Thermodynamics of phase equilibria in the systems with polymorphic transitions
I. Systems forming no compounds and no solid solutions

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A systematic thermodynamic analysis of phase equilibria in binary systems forming neither compounds nor solid solutions in which one component forms polymorphic "overeutectic" modifications of the enantiotropic type is presented. A procedure is proposed which enables to determine the following numerical values of quantities which are not accessible to the measurement at equilibrium conditions:

— the hypothetical temperatures of fusion of the polymorphic modifications,

— the hypothetic temperatures of transition points,

— the activities of the given component in hypothetical solutions having composition and temperature corresponding to the hypothetical transition points,

— the ratio of slopes of tangents to the curves of monovariant equilibrium at the hypothetical transition points.

It was proved that the experimental data obtained for real transition points are sufficient for total thermodynamic characteristic of phase equilibria in regions which are not accessible to an equilibrium measurement.

Осуществлено систематическое термодинамическое рассмотрение фазовых равновесий в бинарных системах без соединений и твердых растворов, в которых один из компонентов образует полиморфные «сверхэвтектические» модификации энантиотропного типа. Был разработан ход определения нумерических значений следующих величин, которые невозможно определить в условиях равновесия:

— гипотетических температур плавления полиморфных модификаций,

— гипотетических температур точек перехода,

— активностей компонентов в гипотетических растворах при составе и температуре гипотетических точек перехода,

— отношений углов наклона касательных кривых моновариантного равновесия в гипотетических точках перехода.

Было доказано, что экспериментальные данные, полученные для реальных точек перехода, вполне достаточны для полной термодинамической характеристики фазовых равновесий в областях, в которых нельзя получить равновесные значения величин.

The phenomenon of polymorphism is wide-spread. Many substances with polymorphic modifications are employed in technical praxis. Despite of that the influence of polymorphic transitions on the character of phase diagrams of corresponding systems has not been paid an adequate attention. Even in well--known monographs on phase diagrams as those by *Ricci* [1], *Vogel* [2], *Anosov et al.* [3] the phase diagrams of the systems containing components with polymorphic transitions are not treated systematically. Actually one can find in literature only a small number of phase diagrams and these are explained exclusively from the point of view of "geometrical" thermodynamics. In this work we shall apply another approach to this topic:

 i) We shall present a systematic survey of phase diagrams with polymorphic transitions and we shall classify them according to certain common features.

 ii) Besides the geometrical analysis we shall present also the thermodynamic analysis of the course of curves of monovariant phase equilibrium with special attention to the neighbourhood of remarkable points in the phase diagrams.

Many of these points and parts of the curves are not accessible to the experimental determination at equilibrium conditions. Despite of that it is possible to apply for this type of phase diagrams the same approach as for the solidus—liquidus equilibria. This thermodynamic analysis allows to derive a series of new quantitative relationships which are important for a systematic forming of the theory of phase equilibria in condensed systems of a given type.

In the first part of this series of papers we shall discuss the binary systems in which neither solid solutions nor complex compounds are formed. The case when one component forms two, three or four polymorphic modifications of enantiotropic type is dealt with in detail. A generalization of the obtained relationships for unlimited number of polymorphic modifications is derived.

General laws valid in the systems of given type

Since the phenomenon of polymorphic transitions is connected with pure components of the system, we shall discuss first briefly the laws valid for individual substances.

A scheme of dependence of molar enthalpies of pure liquid substance A and its solid polymorphic enantiotropic modifications on temperature is presented in

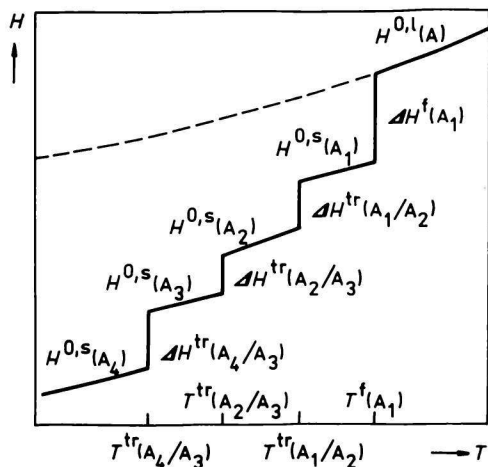Fig. 1. The modifications are denoted A_1, A_2, A_3, *etc.* in direction of the decrease of temperature.

Fig. 1. Dependence of the molar enthalpy of pure liquid substance $A^{0,l}$ and of its solid polymorphic modifications $A_i^{0,s}$ $(i = 1\text{---}4)$ on temperature $(P = \text{const})$.

It holds that

$$H^{0,l}(A) - H^{0,s}(A_1) = \Delta H^f(A_1)$$

$$H^{0,l}(A) - H^{0,s}(A_2) = \Delta H^f(A_2)$$

The symbols $H^{0,s}(A_i)$ denotes the molar enthalpy of the pure solid i-th modification of component A.

If the quantities $H^{0,l}(A)$, $H^{0,s}(A_i)$ do not depend on temperature or if the considered temperature interval is sufficiently narrow (usually if it is less than 100 K) then it holds

$$\Delta H^f(A_2) = \Delta H^f(A_1) + \Delta H^{tr}(A_1/A_2) \tag{1}$$

$$\Delta H^f(A_3) = \Delta H^f(A_1) + \Delta H^{tr}(A_1/A_2) + \Delta H^{tr}(A_2/A_3) \tag{2}$$

or we can write generally that

$$\Delta H^f(A_k) = \Delta H^f(A_1) + \sum_{i=1}^{k-1} \Delta H^{tr}(A_i/A_{i+1}) \tag{3}$$

Dependence of the molar Gibbs energy of pure liquid substance A and its polymorphic modifications on temperature is schematically plotted in Fig. 2. Five curves $G^{0,l}(A)$, $G^{0,s}(A_i)$ $(i = 1\text{---}4)$ intersect in $\binom{5}{2} = 10$ points. The intersections of pairs $G^{0,l}(A)$ and $G^{0,s}(A_i)$ correspond to the melting points of the i-th
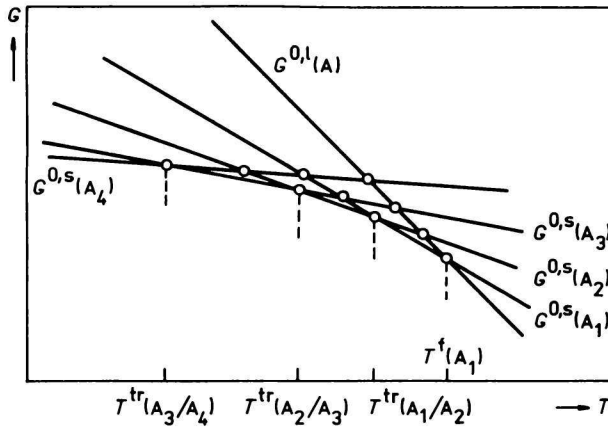
Fig. 2. Dependence of the molar Gibbs energy of pure liquid substance $A^{0,1}$ and of its solid polymorphic modifications $A_i^{0,s}$ ($i = 1$—4) on temperature ($P = $ const).

modification of substance A. However, only the first intersection ($i = 1$) is accessible to an equilibrium measurement.

The intersections of pairs $G^{0,s}(A_i)$ and $G^{0,s}(A_j)$ correspond to the transition temperatures at which a reversible transformation of modification A_j into A_i and oppositely takes place. To equilibrium measurement are accessible only those points for which it holds that $j = i + 1$.

Let us consider the phase equilibrium which occurs in temperature interval between the melting point of high temperature modification, *i.e.* $T^f(A_1)$ and transition point $T^{tr}(A_1/A_2)$ (Fig. 3). In this temperature interval the pure solid high
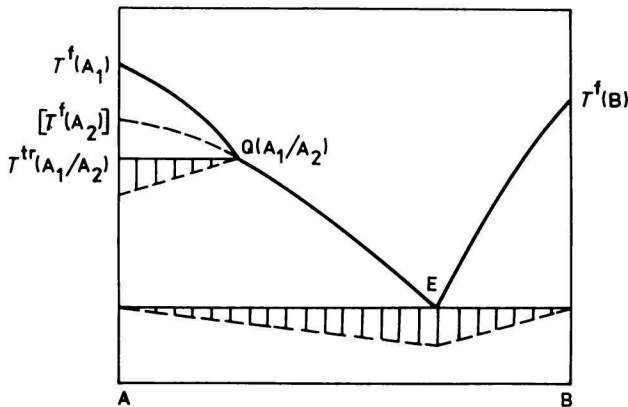

Fig. 3. Isobaric phase diagram of the system A_1 (A_2)—B forming neither compounds nor solid solutions.

temperature modification $A_1^{0,s}$ coexists with solution which is saturated with substance A. We shall denote this solution as $\bar{A}^1$ and the corresponding curve of monovariant equilibrium (*i.e.* the liquidus curve) as $\bar{A}^1/A_1^{0,s}$. Similarly the part of liquidus of the component A in the temperature interval from $T^{tr}(A_1/A_2)$ to $T^{tr}(A_2/A_3)$ will be denoted by the symbol $\bar{A}^1/A_2^{0,s}$, *etc.* (Figs. 4 and 5).
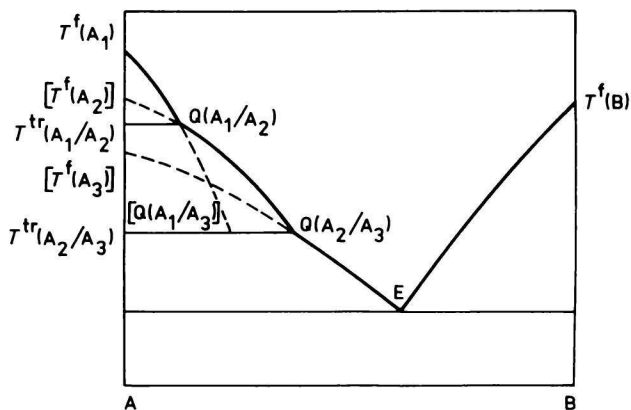

Fig. 4. Isobaric phase diagram of the system A_1 (A_2, A_3)—B forming neither compounds nor solid solutions.
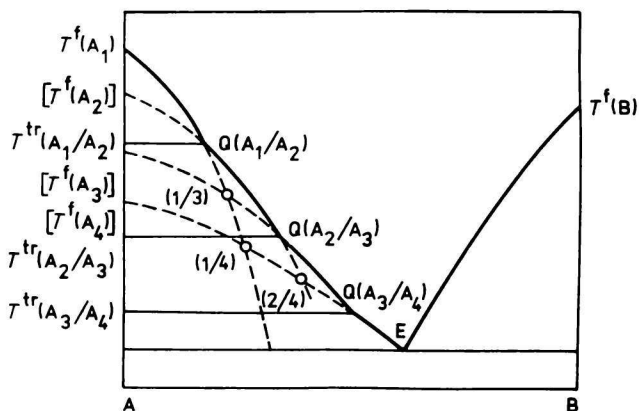

Fig. 5. Isobaric phase diagram of the system A_1 (A_2, A_3, A_4)—B forming neither compounds nor solid solutions.

For the slope $k^0(A_1)$ of the tangent to liquidus curve $\bar{A}^1/A_1^{0,\,s}$ at the point $T^f(A_1)$ it holds, regardless of the concrete shape of the functional dependence $a(A) = f[x(A)]$

$$k^0(A_1) = \frac{R[T^f(A_1)]^2}{\Delta H^f(A_1)} \cdot k^{St}(B/A) \qquad (4)$$

In this "cryometric" relationship $T^f(A_1)$ denotes the temperature of fusion of modification A_1, $\Delta H^f(A_1)$ is the molar enthalpy of fusion of modification A_1 and $k^{St}(B/A)$ is the Stortenbeker's correction factor. This factor equals the number of species which are formed in the system of pure molten component A as a result of addition of 1 molecule of substance B.

The relationship (4) which determines the shape of liquidus curve $\bar{A}^1/A_1^{0,\,s}$ in the vicinity of melting point $T^f(A_1)$ has been denoted as the Ist criterion of thermodynamic consistency [4] (abbreviation CTC I). It is often used for calculation of the quantity $\Delta H^f(A_1)$.

The curves of monovariant equilibria $\bar{A}^1 \rightleftarrows A_i^{0,\,s}$ $(i = 1-4)$ intersect in the transition points $Q(A_i/A_j)$. If there are three or more polymorphic modifications of given component in a system we obtain in the corresponding phase diagram two types of sets of transition points (Fig. 5): real $Q(A_i/A_j)$ for $j = i+1$ and hypothetical $Q(A_i/A_j)$ for $j \geqslant i+2$ which are not accessible to an equilibrium measurement.

It can be proved [5] that the composition coordinate of a transition point $Q(A_i/A_j)$ is related with the Stortenbeker's correction factor by the relation

$$x_B[Q(A_i/A_j)] \cdot k^{St}(B/A) \approx \text{const} \qquad (5)$$

This relationship is fulfilled the more precisely the smaller is the mole fraction of component B in the transition point $Q(A_i/A_j)$. Therefore this relation can be used for determination of numerical value of the quantity $k^{St}(B/A)$ [6].

For the course of liquidus curves $\bar{A}^1/A_i^{0,\,s}$ and $\bar{A}^1/A_j^{0,\,s}$ (whether they are real or hypothetical) in the vicinity of the transition point $Q(A_i/A_j)$ the so-called IIIrd criterion of thermodynamic consistency (CTC III) must be fulfilled [4]

$$\Delta \bar{H}^{1/0,\,s}(A_i) \cdot k(A_i) = \Delta \bar{H}^{1/0,\,s}(A_j) \cdot k(A_j) \qquad (6)$$

$\Delta \bar{H}^{1/0,\,s}(A_i)$, $\Delta \bar{H}^{1/0,\,s}(A_j)$ are the changes in partial molar enthalpy for processes $A_i^{0,\,s} \to \bar{A}^1$ and $A_i^{0,\,s} \to \bar{A}^1$ at the point $Q(A_i/A_j)$. The result of these processes is the formation of the same (it does not matter if real or hypothetical) solution the composition and temperature of which correspond to the transition point $Q(A_i/A_j)$; $k(A_i)$, $k(A_j)$ are the slopes of tangents to the liquidus curves $\bar{A}^1/A_i^{0,\,s}$ and $\bar{A}^1/A_j^{0,\,s}$ at the point $Q(A_i/A_j)$.

It holds

$$\Delta \bar{H}^{1/0, s}(A_i) = \bar{H}^1(A) - H^{0, s}(A_i) =$$
$$= [\bar{H}^1(A) - H^{0,1}(A_i)] + [H^{0,1}(A) - H^{0,s}(A_i)]$$

where $\bar{H}^1(A)$ is the partial molar enthalpy of component A in saturated solution, $H^{0,1}(A)$ is the molar enthalpy of pure liquid component A. $H^{0,s}(A_i)$ is the molar enthalpy of the pure solid i-th polymorphic modification of component A.

If we can neglect the temperature dependence of enthalpy of phase transition $\Delta H^{0, 1/0, s}(A_i)$ it holds

$$\Delta \bar{H}^{1/0, s}(A_i) = \Delta \bar{H}^{1/0, 1}_{\text{mix}}(A) + \Delta H^{0, 1/0, s}(A_i) = \Delta \bar{H}^{1/0, 1}_{\text{mix}}(A) + \Delta H^t(A_i) \qquad (7)$$

For solutions the behaviour of which is not very far from ideality eqn (6) reduces to the relationship (8)

$$\Delta H^t(A_i) \cdot k(A_i) \approx \Delta H^t(A_j) \cdot k(A_j) \qquad (8)$$

For the course of liquidus curves $\bar{A}^1/A_4^{0, s}$ and $\bar{B}^1/B^{0, s}$ in the vicinity of the eutectic point E (Fig. 5) the relationship derived by *Dodé* and *Hagège* [7, 8] holds. This relationship has been denoted as CTC II [4]

$$x(A) \cdot \Delta \bar{H}^{1/0, s}(A_i) \cdot k(A_i) = x(B) \cdot \Delta \bar{H}^{1/0, s}(B) \cdot k(B) \qquad (9)$$

$x(A)$, $x(B)$ are the mole fractions of components A and B at the point E, $\Delta \bar{H}^{1/0, s}(A_i)$, $\Delta \bar{H}^{1/0, s}(B)$ are the changes of partial molar enthalpy connected with processes $A_i^{0, s} \rightarrow \bar{A}^1$ and $B^{0, s} \rightarrow \bar{B}^1$ at this point; $k(A_i)$, $k(B)$ are the slopes of tangents to liquidus curves $\bar{A}^1/A_i^{0, s}$ and $\bar{B}^1/B^{0, s}$ at the point E. If the behaviour of solutions is not very far from ideality, a simplified form of the CTC II can be used

$$x(A) \cdot \Delta H^t(A_i) \cdot k(A_i) \approx x(B) \cdot \Delta H^t(B) \cdot k(B) \qquad (10)$$

For a total thermodynamic description of the phase equilibria in the systems in question expressions for determination of several parameters are to be derived. The parameters are:

1. temperature of fusion $T^t(A_i)$ of the i-th modification of component A ($i \geqslant 2$),

2. temperature $T^{tr}(A_i/A_j)$ corresponding to hypothetical transition points $Q(A_i/A_j)$,

3. activity of component A in solutions corresponding to the hypothetical transition points,

4. ratio of the slopes of tangents to the curves of monovariant phase equilibrium $\bar{A}^1/A_i^{0, s}$ at the hypothetical transition points.

Special laws valid in the systems of given type

1. The system A_1 (A_2)—B

There is only one real transition point $Q(A_1/A_2)$ in this system. It is identical with the intersection point of the liquidus curve $\bar{A}^1/A_1^{0,s}$ (it is the liquidus curve of the high temperature modification of A) and the liquidus curve $\bar{A}^1/A_2^{0,s}$ (it is the curve corresponding to the low temperature modification of substance A) (Fig. 3).

The activity of substance A in saturated solution having composition and temperature of the point $Q(A_1/A_2)$ can be calculated from a simplified form of the LeChatelier—Shreder equation

$$\ln a[A, Q(A_1/A_2)] = \frac{\Delta H^t(A_1)}{R} \cdot \left[\frac{1}{T^t(A_1)} - \frac{1}{T^{tr}(A_1/A_2)} \right] \tag{11}$$

$$\ln a[A, Q(A_1/A_2)] = \frac{\Delta H^t(A_2)}{R} \cdot \left[\frac{1}{T^t(A_2)} - \frac{1}{T^{tr}(A_1/A_2)} \right] \tag{12}$$

The quantity $T^t(A_2)$, which cannot be measured at equilibrium conditions, cannot be calculated from eqn (12) as well because we do not know the quantity $a(A)$. Therefore we proceed in such a way that we eliminate the term $\ln a[A, Q(A_1/A_2)]$ from eqns (11) and (12). After rearrangement we obtain

$$T^t(A_2) = \frac{\Delta H^t(A_2) \cdot T^t(A_1) \cdot T^{tr}(A_1/A_2)}{\Delta H^t(A_1) \cdot T^{tr}(A_1/A_2) + \Delta H^{tr}(A_1/A_2) \cdot T^t(A_1)} \tag{13}$$

and after introducing the relation (1) we get

$$T^t(A_2) = \frac{[\Delta H^t(A_1) + \Delta H^{tr}(A_1/A_2)] \cdot T^t(A_1) \cdot T^{tr}(A_1/A_2)}{\Delta H^t(A_1) \cdot T^{tr}(A_1/A_2) + \Delta H^{tr}(A_1/A_2) \cdot T^t(A_1)} \tag{14}$$

All quantities which appear on the right side of eqn (14) can be measured at equilibrium conditions.

2. The system A_1 (A_2, A_3)—B

In this system (Fig. 4) the following quantities can be obtained by measurement at equilibrium conditions: $T^t(A_1)$, $T^{tr}(A_1/A_2)$, $T^{tr}(A_2/A_3)$, and parameters of the points $Q(A_1/A_2)$, $Q(A_2/A_3)$.

a) Calculation of $T^t(A_i)$, $i = 2, 3$

The temperature of fusion $T^t(A_2)$ of the modification $A_2^{0,s}$ can be calculated from eqns (13) and (14). The temperature of fusion $T^t(A_3)$ of modification $A_3^{0,s}$ at the point $Q(A_2/A_3)$ can be determined after elimination of the term $\ln a[A, Q(A_2/A_3)]$ from the equations

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$$\ln a[A, Q(A_2/A_3)] = \frac{\Delta H^f(A_2)}{R} \cdot \left[\frac{1}{T^f(A_2)} - \frac{1}{T^{tr}(A_2/A_3)} \right] \tag{15}$$

$$\ln a[A, Q(A_2/A_3)] = \frac{\Delta H^f(A_3)}{R} \cdot \left[\frac{1}{T^f(A_3)} - \frac{1}{T^{tr}(A_2/A_3)} \right] \tag{16}$$

Then it follows

$$T^f(A_3) = \frac{\Delta H^f(A_3) \cdot T^f(A_2) \cdot T^{tr}(A_2/A_3)}{\Delta H^f(A_2) \cdot T^{tr}(A_2/A_3) + \Delta H^{tr}(A_2/A_3) \cdot T^f(A_2)} \tag{17}$$

or, after using eqns (1) and (2),

$$T^f(A_3) =$$

$$= \frac{[\Delta H^f(A_1) + \Delta H^{tr}(A_1/A_2) + \Delta H^{tr}(A_2/A_3)] \cdot T^f(A_2) \cdot T^{tr}(A_2/A_3)}{[\Delta H^f(A_1) + \Delta H^{tr}(A_1/A_2)] \cdot T^{tr}(A_2/A_3) + \Delta H^{tr}(A_2/A_3) \cdot T^f(A_2)} \tag{18}$$

The quantity $T^f(A_2)$ can be substituted into eqn (18) from eqn (14). Then after rearrangement we obtain

$$T^f(A_3) = \frac{[\Delta H^f(A_1) + \Delta H^{tr}(A_1/A_2) + \Delta H^{tr}(A_2/A_3)] \cdot T^f(A_1) \cdot T^{tr}(A_1/A_2)}{M + N + U} \cdot T^{tr}(A_2/A_3)$$

$$(19)$$

where $M = \Delta H^f(A_1) \cdot T^{tr}(A_1/A_2) \cdot T^{tr}(A_2/A_3)$,
$N = \Delta H^{tr}(A_1/A_2) \cdot T^f(A_1) \cdot T^{tr}(A_2/A_3)$,
$U = \Delta H^{tr}(A_2/A_3) \cdot T^f(A_1) \cdot T^{tr}(A_1/A_2)$.

b) Calculation of the temperature $T^{tr}(A_1/A_3)$ corresponding to the hypothetical transition point $Q(A_1/A_3)$

The quantity $T^{tr}(A_1/A_3)$ which is to be determined occurs in the following equations

$$\ln a[A, Q(A_1/A_3)] = \frac{\Delta H^f(A_1)}{R} \cdot \left[\frac{1}{T^f(A_1)} - \frac{1}{T^{tr}(A_1/A_3)} \right] \tag{20}$$

$$\ln a[A, Q(A_1/A_3)] = \frac{\Delta H^f(A_3)}{R} \cdot \left[\frac{1}{T^f(A_3)} - \frac{1}{T^{tr}(A_1/A_3)} \right] \tag{21}$$

After elimination of the expression $\ln a[A, Q(A_1/A_3)]$ we obtain

$$T^{tr}(A_1/A_3) = \frac{[\Delta H^f(A_3) - \Delta H^f(A_1)] \cdot T^f(A_1) \cdot T^f(A_3)}{\Delta H^f(A_3) \cdot T^f(A_1) - \Delta H^f(A_1) \cdot T^f(A_3)} \tag{22}$$

Dividing the numerator and denominator of this equation by the product $T^f(A_1) \cdot T^f(A_3)$ we obtain the expression

$$T^{tr}(A_1/A_3) = \frac{\Delta H^t(A_3) - \Delta H^t(A_1)}{\Delta S^t(A_3) - \Delta S^t(A_1)} \qquad (23)$$

The quantities $\Delta S^t(A_i) = \Delta H^t(A_i)/T^t(A_i)$ are the molar entropies of fusion of modification A_i. From Fig. 1 it follows that $\Delta H^t(A_3) > \Delta H^t(A_1)$. Because $T^{tr}(A_1/A_3) > 0$, it must hold with respect to eqn (23) that also $\Delta S^t(A_3) > \Delta S^t(A_1)$. We shall prove the validity of this inequality also in another way. It holds that

$$[\Delta H^t(A_3) > \Delta H^t(A_1)] : T^t(A_1) > 0$$

$$\frac{\Delta H^t(A_3)}{T^t(A_1)} > \frac{\Delta H^t(A_1)}{T^t(A_1)} = \Delta S^t(A_1) \qquad (24)$$

And further it holds also

$$T^t(A_3) < T^t(A_1)$$

and therefore

$$\left[\frac{1}{T^t(A_3)} > \frac{1}{T^t(A_1)}\right] \cdot \Delta H^t(A_3)$$

$$\frac{\Delta H^t(A_3)}{T^t(A_3)} = \Delta S^t(A_3) > \frac{\Delta H^t(A_3)}{T^t(A_1)} \qquad (25)$$

Combining the inequality (24) with eqn (25) we confirm the validity of the relation

$$\Delta S^t(A_3) > \Delta S^t(A_1) \qquad (26)$$

The temperature $T^t(A_3)$ which occurs in eqn (22) is not accessible to measurement at equilibrium conditions. We can, however, to eliminate this quantity using eqn (19). After rearrangement we obtain the relationship

$$T^{tr}(A_1/A_3) =$$

$$= \frac{[\Delta H^{tr}(A_1/A_2) + \Delta H^{tr}(A_2/A_3)] \cdot T^{tr}(A_1/A_2) \cdot T^{tr}(A_2/A_3)}{\Delta H^{tr}(A_1/A_2) \cdot T^{tr}(A_2/A_3) + \Delta H^{tr}(A_2/A_3) \cdot T^{tr}(A_1/A_2)} \qquad (27)$$

at the derivation of eqn (27) we used the expression

$$\Delta H^{tr}(A_1/A_2) + \Delta H^{tr}(A_2/A_3) = \Delta H^t(A_3) - \Delta H^t(A_1)$$

which is identical with eqn (2).

All quantities which occur on the right side of eqn (27) are accessible to experimental determination at equilibrium conditions.

c) Calculation of the activity of component A at the point $Q(A_1/A_3)$

If we know value of the quantity $T^{tr}(A_1/A_3)$, the activity (respectively its logarithm) can be determined from eqn (20)

$$\ln a[A, Q(A_1/A_3)] =$$

$$= \frac{\Delta H^t(A_1)}{R} \cdot \frac{\Delta H^t(A_3) \cdot [T^t(A_3) - T^t(A_1)]}{[\Delta H^t(A_3) - \Delta H^t(A_1)] \cdot T^t(A_1) \cdot T^t(A_3)} \qquad (28)$$

Eqn (28) can be rearranged to the form

$$\ln a[A, Q(A_1/A_3)] = \frac{[1/T^t(A_1) - 1/T^t(A_3)]}{R \cdot [1/\Delta H^t(A_1) - 1/\Delta H^t(A_3)]} \qquad (29)$$

If we substitute for $T^t(A_3)$ from eqn (19) into eqn (28), we obtain

$$\ln a[A, Q(A_1/A_3)] =$$

$$= \frac{\Delta H^t(A_1)}{R \cdot T^t(A_1)} \cdot \frac{V + Z}{[\Delta H^{tr}(A_1/A_2) + \Delta H^{tr}(A_2/A_3)] \cdot T^{tr}(A_1/A_2)} \cdot \frac{1}{T^{tr}(A_2/A_3)} \qquad (30)$$

Here

$$V = \Delta H^{tr}(A_1/A_2) \cdot T^{tr}(A_2/A_3) \cdot [T^{tr}(A_1/A_2) - T^t(A_1)]$$

$$Z = \Delta H^{tr}(A_2/A_3) \cdot T^{tr}(A_1/A_2) \cdot [T^{tr}(A_2/A_3) - T^t(A_1)]$$

d) Determination of ratio of the slopes of tangents to the curves of phase equilibrium at the hypothetical transition point $Q(A_1/A_3)$

For solution of this problem we shall use a simplified form of the CTC III. If the system $A_1 (A_2, A_3)$—B is not very far from ideal behaviour then for each transition point the following relations are valid

$$Q(A_1/A_2): \Delta H^t(A_1) \cdot k^{1/2}(A_1) = \Delta H^t(A_2) \cdot k^{1/2}(A_2) \qquad (31)$$

$$Q(A_1/A_3): \Delta H^t(A_1) \cdot k^{1/3}(A_1) = \Delta H^t(A_3) \cdot k^{1/3}(A_3) \qquad (32)$$

$$Q(A_2/A_3): \Delta H^t(A_2) \cdot k^{2/3}(A_2) = \Delta H^t(A_3) \cdot k^{2/3}(A_3) \qquad (33)$$

From equilibrium measurement we can determine the slopes of tangents to the liquidus curves $\bar{A}'/A_1^{0,s}$, and $\bar{A}'/A_2^{0,s}$ at the point $Q(A_1/A_2)$. We can determine this quantity also for liquidus curves $\bar{A}'/A_2^{0,s}$ and $\bar{A}'/A_3^{0,s}$ at the point $Q(A_2/A_3)$. The ratio of parameters $k(A_1)$ and $k(A_3)$ at the point $Q(A_1/A_3)$ which cannot be determined at equilibrium can be obtained from eqn (32)

$$\frac{k^{1/3}(A_1)}{k^{1/3}(A_3)} = \frac{\Delta H^t(A_3)}{\Delta H^t(A_1)} \qquad (34)$$

From eqn (33) we obtain for $\Delta H^t(A_3)$

$$\Delta H^t(A_3) = \frac{\Delta H^t(A_2) \cdot k^{2/3}(A_2)}{k^{2/3}(A_3)} \qquad (35)$$

and for $\Delta H^t(A_2)$ we obtain according to eqn (31)

$$\Delta H^t(A_2) = \frac{\Delta H^t(A_1) \cdot k^{1/2}(A_1)}{k^{1/2}(A_2)} \qquad (36)$$

After inserting $\Delta H^t(A_2)$ from eqn (36) into eqn (35) and from that into eqn (34) we obtain

$$\frac{k^{1/3}(A_1)}{k^{1/3}(A_3)} = \frac{k^{1/2}(A_1)}{k^{1/2}(A_2)} \cdot \frac{k^{2/3}(A_2)}{k^{2/3}(A_3)} \qquad (37)$$

respectively

$$K^{1/3} = K^{1/2} \cdot K^{2/3} \qquad (38)$$

$K^{i/j}$ denotes here the ratio of the slopes of tangents at given transition point $Q(A_i/A_j)$. It follows that it is possible to calculate this parameter in a hypothetical transition point $Q(A_1/A_3)$ on the basis of knowledge of the analogous parameters at the real transition points $Q(A_1/A_2)$ and $Q(A_2/A_3)$. It should be pointed out that it is not necessary to know the changes in enthalpy of the corresponding phase transitions.

3. The system A_1 (A_2, A_3, A_4)—B

One liquid phase L and four solid phases $A_i^{0,\,s}$ form together $\binom{5}{2} = 10$ coexisting pairs. Four are of the type $L/A_i^{0,\,s}$ and they correspond to melting points of the four polymorphic modifications. Six pairs of the type A_i/A_j ($i = 1$—3, $j = 2$—4, $j - i \geq 1$) correspond to the transition points $Q(A_i/A_j)$. Only four of these ten characteristic points are accessible to equilibrium measurement, viz. $T^t(A_1)$, $Q(A_1/A_2)$, $Q(A_2/A_3)$, and $Q(A_3/A_4)$ (Fig. 5).

a) Calculation of $T^t(A_i)$, $i > 1$

The temperature of fusion $T^t(A_2)$ of the modification A_2 can be determined using eqn (14) and the temperature $T^t(A_3)$ from eqn (19). The temperature of fusion $T^t(A_4)$ can be determined similarly as in the preceding section. For the point $Q(A_3/A_4)$ it holds

$$\ln a[A, Q(A_3/A_4)] = \frac{\Delta H^t(A_3)}{R} \cdot \left[\frac{1}{T^t(A_3)} - \frac{1}{T^{tr}(A_3/A_4)} \right] \qquad (39)$$

$$\ln a[A, Q(A_3/A_4)] = \frac{\Delta H^t(A_4)}{R} \cdot \left[\frac{1}{T^t(A_4)} - \frac{1}{T^{tr}(A_3/A_4)} \right] \qquad (40)$$

Using eqn (3) we can write after rearrangement

$$T^t(A_4) =$$

$$= \frac{[\Delta H^t(A_1) + \Delta H^{tr}(A_1/A_2) + \Delta H^{tr}(A_2/A_3) + \Delta H^{tr}(A_3/A_4)] \cdot T^t(A_3) \cdot T^{tr}(A_3/A_4)}{[\Delta H^t(A_1) + \Delta H^{tr}(A_1/A_2) + \Delta H^{tr}(A_2/A_3)] \cdot T^{tr}(A_3/A_4) + \Delta H^{tr}(A_3/A_4) \cdot T^t(A_3)} \tag{41}$$

We can substitute for $T^t(A_3)$ from eqn (19) and thus

$$T^t(A_4) = \frac{(\Sigma \Delta H) \cdot T^t(A_1) \cdot T^{tr}(A_1/A_2) \cdot T^{tr}(A_2/A_3) \cdot T^{tr}(A_3/A_4)}{Z} \tag{42}$$

where

$$\Sigma \Delta H = \Delta H^t(A_1) + \Delta H^{tr}(A_1/A_2) + \Delta H^{tr}(A_2/A_3) + \Delta H^{tr}(A_3/A_4)$$

$$\begin{aligned}
Z = &\Delta H^t(A_1) \cdot T^{tr}(A_1/A_2) \cdot T^{tr}(A_2/A_3) \cdot T^{tr}(A_3/A_4) + \\
&+ \Delta H^{tr}(A_1/A_2) \cdot T^t(A_1) \cdot T^{tr}(A_2/A_3) \cdot T^{tr}(A_3/A_4) + \\
&+ \Delta H^{tr}(A_2/A_3) \cdot T^t(A_1) \cdot T^{tr}(A_1/A_2) \cdot T^{tr}(A_3/A_4) + \\
&+ \Delta H^{tr}(A_3/A_4) \cdot T^t(A_1) \cdot T^{tr}(A_1/A_2) \cdot T^{tr}(A_2/A_3)
\end{aligned}$$

b) Calculation of the temperatures $T^{tr}(A_i/A_j)$ at the hypothetical transition points $Q(A_i/A_j)$

The value of $T^{tr}(A_1/A_3)$ can be calculated from eqn (22) or from eqn (27). $T^{tr}(A_2/A_4)$ can be determined in the following way. From the simplified form of the LeChatelier—Shreder equation we can write for the activity $a(A)$ at the point $Q(A_2/A_4)$ either

$$\ln a[A, Q(A_2/A_4)] = \frac{\Delta H^t(A_2)}{R} \cdot \left[\frac{1}{T^t(A_2)} - \frac{1}{T^{tr}(A_2/A_4)} \right] \tag{43}$$

or

$$\ln a[A, Q(A_2/A_4)] = \frac{\Delta H^t(A_4)}{R} \cdot \left[\frac{1}{T^t(A_4)} - \frac{1}{T^{tr}(A_2/A_4)} \right] \tag{44}$$

Solving these equations we obtain

$$T^{tr}(A_2/A_4) = \frac{[\Delta H^t(A_4) - \Delta H^t(A_2)] \cdot T^t(A_2) \cdot T^t(A_4)}{\Delta H^t(A_4) \cdot T^t(A_2) - \Delta H^t(A_2) \cdot T^t(A_4)} \tag{45}$$

Substituting $T^t(A_2)$ from eqn (14) and $T^t(A_4)$ from eqn (42) we obtain after rearrangement

$$T^{tr}(A_2/A_4) =$$

$$= \frac{[\Delta H^{tr}(A_2/A_3) + \Delta H^{tr}(A_3/A_4)] \cdot T^{tr}(A_2/A_3) \cdot T^{tr}(A_3/A_4)}{\Delta H^{tr}(A_2/A_3) \cdot T^{tr}(A_3/A_4) + \Delta H^{tr}(A_3/A_4) \cdot T^{tr}(A_2/A_3)} \qquad (46)$$

The quantity $T^{tr}(A_1/A_4)$ can be determined in the following way. Again we calculate the activity of component A at the point $Q(A_1/A_4)$ using the simplified form of the LeChatelier—Shreder equation. We obtain expressions similar to eqns (43) and (44). After elimination of the term $\ln a[A, Q(A_1/A_4)]$ we find

$$T^{tr}(A_1/A_4) = \frac{[\Delta H^f(A_4) - \Delta H^f(A_1)] \cdot T^f(A_1) \cdot T^f(A_4)}{\Delta H^f(A_4) \cdot T^f(A_1) - \Delta H^f(A_1) \cdot T^f(A_4)} \qquad (47)$$

$T^f(A_4)$ can be substituted from eqn (42). From eqn (3) it further follows that

$$\Delta H^f(A_4) - \Delta H^f(A_1) = \Delta H^{tr}(A_1/A_2) + \Delta H^{tr}(A_2/A_3) + \Delta H^{tr}(A_3/A_4)$$

The expression for $T^{tr}(A_1/A_4)$ results in

$$T^{tr}(A_1/A_4) = \frac{(\Sigma \Delta H) \cdot T^{tr}(A_1/A_2) \cdot T^{tr}(A_2/A_3) \cdot T^{tr}(A_3/A_4)}{U + V + Z} \qquad (48)$$

where $\Sigma \Delta H = \Delta H^{tr}(A_1/A_2) + \Delta H^{tr}(A_2/A_3) + \Delta H^{tr}(A_3/A_4)$
$U = \Delta H^{tr}(A_1/A_2) \cdot T^{tr}(A_2/A_3) \cdot T^{tr}(A_3/A_4)$
$V = \Delta H^{tr}(A_2/A_3) \cdot T^{tr}(A_1/A_2) \cdot T^{tr}(A_3/A_4)$
$Z = \Delta H^{tr}(A_3/A_4) \cdot T^{tr}(A_1/A_2) \cdot T^{tr}(A_2/A_3)$

c) Calculation of the activity of component A in solutions corresponding to hypothetical transition points

The quantity $a(A)$ at the point $Q(A_1/A_3)$ can be calculated from eqn (30). For the quantity $\ln a[A, Q(A_2/A_4)]$ in hypothetical solution it holds

$$\ln a[A, Q(A_2/A_4)] = \frac{\Delta H^f(A_2)}{R} \cdot \left[\frac{T^{tr}(A_2/A_4) - T^f(A_2)}{T^{tr}(A_2/A_4) \cdot T^f(A_2)} \right]$$

We can substitute for $T^f(A_2)$ from eqn (14) and for $T^{tr}(A_2/A_4)$ from eqn (46). Further we can utilize the relation

$$\Delta H^f(A_2) = \Delta H^{tr}(A_1) + \Delta H^{tr}(A_1/A_2)$$

After rearrangement we obtain

$$\ln a[A, Q(A_2/A_4)] = \frac{M - N}{R[\Delta H^{tr}(A_2/A_3) + \Delta H^{tr}(A_3/A_4)]} \cdot \frac{1}{U} \qquad (49)$$

where

$$M = [\Delta H^{tr}(A_2/A_3) + \Delta H^{tr}(A_3/A_4)] \cdot [\Delta H^{tr}(A_1) \cdot T^{tr}(A_1/A_2) +$$
$$+ \Delta H^{tr}(A_1/A_2) \cdot T^f(A_1)] \cdot T^{tr}(A_2/A_3) \, T^{tr}(A_3/A_4)$$

$$N = [\Delta H^{tr}(A_1) + \Delta H^{tr}(A_1/A_2)] \, [\Delta H^{tr}(A_2/A_3) \cdot T^{tr}(A_3/A_4) + \\ + \Delta H^{tr}(A_3/A_4) \cdot T^{tr}(A_2/A_3)] \cdot T^t(A_1) \cdot T^{tr}(A_1/A_2)$$

$$U = T^t(A_1) \cdot T^{tr}(A_1/A_2) \cdot T^{tr}(A_2/A_3) \cdot T^{tr}(A_3/A_4)$$

It follows again that all quantities present on the right side of eqn (49) are directly measurable, *i.e.* experimentally accessible.

For the quantity $\ln a[A, Q(A_1/A_4)]$ in the hypothetical solution which corresponds to the point $Q(A_1/A_4)$ it holds

$$\ln a[A; Q(A_1/A_4)] = \frac{\Delta H^t(A_1)}{R} \cdot \frac{T^{tr}(A_1/A_4) - T^t(A_1)}{T^{tr}(A_1/A_4) \cdot T^t(A_1)}$$

or, after substitution for $T^{tr}(A_1/A_4)$ from eqn (47)

$$\ln a[A, Q(A_1/A_4)] =$$

$$= \frac{\Delta H^t(A_1)}{R} \cdot \frac{\Delta H^t(A_4) \cdot [T^t(A_4) - T^t(A_1)]}{[\Delta H^t(A_4) - \Delta H^t(A_1)] \cdot T^t(A_1) \cdot T^t(A_4)} \qquad (50)$$

respectively

$$\ln a[A, Q(A_1/A_4)] = \frac{[1/T^t(A_1) - 1/T^t(A_4)]}{R[1/\Delta H^t(A_1) - 1/\Delta H^t(A_4)]} \qquad (51)$$

In eqns (50) and (51) there is no quantity related to the transition points $Q(A_i/A_j)$. If we substitute into eqn (50) for $T^t(A_4)$ from eqn (42) we obtain after rearrangement

$$\ln a[A, Q(A_1/A_4)] =$$

$$= \frac{\Delta H^t(A_1)}{RT^t(A_1)} \cdot \frac{M + N + U}{\Sigma\Delta H \cdot T^{tr}(A_1/A_2) \cdot T^{tr}(A_2/A_3) \cdot T^{tr}(A_3/A_4)} \qquad (52)$$

where

$$M = \Delta H^{tr}(A_1/A_2) \cdot T^{tr}(A_2/A_3) \cdot T^{tr}(A_3/A_4) \cdot [T^{tr}(A_1/A_2) - T^t(A_1)]$$
$$N = \Delta H^{tr}(A_2/A_3) \cdot T^{tr}(A_1/A_2) \cdot T^{tr}(A_3/A_4) \cdot [T^{tr}(A_2/A_3) - T^t(A_1)]$$
$$U = \Delta H^{tr}(A_3/A_4) \cdot T^{tr}(A_1/A_2) \cdot T^{tr}(A_2/A_3) \cdot [T^{tr}(A_3/A_4) - T^t(A_1)]$$
$$\Sigma\Delta H = \Delta H^{tr}(A_1/A_2) + \Delta H^{tr}(A_2/A_3) + \Delta H^{tr}(A_3/A_4)$$

d) Determination of ratio of the slopes of tangents to the curves of phase equilibria at the hypothetical transition points $Q(A_i/A_j)$

For the point $Q(A_1/A_3)$ the relations (37) and (38) hold. Using the simplified form of CTC.III we obtain for the ratio in question calculated at the point $Q(A_2/A_4)$ the following equations

$$Q(A_2/A_3): \Delta H^t(A_2) \cdot k^{2/3}(A_2) = \Delta H^t(A_3) \cdot k^{2/3}(A_3) \qquad (33)$$

$$Q(A_2/A_4): \Delta H^f(A_2) \cdot k^{2/4}(A_2) = \Delta H^f(A_4) \cdot k^{2/4}(A_4) \tag{53}$$

$$Q(A_3/A_4): \Delta H^f(A_3) \cdot k^{3/4}(A_3) = \Delta H^f(A_4) \cdot k^{3/4}(A_4) \tag{54}$$

Then from eqn (53) it follows

$$\frac{k^{2/4}(A_2)}{k^{2/4}(A_4)} = \frac{\Delta H^f(A_4)}{\Delta H^f(A_2)} \tag{55}$$

The quantity $\Delta H^f(A_4)$ can be determined from eqn (54) and the quantity $\Delta H^f(A_2)$ from eqn (33). After substituting into eqn (55) we obtain after rearrangement

$$\frac{k^{2/4}(A_2)}{k^{2/4}(A_4)} = \frac{k^{2/3}(A_2)}{k^{2/3}(A_3)} \cdot \frac{k^{3/4}(A_3)}{k^{3/4}(A_4)} \tag{56}$$

which can be written also in the form

$$K^{2/4} = K^{2/3} \cdot K^{3/4} \tag{57}$$

It remains to determine the ratio of the slopes of tangents to liquidus curves at the "internal" hypothetical transition point $Q(A_1/A_4)$.

For solution of this problem we shall use the value of this ratio at real transition points $Q(A_1/A_2)$, $Q(A_2/A_3)$, and $Q(A_3/A_4)$ (Fig. 5). These quantities are deter-
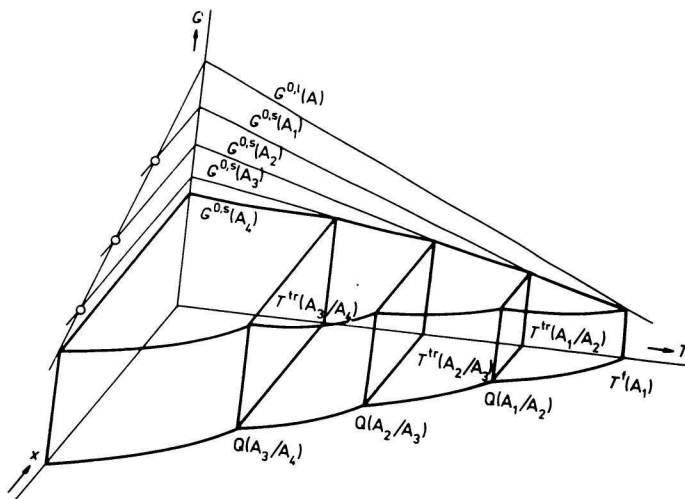

Fig. 6. Part of the phase diagram of the system A_1 (A_2, A_3, A_4)—B corresponding to the composition interval from eutectic point to pure substance A. The diagram is presented as a projection of intersection of five surfaces representing molar Gibbs energies $G^{0,\cdot}(A_i) = f(T)$, $(i = 1—4)$ and $\bar{G}^{0,\cdot}(A) = f[T, x(A)]$.

mined by eqns (31), (33), and (54), respectively. Using a procedure similar to the former one we obtain for this case the following relation

$$\frac{k^{1/4}(A_1)}{k^{1/4}(A_4)} = \frac{k^{1/2}(A_1)}{k^{1/2}(A_2)} \cdot \frac{k^{2/3}(A_2)}{k^{2/3}(A_3)} \cdot \frac{k^{3/4}(A_3)}{k^{3/4}(A_4)} \qquad (58)$$

which can be written also as

$$K^{1/4} = K^{1/2} \cdot K^{2/3} \cdot K^{3/4} \qquad (59)$$

As it follows from Fig. 6 the phase diagram (if component A has four polymorphic modifications) of a binary system A—B corresponds to the orthogonal projection of surfaces representing the quantities $G^{0,s}(A_i) = f(T)$ and $\bar{G}^l(A) = f(T, x)$, $(i = 1$—$4)$ on the basic plane (T, x).

4. The system $A_1 (A_2, ..., A_n)$—B

The thermodynamic analysis of phase diagram of the systems in question can be generalized for the case when the component A forms an arbitrary number of polymorphic enantiotropic modifications.

a) Calculation of $T^t(A_i)$

These considerations are based on coordinates of the transition point $Q(A_i/A_{i+1})$ which can be determined experimentally at equilibrium conditions. This point corresponds to the intersection of two liquidus curves $\bar{A}^l/A_i^{0,s}$ and $\bar{A}^l/A_{i+1}^{0,s}$. We shall apply the Le Chatelier—Shreder equation to these points which gives

$$\ln a[A, Q(A_i/A_{i+1})] = f_1[T^t(A_i), \Delta H^t(A_i)] \qquad (60)$$

$$\ln a[A, Q(A_i/A_{i+1})] = f_2[T^t(A_{i+1}), \Delta H^t(A_{i+1})] \qquad (61)$$

As we know the quantities $\Delta H^t(A_1)$ and $\Delta H^{tr}(A_i/A_{i+1})$ are accessible to a direct measurement. Thus using eqn (3) we are able to determine the value of an arbitrary quantity $\Delta H^t(A_i)$.

From eqns (60) and (61) we shall further eliminate the term containing the activity of component A. After rearrangement we obtain (the enthalpic terms are not written for the sake of simplicity)

$$T^t(A_{i+1}) = f_3[T^t(A_i)] \qquad (62)$$

Therefore it follows that for determination of the quantity $T^t(A_{i+1})$ it is sufficient to know the quantity $T^t(A_i)$. Since the relation (62) holds for all values of i, starting from $i = 1$, and because the quantity $T^t(A_1)$ is experimentally accessible eqn (62) gives a recursion formula for determination of an arbitrary temperature of fusion of the $(i+1)$th polymorphic modification of component A.

b) Calculation of the temperature $T^{tr}(A_i/A_j)$ and the activity $a[A, Q(A_i/A_j)]$ at an arbitrary transition point $Q(A_i/A_j)$, $j-i \geq 2$

Let us apply the LeChatelier—Shreder equation to the figurative point $Q(A_i/A_j)$. We obtain the following relations (the enthalpic terms are omitted)

$$\ln a[A, Q(A_i/A_j)] = f[T^t(A_i), T^{tr}(A_i/A_j)] \qquad (63)$$

$$\ln a[A, Q(A_i/A_j)] = f[T^t(A_j), T^{tr}(A_i/A_j)] \qquad (64)$$

The quantities $T^t(A_i)$ and $T^t(A_j)$ can be obtained in the same way as in the preceding paragraphs. Then we have the set of two equations ((63) and (64)) with two variables (*viz.* $\ln a[A, Q(A_i/A_j)]$ and $T^{tr}(A_i/A_j)$) which can be therefore unambiguously determined.

c) Determination of ratio of the slopes of tangents to the curves of phase equilibrium at an arbitrary hypothetical transition point $Q(A_i/A_j)$, $j-i \geq 2$

For the determination of ratio of the slopes of tangents at the hypothetical transition point $Q(A_i/A_j)$ we shall use the data which are experimentally accessible, namely $Q(A_i/A_{i+1})$, $Q(A_{i+1}/A_{i+2})$, ..., $Q(A_{j-1}/A_j)$. For all these points it holds

$$\frac{\Delta H^t(A_{i+1})}{\Delta H^t(A_i)} = \frac{k_i^{i/(i+1)}}{k_{i+1}^{i/(i+1)}} = K^{i/(i+1)} \qquad (65a)$$

$$\frac{\Delta H^t(A_{i+2})}{\Delta H^t(A_{i+1})} = K^{(i+1)/(i+2)} \qquad (65b)$$

$$\vdots$$

$$\frac{\Delta H^t(A_{j-1})}{\Delta H^t(A_{j-2})} = K^{(j-2)/(j-1)} \qquad (65y)$$

$$\frac{\Delta H^t(A_j)}{\Delta H^t(A_{j-1})} = K^{(j-1)/j} \qquad (65z)$$

After multiplying the left and right sides of eqns ($65a$—z) we obtain after rearrangement

$$\frac{\Delta H^t(A_j)}{\Delta H^t(A_i)} = K^{i/(i+1)} \cdot K^{(i+1)/(i+2)} \ldots K^{(j-1)/j}$$

which can be written also as

$$\frac{\Delta H^f(A_j)}{\Delta H^f(A_i)} = \prod_i^{j-1} K^{i/(i+1)} \qquad (66)$$

Applying the simplified form of the CTC III to the point $Q(A_i/A_j)$ we obtain the general law

$$\frac{\Delta H^f(A_j)}{\Delta H^f(A_i)} = \frac{k_i^{i/j}}{k_j^{i/j}} = K^{i/j} \qquad (67)$$

Comparison of eqns (66) and (67) gives the final relationship

$$K^{i/j} = \prod_i^{j-1} K^{i/(i+1)} \qquad (68)$$

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