Topology of Potential Phase Diagrams Composed of Three Chemical Elements

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A detailed analysis of the topology of two-dimensional isothermal potential phase diagrams for systems composed of three chemical elements is presented. Chemical potentials (or derived properties as activities or partial pressures) of two independent components or their combinations are used as coordinates of such diagrams. The chemical potentials of other species are constant at the given temperature (i.e., stoichiometric, single-species condensed phases, or components of a multicomponent phase of fixed composition). It was shown that only invariant point can change the topology of the diagram. A method for the determination of invariant points is proposed. The set of invariant points is divided into four classes, and each class is demonstrated by a practical example.

1. Introduction

Phase diagrams are usually used for the graphic representation of equilibrium phase relations in heterogeneous systems, as a function of intensive variables. The diagrams can often be constructed two-dimensionally. Any pair of intensive variables (e.g., temperature-pressure, temperature-composition, pressure-composition, chemical potential [partial pressure]-chemical potential [partial pressure]) can be chosen as coordinates. The diagrams at constant temperature, the coordinates of which are chemical potentials (μ_i) or combinations of chemical potentials ($\mu_{ij} = \alpha\mu_i - \beta\mu_j$, where α and β are arbitrary real numbers), or derived variables such as activities (a_i) or partial pressures (p_i) are called isothermal potential phase diagrams (PPDs) [1998Hil]. As typical examples of PPDs for systems composed of three elements (A-B-C), the Kellogg phase stability diagrams or chemical potential diagrams proposed by Yokokawa and colleagues [1989Yok, 1999Yok] can be given. The former describe the stability of single-species condensed phases in the gaseous atmosphere as a function of log p_A and log p_B [1981Gas, 1991Pel], whereas the latter use $\log(a_A/a_B)$ and log p_c as coordinates.

The construction and application of PPDs have been well described in the literature [1986Bal, 1988Rus, 1990Bal, 1990Wan, 1993Lei]. However, the classification and topology of PPDs have almost never been discussed. In this work, we use the definition that two PPDs have different topology if they have either a different number of isothermal invariant points or a different phase composition of some isothermal invariant points. The definition of topology is somewhat ambiguous in the literature. [1990Bal] has studied the topology of intersecting domains in two-metal (i.e., four elements) PPDs and has introduced two different

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types of topologies, "X" and "Y." [1991Pel] has classified three-element PPDs and a *p-T* diagram of pure substance into the same group of diagrams in which, for example, a three-phase point in an isothermal PPD corresponds with the triple point in a *p-T* diagram of a pure substance or a two-phase line in a PPD corresponds with a two-phase saturated curve in *p-T* diagram. [1981Gas] has also discussed three-element PPDs and mentioned the existence of a special type of isothermal invariant point at which four stoichiometric condensed substances are in equilibrium at a particular temperature. An example of such a type of isothermal invariant point for an Fe-O-S system [FeS_2, Fe_3O_4, Fe_2O_3, and $Fe_2(SO_4)_3$] has been given by [1988Rus].

In this article, a detailed topology analysis of isothermal PPDs for systems composed of three chemical elements is presented. Several substances of fixed chemical potential (i.e., stoichiometric single-species condensed phases or components of a multicomponent phase of fixed composition) are considered. Chemical potentials (or activities or partial pressures) of two independent components, X_1 and X_2 (e.g., components of a gaseous phase being in equilibrium with stoichiometric single-species condensed phases) or their combinations are used as coordinates of such PPDs.

2. Equilibrium Conditions

Let us consider a closed system in which there is no work involved other than that related to volume change (pressure – volume work). The determination of the chemical equilibrium of such a system at constant temperature T and pressure p is equivalent to finding a global minimum point of the total Gibbs energy G on a set of points $n = (n_1, n_2, \ldots, n_N)$ satisfying the material balance equations. The problem can be conceived in the following manner:

$$\min G; \quad G = \sum_{i=1}^{N} \mu_i \, n_i \qquad \text{(Eq 1)}$$

$$\sum_{i=1}^{N} a_{ji}\, n_i = b_j \quad 1 \le j \le M; \quad n_i \ge 0 \quad 1 \le i \le N \qquad \text{(Eq 2)}$$

where N is the number of species, n_i the number of moles of the ith species, M is the number of chemical elements the system is composed of, and μ_i is the chemical potential of the ith species in the phase in which the ith species is considered. Matrix $A = \{a_{ji}\}$ is the matrix of constitution coefficients (or the formula matrix), where a_{ji} is the number of atoms of the jth element in a molecule (or in a formula unit) of the ith species and b_j is the total number of moles of the jth element in the system. We shall always assume $N > M$ and rank(A) = M. If rank(A) < M, then the linearly dependent rows of the matrix A are removed and a new value of M, M = rank(A), is considered.

The following relations hold for the respective chemical potentials:

$$\mu_i^g = \mu_i^{o,g}(T) + \boldsymbol{R}T \ln \frac{p_i}{p_{st}} \qquad \text{(Eq 3)}$$

$$\mu_i^c = \mu_i^{o,c}(T) + \boldsymbol{R}T \ln a_i^c \qquad \text{(Eq 4)}$$

where the superscripts g, c, and o stand for gaseous phase, condensed phase, and standard state, respectively. Symbol p_i represents partial pressure of the ith gaseous species, and p_{st} is standard pressure. The pressure dependence of $\mu_i^{o,c}$ is neglected. The activity a_i^c is equal to unity for a single-species condensed phase or, in general, it is equal to a specific value if the ith species is a component of a multi-component phase. Values of $\mu_i^o(T)$ can be calculated from the standard thermodynamic functions of pure substances given in many data collections [1991Kna, 1993Bar, 1998Cha].

It follows from the theory of mathematical programming [1976Dan] that the following Kuhn-Tucker conditions must be satisfied in equilibrium [1982Smi]:

$$\text{if } n_i > 0 \text{ then } \mu_i - \sum_{k=1}^{M} a_{ki}\, \lambda_k = 0 \qquad \text{(Eq 5)}$$

$$\text{if } n_i = 0 \text{ then } \mu_i - \sum_{k=1}^{M} a_{ki}\, \lambda_k \ge 0 \qquad \text{(Eq 6)}$$

where $\{\lambda_k\}$ are unknown Lagrangian multipliers. Because all substances have fixed chemical potentials, the total G is a linear function of molar numbers. Consequently, the material balance equations $An = b$, the inequalities $n \ge 0$, and Kuhn-Tucker conditions Eq 5 and 6 are in this case not only necessary but also sufficient equilibrium conditions.

3. Gibbs Phase Rule

The phase rule introduced by Gibbs allows the determination of the number of independently adjustable intensive variables in a system where F phases are in equilibrium.

This number is called the number of degrees of freedom (f) and is given as a difference between the total number of independent intensive variables that are necessary for the unambiguous determination of the system and the number of independent equilibrium conditions.

Let us consider an equilibrium system containing F_c stoichiometric single-species condensed phases. Temperature is the only intensive variable in such an equilibrium system (influence of pressure is neglected), and therefore $f = 1 - R$, where R ($R \le 1$) is the number of independent chemical reactions describing the chemical change of such a system. The relation $R = F_c - \text{rank}(A)$ follows from the Gibbs stoichiometric rule. Therefore, for a considered system of stoichiometric single-species condensed phases the Gibbs phase rule assumes the form $f = M + 1 - F_c$. Obviously, the maximum number of single-species condensed phases is $M + 1$. Such an equilibrium state ($f = 0$) can be achieved only for a particular value of temperature (i.e., the invariant temperature T_{inv}). The point corresponding to this state is an invariant point. The denotation *isothermal invariant point* is used for isolated points in isothermal PPDs at which only M single-species phases are obviously in equilibrium.

4. Calculation of Invariant Points

Let us choose any subset of $M + 1$ phases from the total number N of single-species condensed phases where rank(A^{M+1}) = M and A^{M+1} is a matrix of constitution coefficients of these $M + 1$ species. Let us further assume, without loss of generality, that the sequence numbers of these species are $1, 2, \ldots, M + 1$. It follows from Eq 3 and 4 that necessary and sufficient conditions for an invariant point have the form of the following set of $M + 1$ equations:

$$\mu_i(T_{inv}) - \sum_{k=1}^{M} a_{ki}\, \lambda_k = 0 \quad i = 1, 2, \ldots, M + 1 \qquad \text{(Eq 7)}$$

and the following set of inequalities:

$$\mu_i(T_{inv}) - \sum_{k=1}^{M} a_{ki}\, \lambda_k > 0 \quad i = M + 2, \ldots, N \qquad \text{(Eq 8)}$$

where $M + 1$ unknowns $T_{inv}, \lambda_1, \ldots, \lambda_M$ that were calculated from Eq 7 must satisfy the inequalities of Eq 8. A hypothetical case $f < 0$ is not accepted, and therefore the inequality "$\ge$" in Eq 6 is replaced by inequality ">" in Eq 8. Nevertheless, for a particular choice of the right-hand side of material balance equations $An = b$, one or more values of n_i, $i = 1, \ldots, M + 1$ are allowed to be equal zero. Because rank(A^{M+1}) = M, there exists only one independent chemical reaction between considered single-species phases (generally speaking, in some of the stoichiometric coefficients of such a reaction, v_i, $i = 1, \ldots, M + 1$ can indeed be zero). Let us multiply the ith equation in Eq 7 by v_i, and let us make a sum of them. It follows from relations $\Sigma a_{ji} v_i = 0$, $j = 1, \ldots, M$ that the temperature of the invariant point T_{inv} must satisfy the equation $\Sigma v_i \mu_i(T_{inv}) =$

$\Delta G_r(T_{inv}) = 0$. The values of Lagrangian multipliers are determined from the set of M linear equations because fixing T_{inv} makes just one equation of the set in Eq 7 linearly dependent (rank $A^{M+1} = M$). the chemical potentials of both independent components X_1 and X_2 (coordinates of invariant point in a PPD) being in equilibrium with the $M + 1$ phases can be easily determined from two separate equations:

$$\mu_i(T_{inv}) = \sum_{k=1}^{M} a_{ki} \lambda_k \quad i = X_1, X_2 \qquad \text{(Eq 9)}$$

The invariant point is represented by a $(M + 1)$-component vector, the components of which are equal to the sequence numbers of considered single-species phases. The total number of such vectors amounts to $C(M + 1, F_c)$, where C is a symbol for a combinatorial number. These vectors can be divided into four classes:

- $Rank(A^{M+1}) < M$, thus, a set of equations in Eq 7 has no solution because there are at least two independent chemical reactions describing chemical changes in the system ($f < 0$)
- $Rank(A^{M+1}) = M$, but the equation $\Delta G_r(T) = 0$ has no physical solution
- $Rank(A^{M+1}) = M$, and the equation $\Delta G_r(T) = 0$ has a solution in the considered temperature interval, but the inequalities in Eq 8 are not valid, and in such a case the solution is said to be unstable
- Invariant points

5. Potential Phase Diagrams for $M = 3$

Two essential characteristics of invariant points will be shown in this section:

- An invariant point originates from merging two (or more) isothermal invariant points and vanishes by an inverse process splitting into two (or more) isothermal invariant points.
- Nothing but the invariant point changes the topology of a PPD. A new phase originates only at an invariant point (an inverse theorem does not hold, i.e., each invariant point is not associated with the origin of a new phase).

Consider the Fe-O-S system [Fe, Fe_3O_4, FeO, FeS_2, $Fe_2(SO_4)_3$, $FeSO_4$, Fe_2O_3, FeS, $O_2(g)$, $S_2(g)$] containing eight single-species solid phases as an example. Species $O_2(g)$ and $S_2(g)$ were chosen as two independent components. The set Ω has $C(4,8) = 70$ vectors where one of them {Fe, FeO, Fe_2O_3, Fe_3O_4} belongs to the first class (rank(A^4) = 2), 12 of them belong to the second class (temperature interval 300-1100 K), 55 of them belong to the third class, and only two represent invariant points: {Fe_2O_3, Fe_3O_4, FeS_2, $FeSO_4$; $T = 787$ K} and {Fe, FeO, FeS, Fe_3O_4; $T = 843$ K}. The necessary thermodynamic data were taken from [1991Kna].

Let us discuss the first invariant point. A part of the phase stability diagram at a temperature of 600 K is shown in Fig. 1(a). Three single-species phases, FeS_2, Fe_3O_4, and
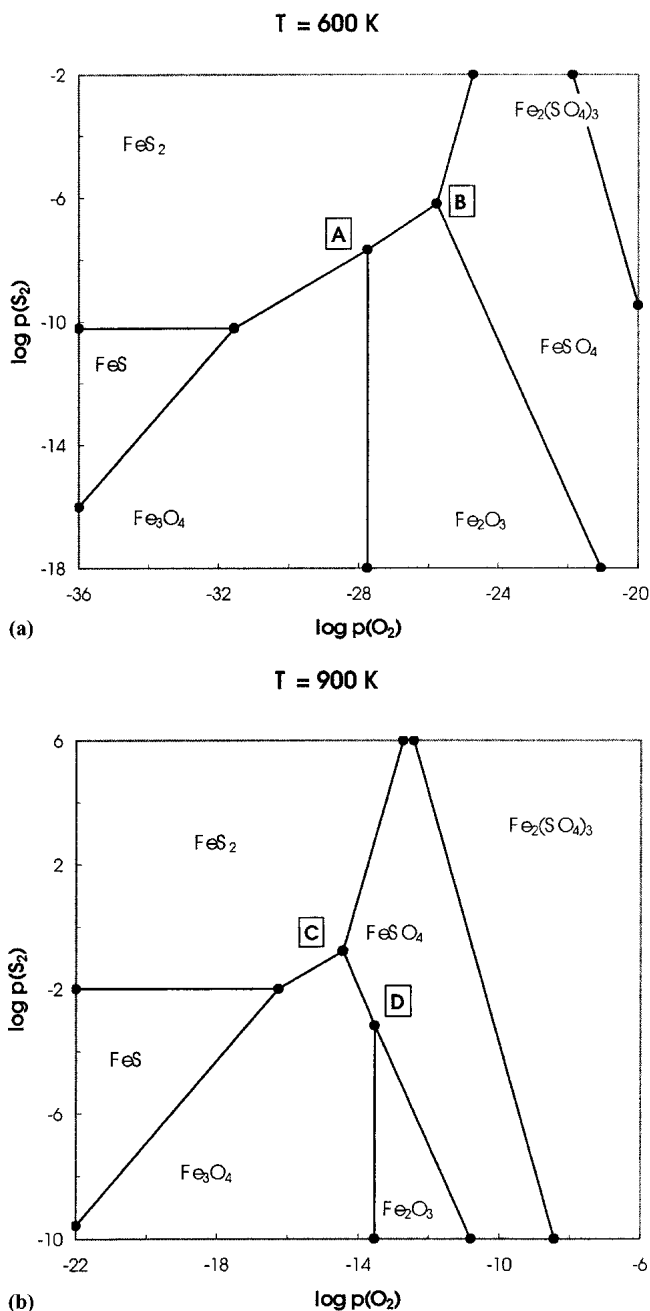

Fig. 1 Phase stability diagram of the system Fe-O-S at (a) 600 K and (b) 900 K

Fe_2O_3, coexist in the isothermal invariant point denoted as **A**, and three single-species phases, FeS_2, Fe_2O_3 and $FeSO_4$, coexist in the isothermal invariant point denoted as **B**. Both points have two common phases, FeS_2 and Fe_2O_3 (the third phase is different). The common phases coexist on the line connecting both points. A phase stability diagram at 900 K is given in Fig. 1(b). Three phases, FeS_2, Fe_3O_4, and $FeSO_4$, coexist in the isothermal invariant point **C**, and three phases, Fe_3O_4, Fe_2O_3, and $FeSO_4$, coexist in the isothermal invariant point **D** where Fe_3O_4 and $FeSO_4$ represent the common pair. Obviously, there exists a temperature T_{inv} between 600
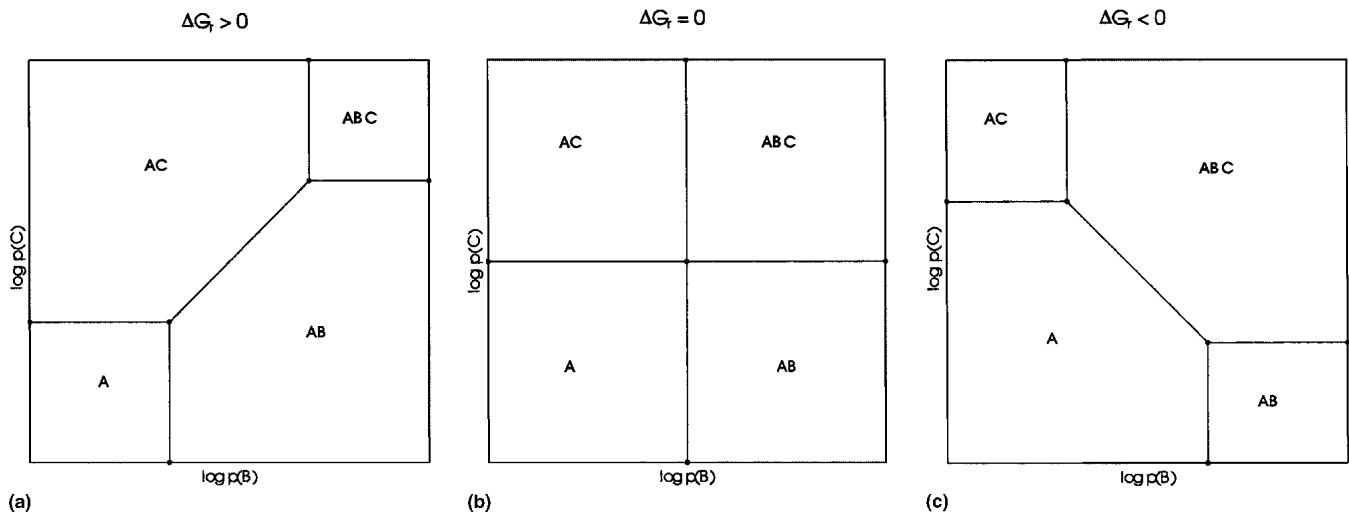
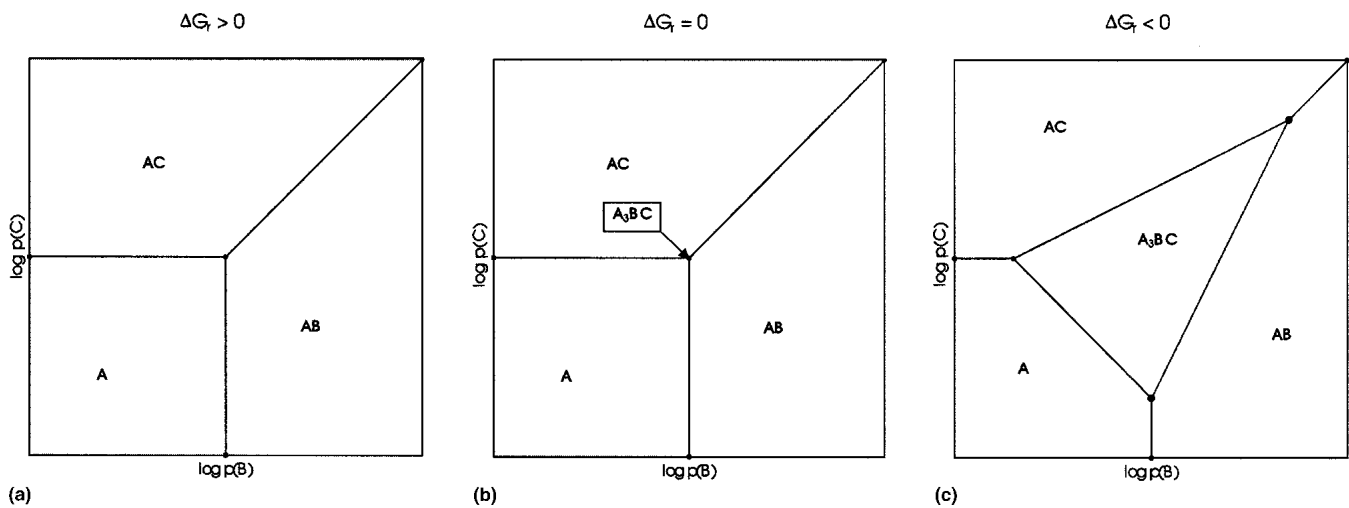**Fig. 2** Change of topology in the invariant point 2 + 2

Fig. 3 Change of topology in the invariant point 3 + 1

and 900 K for which the common pair at 600 K and the common pair at 900 K are in equilibrium state (i.e., points **A, B, C**, and **D** merge into one point). The temperature T_{inv} was calculated from equation $\Delta G_r(T) = 0$ for chemical reaction:

$$FeS_2(s) + 20\ Fe_2O_3(s) = 13\ Fe_3O_4(s) + 2\ FeSO_4(s) \quad (Eq\ R1)$$

As mentioned above, $T_{inv} = 787$ K. The invariant point changes the topology of the isothermal diagram (i.e., the number or composition of isothermal invariant points), but in this case it is not connected with the occurrence of a new phase. The second invariant point will be mentioned later.

Let us consider a hypothetical system composed of three chemical elements, A, B, and C. Let us consider, without loss of generality, B(g) and C(g) as two independent species in the gaseous phase, and $\log p_B$ and $\log p_C$ as coordinates of the isothermal PPD. Furthermore, the element A is supposed to be contained in all single-species condensed

phases, for example, A, AB, AC, ABC, A_2BC, A_3BC, and AB_3C_2.

The set of invariant points for $M = 3$ can be divided into the four basic classes:

Class 1. Four single-species condensed phases, A, AB, AC, and ABC (Fig. 2), where the chemical change of the system is described by the reaction:
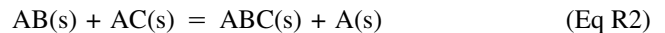
$$AB(s) + AC(s) = ABC(s) + A(s) \quad (Eq\ R2)$$

Figure 2(a) to (c) represents three isothermal PPDs corresponding to three different values of ΔG_r for Eq R2: $\Delta G_r > 0$ (a), $\Delta G_r = 0$ (b), and $\Delta G_r < 0$ (c), respectively. The invariant point (Fig. 2b) changes the diagram topology (isothermal invariant points in Fig. 2a, c, have different phase compositions), but the number of phases remains constant. Two species on the left-hand side and two species on the right-hand side are involved in the given chemical reaction. Therefore, the invariant point is said to belong to the class
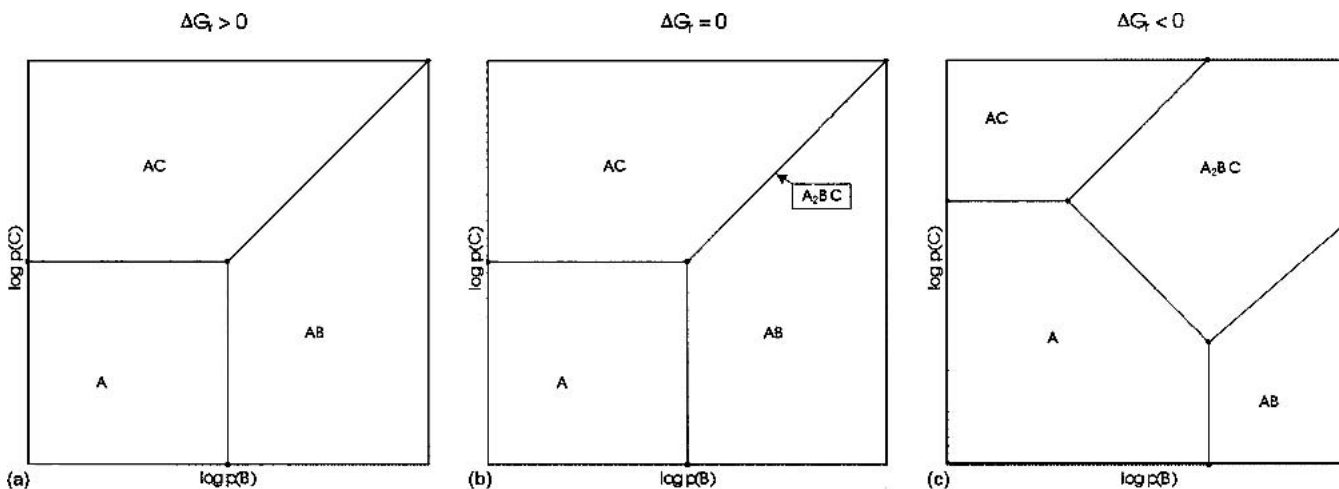
Fig. 4 Change of topology in the invariant point 2 + 1
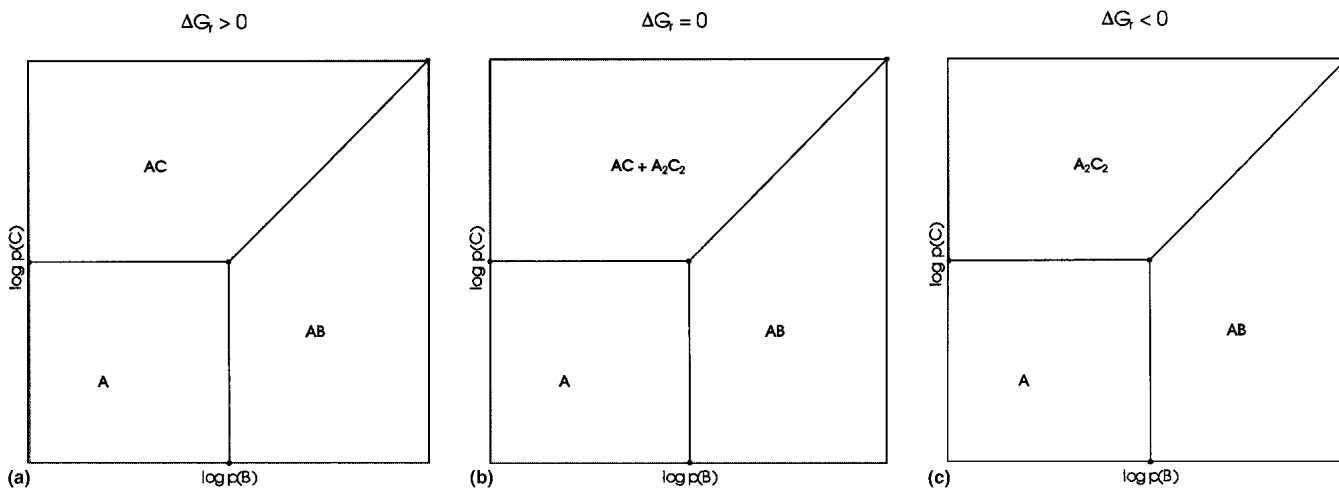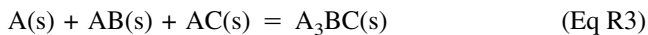

Fig. 5 Change of topology in the invariant point 1 + 1

(2 + 2). The first invariant point in the system Fe-O-S (see Eq R1) can be given as a real example.

Class 2. Four single-species condensed phases, A, AB, AC, and A_3BC (Fig. 3), are considered. The chemical reaction has the following form:

$$A(s) + AB(s) + AC(s) = A_3BC(s) \qquad (Eq\ R3)$$

In this case, the invariant point (Fig. 3b) splits up into three separate isothermal invariant points. The number of phases is changed and a new "closed" phase stability field containing A_3BC starts to develop or disappears according to the sign of ΔG_r for the reaction (R3). The chemical reaction (R3) has three species on the left side and one species on the right side. Accordingly, such an invariant point belongs to the class (3 + 1). As an example, the system Cu-O-S with an invariant point $\{Cu_2O, Cu_2S, CuSO_4, Cu_2SO_4; T = 831\ K\}$ can be presented. The relevant reaction to that invariant point has the form:

$$4\ Cu_2O(s) + 2\ Cu(s) + 8\ CuSO_4(s) = 9\ Cu_2SO_4(s)\ \ (Eq\ R4)$$

Class 3. Four single-species condensed phases, A, AB, AC, and A_2BC (Fig. 4), where the chemical reaction assumes the form:

$$AB(s) + AC(s) = A_2BC(s) \qquad (Eq\ R5)$$

that is, one species (A) does not participate in the reaction in Eq R5. If $\Delta G_r = 0$, three phases, AC, AB, and A_2BC, are in equilibrium on the two-phase line separating AC and AB (Fig. 4b). The invariant point changes the number of phases, and a change of temperature causes an "open" phase stability field of A_2BC to be formed or disappear according to the sign of ΔG_r for the reaction in Eq R5. In this case, the invariant point belongs to the class (2 + 1). The invariant point $\{Ti_2O_3, Na_2TiO_3, Ni_2Ti_2O_5, Ni_2Ti_3O_7; T = 1075\ K\}$ with the reaction:

$$Na_2TiO_3(s) + Na_2Ti_3O_7(s) = 2\ Na_2Ti_2O_5(s) \qquad (Eq\ R6)$$
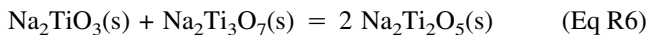
is an example of such a change of PPD topology. Note that

the invariant point {Fe, FeO, FeS, Fe$_3$O$_4$} in the above-mentioned Fe-O-S system with the reaction:

$$\text{Fe(s)} + \text{Fe}_3\text{O}_4 \text{ (s)} = 4\text{FeO(s)} \qquad \text{(Eq R7)}$$
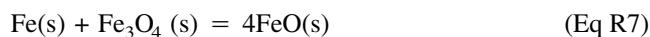
belongs to this class.

Class 4. The last class is denoted (1 + 1). From the four considered single-species condensed phases, A, AB, AC, and A$_2$C$_2$, only two participate in the corresponding chemical reaction:

$$2 \text{ AC(s)} = \text{A}_2\text{C}_2\text{(s)} \qquad \text{(Eq R8)}$$
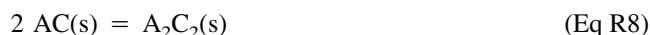
In this case (Fig. 5), the number of phases is retained, and only the composition of the isothermal invariant point is changed (an analogous situation to that in the class [2 + 2]). The discontinuity of the diagram is significant because the entire AC area is converted into the A$_2$C$_2$ area. Three phases are in equilibrium on the boundaries A-AC(A$_2$C$_2$) and AB-AC(A$_2$C$_2$), whereas two phases, AC and A$_2$C$_2$, coexist in the AC(A$_2$C$_2$) stability field. Perhaps a more typical representative of this class is a set of four single-species condensed phases, A(s), AB(s), AC(s1) and AC(s2), containing two different modifications of a solid substance AC. Evidently only one reaction:

$$\text{AC(s1)} = \text{AC(s2)} \qquad \text{(Eq R9)}$$

takes place in such a subsystem.

6. Conclusions

The determination of invariant points allows the study of the topology of PPDs over a wide range of temperatures. Even if the number of invariant points can be generally high—i.e., $\leq \text{C}(M + 1, F_c)$—the real number is, by experience, significantly less (see the results for the Fe-O-S system).

In this study, we have examined in detail the systems with three elements ($M = 3$). We have found four classes of invariant points, which are described in the previous section and correspond with the stoichiometry of the corresponding chemical reaction: 2 + 2 (two species on the left-hand side and two species on the right-hand side of the chemical reaction), 3 + 1, 2 + 1, and 1 + 1. Hence, the knowledge of the reaction stoichiometry enables the identification of the relevant class of the invariant point.

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