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GENERALIZED LEVER RULE

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As is known, to determine the mass ratio of the phases of an equilibrium two-phase system, the lever rule is used. Its generalization to the case of equilibrium of a three-phase system is the rule of the center of gravity; for the case of a multicomponent multiphase equilibrium system containing an arbitrary number of components, we have proposed a generalized rule of the center of gravity ([1]). This rule is applied to the quantitative study of equilibrium states of complex multicomponent heterogeneous systems and has been used to derive certain general regularities and rules relating to the structure of equilibrium diagrams of such systems ([2], [3]).

In this article a generalized lever rule is proposed, representing a certain new generalization of the rules indicated above. It consists in the following: in studying various processes in equilibrium multicomponent systems, instead of the figurative points of each of the phases separately, we shall consider the figurative points of certain (two) conglomerates of phases (see below) that are in equilibrium. Such a generalization will make it possible to study more easily (stepwise or continuously) the most complex processes in multiphase systems, which appear intricate when considered by the usual methods.

Let M be the figurative point (or the corresponding composition vector inside the concentration simplex ([3])) representing as a whole an equilibrium multicomponent heterogeneous system of unit mass. Then

$$M = \sum_i X_i A_i = \sum_j m_j B_j = \sum_k v_k C_k, \tag{1}$$

where A_i is the vertex corresponding to the i-th component of the concentration simplex (or the vector of the i-th component); X_i is the concentration of the i-th component in the system; B_j is the j-th vertex in the phase simplex (the vector of the j-th phase); m_j is the mass of the j-th phase; C_k is the vector of the k-th conglomerate; v_k is the mass of the k-th conglomerate; $i = 1, 2, \ldots, n$

is the number of the component; $j = 1, 2, \dots, r$ is the number of the phase; $k = 1, 2, \dots, s$ is the number of the conglomerate of phases.

Formula (1) describes the indicated system M through its components A_i, through the coexisting phases B_j entering into it, or through the conglomerates of phases C_k into which the system M decomposes. Equations (1) simultaneously provide a transition from one barycentric coordinate system (the components of the system) to another (its phases or conglomerates of phases). In this case the geometrical dimensions R_A, R_B, and R_C of the concentration, phase, or conglomerate simplexes may in general be different. Thus, for example, for a three-component two-phase system the concentration simplex is the Gibbs triangle ($R_A = 2$), and the phase simplex is a line segment—the tie-line ($R_B = 1$); for a four-component three-phase system the concentration simplex is the Roozeboom–Fedorov tetrahedron ($R_A = 3$), while the phase simplex is a triangle ($R_B = 2$), etc. The dimensions R_A and R_B may also be identical—

for example, for a three-component three-phase system ($R_A = R_B = 2$), for a four-component four-phase system ($R_A = R_B = 3$), etc.

In the case $s = 2$ ($R_C = 1$), i.e., when the system decomposes into two conglomerates of phases, equations (1) become the equation of the generalized lever rule

$$M = \sum_i X_i A_i = \sum_i m_j B_j = \nu L + (1 - \nu) D, \tag{2}$$

where L and D are the vectors of two conglomerates of phases with masses ν and $(1 - \nu)$, respectively. For example, in the case of crystallization of a multicomponent alloy, L corresponds to the liquid phase (or conglomerate of liquid phases), and D to the conglomerate of all solid phases that have separated out before the present equilibrium moment.

Proceeding from the law of conservation of mass for each of the n components of the system, we have

$$\nu x_{iL} + (1 - \nu) x_{iD} = X_i \quad (i = 1, 2, 3, \dots, n), \tag{3}$$

where x_{iL}, x_{iD}, X_i are the concentrations of the i-th component, respectively, in the liquid phase, in the conglomerate of solid phases, and in the entire system M as a whole; ν and $(1 - \nu)$ are the masses of the liquid phase and of the conglomerate of solid phases.

The solution of equations (3) is

$$\nu = \frac{X_i - x_{iD}}{x_{iL} - x_{iD}}, \qquad 1 - \nu = \frac{x_{iL} - X_i}{x_{iL} - x_{iD}}, \tag{4}$$

whence follow the equations of the generalized lever rule

Fig. 1

Figure 1: Fig. 1

$$\frac{\nu}{1-\nu} = \frac{X_i - x_{iD}}{x_{iL} - X_i}. \tag{5}$$

With the aid of equations (5) one can calculate the ratios of the masses ν and $(1-\nu)$ of the coexisting liquid phase and conglomerate of solid phases, if the concentrations x_{iL}, x_{iD}, and X_i are specified; or else calculate (analytically) the overall composition of the conglomerate x_{iD} for given ν, x_{iL}, and X_i in an equilibrium system containing an arbitrary number of components, etc.

Thus, when a multicomponent system M decomposes into two subsystems—the liquid phase and the conglomerate of solid phases, represented by the figurative points L and D—the "conglomerate simplex" degenerates into an ordinary (one-dimensional) tie-line, to which the ordinary lever rule is applicable.

In the course of a reversible process, at any of its stages the points M, L, and D lie on one common straight line LMD, situated in the $(n-1)$-dimensional space of the concentration simplex (and at the same time in the $(r-1)$-dimensional space of the phase simplex). Throughout the entire process the point M, obviously, always remains fixed, while the points L and D may move simultaneously within the concentration simplex (sliding along the boundary between regions of phase states) or may alternately remain fixed (in which case one of the points will move along a straight line within a single-phase region). The tie-line (straight-line segment) LMD, and together with it the segments LM and MD, may rotate in the multidimensional concentration simplex about the point M, or may retain their direction, lengthening or shortening (but only not bending). In this case the vector D at any moment of the reversible process can be decomposed into its constituent vectors, representing individual phases or other, simpler conglomerates of phases (eutectics, etc.), which makes it possible to record easily any state of the system throughout the entire process under study.

With the aid of the generalized lever rule it is possible to describe very complex crystallization processes. As an example, let us consider the process

crystallization of the three-component system A–B–C, in which a ternary compound S is formed with an incongruent melting point (in the liquid state there is complete mutual solubility, and in the solid state complete insolubility of the components). Let us follow the crystallization process for some composition from the very beginning to its complete completion.

In Fig. 1 the projection of the liquidus surfaces onto the concentration triangle ABC is shown. The region EP_2P_1E of primary crystallization of S

Fig. 1

lies outside the point S, which corresponds to the composition of the solid ternary compound. The ternary point P_1 corresponds to a nonvariant, singly incongruent crystallization process $(-L-A+B+S)$. The plus and minus signs were determined on the basis of the center-of-gravity rule: the plus sign corresponds to a congruent process, the minus sign to an incongruent process (for example, at point P_1 crystals of S and B separate out, while A disappears together with the liquid). Point P_2 corresponds to a nonvariant, doubly incongruent process $(-L-A-C+S)$; point E to a nonvariant congruent process $(-L+B+C+S)$, in which the ternary eutectic $(B+C+S)$ crystallizes.

The line P_1E represents a monovariant congruent process $(-L+B+S)$, while the lines P_2P_1 and P_2E represent monovariant incongruent crystallization processes $(-L-A+S$ and $-L-C+S)$, etc. The arrows indicate the direction of decreasing temperature during the crystallization process.

In Fig. 1 the stages of crystallization from a liquid whose initial composition is indicated by point 19 are shown by heavy lines. As is evident from Fig. 1, on the basis of the generalized lever rule it is easy to establish the trajectories of the figurative points of the liquid phase and, correspondingly, of the conglomerate of solid phases coexisting at any moment of the crystallization process. For point 19 there arise 7 stages of crystallization, designated by Roman numerals.

with the sectors: I—VII for the liquid phase and I'—VII' for the conglomerate of solid phases. At the various stages of crystallization, the following solid phases coexist in the conglomerates:

$$I'(A); \quad II'(A+C); \quad III'(A+C+S); \quad IV'(C+S);$$

$$V'(S); \quad VI'(B+S); \quad VII'(B+C+S).$$

During these 7 stages the variance of the system changes as follows: $y = 2,1,0,1,2,1,0$. The mass ratio $\frac{v}{1-v}$ is readily calculated for any moment of crystallization. With the aid of the proposed rule it is easy to establish all stages of crystallization for any other compositions of the A—B—C system.

We have applied the proposed rule to the construction of various polythermal sections (for example, $A\alpha$, $\gamma_1\alpha_1$, $\gamma_2\alpha_2$, $\beta\alpha_3$, etc.), on the basis of which the entire spatial equilibrium-state diagram of the indicated complex ternary system can be represented.

In the case of multicomponent heterogeneous systems $(n \geq 4)$, the generalized lever rule loses its visual clarity, but it can be used in analytical form (equations (4) and (5)).

Thus, from equations (5), when experimental values of X_x, x_{iD}, and $\frac{v}{1-v}$ are available, one can find analytically the equation of the trajectory of the figurative point x_L in the multidimensional concentration simplex. From such data,

important information can be extracted about the structure of the equilibrium diagram of a multicomponent system.

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.