Comments

Discussion on the Hierarchy of Metastable Phases

"In a very enlightening paper on metastable phase equilibria, J.W. Cahn [1] recently discussed the hierarchy of phases by which is meant that all possible phases in a system can be arranged in a hierarchical order such that a spontaneous change can occur by the transformation of a phase to another phase further down in the hierarchical order but not to a phase further up in the order. If such an order exists, then it follows that a phase cannot spontaneously disappear and then reappear later on. Cahn pointed out that such a definite hierarchy of phases exists in open systems, for instance in a single-component system at constant pressure and temperature or in a multicomponent system at constant pressure, temperature and chemical potentials. He demonstrated that no simple hierarchy exists in a multicomponent system when it is closed in the sense that it has a fixed composition. The purpose of this note is simply to emphasize that we meet the same situation as soon as the system is closed in any respect, and it can thus occur in a single-component system as well.

"Let us examine a single-component system using temperature and volume as the independent variables. We would then have a phase diagram of the type shown in Fig. 1. The metastable extension of the $\beta + \gamma$ equilibrium toward low temperatures has been drawn with dashed lines. It is evident that a system kept at point V_1, T_1 could be in a state of single phase β . If γ would then nucleate, β would dissolve and disappear com-

Fig. 1 Single-component System Exhibiting Metastability of γ Phase at Low Temperatures

See text for explanation.

pletely. However, after α has nucleated, β may reappear and establish the final state of equilibrium, $\beta + \alpha$. Consequently, this is a case where a "stable phase", β , dissolves in a "metastable phase", γ , in a single-component system."

Reference

1. J. W. Cahn, *Bull. Alloy Phase Diagrams*, 1(2), p 27 (1980).

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See J. W. Cahn's response below.

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Addenda

Some Additional Thoughts on Metastable Hierarchies

In reference to Mats Hillert's comment (see above), I fully concur that his extension of the concepts of open and closed systems reveals general principles that deserve a fuller discussion. In thermodynamics of phase equilibria, it is useful to distinguish between intensive variables, such as temperature, pressure and chemical potentials, each of which has the same value in all coexisting phases, and variables related to extensive variables, such as molar entropy, density and compositions, which can be different in the different phases at equilibrium. To fix the size of the system, at least one condition is imposed on the extensive variables. The conventional definition used in my paper holds that a system is open if matter could be added, closed if not. In Hillert's more general definition, a system is open if any extensive variable is allowed to vary, as it would be if the corresponding intensive variable were held

fixed, and closed if all extensive variables are held fixed. Hillert could have considered fixing not only volume but also entropy. In all open systems, we must specify which extensive variables are allowed to vary.

It is important to note that Hillert's argument applies equally well to single-component adiabatic systems held at either constant volume or constant pressure. Because many phase changes occur so rapidly that adiabatic conditions hold, this is not only an important case of his kind of "open" system, but also one in which it will be easy to check some of the consequences. Hillert's diagram is equally applicable if the axes are entropy instead of volume and pressure instead of temperature.

Let us reexamine the case in which a small amount of stable phase can dissolve into a metastable one after they are brought in contact. For the multicomponent case, closed with respect to material, but held at constant pressure and temperature, the two phases are at the same temperature and pressure but differ in chemical potentials. In Hillert's example of the one-component system held at constant volume, the two

phases are initially at different pressures and/or different chemical potentials whereas, in the adiabatic example, they are initially at different temperatures and/or different chemical potentials, the stable phase being in a temperature range where that phase is stable. In each case, there is a difference in an intensive property, and there exist conditions where the stable phase will be the one that disappears. It somehow seems less surprising that a small amount of stable phase could dissolve into a metastable phase at a different temperature, than into one with different chemical potentials.

In an isothermal multicomponent system, closed with respect to material, chemical potentials did not need to change monotonically as the system approached equilibrium. In Hillert's kinds of closed systems, pressure and temperature do not need to change monotonically. It should be possible to have a series of metastable adiabatic equilibria, in which the temperature takes on values on either or both sides of the final equilibrium temperature. The same thing is possible for pressure, but inertial effects (such as sound waves), which are usually not included in thermodynamics of phase equilibria, can also give oscillatory pressure changes.

Consider, for example, a liquid held adiabatically below its triple-point pressure. For a wide range of initial temperature, the entropy content is such that the final equilibrium is solid plus vapor. Depending on whether solid or vapor nucleates first, the temperature will respectively either rise or fall. In some of these cases, the temperature will initially move further away from its final equilibrium temperature.

During fast reactions, large systems often approximate adiabatic conditions. Undercooling is often observed to terminate with rapid thermal changes. Temperature and pressure, unlike chemical potential, are easier to monitor during a metastable reaction sequence. A system closed with respect to volume and heat could indeed give valuable information about metastable reactions.

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The Al-Au (Aluminum-Gold) System

On page 72 of Vol. 2, No. 1, Fig. 3 should be changed as shown in the following figure.

In Reference 38 on page 74 of Vol. 2, No. 1, the authors should read "M.E. Straumanis and J.S. Shah".

Evaluations of Alloy Systems

On page 43, line 10 of Vol. 1, No. 2, in the sentence, "The third set consists of six previously unpublished U-X binary diagrams (where X = Cd, H, Hg, Mg, Sb or Zn) that were recently evaluated by Chiotti", the words "previously unpublished" should have been deleted because most of these phase diagrams have been previously published as acknowledged in the references.

The H-U (Hydrogen-Uranium) System

On page 101 of Vol. 1, No. 2, the constant term in Table 1, Equation 6, should be 6.415.

The V (Vanadium) System

On page 40 of Vol. 2, No. 1, Fig. 2 should be replaced by the following figure.

Fig. 1 Heat Capacity Versus Temperature for V

J.F. Smith, 1980.