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Configurational Transformation of Complex Phase Diagrams under Constrained Conditions—A Phenomenon of General Significance

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The phase diagrams of multiphase, multicomponent systems under specified thermodynamic conditions are frequently met in petrology, geochemistry, materials, metallurgy and physical chemistry. The topological configurations of these phase diagrams often vary with the thermodynamic conditions, where the condition parameters are typically restricted temperature, pressure, or specific intensive properties of components (such as chemical potential, composition, concentration, fugacity, activity, etc.). The configurational transformation of phase diagrams under constrained conditions is very important for understanding the formation or stability conditions of phases or phase assemblages. The topological analysis theory of phase diagrams (Cheng and Greenwood, 1990; Zen, 1966, 1967; Zen and Roseboom, 1972) is a very useful tool for discovering the regularity of the configurational variation of complex phase diagrams.

In order to avoid making things too complicated, taking a simple system as example should be a good choice. In this work, the log$f(O_2)$–log$a(SiO_2)$ diagrams of the CaO-FeO-SiO_2-O_2 system under different temperatures and pressures are used as example, which includes magnetite (Mt, Fe_3O_4), andradite (Andr, $Ca_3Fe_2Si_3O_{12}$), hedenbergite (Hd, $CaFeSi_2O_6$), fayalite (Fa, Fe_2SiO_4), kirschsteinite (Kst, $CaFeSiO_4$), wollastonite (Wo, $CaSiO_3$) and hematite (H, Fe_2O_3). These minerals or their assemblages can form or exist under very different temperatures (T), pressures (P), oxygen fugacities [$f(O_2)$], and silica activities [$a(SiO_2)$]. The thermodynamic data for minerals or components (O_2 and SiO_2) are taken from Holland and Powell (1998) and Sommacal (2004), and the activity coefficient model of the Fa-Kst solid solution is taken from Mukhopadhyay and Lindsley (1983).

In this work, all phase assemblages are labeled with their absent phases. For example, if an invariant

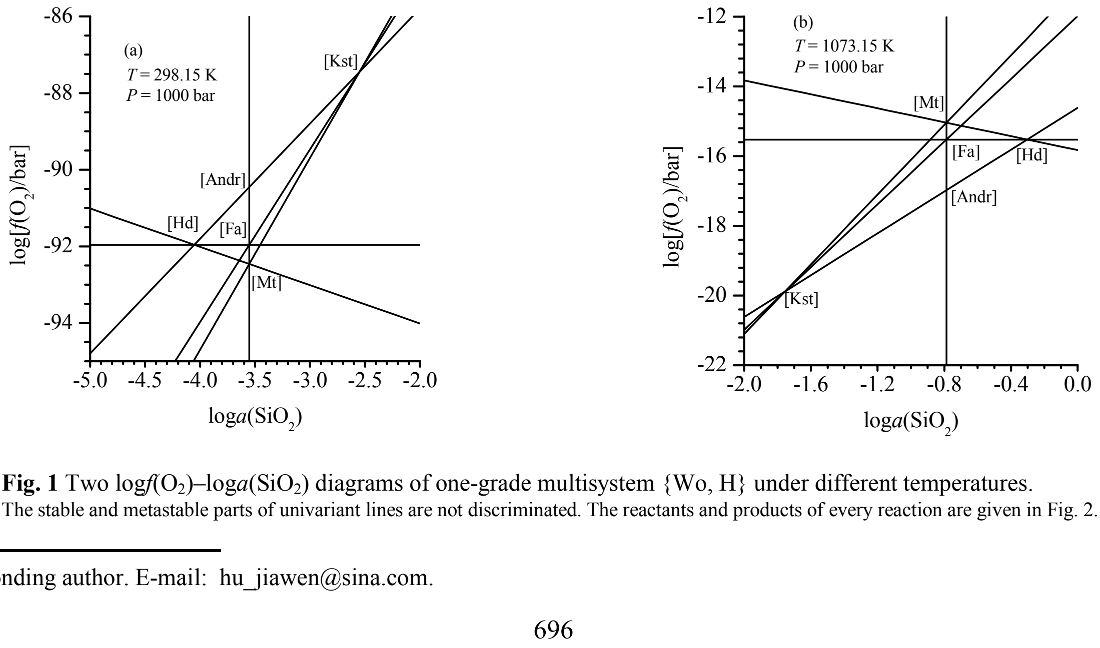

Fig. 1 Two log$f(O_2)$–log$a(SiO_2)$ diagrams of one-grade multisystem {Wo, H} under different temperatures.
The stable and metastable parts of univariant lines are not discriminated. The reactants and products of every reaction are given in Fig. 2.

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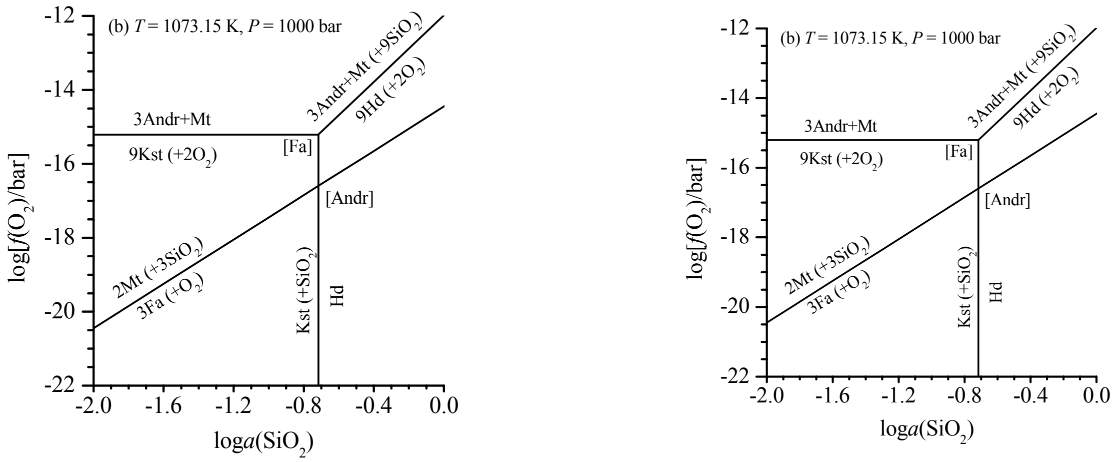

Fig. 2 The stable parts of two nets of one-grade multisystem {Wo, H} under different conditions.

assemblage misses phase A, it will be labeled as [A]. Similarly, the univariant assemblage missing A and B is labeled as (A, B). For simplicity, the invariant points and univariant lines corresponding to the above assemblages are also labeled with the same symbols, respectively. According to the topological analysis theory of phase diagrams, if a system has more than one invariant assemblage, it can also be called "a multisystem" (Korzhinskii, 1959). If m new phases are added to an invariant assemblage, it will form an m-grade (or m-level) multisystem (Hu et al., 2004; Hu, 1998). To be consistent in notation, multisystems are also labeled with their absent phases, e.g. one-grade multisystem Fa-Kst-Hd-Mt-Wo can be labeled as {Andr, H} (relative to the seven-phase system).

In this work, all thermodynamic calculation and discrimination are made in the framework of one-grade multisystems, where the stability fields of reactant or product assemblages, the stable and metastable invariant points and the stable and metastable parts of univariant lines are determined with the approach of Hu et al. (2000). The calculated results show that the phase diagrams of one-grade multisystems {Fa, H} and {Wo, H} both change their configurations with temperature or pressure. Before and after a configurational transformation, the stable and metastable parts of the equilibrium line of the same univariant assemblage show 180° -rotational symmetry (Fig. 1). After the transformation, every invariant point changes its stability. That is, the *stable* and *metastable* invariant points under certain conditions change into the *metastable* and *stable* invariant points at new conditions, respectively (Fig. 2). For example, at given pressure (e.g. 1000 bar), the log$f$(O_2)–log$a$(SiO_2) diagrams of {Fa, H} and {Wo, H} both have such configurational transformation between 298.15 K and 1073.15 K, so the phase diagram of the whole system (seven phases) undergoes two configurational transformations. The transformations result in three configurations (Shi et al. 2011), which exist in three temperature intervals divided by the two configurational transformation temperatures.

According to the topological analysis theory of phase diagrams, the invariant points of a one-grade multisystem and the univariant lines about them cannot be all stable under specified conditions. The stable parts form a stable net, and the metastable parts form a metastable net, which is a residual net of the former. For a one-grade multisystem, if its phase diagram undergoes a configurational transformation, the stable net and its metastable residual net will simultaneously change their stabilities as a whole (Fig. 2). It is found that pressure has obvious influence on the configurational transformation temperatures (T_{tr}) of log$f$(O_2)–log$a$(SiO_2) diagrams of {Fa,

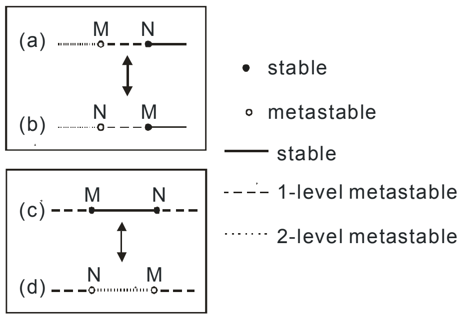

Fig. 3 Change of the stability levels of invariant points and univariant lines of a one-grade multisystem due to the change of thermodynamic conditions.

The configurations in (a) and (b), or in (c) and (d) exist under different thermodynamic conditions, and can transform into each other in the variation of thermodynamic conditions. The 2-level metastable part of a univariant line is the segment on which the metastable parts of the univariant lines emanating from two invariant points coincide.

H} and {Wo, H}. The P–T_{tr} relations of the two one-grade multisystems are very close to linear functions.

In principle, for a phase diagram of a one-grade multisystem under given conditions, there are two invariant points on a *non-degenerate* univariant line, and there must be such lines on which one invariant point is stable and the other is metastable, e.g. Fig. 3 [(a) or (b)]. Suppose the two invariant points are M and N, respectively, whose horizontal (or vertical) coordinates are X_M and X_N, respectively. Apparently, the distance between M and N must vary with the conditions of the system. If M and N move towards each other and the variation ranges of condition parameters are *big* enough, X_M–X_N may change sign. That is, M and N may move across each other (Figs. 3a and 3b). In this case, M and N will exchange their stabilities. At the same time, the stable and metastable parts of univariant lines about M and N also exchange their stabilities. Similarly, if M and N are both stable, they can simultaneously change into metastable, and vice versa, e.g. Figs. 3c and 3d. Besides the above conditions, no other special conditions are needed in the configurational transformation. This suggests that the configurational transformations of phase diagrams should be common in the various constrained phase diagrams. However, to our knowledge, there are few systematic investigations on such configurational transformations. This may be attributed to the following reasons: (1) In most cases, thermodynamic calculation or experimental study is focused on a single phase diagram under specific conditions, or on some phase diagrams of a limited range of condition parameters, which is not big enough to pass through the boundary conditions of the configurational transformation. (2) The boundary conditions of the configurational transformation are beyond in the physically possible range. (3) Before the configurational transformation, the variation of condition parameters leads to the disappearing of old phase(s) or the presence of new phase(s). Despite these factors, the configurational transformations of constrained phased diagrams should have general significance. Before getting a complete knowledge of the phase relations in a high-grade multisystem (m>1), one must try to get all possible phase diagram configurations. The key to this problem is the transformation conditions of different configurations of one-grade multisystem phase diagrams.

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