Concentration vectors in phase diagrams*

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Received 28 November 1973

The substance of the method of concentration vectors and its application to phase diagrams of condensed isobaric and isothermal-isobaric systems has been explained. It has been proved that the application of this method gives the possibility rationally to justify several regularities traditionally denoted as rules used for the characterization of processes in phase diagrams, as *e.g.* the rule by van Rijn, the triangle, trapezoid, and tangent rules. In addition, the method of concentration vectors is successful even when some of these rules cannot be applied. Further it provides the possibility to determine the character of crystallization processes occurring in invariant points of phase diagrams.

In the study of phase equilibria in multicomponent condensed systems we often encounter with three problems. Firstly, the direction has to be determined, in which the figurative point (FP) of the liquid phase coexisting in equilibrium with several solid phases moves when the independent parameters of the system are changed. This motion of the FP of the liquid phase for isobaric systems is caused by taking the heat away. In the case of isothermal-isobaric phase diagrams the motion is caused by removing one of the components (*e.g.* water) from the system.

Another important problem is to determine the character of the process accompanying the above-mentioned motion of the FP of the liquid phase. In principle, the question is whether it is a process of the eutectic type

$$\mathrm{L} \rightleftarrows \mathrm{S}_1 + \mathrm{S}_2 + \mathrm{S}_3 + \mathrm{S}_4 + \dots \tag{A}$$

or of the peritectic type, *e.g.* of the first order

$$\mathrm{L} + \mathrm{S}_1 \rightleftarrows \mathrm{S}_2 + \mathrm{S}_3 + \mathrm{S}_4 + \dots \tag{B}$$

or of the second order

$$\mathrm{L} + \mathrm{S}_1 + \mathrm{S}_2 \rightleftarrows \mathrm{S}_3 + \mathrm{S}_4 + \dots, \tag{C}$$

where L is the liquid phase, S_1, S_2, *etc.* denote the solid phases being in equilibrium with the liquid phase.

The third problem concerns the phase diagrams of the systems, in which a reversible inversion of the eutectic crystallization according to eqn (*A*) to the peritectic crystallization according to eqn (*B*) or (*C*) takes place. The question is to determine the point of inversion, *i.e.* that point on the univariant equilibrium curve, in which one process changes to the other.

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* Presented at the 2nd Czechoslovak Seminar on "Molten Salt Systems", Bratislava, April 11–12, 1973.

For isobaric systems the first problem is solved by applying the rule by van Rijn van Alkemade ([1], pp. 572—573): "The line segment connecting in a phase diagram the figurative points of two solid phases, intersects the univariant curve, dividing the regions of primary crystallization of these phases in a point which is the (real or unreal) temperature maximum on this univariant curve."

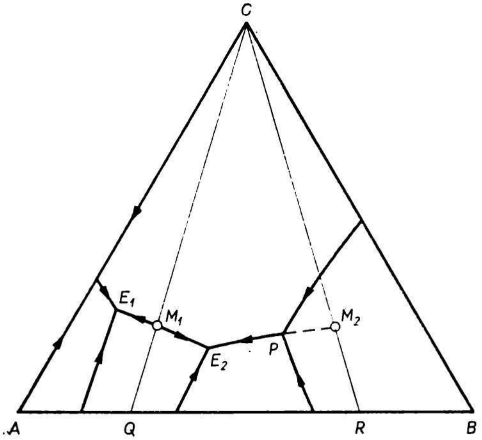

Fig. 1. Isobaric phase diagram of a ternary system with the congruently melting binary compound Q and the incongruently melting binary compound R.

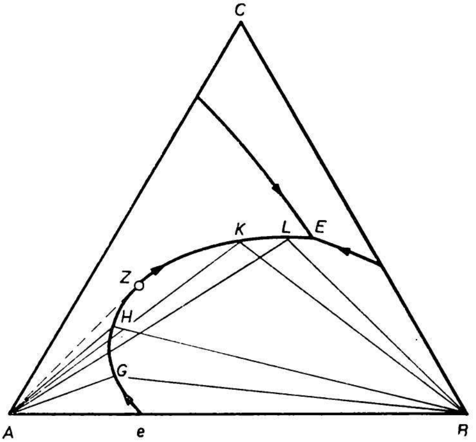

Fig. 2. Isobaric phase diagram of a ternary system, in which on the univariant curve eE the eutectic crystallization changes to a peritectic process. The inversion point Z is marked.

For the illustration of the use of this rule the projection of the phase diagram of the ternary system A—B—C may serve, containing a congruently melting binary compound Q and an incongruently melting binary compound R (Fig. 1). In the first case it concerns the solid phases C and Q, the primary crystallization regions of which are in contact along the curve E_1E_2. The line segment connecting the FPs of the phases C and Q intersects this curve in the point M_1, being the temperature minimum on the straight line segment C—Q and at the same time the temperature maximum on the curve E_1E_2. The point exhibiting these properties is often called the saddle point or the van Rijn point ([1], p. 572). Therefore on the curve E_1E_2 the temperature decreases from the point M_1 in both directions to points E_1 and E_2 as shown by arrows in Fig. 1.

An analogous consideration of the coexistence of the solid phases C and R shows that the primary crystallization regions of these phases are in contact along the univariant curve PE_2. Its extrapolated part intersects the straight line segment C—R in the point M_2, being the unreal temperature maximum on the curve M_2PE_2. Thus the temperature decreases along the univariant curve from M_2 to P and from there to E_2.

In its original form the van Rijn rule cannot be applied to an isothermal-isobaric diagram (usually the systems containing water as one of the components).

The second problem, namely the determination of the character of processes occurring along the univariant equilibrium curves is solved using the following rules: Let the points

P and Q be the FPs on the univariant equilibrium curve L + A_s + B_s (index "s" denotes the solid phase). If the whole triangle APB is a part of the triangle AQB, the process shows a eutectic character. If the triangle APB partly overlaps the triangle AQB (*i.e.* if the formation APQB is in general a trapezoid), the process is of peritectic nature. These rules may be cleared up by means of Fig. 2. On the whole curve of univariant equilibrium, along which the phases L, A_s, and B_s coexist in equilibrium, the temperature falls from e to E.

Let P = G and Q = H. Then the triangle AGB forms a part of the triangle AHB and therefore the process on the segment PQ is a eutectic one (*i.e.* $L \rightleftarrows A_s + B_s$).

For P = K and Q = L the triangles AKB and ALB partially overlap (the points AKLB form a trapezoid) and the process running on the segment KL is a peritectic one (in the given case $L + B_s \rightleftarrows A_s$).

Both the rules, *i.e.* that of the "triangle" and that of the "trapezoid" fail, if they are applied to two points on the same univariant curve, each of them corresponding to the other process (see, *e.g.* the triangles AGB and AKB, Fig. 2).

The third problem, namely the determination of the position of the inversion point, is solved as follows. From the FP of one of the solid phases being in equilibrium along the univariant curve with the liquid phase of variable composition a tangent is laid to the univariant equilibrium curve. Then the common point of this tangent and the univariant curve (in Fig. 2 marked with Z) is the inversion point searched for.

All the said regularities, namely, those by van Rijn, the triangle, trapezoid, and tangent rules, are the consequence of the lever rule. The same laws can be obtained using the concept of the vectors of concentration changes (concentration vectors). It has to be noted that the application of concentration vectors appears to be successful without any exception.

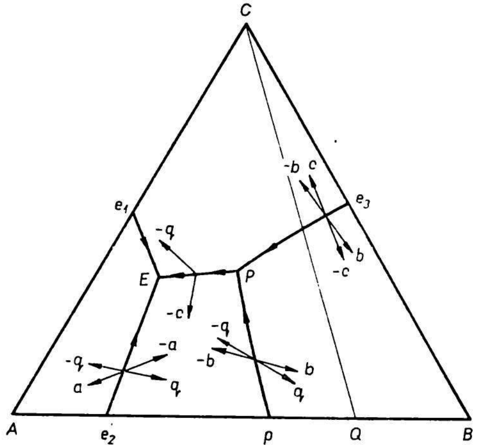

Fig. 3. Isobaric phase diagram of a ternary system containing the binary compound Q with an incongruent melting point. On the curves of the univariant equilibria the concentration vectors are marked belonging to the solid phases that coexist with the liquid phase.

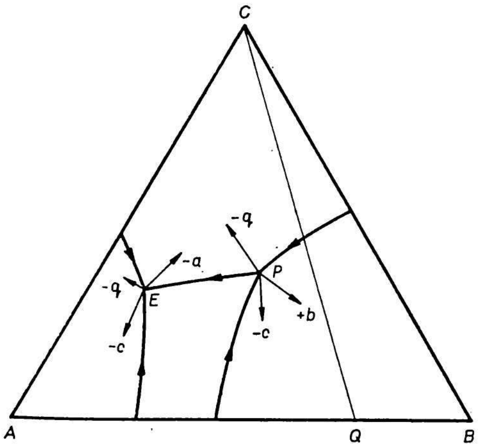

Fig. 4. Isobaric phase diagram of a ternary system, in which the binary compound Q with an incongruent melting point exists. The figure represents the invariant points E and P expressed by vectors.

The concept of "composition" or "motion" vectors and their relationship with crystallization processes has been presented by *Ricci* ([2], pp. 224, 420). *Abramov et al.* ([3], p. 394) have used such vectors to elucidate the observed changes in the composition of the electrolyte for the production of aluminium during electrolysis.

The method of concentration vectors in phase diagrams has not yet been systematically developed, nor have been demonstrated the possibilities being given by its application.

In our considerations the concentration vector of a particular constituent is defined as an arrow (a line segment), representing in the phase diagram the course of the FP of the liquid phase, if the concentration of this constituent in the liquid phase changes. The signs "+" and "−" denote respectively the concentration increase and decrease of the given constituent in the liquid phase.

Vectors are quantities having both magnitude and direction. The physical meaning of the direction of a concentration vector in a phase diagram has been explained. The magnitude of a concentration vector may be chosen arbitrarily; it is evident that the FP of a liquid phase if determined as the sum of concentration vectors can be situated only on univariant curves or invariant points of the given phase diagram.

For the sake of simplicity let us consider an isobaric phase diagram of a ternary system without solid solutions (Fig. 3).

The liquid phase L coexists along the curve of the univariant equilibrium with two solid phases ($\boldsymbol{v} = \boldsymbol{k} - \boldsymbol{f} + 1 = 3 - 3 + 1 = 1$) and the projection of the univariant curve is thus given by the vector sum of the concentration vectors of both solid phases, *e.g.* of B and C.

Apparently there are four possible combinations of these vectors marked as $\boldsymbol{b}$ and $\boldsymbol{c}$: $(\boldsymbol{b}, \boldsymbol{c})$, $(\boldsymbol{b}, -\boldsymbol{c})$, $(-\boldsymbol{b}, \boldsymbol{c})$, and $(-\boldsymbol{b}, -\boldsymbol{c})$. The course of the univariant curve indicates that two of these couples are unreal. From the remaining vector couples it may be readily found, which of them may be applied to the demanded parameter change of the given system. The application of the concentration vectors is schematically shown in Fig. 3. Thus *e.g.* the univariant curve e_3P, along which the solid phases B_s and C_s are in equilibrium with the liquid phase L, may be realized as the sum of $(\boldsymbol{b}) + (\boldsymbol{c})$ (at increasing temperature) or as that of $(-\boldsymbol{b}) + (-\boldsymbol{c})$, when the temperature falls. The same is valid for the curves e_1E and e_2E.

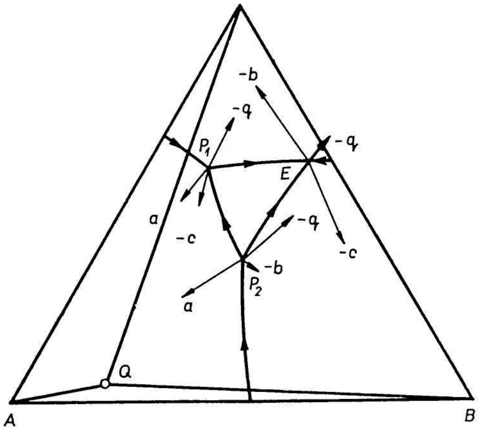

Fig. 5. Isobaric phase diagram of a ternary system containing one ternary compound Q with an incongruent melting point. The invariant points in the given system are represented by vectors.

The univariant curve PE may be apparently realized as the vector sum of $(-\boldsymbol{c}) + (-\boldsymbol{q})$ and since an elimination of the solid phases takes place at decreasing temperature, the FP of the liquid phase moves from the point P to E. This corresponds to the van Rijn rule.

In general it holds: if both the vectors have the same signs, the corresponding process shows a eutectic character.

The curve pP may be realized however only as $(-\boldsymbol{q}) + (\boldsymbol{b})$, or as $(\boldsymbol{q}) + (-\boldsymbol{b})$, respectively. If the two vectors have opposite signs, the general rule holds that the corresponding process exhibits a peritectic character.

The method of concentration vectors provides significant information also on the character of the invariant points in the phase diagrams of systems. For the point E (Fig. 4) *e.g.*, the relation holds: $(-\boldsymbol{a}) + (-\boldsymbol{b}) + (-\boldsymbol{q}) = 0$, corresponding to the eutectic reaction $L_E \rightleftarrows A_s + B_s + Q_s$. For the point P in the same diagram it holds: $(+\boldsymbol{b}) + (-\boldsymbol{c}) + (-\boldsymbol{q}) = 0$, corresponding to the peritectic reaction $L_P + B_s \rightleftarrows C_s + Q_s$.

Thus if all vectors have the same sign, it is a eutectic process; if the signs are different, the crystallization process exhibits a peritectic character.

When in the phase diagram of the system there is a ternary compound Q with an incongruently melting point (Fig. 5), the following cases may arise:

Point E: $(-\boldsymbol{b}) + (-\boldsymbol{c}) + (-\boldsymbol{q}) = 0$; process: $L_E \rightleftarrows B_s + C_s + Q_s$.

Point P$_1$: $(+\boldsymbol{a}) + (-\boldsymbol{c}) + (-\boldsymbol{q}) = 0$; process: $L_{P_1} + B_s \rightleftarrows C_s + Q_s$.

Point P$_2$: $(+\boldsymbol{a}) + (+\boldsymbol{b}) + (-\boldsymbol{q}) = 0$; process: $L_{P_2} + B_s + A_s \rightleftarrows Q_s$.

For the invariant point P$_1$ it is a first-order peritectic process. For the point P$_2$ it is a peritectic process of the second order (a "twofold" peritectic process; [4], p. 160).

Peritectic processes of the order higher than three cannot exist in a ternary system, as it clearly follows from the phase rule of Gibbs.

Finally let us show the way how the method of concentration vectors solves the third problem, namely the transition of the eutectic process to the peritectic along the same univariant curve. It holds for the line eZ, except point Z (Fig. 2), that it is given by the sum $(-\boldsymbol{a}) + (-\boldsymbol{b})$. Likewise it holds for the line ZE, except Z, that it equals the vector sum $(-\boldsymbol{a}) + (+\boldsymbol{b})$. Just in the point Z there exists a single infinitesimally small vector $(-\boldsymbol{a})$ only. Thus the point Z is a common point of the curve eE and the tangent laid from point A to this curve.

References

1. Anosov, V. Yu. and Pogodin, S. A., *Osnovnye nachala fiziko-khimicheskogo analiza.* (Fundamentals of Physicochemical Analysis.) Publishing House of the Academy of Sciences USSR, Moscow—Leningrad, 1947.
2. Ricci, J. E., *The Phase Rule and Heterogeneous Equilibrium.* Van Nostrand, Toronto, 1951.
3. Abramov, G. A., Vetyukov, M. M., Gupalo, I. P., Kostyukov, A. A., and Lozhkin, L. N., *Teoreticheskie osnovy elektrometallurgii alyuminiya.* (Theoretical Principles of the Electrometallurgy of Aluminium.) Metallurgizdat, Moscow, 1953.
4. Petrov, D. A., *Troinye sistemy.* (Ternary Systems.) Publishing House of the Academy of Sciences USSR, Moscow, 1953.

Translated by M. Malinovský and T. Guttmannová