation for systems of the given type is constant as it follows from the Gibbs phase law ($v = k - f + 1$, $v = 2 - 3 + 1 = 0$).

Let us consider a similar system B—C with the same component B, where one molecule of substance C introduced into pure component B another number of particles than the substance A; thus $k_{A/B}^{St} \neq k_{C/B}^{St}$ [1]. A schematic representation of the systems under consideration is shown in Fig. 2.

Now let us consider the equilibrium $\bar{B}^1 \rightleftharpoons B^{0,s}$ in the system A—B at the temperature of transformation T^{tr} . The equilibrium is conditioned by the equality of Gibbs mole energies of component B at $T, P = \text{const}$

$$\bar{G}_{B(A-B)}^1 = G_B^{0,s} \quad (1)$$

The condition of the equilibrium $\bar{B}^1 \rightleftharpoons B^{0,s}$ in the system B—C, at the same temperature T^{tr} is expressed by the relation

$$\bar{G}_{B(B-C)}^1 = G_B^{0,s} \quad (2)$$

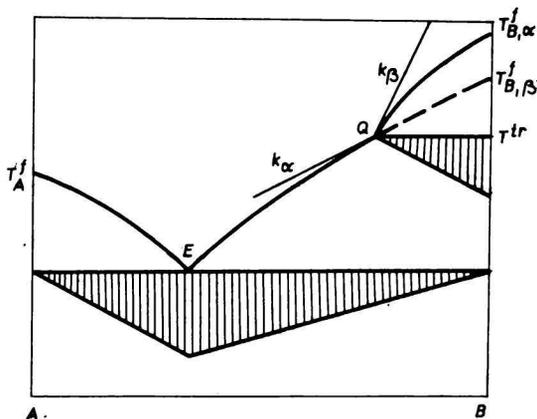


Fig. 1. Phase diagram of the system A—B with no solubility of components in the solid state, in which component B shows a polymorphous transformation at the temperature T^{tr} .

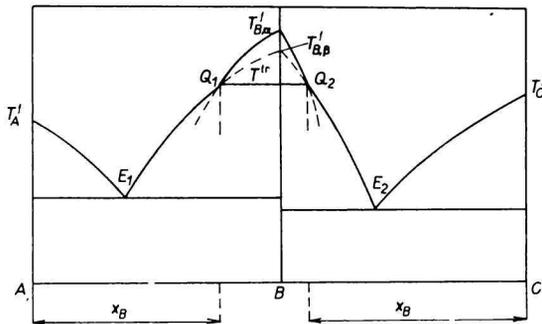


Fig. 2. Phase diagrams of the binary systems A—B and B—C in which component B shows polymorphous transformation at the temperature T^I .

From eqns (1) and (2) we obtain $\bar{G}_{B(A-B)}^I = \bar{G}_{B(B-C)}^I$ and since $\bar{G}_B^I = G_B^{0,1} + RT \ln a_B^I$, after modification the relation holds

$$a_{B(A-B)}^I = a_{B(B-C)}^I. \quad (3)$$

For further considerations we use the actual form of the dependence $a_i = f(x_i)$. We take the so-called universal relationship [2]

$$a_i = x_i^{k_{ii}^{St}}, \quad (4)$$

where in our case $i = B$ and $j = A$ or C . Then eqn (3) is represented in the form

$$x_{B(A-B)}^{k_{A/B}^{St}} = x_{B(B-C)}^{k_{C/B}^{St}} \quad (5)$$

or

$$k_{A/B}^{St} \cdot \ln x_{B(A-B)} = k_{C/B}^{St} \cdot \ln x_{B(B-C)}. \quad (6)$$

The validity of relation (6) is limited by the validity of the universal relationship for the activity of the i -th component [2]. Considering an ideal "universal solution", the relation (6) would hold in the whole composition range of x_i . In general, the universal relationship complies especially for $0.9 \leq x_i < 1$; then eqn (6) can be further simplified. We use the possibility of expanding the logarithmic function into a series and we limit ourselves to the first member.

Since $x_i + x_j = 1$, it holds

$$\ln x_i = \ln (1 - x_j) \doteq -x_j. \quad (7)$$

The inaccuracy arising from the use of the approximate eqn (7) can be seen in

Table 1. For $x = 0.9$ the use of the approximate eqn (7) causes a deviation of 0.005. By introducing this simplification into relation (6) we obtain the simple expression

$$x_{A(A-B)} \cdot k_{A/B}^{St} = x_{C(B-C)} \cdot k_{C/B}^{St} \quad (8)$$

Table 1

Deviations resulting from the relation $\ln x_i = -x_i$ (7)

	$-\ln x_i$	x_i	Error
0.99	0.0100393	0.01	0.0000393
0.98	0.0201937	0.02	0.0001937
0.97	0.0304633	0.03	0.0004633
0.96	0.0408249	0.04	0.0008249
0.95	0.0513017	0.05	0.0013017
0.94	0.0618706	0.06	0.0018706
0.93	0.0725776	0.07	0.0025776
0.92	0.0833768	0.08	0.0033768
0.91	0.0943141	0.09	0.0043141
0.90	0.1053665	0.10	0.0053665

Experimental

For experimental verification of relations (6) and (8) we used as component B barium chloride, BaCl_2 , that exhibits two polymorphous modifications, and the temperature of its polymorphous transformation is near to its melting point ($T_{B,\alpha}^t = 955^\circ\text{C}$, $T^r = 920^\circ\text{C}$). The change of the enthalpy accompanying this transformation is relatively high ($\Delta H^r = 17.165 \times 10^3 \text{ J mol}^{-1}$ [3]) and thus the breaks on the cooling curves can be reliably evaluated.

As the second component we used in the first case sodium chloride, NaCl , one molecule of which introduces one new particle into the melt of BaCl_2 and therefore $k^{St} = 1$. In the next system the second component was NaF providing two new particles and in the third one it was Na_2SO_4 with three new particles introduced by one molecule.

The systems were studied in such a composition range as to determine unambiguously the liquidus line in the vicinity of the transition point.

BaCl_2 — NaCl

The phase diagram presented by *Vortisch* [4] provided the following parameters of the transition point: 97 mole % BaCl_2 , 3 mole % NaCl , and $T^r = 925^\circ\text{C}$. (These data are taken from *Levin's* monograph [5].)

We measured the liquidus line of BaCl_2 using the TA method (as described in [6]) in the composition range from 0 to 14 mole % NaCl . The experimentally found transition point has the parameters: 95.6 mole % BaCl_2 , 4.4 mole % NaCl , $T^r = 920^\circ\text{C}$. The experimental data may be found in Table 2.

Table 2

System $\text{BaCl}_2\text{—NaCl}$
Experimental data of TPC and T^r

NaCl mole %	BaCl_2 mole %	TPC °C	T^r °C
—	100.0	955.0	920.0
0.5	99.5	951.0	919.5
1.0	99.0	947.0	920.0
1.5	98.5	943.0	920.0
2.0	98.0	939.0	920.5
2.5	97.5	935.0	920.0
3.0	97.0	930.5	920.0
3.5	96.5	926.5	919.5
4.0	96.0	923.0	920.0
4.5	95.5	919.0	—
5.0	95.0	917.5	—
6.0	94.0	914.0	—
7.0	93.0	910.0	—
8.0	92.0	905.0	—
9.0	91.0	900.0	—
10.0	90.0	896.0	—
12.0	88.0	887.5	—
14.0	86.0	880.0	—

$\text{BaCl}_2\text{—NaF}$

The phase diagram of the system $\text{BaCl}_2\text{—NaF}$ was investigated by *Kuvakin* [7] as a subsystem of the quasiternary system $\text{BaCl}_2\text{—NaF—AlF}_3$; the author did not mention any polymorphous transformation of BaCl_2 .

We measured the liquidus curve of BaCl_2 in the composition range from 0 to 10 mole % NaF. The transition point showed the parameters: 97.7 mole % BaCl_2 , 2.3 mole % NaF, $T^r = 920^\circ\text{C}$. The experimental data are gathered in Table 3.

$\text{BaCl}_2\text{—Na}_2\text{SO}_4$

This system was investigated by *Khakhlova* and *Dombrovskaya* [8]; here again no polymorphous transformation of BaCl_2 was mentioned. We studied experimentally the part of the liquidus curve of BaCl_2 in the interval 0—4 mole % Na_2SO_4 , BaCl_2 being the rest. The results are presented in Table 4. The transition point was found at 98.5 mole % BaCl_2 and 1.5 mole % Na_2SO_4 , the transformation temperature was the same as in the foregoing cases.

Calculation

In order to verify the rule of constancy of the product of the transition point coordinate and the Stortenbeker correction factor, it is necessary to be sure that the experimentally found data are correct.

Table 3

System BaCl₂—NaF
Experimental data of TPC and T^{tr}

BaCl ₂ mole %	NaF mole %	TPC °C	T ^{tr} °C
100.00	0.00	955.0	920.0
99.75	0.25	950.5	920.0
99.50	0.50	949.0	921.0
99.25	0.75	945.0	920.0
99.00	1.00	940.0	920.0
98.75	1.25	935.0	920.0
98.50	1.50	930.0	922.0
98.25	1.75	928.0	920.0
98.00	2.00	925.5	920.0
97.75	2.25	920.5	—
97.50	2.50	920.0	—
97.00	3.00	916.5	—
96.50	3.50	912.5	—
96.00	4.00	909.0	—
95.00	5.00	900.5	—
94.00	6.00	893.0	—
92.00	8.00	878.5	—
90.00	10.00	862.5	—

Table 4

System BaCl₂—Na₂SO₄
Experimental data of TPC and T^{tr}

BaCl ₂ mole %	Na ₂ SO ₄ mole %	TPC °C	T ^{tr} °C
—	100.00	884.8	
100.00	—	955.0	920.0
99.75	0.25	949.5	920.5
99.50	0.50	942.0	920.5
99.25	0.75	938.5	921.3, 920.8
99.00	1.00	932.0	921.0, 920.0
98.75	1.25	925.7	921.5
98.50	1.50	920.7	919.8
98.40	1.60	918.5	—
98.25	1.75	916.5	—
98.00	2.00	914.2	—
97.50	2.50	907.8	—
97.00	3.00	904.0	—
96.50	3.50	897.5	—
96.00	4.00	891.3	—

For the verification of experimental data we may use the criteria of the thermodynamic consistency [9] (CTC I and CTC III) which are generally valid for the course of the liquidus curves regardless of the actual form of the dependence $a_i = f(x_i)$.

According to CTC I the value of the slope of the tangent to the liquidus line for $x \rightarrow 1$ is given by the relation

$$k_{\text{calc}}^0 = \frac{R \cdot (T_b^0)^2}{\Delta H_b^0} \cdot k_{\lambda/\beta}^{\text{st}} \quad (9)$$

For BaCl_2 in the system $\text{BaCl}_2\text{—NaCl}$, where $k_{\lambda/\beta}^{\text{st}} = 1$, it holds

$$k_{\text{calc}}^0 = \frac{8314 \times 1228^2}{1.633 \times 10^7} = 768.3 \text{ K.}$$

The experimentally found liquidus curve of the high-temperature modification of BaCl_2 is practically a straight line; the experimental value for the slope of the tangent taken from Fig. 3 is

$$k_{\text{exp}}^0 = \frac{(955 + 273) - (920 + 273)}{0.044} = 795.4 \text{ K.}$$

In the $\text{BaCl}_2\text{—NaF}$ system $k_{\lambda/\beta}^{\text{st}} = 2$, therefore

$$k_{\text{calc}}^0 = 768.3 \times 2 = 1536.6 \text{ K.}$$

The liquidus curve of BaCl_2 in this system is practically a straight line too, and the experimental value of the slope of the tangent is given by the equation

$$k_{\text{exp}}^0 = \frac{(955 + 273) - (920 + 273)}{0.023} = 1521.7 \text{ K.}$$

In the system $\text{BaCl}_2\text{—Na}_2\text{SO}_4$, where $k_{\lambda/\beta}^{\text{st}} = 3$, the values for the slopes of the tangents are as follows

$$k_{\text{calc}}^0 = 768.3 \times 3 = 2304.9 \text{ K,}$$

$$k_{\text{exp}}^0 = \frac{(955 + 273) - (920 + 273)}{0.015} = 2333.3 \text{ K.}$$

Thus we may state that there is a good agreement between the calculated and the measured values of the slopes of the tangents.

The course of the liquidus lines of the high- and the low-temperature modifications of a component near the transition point is governed by thermodynamic regularities formulated in CTC III, which in its simplified form is expressed by [9]

$$\Delta H_{\beta, \alpha}^t \cdot k_{\alpha}^0 = \Delta H_{\beta, \beta}^t \cdot k_{\beta}^0 \quad (10)$$

Since the liquidus line of the high-temperature modification of BaCl_2 is practically a straight line, for all the mentioned systems the relation is valid

$$k_{\alpha}^0 = k_{\text{exp}}^0.$$

The slopes of the tangents to the liquidus line of the low-temperature modification of BaCl_2 can be read from the experimental diagram. The determined values as well as the evaluation of relation (10) for all the investigated systems are shown in Table 5. There is a good agreement between the calculated and the established values of the slopes of the tangents, which confirms the objectivity of the measured data.

In order to verify the course of the liquidus line of the low-temperature modification of BaCl_2 , it is necessary to know its hypothetical melting temperature. The calculation is based on the equality of the activities of both modifications in the transition point at the transformation temperature [10]. To express the activity, we used the LeChatelier—Schröder equation [2]. We assume that ΔH^t is constant.

This simplifying suggestion does not cause practically any inaccuracy in the calculation, since the transformation of the modification takes place near the melting point of BaCl_2 ($T'_\alpha - T'' = 35^\circ\text{C}$). For the activities at the transformation temperature the relations hold

$$\ln a_\alpha = \frac{\Delta H'_{\text{B},\alpha}}{R} \left[\frac{1}{T'_{\text{B},\alpha}} - \frac{1}{T''} \right], \quad (11)$$

$$\ln a_\beta = \frac{\Delta H'_{\text{B},\beta}}{R} \left[\frac{1}{T'_{\text{B},\beta}} - \frac{1}{T''} \right] \quad (12)$$

Since $a_\alpha = a_\beta$, by means of eqns (11) and (12) we obtain the expression for the hypothetical melting temperature of the low-temperature modification

$$T'_{\text{B},\beta} = \frac{(\Delta H'_{\text{B},\alpha} + \Delta H'') T'_{\text{B},\alpha} T''}{\Delta H'_{\text{B},\alpha} T'' + \Delta H'' \cdot T'_{\text{B},\alpha}} \quad (13)$$

By introducing the thermodynamic parameters of BaCl_2 we obtain

$$a'_{\text{BaCl}_2} = 0.9541, \quad T'_{\text{B},\beta} = 1210 \text{ K} = 937^\circ\text{C}.$$

For the calculation of the actual form of the dependence $a_i = f(x)$, we employ again the universal relationship [2] and compare this method with the *Temkin's* model [11]. In the BaCl_2 — NaCl system $k_{\text{NaCl}/\text{BaCl}_2}^{\text{St}} = 1$ and consequently $a = x$. The system has a common anion and the stoichiometric coefficients for the non-common ion are equal, so that also according to Temkin it holds again $a = x$.

Both methods of calculation of the liquidus line lead to the same result, as it is shown together with the experimental data in Fig. 3.

In the BaCl_2 — NaF system $k_{\text{NaF}/\text{BaCl}_2}^{\text{St}} = 2$, and according to the universal relationship $a = x^2$. According to Temkin's model for the activity of BaCl_2

$$a_{\text{BaCl}_2} = \frac{4x^3}{(x+1)^2} \quad (14)$$

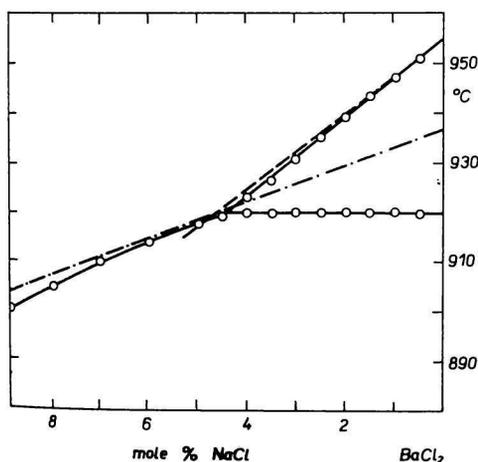


Fig. 3. Part of the phase diagram of the system BaCl_2 — NaCl .

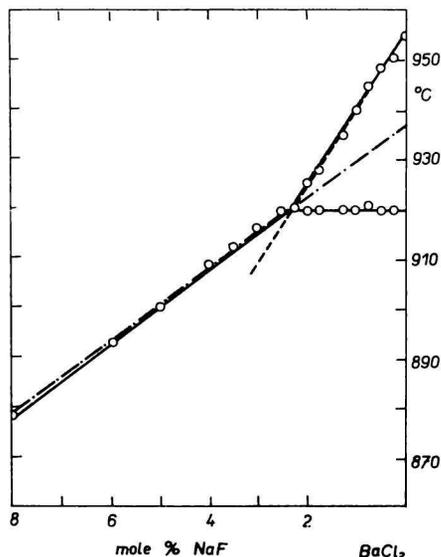


Fig. 4. Part of the phase diagram of the system BaCl_2 — NaF .

The values for the liquidus curve of BaCl_2 calculated by means of the universal relationship are practically the same as those expressed according to Temkin and they are shown together with the experimental values in Fig. 4. For the boundary composition of NaF at $x_{\text{BaCl}_2} = 0.9$, the universal relationship yields for the activity of BaCl_2 the value $a = 0.810$, while according to Temkin we obtain $a = 0.808$. The calculated values for the composition coordinate of the transition point at the transformation temperature are 97.68 mole % BaCl_2 and 2.32 mole % NaF.

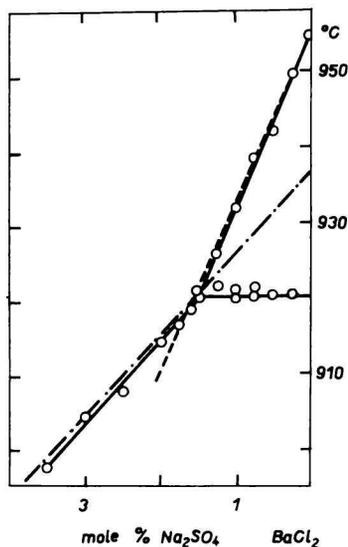


Fig. 5. Part of the phase diagram of the system $\text{BaCl}_2\text{—Na}_2\text{SO}_4$.

In the $\text{BaCl}_2\text{—Na}_2\text{SO}_4$ system $k_{\text{Na}_2\text{SO}_4/\text{BaCl}_2}^{\text{St}} = 3$, therefore according to the universal relationship $a = x^3$; the calculated liquidus line is shown in Fig. 5 together with the experimental data. According to Temkin's model

$$a_{\text{BaCl}_2} = \frac{4x^3}{(2-x) \cdot (x+1)^2} \quad (15)$$

and the calculated values are practically the same as the activities calculated using the universal relationship. For $x = 0.9$ the activity of BaCl_2 equals to 0.729 according to the universal relationship, and to 0.734 according to Temkin. The composition coordinate of the transition point in this system has the value of 98.55 mole % BaCl_2 and 1.45 mole % Na_2SO_4 .

Discussion

The liquidus line of BaCl_2 in the studied systems was submitted to thermodynamic analysis. The criterion of thermodynamic consistency *I* is fulfilled with a maximum deviation of 3.5% [12]. The CTC *III*, verifying the course of the liquidus lines in the vicinity of the transition point, exhibits a maximum deviation of 1.1%. The course of the liquidus lines was calculated by means of the universal

Table 5

Results of the application of CTC III in the studied systems

System	k_p° K	$\Delta H_{B,\alpha}^{\circ} \cdot k_{\alpha}^{\circ}$	$\Delta H_{B,\beta}^{\circ} \cdot k_{\beta}^{\circ}$	Error %
BaCl ₂ —NaCl	390	1.298×10^{10}	1.306×10^{10}	0.7
BaCl ₂ —NaF	750	2.485×10^{10}	2.512×10^{10}	1.1
BaCl ₂ —Na ₂ SO ₄	1140	3.810×10^{10}	3.818×10^{10}	0.5

relationship for the dependence $a_i = f(x_i)$ as well as on the basis of the dependences ensuing from the Temkin's model. The agreement between the calculated and the measured values was very good; in the system BaCl₂—NaCl the experimental and the calculated coordinates of the transition point differed within 0.19 mole %. The correctness of the experimental data and of theoretical calculations for the system BaCl₂—NaCl is indirectly supported also by the results of the measurements of the liquidus curve of the system BaCl₂—KCl [13]. The parameters of the transition point taken from the phase diagram are: 95.2 mole % BaCl₂, 4.8 mole % KCl, $T^u = 924^{\circ}\text{C}$, $T_{\text{BaCl}_2}^l = 961^{\circ}\text{C}$.

The good agreement between the experimental data and the theoretical values for all the three investigated systems indicates the reliability of the method of calculating of the hypothetic melting temperature of the low-temperature modification of the component under consideration. The results also confirmed the applicability of the universal relationship for the calculation of activities in systems of the given type and emphasized its advantage owing to its simplicity. In applying the relations ensuing from the Temkin's model instead of the universal relationship for the activity of the component, we have to solve a cubic equation with respect to x to obtain the composition coordinates of the transition point. The analysis presented together with the calculations confirmed the correctness of the measured values.

Table 6

Verification of the validity of relation (6) and of the rule of constancy (8) of the product of the Stortenbeker correction factor and the composition coordinate of the minor component $k_{ji}^{\text{St}} \cdot x_j$

System	x_j exp	$k_{ji}^{\text{St}} \cdot x_j$ (8)	$k_{ji}^{\text{St}} \cdot \ln x_j$ (6)
BaCl ₂ —NaCl	0.044	0.0459	0.0459
BaCl ₂ —NaF	0.023	0.046	0.0464
BaCl ₂ —Na ₂ SO ₄	0.015	0.045	0.0465

For the given systems it has been proved that the rule of constancy of the product of the Stortenbeker correction factor and the composition coordinate of the minor component in the transition point on the liquidus line of the component with a polymorphous transformation is fulfilled within the limits of experimental error (Table 6). This relationship allows *e.g.*, to calculate the unknown value of the Stortenbeker correction factor, if the value of the mentioned product for the given substance is known.

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Symbols

a_B^l	activity of component B in a liquid solution
a_B^tr	activity of component B in the transition point
$a_{B(A-B)}$	activity of component B in the system A—B
$B^{0,s}$	pure solid component B
\bar{B}^l	component B in a liquid solution
CTC I, III	criteria of thermodynamic consistency I and III
$G_B^{0,s}$	Gibbs energy of pure substance B in the solid state
$\bar{G}_{B(A-B)}^l$	Gibbs energy of substance B in the liquid state in the system A—B
$\Delta H_{B,\alpha}^f$	melting enthalpy of the α -modification of substance B
$\Delta H_{B,\beta}^f$	melting enthalpy of the β -modification of substance B
ΔH^{tr}	change of enthalpy at the transformation of a modification (polymorphous transformation)
k_{calc}^0	theoretically calculated slope of the tangent to the liquidus line at the temperature T^l
k_{exp}^0	experimentally determined slope of the tangent to the liquidus line at the temperature T^l
$k_{\alpha,\beta}^0$	slope of the tangent to the liquidus line of the α - and β -modification, respectively, of the component in the transformation point
$k_{j/i}^{St}$	Stortenbeker correction factor for substance j introduced into substance i
Q	transition point on the liquidus line of the component with polymorphous transformation
$T_{B,\alpha}^f$	melting temperature of the α -modification of component B
T^{tr}	temperature of polymorphous transformation
TA	thermal analysis
TPC	temperature of the primary crystallization

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