

A rule for a joint of three boundary lines in phase diagrams

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DOI: 10.3367/UFNe.0183.201304d.0417

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Abstract. The rule governing the mutual position of three boundary lines meeting at one point in a two-dimensional phase diagram is derived in a new way using the fact that a boundary can be extended into the metastable region beyond the point of its intersection with another line. An improved formulation of the rule is proposed, which makes it independent of the diagram axes chosen and suitable for the analysis of two-dimensional sections of phase diagrams of heterogeneous systems with any number of components. Conditions for and some aspects of the application of the rule are considered using phase diagrams of one-, two-, and three-component systems as examples.

1. Introduction

A joint of three boundary lines is a common element of two-dimensional phase diagrams and two-dimensional sections of phase diagrams of a higher dimension. In the construction of equilibrium phase diagrams and for checking their correctness, a rule is of great utility which in the most general form can be formulated as follows:

The extension of the boundary line between two phase regions beyond the point of intersection with the boundaries of a third region should lie inside this third region.

An equivalent formulation can also be found:

The angles between the boundary lines of three phase regions meeting at one point should be less than 180° .

Surprisingly enough, we could only retrieve two publications [1, 2] in which proofs are given for the rule of triple joints, the proofs being made by two different methods for two different types of diagrams.

In Ref. [1] representing one of the most complete and detailed textbooks on phase diagrams, the rule of triple joints is proven for the diagrams of eutectic invariant equilibrium in the temperature–composition (T – X) coordinates in two-component systems at a constant pressure P . The thermodynamic potential method applied in Ref. [1] also allows one to prove the rule of triple joints for the T – X diagrams of other types of invariant equilibrium in two-component systems and can be extended to the diagrams of invariant equilibria in the temperature–volume (T – V) coordinates for one-component systems. This method, however, is inapplicable to the T – P diagrams of one-component systems and for two-dimensional sections of phase diagrams of systems with more than two components.

In some textbooks and handbooks (e.g., in textbook [3]), it is noted that the rule of triple joints for the T – P diagrams of one-component systems can be proved based on the Clausius–Clapeyron equation; however, we have failed to find such a proof in the literature. A proof of the rule for this particular but important type of diagrams has been given in the famous work by Schreinemakers [2], who developed an original (and used up to date) method for analysis of phase diagrams. That proof was based on the possibility to extend each of the three lines of phase equilibria into the metastable region beyond the point of their intersection.

The present paper will show that the sufficient condition for the rule of triple joints to be valid is that two of the three boundary lines have metastable extensions beyond the point of the joint. This finding permitted us to employ the concept of metastable extensions of the boundary lines for an analysis of the applicability of this rule to triple joints in the diagrams of systems with any number of components.

The proven rule reads as follows:

Let it be a point of a joint of three boundary lines in a two-dimensional diagram of phase equilibria or in a two-dimensional section of a diagram. If at least two of these lines allow a metastable extension beyond the point of the joint, the extension of each of the three lines should lie in the phase region bounded by the two other lines.

Proving the rule in this paper is followed by a discussion of the main types of phase diagrams and phase equilibria that must obey this rule. Examples of violation of the rule

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Received 3 May 2012, revised 8 June 2012
Uspekhi Fizicheskikh Nauk 183 (4) 417–422 (2013)
DOI: 10.3367/UFNr.0183.201304d.0417
Translated by S N Gorin; edited by A Radzig

are also given and the reasons for the violation are explained.

2. Proof of the rule of triple joints

The metastable extension of a boundary line describes the same equilibrium as the very line does because the state of the system corresponds, as before, to the minimum of the appropriate thermodynamic potential of the system, but this minimum is not the deepest one. If a certain phase composition of the system becomes more stable than another after crossing the boundary line, this composition will also be more stable after crossing the metastable extension of the line.

It follows from this, in particular, that if the boundary line has a metastable extension beyond the point of the joint with two other boundary lines, these two lines (rays) of the stable equilibrium should lie on opposite sides of the extended line.

Indeed, as in Fig. 1a, let the boundary lines ob and oc lie to the left of the line oa and of its metastable extension od shown by a dashed line. Phase state $\{A\}$ is the most stable state of the system in the aob sector; state $\{B\}$, in the boc sector, and state $\{C\}$, in the entire coa sector, including the cod sector. On the other hand, since state $\{A\}$ is more stable than state $\{C\}$ to the left of line oa , it should also remain more stable to the left of the od line, including the cod sector. This contradicts the initial condition that $\{C\}$ is the most stable phase state in the cod sector. Such a sector cannot exist and, therefore, the oc line should lie to the right of the aod line.

Now, along with the oa line, let one more boundary line, e.g., the ob line, be extended metastably beyond the point of the triple joint. In accordance with the proof given above, the oa and oc lines should lie on opposite sides of the ob line and its extension oe . In combination with the requirement that the oc line be located to the right of the aod line, this allows the oc line to lie only in the doe sector, as in Fig. 1b. As a result, the extension of of the oc line should be found in the boa sector irrespective of whether of represents a metastable equilibrium or not. Thus, we come to a situation depicted in Fig. 1c, where the extension of each of the three lines lies in the phase field whose boundaries are the two other lines.

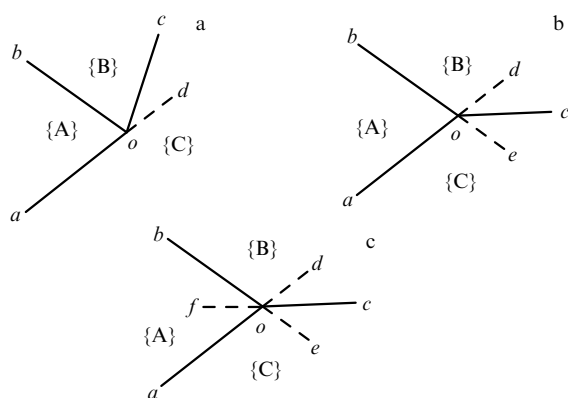


Figure 1. Boundaries between phase regions (solid lines) and metastable extensions of these boundaries (dashed lines) near the point o of the triple joint. The phase states $\{A\}$, $\{B\}$, and $\{C\}$ may differ in both the full number and the set of phases.

Notice that the above-proved rule of the joint of three boundary lines can be used ‘in parts’. If the boundary between two phase fields can have a metastable extension beyond the point of intersection with the boundaries of the third phase field, this extension should necessarily lie between the boundaries of the third region. If the metastable extensions are possible for two boundaries, the extension of each of the three boundaries lies in the region between two other boundaries.

3. Applicability conditions of the rule

When proving the rule, it was assumed that one and only one phase equilibrium state of the system corresponds to each point in the diagram. Gibbs [4] has shown that this condition can be fulfilled for heterogeneous systems in which each of the components is present in each of the phases, the pressure P is isotropic everywhere, and the effects due to the interfaces between different phases and due to the applied external fields (electric, gravitational, etc.) are negligibly small. The phase state of such systems is determined in a unique fashion by the choice of the total amount of each component and by the values of two external parameters. Four different pairs of external parameters are possible, namely, the entropy S and the volume V of the system (the equilibrium corresponds to the minimum of the internal energy E of the system); S and P (minimum of the enthalpy $H = E + PV$); T and V (minimum of the Helmholtz energy $F = E - TS$), and T and P (minimum of the Gibbs energy $G = E + PV - TS$).

When studying phase equilibria, two pairs of external parameters are usually employed: either T and P or T and V . Thus, a diagram whose points unambiguously determine all possible phase states of an n -component system can be constructed on $n + 1$ independent axes. Along two of these axes, the values of the external parameters should be applied, T and P or T and V ; along the other $n - 1$ axes, the values of $n - 1$ concentrations of different components of the system (e.g., $n - 1$ molar or weight fractions X_i ; with the concentration of the n th component being determined in this case from the condition $X_n = 1 - \sum_{i=1}^{n-1} X_i$). The points of any section of the complete $(n + 1)$ -dimensional diagram will also unambiguously determine the phase states of the system, but this will only be a certain fraction of the states and not all of them.

Following the standard practice, we will for brevity call the sections of phase diagrams merely diagrams in those cases where it is obvious or insignificant which parameters of the system were fixed in obtaining the section.

3.1 One-component systems

To begin the discussion of the applicability of the above-proved rule to various two-dimensional phase diagrams and two-dimensional sections of phase diagrams of a higher dimension, it is convenient to start with the T – P diagram of water in the vicinity of the triple point (solid + liquid + gas), which is given schematically in Fig. 2a. A distinctive feature of the phase diagram of this one-component system is a decrease in the equilibrium melting temperature T_m with increasing pressure, which is due to the smaller specific volume of the liquid phase compared to that of the solid phase (upon melting, $\Delta S > 0$, and in combination with the inequality $\Delta V < 0$, the Clausius–Clapeyron equation gives $dT_m/dP = \Delta V/\Delta S < 0$). Because of a decrease in T_m under pressure, some regions of the P – V diagram of water (Fig. 2c) represent

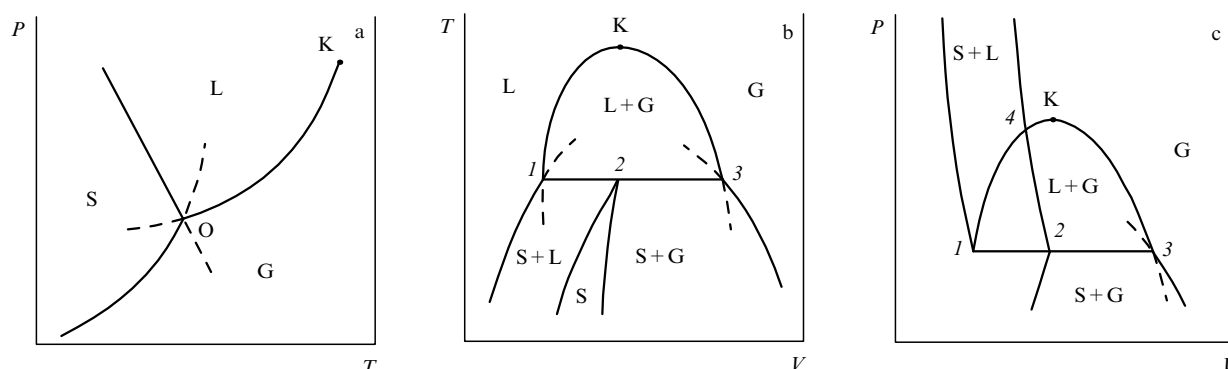


Figure 2. Schematic diagram illustrating phase equilibria in water in various coordinates: (a) T and P ; (b) T and V , and (c) P and V . In each diagram, S labels the solid phase (ice); L, the liquid phase; G, the gas phase (water vapor), and K, the critical point. Dashed lines depict the metastable extensions of phase boundaries beyond the points of triple joints.

the state of the system ambiguously, which permits us, at the end of this section, to discuss the related limitations on the application of the rule of triple joints.

As to the T – P diagram (Fig. 2a), it should be noted, first of all, that neither the Gibbs energy nor any physical properties of the phases of water have singularities at the boundaries between regions {S}, {L}, and {G}. At the intersection of the boundary, the Gibbs energy of one phase of water becomes higher than the energy of the other phase; however, the atomic configuration of the first phase continues corresponding to the minimum Gibbs energy, but this minimum is not the deepest now. The conversion of one aggregate state of a substance into another one occurs through the formation of intermediate states that are nonequilibrium and therefore possess a higher Gibbs energy, producing a potential barrier between the initial and final states. The barrier may be very small, but due to its presence each phase of water can exist for a finite time in a metastable state in a certain range outside the region of its absolute stability in the T – P diagram and, in particular, can be in equilibrium with some other metastable phase.

Experimentally, the metastable equilibria are usually observed if the formation of a new phase proceeds via a homogeneous nucleation and growth of nuclei. For this to occur, the nuclei should acquire, as a result of thermal fluctuations, additional energy necessary for the formation of an interface with the old phase. For example, in the absence of heterogeneous nucleation of particles of the solid phase (ice), the liquid state of water admits strong undercooling, and a metastable equilibrium between the liquid L and gas G can really be observed (including natural water reservoirs) in the stability region of the solid phase S, as is indicated by a dashed line in Fig. 2a.

The overheating of ice, as of most other crystalline phases, is only possible by employing some special methods, since the liquids (with rare exceptions) completely wet the surface of a solid phase of the same substance, and the formation of a liquid layer on the surface of a melting body does not require the expenditure of energy for the formation of a new interface [5]. For example, aluminum single crystals can be overheated in a shock wave by 60 K above the equilibrium melting point [6], and polycrystalline selenium can be overheated by 5 K by creating a specific microstructure [7]. Ice single crystals can be overheated by 0.3 K applying a high-frequency electric field [8], and by 5 K using a jumpwise increase in pressure [9]. However, for the rule of

triple joints to be operative, it is unessential precisely which method was utilized to delay the transition of the system to the equilibrium state, and how far beyond the triple point the metastable line of equilibrium could be extended in experiment.

In order to determine whether or not, in principle, the line of equilibrium between two phases admits extension beyond the point of intersection with the boundaries of the stability region of a third phase, let us imagine that this third phase, for some reasons (e.g., for kinetic ones), fails to form. If the absence of the third phase does not disturb the phase equilibrium described by the line of interest, then the metastable extension of this line is possible. In the absence of the liquid L phase, as is seen from Fig. 2a, nothing prevents the establishment of the equilibrium between the solid and gas phases of water beyond the triple point in the {L} region. The absence of the gas phase allows the establishment of an equilibrium between the liquid and solid phases in the {G} region. Thus, all three equilibrium lines in Fig. 2a can be extended metastably beyond the point of intersection; therefore, their disposition in the vicinity of this point should obey the rule of triple joints.

In general, we cannot rule out the possibility that the critical point in the line of liquid–gas equilibrium, which is labelled by the letter K in Fig. 2a, will lie close to the triple point or even coincide with it. The entropy and the volume are functions of the state of the system; therefore, when going around the triple point, the sums of the jumps in the entropy and volume at the boundary lines between the stability regions of the liquid, gas, and solid phases should be equal to zero:

$$\Delta S_{LG} + \Delta S_{GS} + \Delta S_{SL} = 0 \text{ and } \Delta V_{LG} + \Delta V_{GS} + \Delta V_{SL} = 0. \quad (1)$$

At the critical point, the distinctions between the liquid and gas disappear, and for the transition between these phases we have $\Delta S_{LG} = 0$ and $\Delta V_{LG} = 0$. If the critical point coincides with the triple point, conditions (1) transform into $\Delta S_{GS} = -\Delta S_{SL}$ and $\Delta V_{GS} = -\Delta V_{SL}$, and, according to the Clausius–Clapeyron equation, the slopes of the ‘gas–solid’ and ‘solid–liquid’ boundary lines become identical: $dT_{GS}/dP = \Delta V_{GS}/\Delta S_{GS} = (-\Delta V_{SL})/(-\Delta S_{SL}) = dT_{SL}/dP$. Thus, the closer the critical point in the ‘liquid + gas’ equilibrium line to the triple point, the closer the angle between the two other equilibrium lines to 180° .

Based on the same property of the critical point — equality of the entropy and volume jumps to zero — we can find in a similar way that if the line of equilibrium between two crystalline phases is terminated at the critical point¹ lying in the melting curve or in the curve of transition to some other crystalline phase, then no bending will be observed on this curve at the point of the joint.

In the $T-V$ diagram of water (Fig. 2b), the two-phase invariant equilibria are represented by two-dimensional regions, while the three-phase invariant equilibrium by superposing tie-lines 1–2, 2–3, and 1–3, where the points 1, 2, and 3 represent the equilibrium values of the volumes of the liquid, solid, and gas phases, respectively. At point 3, three phase regions meet: {G}, {S + G}, and {L + G}. If we inhibit the formation of the L phase, the boundary between regions {G} and {S + G} can be extended metastably beyond point 3 and, in accordance with the rule of triple joints, this extension will be projected into region {L + G} (dashed line in Fig. 2b). If the S phase fails to form, then the boundary between regions {G} and {L + G} can be extended beyond point 3 and the resulting line will reside in region {S + G}, which is also shown in Fig. 2b by a dashed line.

The boundary between regions {S + G} and {L + G} cannot be extended metastably beyond point 3, since this boundary is pinned to points 1, 2, and 3, and the position of these points is uniquely determined by the conditions of the invariant equilibrium. Nevertheless, the formal extension of the {S + G}/{L + G} boundary beyond point 3 should fall into region {G}, in accordance with the rule of triple joints, since the existence of the metastable extensions for the other two boundaries meeting at point 3 ensures the fulfillment of this rule for all three boundaries. Analogous considerations lead to a conclusion on the validity of the rule of triple joints for point 1 as well.

Equilibria that include liquid and gas phases in one-component systems are frequently illustrated in $P-V$ diagrams. At the same time, P and V do not belong to the pairs of external parameters that unambiguously determine the phase state of the system. In those places of the $P-V$ diagram where one and only one phase state corresponds to each point of the plane (e.g., in the vicinity of point 3 in Fig. 2a), the rule of triple joints is fulfilled. However, places can exist where such an unambiguous correspondence is violated. For example, two-phase regions {S + L} and {L + G}, referring to different temperatures, overlap in the curvilinear triangle 1–2–4 in Fig. 2c. The rule of triple joints for point 1 is not fulfilled.

3.2 Two-component systems

The application of the rule of triple joints to the phase diagrams of two-component systems can be considered for

¹ In some studies (see, e.g., monograph [5], Ch. 8), it is stated that the line of equilibrium between the crystalline phases cannot terminate at a critical point, since the different crystalline modifications of a substance differ qualitatively between themselves because of the different internal symmetry. This statement, however, does not take into account the existence of transformations between isomorphic phases, whose crystal structures have the same symmetry and differ only in the values of their lattice parameters. An example of a substance with such a transformation is given by cerium, in which a transition between two modifications with a face-centered cubic structure is observed under pressure. At room temperature, the transition is accompanied by a jumpwise decrease in volume reaching 8%. With increasing temperature and pressure, the thermal and volume effects of the transition weaken, and at $T \approx 550$ K and $P \approx 1.9$ GPa these both simultaneously decrease to zero — the line of the phase equilibrium terminates at a critical point [10, 11].

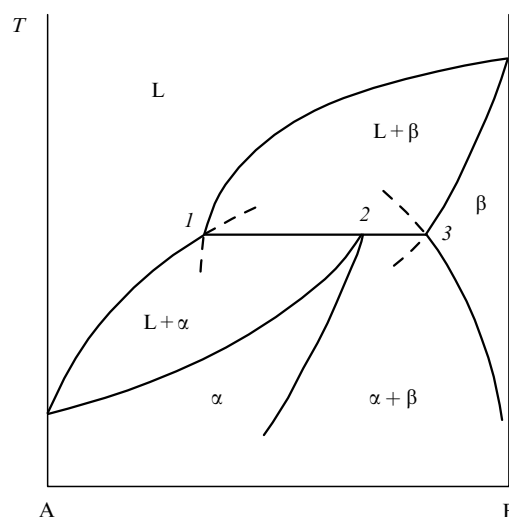


Figure 3. $T-X$ diagram of a two-component system with a peritectic equilibrium $L + \beta = \alpha$, where L stands for liquid, and α and β are two different crystalline phases.

the example of a $T-X$ diagram of a system with peritectic equilibrium, shown in Fig. 3 (to be exact, this diagram represents a $T-X$ section of the full $T-P-X$ diagram of the system cut by the plane $P = \text{const}$). The peritectic equilibrium $L + \beta = \alpha$ shown in Fig. 3 is invariant; the positions of the points 1, 2, and 3 representing the equilibrium compositions of the liquid L, phase α , and phase β cannot change; therefore, the horizontal boundary 1–2–3 cannot be metastably extended either to the left (beyond point 1) or to the right (beyond point 3).

Point 1 is the meeting point of the boundaries of three phase regions: {L}, {L + α }, and {L + β }. Upon transition near point 1 from region {L} to region {L + β }, crystals of the β -phase with the composition of point 3 should begin to precipitate from a liquid with the composition of point 1. Upon transition near point 1 from region {L + α } to region {L + β }, the crystals of the α -phase with the composition of point 2 should disappear, by converting into a mixture of the liquid with the composition of point 1 and the β -phase with the composition of point 3. In addition to the potential barriers for the formation and growth of nuclei of new phases in all these processes, a diffusive redistribution of the components between the phases should also occur, since their compositions are different. Consequently, the process of the formation of the β -phase can, in principle, be delayed, and then the boundary between regions {L} and {L + α } will be extended metastably beyond point 1 into the region {L + β }. Quite similarly, the formation of the α -phase can also be delayed in region {L + α }, and the {L}/{L + β } boundary can be extended into this region metastably. The existence of the metastable extensions of these two phase boundaries ensures the fulfillment of the rule of triple joints for point 1; therefore, the extension of the horizontal boundary 1–2–3 should lie in region {L}.

An analogous consideration indicates that the rule of triple joints should be fulfilled for point 3 of the peritectic diagram given in Fig. 3. In the same way, it can be proven that the rule of triple joints is fulfilled at the endpoints of the horizontal lines of the invariant equilibrium in the $T-X$ diagrams of two-component systems with an eutectic, monotectic, syntectic, metatectic, and other types of invar-

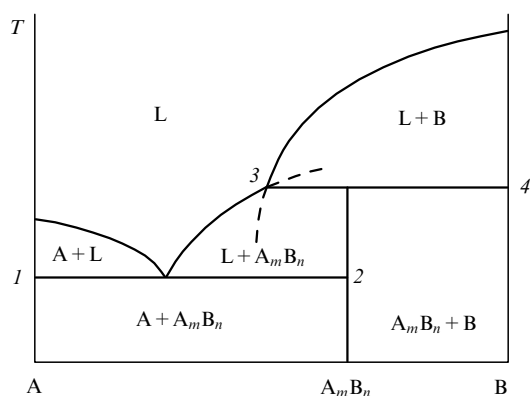


Figure 4. T - X diagram of a two-component system without solid solutions. Horizontal line 1-2 represents the eutectic equilibrium $L = A + A_mB_n$; horizontal line 3-4 represents the peritectic equilibrium $L + B = A_mB_n$. Dashed lines show the metastable extensions of the lines of liquidus of the B component and of the stoichiometric A_mB_n compound beyond the point of intersection with the horizontal 3-4.

iant equilibria. The condition that warrants the validity of the rule for these T - X diagrams is the presence of each component in each phase involved in the equilibria under consideration.

In the systems with two or more components, however, there can be phases in which one or several components are absent. If such a phase resides in the region of the diagram adjacent to the point of a triple joint, two of the three boundaries that meet at this point can be extensions of each other, and the joint will acquire a T-like shape. As an example, Fig. 4 displays a T - X section of a T - P - X diagram of a two-component system in which the A and B components and A_mB_n compound forms no solid solutions. As is seen from this figure, the rule of triple joints is fulfilled only for point 3, while the joints at points 1, 2, and 4 have a degenerate, T-like shape.

3.3 Three-component systems

It should be noted that the variety of phase boundaries admitting a metastable extension beyond the point of a triple joint is not limited with the curved lines or sections of curved boundary surfaces, considered above. These may also be sections of ruled surfaces formed by tie-lines; correspondingly, the rule of triple joints can be applied to two-dimensional sections of phase diagrams with three or more components.

As an example, Fig. 5a presents a vertical ('polythermal') section of a three-dimensional T - X_1 - X_2 diagram (to be exact, this is an isobaric section of a four-dimensional T - P - X_1 - X_2 diagram) of a three-component system with an invariant eutectic equilibrium $L = \alpha + \beta + \gamma$. In this section there are two triple joints of boundary lines at points 1 and 3. The 1-2-3 line represents a section of the horizontal plane of invariant equilibrium; therefore, as in the preceding cases, this line cannot be extended either to the right or to the left.

The boundaries of the phase regions $\{L + \beta + \gamma\}$, $\{\beta + \gamma\}$, and $\{\alpha + \beta + \gamma\}$ meet at point 3. Both the $\{L + \beta + \gamma\}/\{\beta + \gamma\}$ and $\{\beta + \gamma\}/\{\alpha + \beta + \gamma\}$ boundaries are sections of ruled surfaces separating the corresponding bulk phase regions in the three-dimensional T - X_1 - X_2 diagram. As is seen from the phase composition of the regions, the boundary $\{L + \beta + \gamma\}/\{\beta + \gamma\}$ line can be extended metastably

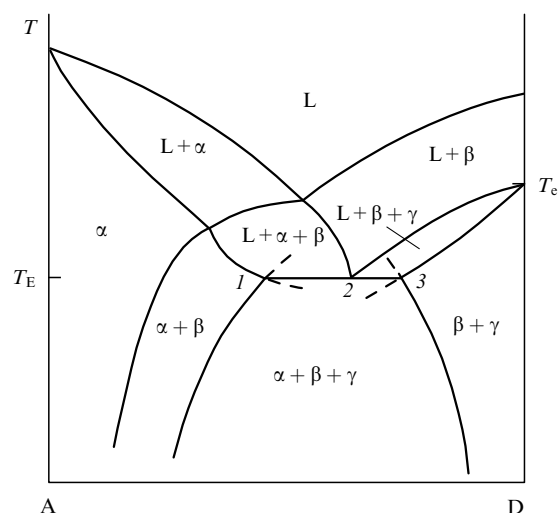


Figure 5. Vertical ('polythermal') section through a three-dimensional T - X_1 - X_2 diagram of a three-component system with an invariant eutectic equilibrium $L = \alpha + \beta + \gamma$ at the temperature T_E . The point D lies on the BC side of the concentration triangle ABC. The symbol T_e marks the point of intersection of the horizontal line of the eutectic equilibrium $L = \beta + \gamma$ in the constituent binary BC system.

beyond point 3 into the region $\{\alpha + \beta + \gamma\}$ if the α -phase fails to appear. The boundary $\{\beta + \gamma\}/\{\alpha + \beta + \gamma\}$ line can be metastably extended beyond point 3 into region $\{L + \beta + \gamma\}$ if no phase L forms. Since two boundaries admit a metastable extension beyond the intersection point, the rule of triple joints is valid for point 3, and the extension of the horizontal boundary 1-2-3 should lie in region $\{\beta + \gamma\}$.

It follows from analogous considerations that the disposition of the phase boundary lines in the vicinity of point 1 also obeys the rule of triple joints.

4. Conclusions

The finding that the rule of triple joints should already be valid if only two out of three boundary lines can have a metastable extension beyond the point of intersection allowed us to formulate this rule in a form applicable to the analysis of a large variety of the types of diagrams of phase equilibria in the systems with an unlimited number of components. The flexibility of the rule is to a significant extent due to the fact that it does not specify exactly which coordinate axes are utilized for constructing the phase diagram.

At the same time, the application of the rule in the suggested formulation requires a more rigorous understanding of the term 'metastable extension' of a phase boundary compared to its commonly accepted meaning. A necessary condition for the existence of such an extension is that the phase equilibrium described by the boundary line remain thermodynamically feasible beyond the point of its intersection with another boundary line. To the best of our knowledge, the possibility of the absence of a metastable extension for phase boundaries of one type or another has not been discussed previously in the literature (most likely because of the absence of practically important consequences). Nevertheless, some phase boundaries cannot certainly be extended, e.g., no metastable extension is possible for the horizontal lines of invariant equilibria in the above-considered T - X diagrams. Moreover, except for the T - P diagrams of one-

component systems, we have found no example of phase diagrams with a joint of three boundary lines in any two-dimensional section such that all these three lines could have metastable extensions beyond the point of the joint. Our paper gives recommendations of how to determine whether the boundary line admits a metastable extension or not.

The rule of the joint of three boundary lines proved in this paper can be used ‘in parts’. If the boundary between two phase fields allows a metastable extension beyond the point of its intersection with the boundaries of a third region, the extension should lie between the boundaries of this third region.

The rule is only applicable to the diagrams which uniquely represent the phase compositions of the regions adjoining the triple joint. This condition is always fulfilled for the $T-P-X$ and $T-V-X$ diagrams of heterogeneous systems for which the Gibbs phase rule [4] is known to be valid, i.e., for the systems in which each phase contains all the components, the pressure is isotropic everywhere, and the effects due to interfaces between different phases and due to the external fields are negligible. If a diagram is constructed on other coordinate axes, it can describe the state of the system ambiguously in the vicinity of some triple joints, and the rule that has been proved in this paper cannot be applied to these joints (as an illustration, the paper considered the violation of the rule for one of the triple joints in the $P-V$ diagram of water presented schematically in Fig. 2c). Notice also that in the case if one or several components is missing in a phase or phases presented in the region of the diagram adjoining the point of the triple joint, then two of the three phase boundaries meeting at this point can be the extensions of one another, and the joint acquires a degenerate T-shape (see Fig. 4).

Acknowledgments

This work was supported in part by the Russian Foundation for Basic Research, project No. 11-02-00401.

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