



Proving the contact rules for phase regions: Implications to phase diagrams of metal–hydrogen systems



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ABSTRACT

The rule of triple joints has recently been proved for two-dimensional phase diagrams and two-dimensional sections of phase diagrams of a higher dimension (Antonov, 2013). The present paper is extending this rule to phase diagrams of binary metal–hydrogen systems composed of a metal immersed in a hydrogen gas. The rule is shown to be valid for every triple point in the temperature–pressure phase diagrams of these systems, including the points with the intersecting boundary lines tangent to each other. The paper also considers the sufficient conditions for the application of the rule to triple points in the projections of phase diagrams onto the temperature–concentration plane.

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1. Introduction

The rules (or theorems) related to the topology of phase diagrams are very few. These include the Palatnik–Landau contact rule for phase regions [1] and two its consequences, the cross rule [1] and the Rhines phase rule [2], and also the rule of triple joints. The paper below will present the part of the talk concerning the rule of triple joints. This rule places limitations on the mutual position of three boundary lines meeting at one point in a two-dimensional phase diagram or in a two-dimensional section of a phase diagram of a higher dimension. The rule is usually 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.

The rule for triple joints is widely used in constructing equilibrium phase diagrams and in the error tests. However, for a very long time, the rule has only been proved for triple joints in the T – P diagrams of one-component systems [3]. The 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. This condition, however, is never fulfilled for the triple points in phase diagrams of other types.

It was only recently that we noticed that the rule of triple joints should already be valid if two out of the three boundary lines can have a metastable extension beyond the point of their intersection. This finding allowed us to advance an improved formulation of the rule [4]:

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.

The rule in this new form is illustrated by Fig. 1.

For the analysis of some phase equilibria, a more detailed formulation of the rule can be recommended:

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 the boundary between two phase regions can have a metastable extension beyond the point of intersection with the boundaries of the third phase region, this extension lies between the boundaries of the third region. If metastable extensions are possible for two boundaries, the extension of each of the three boundaries lies in the region between two other boundaries.

As one can see, the proved rule does not specify the types of the axes on which the diagram is built (pressure P , temperature T , volume V , concentrations x , electric field, etc.), or the number of components of the system, or the type or variance of the phase equilibria presented in the diagram. This makes the rule more flexible and applicable to the analysis of two-dimensional sections of phase diagrams of heterogeneous systems with any given number

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of components. On the other hand, applying the rule in the improved form requires a more rigorous understanding of the term “metastable extension” of a phase boundary compared to its commonly accepted meaning.

Another significant requirement is that the diagram should unambiguously represent phase compositions of the regions adjoining the triple joint. This requirement is always fulfilled for two-dimensional sections of the T - P - x and T - V - x diagrams of heterogeneous systems for which the Gibbs phase rule [5] 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. Before applying the rule to a triple point in a diagram of other type, one have to make sure that the three phase regions only meet at this point and do not overlap.

Conditions and some aspects of the application of the rule to the diagrams of the Gibbs type were considered in Ref. [4]. This paper will consider a special case of phase diagrams of binary metal–hydrogen system, in which a metallic sample is brought in thermodynamical equilibrium with a H_2 gas surrounding it.

2. Temperature–pressure phase diagrams

There are basically two types of phase equilibria in the metal–hydrogen systems.

Many metals (rare earths, titanium, zirconium, etc.) easily absorb hydrogen at low pressures and do not lose it in inert media, even at elevated temperatures. The total hydrogen concentration in these metals can be varied independently of other parameters that also govern the phase state of the system (temperature, pressure, concentrations of different metallic components). Phase diagrams of the metal–hydrogen systems of this type have no specific features compared with the diagrams considered in Ref. [4].

Phase equilibria of another type are observed when a metal sample (one- or multicomponent) is immersed in an atmosphere of molecular hydrogen, and the temperature is high enough to establish the dynamical equilibrium between the hydrogen inside and outside the sample. In this case, the total concentration of hydrogen in the metal cannot be varied at will. Instead, the hydrogen concentration in each of the p_{cond} phases formed in the sample is determined by the equality $\mu_{\text{H}}^{(i)} = \frac{1}{2}\mu_{\text{H}_2}$, where $\mu_{\text{H}}^{(i)}(T, P)$ is the chemical potential of hydrogen in the i -th metallic phase ($i = 1, 2, \dots, p_{\text{cond}}$) and $\mu_{\text{H}_2}(T, P)$ is the chemical potential of molecular hydrogen.

The line of the liquid–gas equilibrium in molecular hydrogen terminates at a critical point at $T_{\text{cr}} \approx 33$ K and $P_{\text{cr}} \approx 13$ bar [6] and the melting line of molecular hydrogen only rises to room temperature at $P \approx 5$ GPa and further to $T = 150$ °C at $P \approx 10$ GPa [7]. In

a wide T - P range above the critical point and the melting line, molecular hydrogen behaves as a homogeneous gas (or fluid) and serves as pressure transmitting medium and a reservoir for loading the metal phase(s) with hydrogen up to the equilibrium concentrations, which vary with the temperature and pressure in a unique fashion.

Of special interest is the important case of systems composed of a one-component metal (or any other condensed substance, solid or liquid) reacting with H_2 gas taken in excess. The total number of phases in such a system with $n = 2$ components is $p = p_{\text{cond}} + 1$, and the Gibbs phase rule gives the variance (number of degrees of freedom)

$$f = n - p + 2 = 2 - (p_{\text{cond}} + 1) + 2 = 1 - p_{\text{cond}} + 2,$$

which looks exactly like that for the usual one-component system. Particularly, the maximum possible number of coexisting phases, p_{cond} , is three. This may occur if the number of degrees of freedom attains its minimum possible value, which is zero.

Correspondingly, the topology of the T - P diagram describing phase states inside a one-component condensed substance surrounded with a hydrogen gas should be the same as that of a one-component system: equilibria between two condensed phases should be represented by curves, and three-phase equilibria by isolated points. The only difference is that the hydrogen concentration in each condensed phase varies with T and P .

By way of illustration, Fig. 2a shows a T - P diagram of the Mn–H system characterized by a rather large variety of phase transformations in the studied range of hydrogen pressures and temperatures. At atmospheric pressure, there are four modifications of manganese: α -Mn and β -Mn with complex cubic lattices, fcc γ -Mn and bcc δ -Mn. The maximum hydrogen solubility in α -Mn and β -Mn is a few atomic percent [8]. The atomic ratio $x = \text{H}/\text{Mn}$ of solid hydrogen solutions in γ -Mn reaches $x = 0.36$ at $P = 0.8$ GPa and $T = 1000$ °C [8] and further increases to $x = 0.41$ at 2 GPa and 800 °C [9] and to no less than $x = 0.72$ at 5 GPa and 900 °C [10]. The hydrogen content of the ϵ hydride (hcp metal lattice) at $T = 350$ °C varies from $x \approx 0.8$ at 1 GPa to $x \approx 0.95$ at 4 GPa [8]. The composition of the ϵ' hydrides ($double\ hcp$ metal lattice) is expected to be similar to that of the ϵ hydrides and the hydrogen content of the Mn–H liquids is not known [10]. The interaction of high-pressure hydrogen with δ -Mn has not been studied. The boundary lines in Fig. 2a show the conditions of decomposition of the hydrides, and these conditions should be close to those of the corresponding phase equilibria (see [11] for discussion and explanation).

The significant differences and variations of hydrogen concentrations in the Mn–H phases have no impact on the applicability of the rule of triple joints to the T - P diagram because the temperature and pressure are the same in these phases. Moreover, the rule must be valid for each triple point in the diagram, because every boundary line representing a two-phase equilibrium can be extended metastably (remains thermodynamically feasible) beyond the point of its intersection with the boundaries of the stability region of a third phase. This can be demonstrated in the same way as with the usual one-component systems [4].

Indeed, let us consider triple point 1 in Fig. 2a and imagine that the γ phase fails to form for some reasons (e.g., for kinetic ones). In the absence of this phase, both α and ϵ phases can exist in the γ region of the diagram and be in equilibrium with each other and this equilibrium will be represented by a metastable extension of the α/ϵ boundary. Similarly, the absence of the ϵ phase allows the extension of the α/γ boundary in the ϵ region, and the ϵ/γ boundary will have a metastable extension in the α region if the α phase does not form.

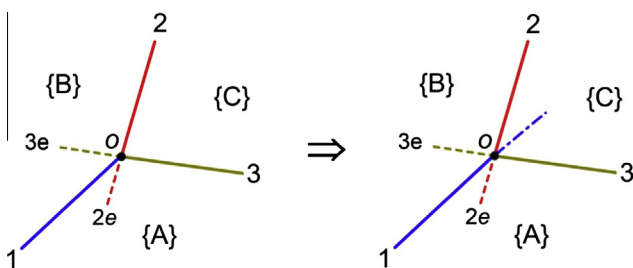


Fig. 1. Boundaries between phase regions (solid lines) and metastable extensions of these boundaries (dashed lines) near the point O of the triple joint. The dash-dotted line in the right-hand diagram represents a formal extension of boundary 3 predicted by the rule of triple joints. The phase states {A}, {B}, and {C} may differ in both the full number and the set of phases.

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