Thermodynamics of phase equilibria in the systems with polymorphic transitions
III. Systems having limiting solid solutions but no compounds

I. KOŠTENSKÁ and M. MALINOVSKÝ

Department of Inorganic Technology, Slovak Technical University,
812 37 Bratislava

Dedicated to Corresponding Member M. Zikmund, in honour of his 60th birthday

In this paper we discuss the systems forming one-side or both-sides limiting solid solutions in which either eutectoid or peritectoid reactions can take place. The equations of the curve of monovariant equilibrium which connects the transition point of polymorphic modification of pure component with eutectoid point are derived. If a pure solid compound is in equilibrium with solid solution it is possible to derive from this equation the relationship similar to the first criterion of thermodynamic consistency describing the course of liquidus curve in the vicinity of melting point of pure substance.

В работе обсуждаются системы, образующие односторонние или двухсторонние твердые растворы, в которых протекают эвтектоидные или перитектоидные реакции. Получены уравнения, связывающие точки перехода полиморфных модификаций чистых компонентов с эвтектоидной точкой. Если чистое твердое соединение находится в равновесии с твердым раствором, возможно из этого уравнения получить отношение похожее на первый критерий термодинамической конзистентности, описывающее ход кривых ликвидуса в окрестности точки плавления чистого вещества.

1. Only eutectoid type reactions occur in the systems

We shall pay attention only to the most characteristic types of these systems, *viz.* to the systems with limiting solid solutions formed on one side, to the systems having limiting solid solutions on both sides and one eutectoid point and lastly to the systems with both-sides limiting solid solutions and two eutectoid points.

Systems having limiting solid solutions on one side

The corresponding phase diagrams are plotted in Figs. 1 and 2. In the first phase diagram (Fig. 1) there is a simple eutectoid point ε. If we take heat from the system
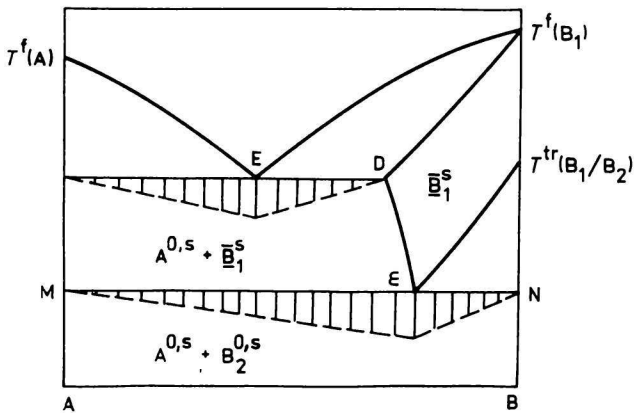
Fig. 1. Phase diagram of the condensed system A—B_1 (B_2) with limiting one-side solid solution formed on the basis of high temperature polymorphic modification B_1^s. ·
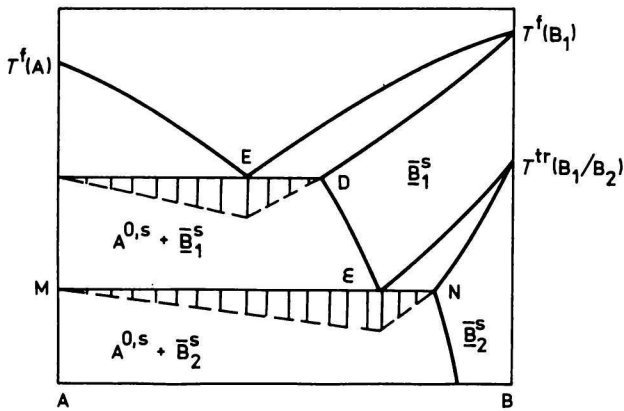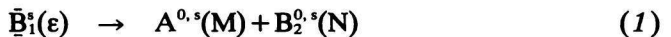

Fig. 2. Phase diagram of the condensed system A—B_1 (B_2) with limiting one-side solid solutions formed on the basis of both polymorphic modifications of component B.

a limiting solid solution $\underline{\bar{B}}_1^s$ which is formed on the basis of the modification B_1 and the composition of which corresponds to the point ε decomposes according to the scheme

$$\underline{\bar{B}}_1^s(\varepsilon) \quad \rightarrow \quad A^{0,\,s}(M) + B_2^{0,\,s}(N) \tag{1}$$

Therefore in equilibrium the solution $\underline{\bar{B}}_1^s$ coexists with pure solid substance A and B_2. Because $v = k - f + 1 = 2 - 3 + 1 = 0$ the equilibrium is nonvariant which is an analogue to a simple eutectic crystallization.

The eutectoid point ε lies on the intersection of the part of binoidal curve (ε, D) (which corresponds to the solubility of component A in solid solution formed on the basis of high temperature modification of the component B) and of the curve (T^{tr}, ε). The latter curve corresponds to the limiting solid solution which is formed on the basis of high temperature modification B_1 and which is saturated with the low temperature modification B_2.
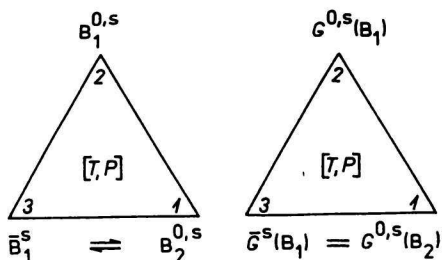

Fig. 3. Three-term cycles for mass and Gibbs energy changes (isothermal-isobaric) used for derivation of the equation of monovariant phase coexistence of the limiting solid solution formed on the basis of high temperature modification B_1 (*i.e.* $\tilde{B}_1^s$) with pure solid phase $B_2^{0,s}$.
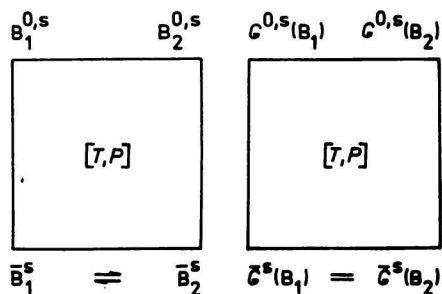
Fig. 4. Four-term cycles for mass and Gibbs energy changes (isothermal-isobaric) used for derivation of the equation of monovariant phase coexistence of limiting solid solutions $\tilde{B}_1^s$ and $\tilde{B}_2^s$.

For derivation of equation of the curve of monovariant equilibrium (T^{tr}, ε) we shall use the method of isothermal-isobaric ΔG cycle as it has been described in [1]. *Førland* and *Krogh-Moe* have solved this problem using another approach [2].

It holds (Fig. 3)

$$\Sigma \Delta G = \Delta G^{2/1} + \Delta G^{3/2} + \Delta G^{1/3} = 0$$

$$\Delta G^{2/1} = G^{0,\,s}(B_1) - G^{0,\,s}(B_2) = \Delta G^{tr}(B_1/B_2)$$

$$\Delta G^{3/2} = \bar{G}^s(B_1) - G^{0,\,s}(B_1) = RT \ln a^s(B_1)$$

The condition of phase equilibrium is

$$\Delta G^{1/3} = G^{0,\,s}(B_2) - \bar{G}^s(B_1) = 0$$

Thus

$$RT \ln a^s(B_1) = -\Delta G^{tr}(B_1/B_2) = -[\Delta H^{tr}(B_1/B_2) - T\Delta S^{tr}(B_1/B_2)]$$

which can be written also as

$$\ln a^s(B_1) = \frac{\Delta H^{tr}(B_1/B_2)}{R} \cdot \left[\frac{1}{T^{tr}(B_1/B_2)} - \frac{1}{T} \right] \qquad (2)$$

The relationship (2) holds exactly when $\Delta H^{tr}(B_1/B_2)$ does not depend on temperature. As usually $T^{tr} - T(\varepsilon) < 100$—150 K it is possible to use eqn (2) with sufficient accuracy even when the assumption on temperature independence of the quantity $\Delta H^{tr}(B_1/B_2)$ is not fulfilled.

Eqn (2) is completely analogous to the LeChatelier—Shreder equation which describes the course of liquidus curves in simple eutectic systems. This circumstance is important not only from the point of view of systematic development of the theory of heterogeneous equilibria but also for laboratory praxis. It is known that course of the curves (D, ε) and (T^{tr}, ε) can be experimentally determined only with difficulties. On the other hand, the quantities $T^{tr}(B_1/B_2)$, $\Delta H^{tr}(B_1/B_2)$, and $T(\varepsilon)$ can be measured relatively easily. Then using eqn (2) we can calculate coordinates of the point ε. It is often sufficient to assume ideal behaviour only of the limiting solid solution which is formed on the basis of modification B_1. In all other cases it is sufficient to employ a simple "universal" relationship [3]

$$a(i) = x(i)[\exp k^{St}(j/i)]; \qquad k^{St}(j/i) = \text{const} \qquad (3)$$

From eqn (2) it follows that

$$\lim_{x(i) \to 1} \frac{\mathrm{d}T}{\mathrm{d}x(i)} = \frac{R(T^{tr})^2}{\Delta H^{tr}} \cdot k^{St}(j/i) \qquad (4)$$

This relationship is the criterion of thermodynamic consistency I modified for equilibrium of the type "solidus I—solidus II". In case of the system presented in Fig. 1 we can, therefore, calculate easily any part of the liquidus curve $[T^t(A), E]$ starting from the point $T^t(A)$ and practically also total curve of monovariant equilibrium $[T^{tr}(B_1/B_2), \varepsilon]$.

Determination of the course of liquidus curve in the vicinity of the point $T^t(B_1)$ requires an assumption on the character of the limiting solid solution which is formed on the basis of modification B_1[4]. The same is true for the liquidus curve in vicinity of the eutectic point E [5].

In the case of the phase diagram which is illustrated in Fig. 2 the eutectoid reaction is more complicated. When we remove heat from the solid solution formed on the basis of modification B_1 which has composition and temperature of the eutectoid point ε, a reversible reaction of decomposition of this solution proceeds, which results in the formation of pure solid phase $A^{0, s}$ and of solid solution formed on the basis of modification B_2

$$\bar{B}_1^s(\varepsilon) \quad \to \quad A^{0, s}(M) + \bar{B}_2^s(N) \qquad (5)$$
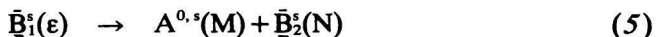
The symbols $\bar{B}_1^s(\varepsilon)$, $\bar{B}_2^s(N)$ in eqn (5) denote the limiting solid solution formed on the basis of modification B_1 and B_2 with composition and temperature of the point ε and N, respectively (Fig. 2).

The equation of the curve of monovariant equilibrium (ε, T^{tr}) can be derived by application of the isothermal-isobaric ΔG cycle having four terms (Fig. 4)

$$\Sigma \Delta G = \Delta G^{2/1} + \Delta G^{3/2} + \Delta G^{4/3} + \Delta G^{1/4} = 0$$

$$\Delta G^{2/1} = G^{0,\,s}(B_2) - \bar{G}^s(B_2) = -RT \ln a^s(B_2)$$

$$\Delta G^{3/2} = G^{0,\,s}(B_1) - G^{0,\,s}(B_2) = \Delta G^{tr}(B_1/B_2)$$

$$\Delta G^{4/3} = \bar{G}^s(B_1) - G^{0,\,s}(B_1) = RT \ln a^s(B_1)$$

$$\Delta G^{1/4} = \bar{G}^s(B_2) - \bar{G}^s(B_1) = 0$$

and therefore

$$RT \ln a^s(B_1) - RT \ln a^s(B_2) = -\Delta G^{tr}(B_1/B_2)$$

After rearrangement we obtain

$$\ln \frac{a^s(B_1)}{a^s(B_2)} = \frac{\Delta H^{tr}(B_1/B_2)}{R} \cdot \left[\frac{1}{T^{tr}(B_1/B_2)} - \frac{1}{T} \right] \tag{6}$$

Often it is possible to replace the ratio of activities on the left side of eqn (6) by the ratio of mole fractions of component B in the coexisting solid solutions. In general case it is necessary to know the functions

$$a^s(B_1) = f[x(B)]; \quad a^s(B_2) = f[x(B)]$$

Systems forming limiting solid solutions on both sides with one eutectoid point

The corresponding phase diagrams are given in Figs. 5 and 6.

When we remove heat from the system having composition of the eutectoid point ε (Fig. 6) the following reversible reaction takes place

$$\bar{\underline{B}}^s_1(\varepsilon) \quad \rightarrow \quad \bar{A}^s(R) + \bar{\underline{B}}^s_2(S) \tag{7}$$
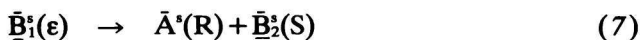
For determination of the course of liquidus curves in the vicinity of the points $T^t(A)$, E, and $T^t(B_1)$ it is necessary to have information on character of the limiting solid solutions formed on the basis of component A and modification B_1, respectively.

For the curve (ε, T^{tr}) (Fig. 5) eqn (2) holds. The curve (ε, T^{tr}) (Fig. 6) obeys the relationship (6).
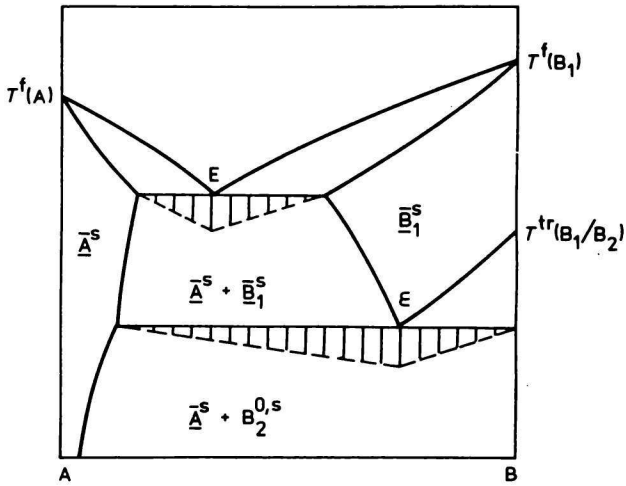
Fig. 5. Phase diagram of the condensed system A—B$_1$ (B$_2$) with solid solutions on both sides and having one simple eutectoid point.
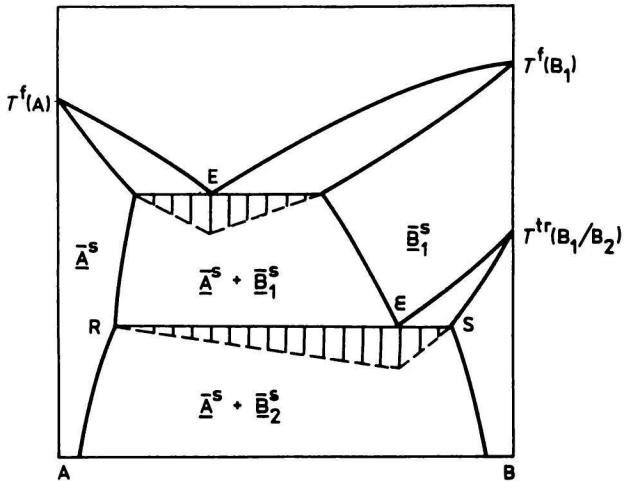

Fig. 6. Phase diagram of the condensed system A—B$_1$ (B$_2$) with solid solutions on both sides and with one eutectoid point.

Systems forming limiting solid solutions on both sides and having two eutectoid points

The phase diagrams of the systems of this type are illustrated in Figs. 7 and 8. For these systems the same rules are valid as for those given in Figs. 5 and 6. From

the point of view of information which can be obtained from knowledge of a phase diagram the system presented in Fig. 7 is especially useful. If we determine experimentally the temperatures $T^{tr}(A_1/A_2)$ and $T^{tr}(B_1/B_2)$ and coordinates of the simple eutectoid points ε_1 and ε_2 we can calculate the enthalpies of polymorphic
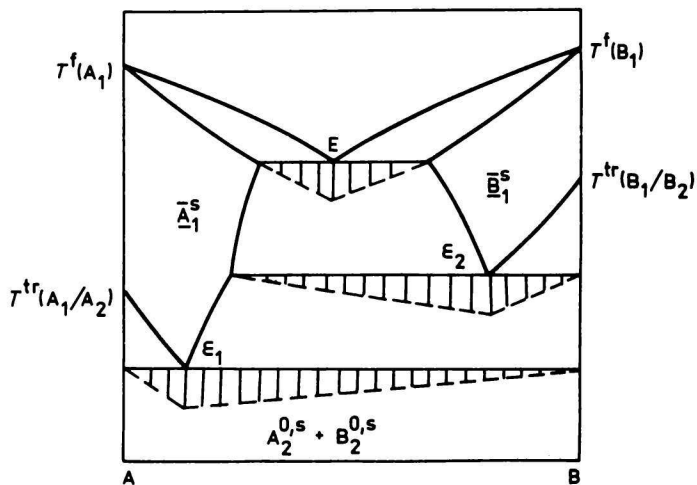

Fig. 7. Phase diagram of the condensed system A_1 (A_2)—B_1 (B_2) with solid solutions formed on the basis of high temperature polymorphic modifications on both sides of the diagram. There are two simple eutectoid points in the subsolidus region.
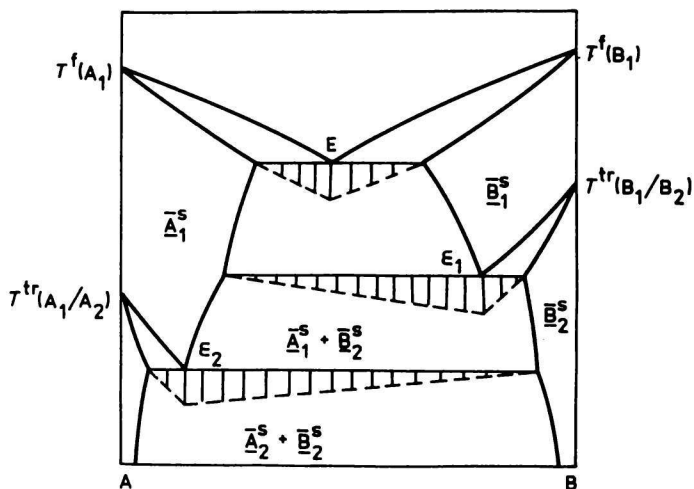

Fig. 8. Phase diagram of the condensed system A_1 (A_2)—B_1 (B_2) with solid solutions on both sides and with two eutectoid points in the subsolidus region.

transitions $\Delta H^{tr}(A_1/A_2)$ and $\Delta H^{tr}(B_1/B_2)$. Oppositely, if we know these values we can determine positions of the points ε_1 and ε_2.

2. Both eutectoid and peritectoid reactions take place in the systems

The main types of phase diagrams of the corresponding systems are given in Figs. 9—14. In the case which is illustrated in Fig. 9 the temperature $T^{tr}(B_1/B_2)$ decreases with addition of substance A. Existence of the eutectoid point is the result of this decrease in temperature. However, the temperature of transition
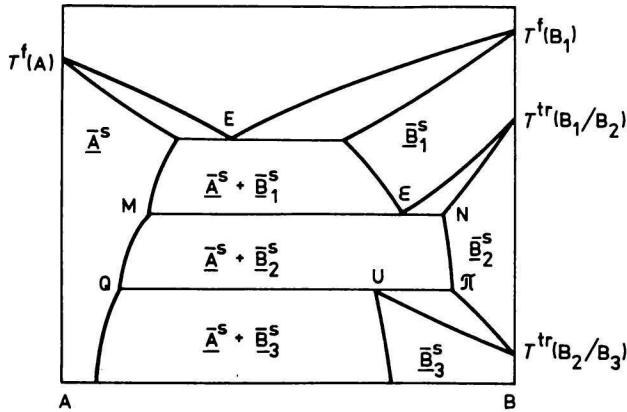

Fig. 9. Phase diagram of the condensed system A—B_1 (B_2, B_3) with solid solutions on both sides. In the subsolidus region there are one eutectoid and one peritectoid points; $T(\pi) < T(\varepsilon)$.
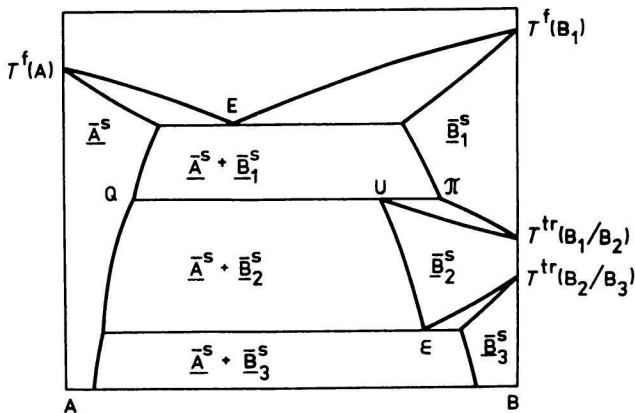

Fig. 10. Phase diagram of the condensed system A—B_1 (B_2, B_3) with solid solutions on both sides. There are one peritectoid and one eutectoid points in the subsolidus region; $T(\pi) < T(\varepsilon)$.
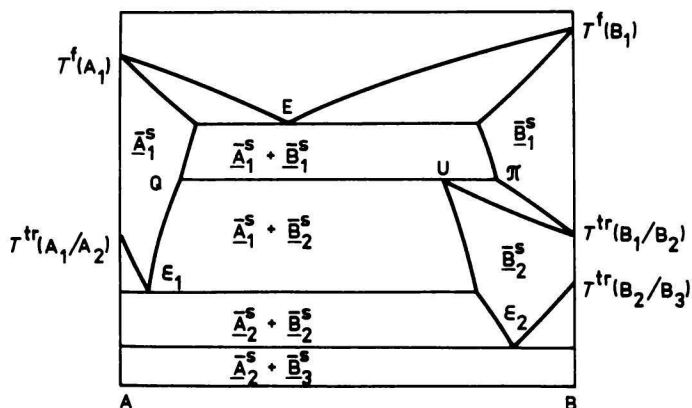
Fig. 11. Phase diagram of the condensed system A_1 (A_2)—B_1 (B_2, B_3). Limiting solid solutions are formed on the basis of the polymorphic modifications A_1, B_1, and B_2. There are one peritectoid and two simple eutectoid points in the subsolidus region.
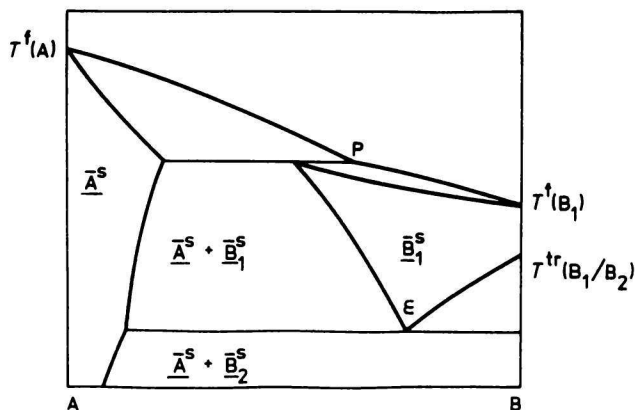

Fig. 12. Phase diagram of the condensed system A—B_1 (B_2) with limiting solid solutions formed on the basis of component A and the high temperature modification B_1. There are one peritectic and one simple eutectoid points in the phase diagram.

$T^{tr}(B_2/B_3)$ is increased by an addition of substance A, which results in occurrence of the peritectoid point π.

When we remove heat from the system then at temperatures $T(\varepsilon)$ and $T(\pi)$ the following reversible nonvariant reactions take place

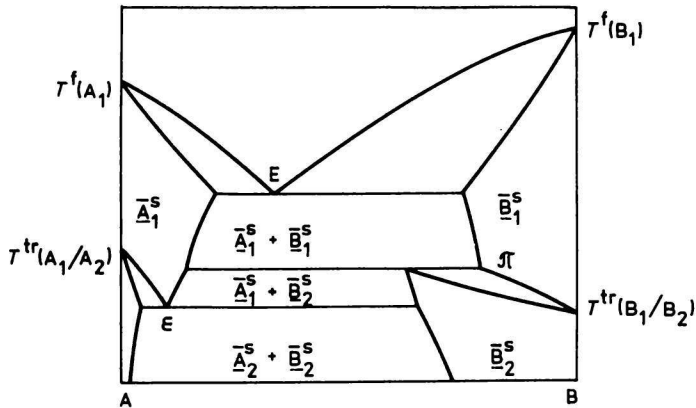$$\bar{\underline{B}}_1^s(\varepsilon) \rightarrow \bar{A}^s(M) + \hat{\underline{B}}_2^s(N) \qquad (8)$$

$$\underline{\bar{A}}^s(Q) + \underline{\bar{B}}_2^s(\pi) \rightarrow \underline{\hat{B}}_3^s(U) \qquad (9)$$

Fig. 13. Phase diagram of the condensed system A_1 (A_2)—B_1 (B_2) with limiting solid solutions on both sides. There are one eutectoid and one peritectoid points in the subsolidus region.
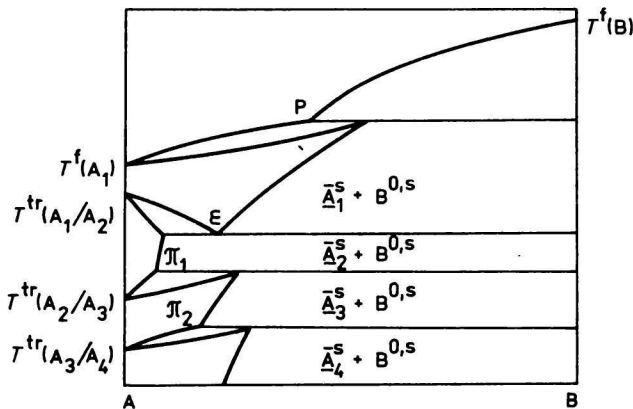

Fig. 14. Phase diagram of the condensed system A_1 (A_2, A_3, A_4)—B with one-side solid solutions formed on the basis of all modifications of component A. There are one eutectoid and two peritectoid points in the subsolidus region; $T(\pi_2) < T(\pi_1) < T(\varepsilon)$.

In this connection it should be mentioned that we may find in literature inconsistent or even wrong description of points at peritectic equilibria. *E.g.* in the well-known monograph by *Anosov et al.* [6] the figure X.11. (p. 133) of a system A—B shows that an addition of substance A increases the temperature $T^{tr}(B_1/B_2)$. The three points corresponding to peritectoid isotherm are denoted here as D—P—D′, P being the peritectoid point. (It corresponds to the point U in Fig. 9 in this paper.)

This inaccuracy is repeated in the text on page 134 where the quoted figure is described.

The systems illustrated in Figs. 9—11 obey the same rules as the diagrams described in former paragraphs of this paper. The simplest case is the calculation of the course of monovariant curves $[T^{tr}(A_1/A_2), \varepsilon_1]$ and $[T^{tr}(B_2/B_3), \varepsilon_2]$ for the system given in Fig. 11. We shall give some examples of the systems of this type. According to *Scarpa* [7] the system KCl—KOH is of the type illustrated in Fig. 12. Phase diagram of the system $PbWO_4$—$PbSO_4$ which was studied by *Jaeger* and *Germs* [8] corresponds to the type given in Fig. 13. And finally, the system NH_4NO_3—$(NH_4)_2SO_4$ measured by *Nikonova* and *Bergman* [9] belongs to the type presented in Fig. 14.

References

1. Malinovský, M., *Chem. Zvesti 30*, 721 (1976).
2. Förland, T. and Krogh-Moe, J., *Acta Chem. Scand. 13*, 1051 (1959).
3. Malinovský, M. and Koštenská, I., *Chem. Zvesti 28*, 493 (1974).
4. Malinovský, M., *Chem. Zvesti 30*, 737 (1976).
5. Hagège, R., *C. R. Acad. Sci.* (Paris) *249*, 956 (1959).
6. Anosov, V. Ya., Ozerova, M. I., and Fialkov, Yu. Ya., *Osnovy fiziko-khimicheskogo analiza.* Nauka, Moscow, 1976.
7. Scarpa, G., *Atti della Reale Accad. dei Lincei 24* (1) 738 (1915); cited according to [10], p. 656.
8. Jaeger, F. M. and Germs, H. C., *Z. Anorg. Allg. Chem. 119*, 145 (1921); cited according to [10], p. 809.
9. Nikonova, I. N. and Bergman, A. G., *Zh. Prikl. Khim. 15*, 437 (1942); cited according to [10], p. 723.
10. *Spravochnik po plavkosti sistem iz bezvodnykh neorganicheskikh solei, Vol. I, Dvoynye sistemy.* Izd. Akad. Nauk SSSR, Moscow, 1961.