Proof of Schreinemakers' Rule for General Phase Diagram Sections

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Following a proposal by Hillert, Schreinemakers' rule is proven to apply in the general case to sections of phase diagrams of systems of any number of components.

The well-known Schreinemakers' rule is illustrated in Fig. 1. In an isothermal isobaric section of a ternary phase diagram, both extensions of the phase boundaries of the α region at point a must pass into the adjacent three-phase region as in Fig. 1(a), or they both must pass into the adjacent two-phase regions as in Fig. 1(b).

Hillert recently proposed that this rule may be useful for general sections of phase diagrams for higher order systems, although no strict proof for such cases was presented. The purpose here is to formulate this proof.

As an example of the general rule, Fig. 2 shows an isobaric section of the Fe-Cr-V-C system at 850 °C and 0.3 wt.% C. The diagram consists of a number of nodal points at which four lines meet. Around each point are found an N-phase field, two (N+1)-phase fields, and an (N+2)-phase field. The general Schreinemakers' rule states that, at any point, either the boundaries of the N-phase field both must pass into the (N+2)-phase field as at points b and i in Fig. 2, or they both must pass into the (N+1)-phase fields as at points c, n, and s.

Consider the ternary system in Fig. 1, and consider first the limiting case where points b and c are coincident with the corners B and C of the composition triangle; that is when phases β and γ are pure components B and C. Point p in Fig. 1(a) is a point in the three-phase field, arbitrarily close to point a. Now, if precipitation of C is prohibited, point p lies in the one-phase metastable α region. Hence, at point p, B will not precipitate unless C also precipitates. That is, precipitation of C from the α phase increases the chemical potential of B:

$$\frac{\partial}{\partial n_C} \mu_B^\alpha = \frac{\partial}{\partial n_C} \left( \frac{\partial G^\alpha}{\partial n_B} \right) < 0$$

(Eq 1)

where $G^\alpha$ is the Gibbs energy of the α-phase at point a.

Because the order of differentiation does not matter, then:

$$\frac{\partial}{\partial n_B} \left( \frac{\partial G^\alpha}{\partial n_C} \right) = \frac{\partial}{\partial n_B} \mu_C^\alpha < 0$$

(Eq 2)

Hence, the other boundary of the α phase region must also pass into the three-phase region. In Fig. 1(b), point p lies in the two-phase ($\alpha + \gamma$) region arbitrarily close to point a. If precipitation of C is prohibited, point p lies in the metastable two-phase ($\alpha + \gamma$) region.

Fig. 1 Isothermal isobaric section of a ternary phase diagram illustrating Schreinemakers' rule.
β) region. Hence, precipitation of C prevents precipitation of B. That is:
\[
\frac{\partial}{\partial n_c} \left( \frac{\partial G^\alpha}{\partial n_B} \right) > 0 \quad \text{(Eq 3)}
\]

Therefore, because the order of differentiation does not matter, the extension of the other boundary of the α phase must pass into the two-phase (α + β) region.

For the more general ternary case, we consider the quantity:
\[
\frac{\partial}{\partial n_\gamma} \left( \frac{\partial G^\alpha}{\partial n_\beta} \right) = \frac{\partial}{\partial n_\beta} \left( \frac{\partial G^\alpha}{\partial n_\gamma} \right) \quad \text{(Eq 4)}
\]

where \( \partial n_\gamma \) and \( \partial n_\beta \) represent transfers of material with overall compositions at points b and c, respectively. According to whether this quantity is negative or positive, the extension at point a will be as in Fig. 1(a) or (b), respectively. This proof is similar to the proof given by Hillert.5

This reasoning may be extended to general sections of higher order systems. In Fig. 2, consider point A, which is in the four-phase region arbitrarily close to point b, and at which (γ + MC) is the metastable phase assemblage if precipitation of α is prohibited. It follows that:
\[
\frac{\partial}{\partial n_\alpha} \left( \frac{\partial G^{\gamma + MC}}{\partial n_{MC}} \right) < 0
\]

where \( G^{\gamma + MC} \) represents the Gibbs energy of an equilibrium mixture of γ and MC phases (alone), where Eq 5 applies at the overall composition of point b, and where \( \partial n_\alpha \) and \( \partial n_{MC} \) represent transfers of material with overall compositions of the α