Obtaining Inferences About Relative Stability and Metastable Phase Sequences From Phase Diagrams

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Phase diagrams that include metastable equilibria can be constructed from empirical observations on metastable phases and extrapolations of data from stable phases. Such diagrams contain useful hierarchical information about metastable phase equilibrium sequences.

Metastable phase equilibrium is an example of constrained equilibrium. The constraint is that one or more of the stable phases is absent. The phases that are actually present reach equilibrium subject to this constraint. This definition of metastable phase equilibrium, focussing on the absence of one or more of the equilibrium phases, does not ascribe any unusual characteristics to the metastable ones present.

Metastable equilibria obey the phase rule and can be mapped on phase diagrams. The same thermodynamic measurements that are made on stable phases can be, and have been, made on metastable phases. Heat capacity, volume, vapor pressure, and other such properties are rigorously defined and have been measured. From such measurements, energy, entropy, and free energy can be rigorously determined. Metastable phases obey the usual solution laws. If they are dilute, Henry's and Raoult's laws apply. They can even be ideal: to wit, a supersaturated vapor at a density far below the critical-point density. It is reasonable to assume that there are no discontinuities in thermodynamic properties as a phase moves from stable to metastable. As a result, metastable equilibria can be estimated from extrapolations of data obtained on stable phases.

A second example of constrained phase equilibrium occurs when a phase change is so rapid that one or more of the components cannot redistribute among the phases in the time scale of the experiment. In a completely partitionless phase change, the temperature at which the two phases have equal free energies traces out to a surface (T_0) on the multicomponent phase diagrams within the two-phase field for these phases and extrapolations. Nucleation theory tells us that there are natural barriers to the formation of new phases from metastable ones. The range of conditions under which a phase can be metastable is bounded by kinetic factors, imposed by nucleation and growth, and thermodynamic limits commonly called spinodals.

This article focuses on metastable equilibria and partitionless transformations, their representation on phase diagrams and the hierarchical laws governing the thermodynamically possible sequences of phases and metastable phase equilibria. Certain basic concepts and relationships described in earlier reviews[1-3] and standard textbooks will be assumed. After the single-component case is discussed, the major complications introduced for multicomponent systems are highlighted.
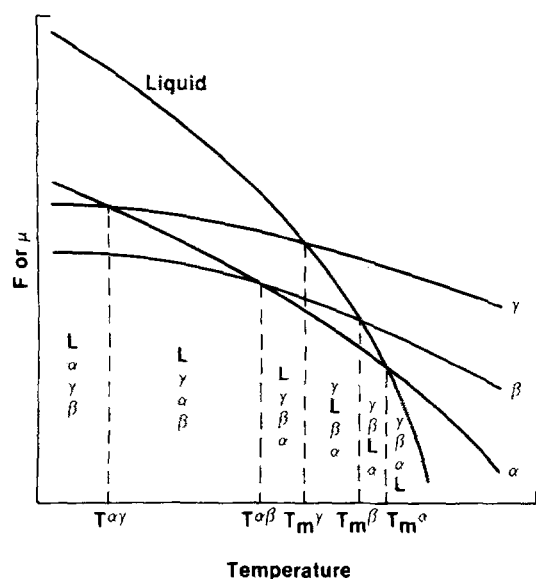
Metastable Phase Equilibria in Single-Component Systems

In a single component system, phases are in equilibrium when the chemical potentials (μ) of the component, which in this case are the same as the molar Gibbs free energies (F), in the several phases are equal. A graph of the free energies of several phases as a function of temperature at constant pressure is shown in Fig. 1. At each temperature, the stable phases are the ones with the lowest value of F. Consistent with the phase rule, only one phase is stable except where the two lowest curves cross. All other phases are metastable. With changing pressure, the free energy curves will shift at a rate proportional to the volumes of each phase, and different phases may become stable.

The phase diagram shown in Fig. 2 is a graph of the domains where each phase is stable. It consists of areas in which a phase is stable bounded by curves in which two phases are the equilibrium. Three curves come together at triple points of three-phase equilibrium. Vapor-liquid critical points where a two-phase curve terminate are of little concern in metallurgy. The axes can be any two independent combinations of T, P, or μ.

Equilibria between metastable phases can also be mapped on this phase diagram. Each of the curves in the metastable phase diagram represents a crossing of two free energies. As in the case of the stable diagram, each curve is identified with the equilibrium of the two phases, one of which is stable on one side of the curve, the other is stable on the other. In Fig. 3, this sidedness of each curve has been identified by labeling the stabler phase on each side. The properties of these two-phase equilibria are unaffected by whether or not there exists a more stable phase. If in some part of the diagram the two-phase equilibrium is stable, the curve representing it can be extrapolated beyond the triple point where it becomes metastable. The stable triple points also have become the crossings of three two-phase curves. The six rays emanating from a stable triple point are alternately stable and metastable.

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Fig. 1 Chemical Potential (Free Energies) of Various One-Component Stable and Metastable Phases as a Function of Temperature at Constant Pressure


The stable phase at each temperature is the one with the lowest μ. Stable and metastable two-phase equilibria occur where two curves cross. Between crossings the hierarchy of phases ranked according to their values of μ is listed.

Fig. 2 One-Component Phase Diagram
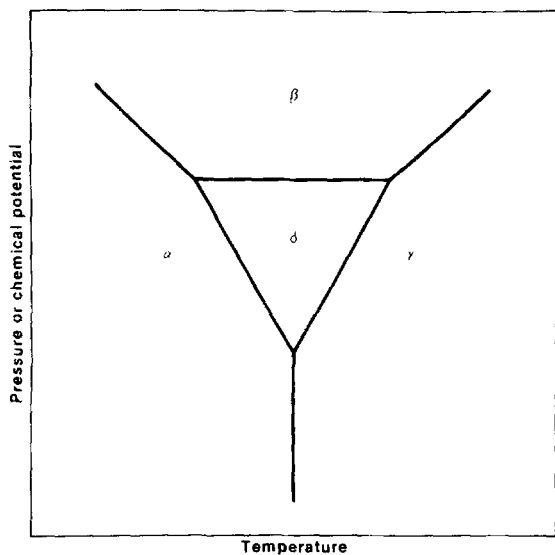
With T, P or μ as axes, showing stable two and three-phase equilibria as curves and (triple) points.

Fig. 3 Metastable Phase Diagram
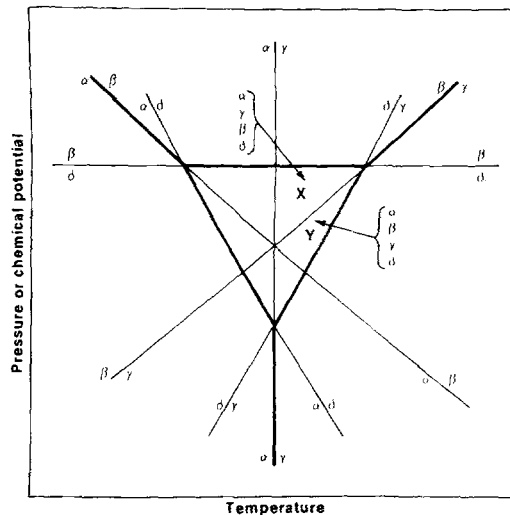
Same phases as shown in Fig. 2. Triple points have become triple crossings with metastable equilibria indicated by light lines. Within each region a given phase hierarchy persists.
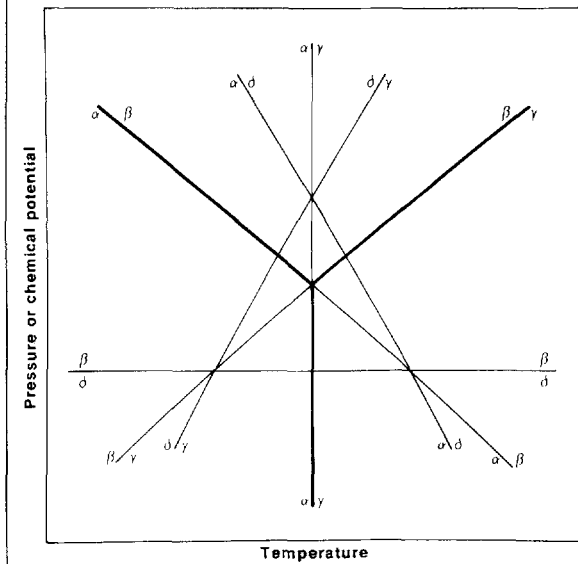
The metastable diagram is seen to consist of many regions bounded by no more than three curves. Within each region, there is a definite hierarchy of phases, which is unchanged over the entire region. The thermodynamic hierarchy for a one-component system ranks phases by their molar free energies. At a bounding curve, a pair of phases change place in the hierarchy and a different hierarchy exists in each adjacent region. In region X, the phase hierarchy is $\alpha \rightarrow \gamma \rightarrow \beta \rightarrow \delta$; while in region Y, the order of β and γ have been reversed by the traversing of the metastable $\beta - \gamma$ equilibrium curve.

Each triple point represents a place where three phases have equal μ. Three two-phase equilibria curves representing the three pairings of the three phases must cross there. The crossings of two curves representing two pairs of two phases with none in common are not triple points.

In thermal processing, the path of heating, cooling, and pressure changes, can move a phase into a region where it is metastable and above one or more phases in the hierarchy. During spontaneous phase changes, this phase can only move down the hierarchy. A liquid undercooled just below its equilibrium melting curve becomes metastable only with respect to the stable crystal. It does not become metastable with respect to a metastable crystal until it has been brought below the melting curve of the metastable phase. This metastable melting curve can often be observed as a reversible phenomenon and can often be estimated from the stable phase diagram if the metastable phase becomes stable elsewhere in phase diagrams.

Figure 3 includes only phases that were stable in some portion of Fig. 2. All curves in Fig. 3 are extrapola-

Fig. 4 Metastable Phase Diagram

Similar to Fig. 3 except that the δ-phase is nowhere stable.

vature. On phase diagrams, the curves representing the metastable equilibria between the amorphous phase and some other phase are continuous through the glass transition, but exhibit a rapid change in slope. If the metastable crystalline phase does not catalyze the nucleation of a stabler crystalline phase, the reversible growth or dissolution of this phase in contact with a glass should be observable.

Observations on phase change sequences at various constant T and P could be used to refine the construction of such a metastable phase diagram. Even though certain phases may not be observed for kinetic reasons, the order in which the observed phases appear unambiguously places limits on the placement of the metastable equilibrium curves.

Multicomponent Phase Equilibria, Partitionless Phase Changes and Metastable Hierarchies

The complications introduced by several components are not obvious at first glance. Metastability of each phase is again common and limited only by spinodals and nucleation and growth kinetics. Thermodynamic properties of metastable phases are smooth extensions of behavior in stable ranges. Equilibria are still dictated by equality of chemical potentials of each component but this no longer implies equal free energies. A phase diagram having as axes T, P, $\mu_2 \ldots \mu_N$ or more symmetrically T, μ_1, $\mu_2 \ldots \mu_N$ would be an $(N + 1)$-dimensional analogue of the single component diagram where N is the number of components. Single phases would occupy $(N + 1)$-dimensional hyper-volumes, bounded by N-dimensional hyper-surfaces representing two-phase equilibria, which intersect at $(N - 1)$-dimensional hyper-surfaces representing three-phase equilibria, etc., until there are points representing $(N + 2)$-phase equilibria. Such a phase diagram is useful for an open system in which material reservoirs keep the chemical potentials fixed by letting compositions change. In a few situations, we do impose open system conditions for some of the components by, e.g., fixing the partial pressures of a gas containing these components; more generally, we fix the composition of our system, which leads to profound complications in the thermodynamics. The open-system metastable diagram would be constructed by extension of all two-phase hyper-surfaces and would divide the space into simplexes in each of which a hierarchy of phase equilibria would exist.

In open systems, the entire phase diagram is occupied by single phase hyper-volumes with multiphase equilibria occupying hyper-surfaces of lower dimension and thus of zero measure. Unless we take pains to fix chemical potentials and temperature to lie precisely on one of these multiphase surfaces, the system will almost always be single phase. If it is multiphase, an infinitesimal shift in conditions off the surface will return it to single phase. The open system metastable phase diagram is a multidimensional version of a one-component phase diagram and the same rules including the hierarchical one apply. Indeed, Fig. 2 through 4 could serve as examples of a two-dimensional section of a multicomponent phase diagram.

tions of curves from the stable phase diagram. Metastable equilibria as well as the metastable hierarchies of all the phases that are stable in some part of a stable phase diagram are thus easy to estimate. It is not surprising that most observed metastable phases appear as stable phases somewhere in phase diagrams either at different pressure, temperature or with small additions of other components.

Many of the metastable phases encountered in materials processing are within a few hundredths eV per atom of the stable phase and it is unlikely that a phase will come that close to the lowest free energy without breaking through at some adjacent pressure, temperature or alloy addition. It is not impossible though. Figure 4 gives a hypothetical case where a metastable phase δ comes close to being stable without ever becoming so, and having a free energy curve which is not parallel to that of any other phase. It is quite straightforward to construct the hypothetical free energy surfaces corresponding to the metastable equilibria of Fig. 4.

While there is no singularity in thermodynamic properties of the liquid at any of the stable or metastable melting points, there is a rapid change in heat capacity near the glass transition.[4] The heat capacity of the amorphous phase at the glass transition is cooling-rate and heating-rate dependent but seems at the slowest rates to approach a well-behaved reversible limit.[5,6] For the faster rates, there is a lack of reversibility, but heating and cooling curves can establish an upper and lower bound to the free energy of a glass when its properties depend on its thermal history. The slow cooling limit of the glass transition seems well defined, and indicates that the free-energy curves of glass and liquid merge smoothly, exhibiting only a rapid change in cur-

Major changes occur when we shift to closed systems in which the overall composition rather than the μ's are fixed. This is the usual situation in processing. Phase diagrams for closed systems have compositions as axes and contain $(N + 1)$-dimensional hyper-volumes of one-, two- and N-phase equilibria with $(N + 1)$ and $(N + 2)$-phase equilibria occupying hyper-surfaces of zero measure. The same phases remain in equilibrium throughout the volume as temperature, pressure and composition shift.

A common graphic method of depicting the multiphase equilibria is the common tangent hyper-plane to the free energy hyper-surfaces for the various phases at a given temperature and pressure. It is fully equivalent to the condition of equal chemical potential of all the components, and the range of the line segment between tangent points readily demonstrates how the same two phases can remain in equilibrium over a wide composition range (Fig. 5).

The stable multiphase equilibria are those where the hyper-plane tangent to the free energy surface of the equilibrium phase does not cross the free energy surface of any phase. If it does cross, the equilibrium is metastable with respect to the formation of the phase.

It is immediately apparent from Fig. 5 that there is a hierarchy of metastable phases denoted by free energy curves (or hyper-surfaces) and phase equilibria denoted by tangent line segments (or hyper-planes). The boundaries to a given hierarchy are given first of all by the tangent points on the free energy curves. These tangents map out the stable and metastable phase diagram (Fig. 6).

Three other features mark changes in the hierarchy. The intersections of free energy curves (or hyper-surfaces) define the T_0 curve (or hyper-surface) which can appear on phase diagrams. It defines a restricted equilibrium for partitionless transformation. The T_0 curves do not denote a stable or metastable equilibrium. They do pass through congruent points on the phase diagram and lie within the corresponding two-phase field. They also intersect at T_0 triple points (or hyper-curves) where three phases have the same free energy.

T_1 curves in Fig. 6 mark the intersections of tangent planes and therefore form ruled hyper-surfaces on phase diagrams. T_2 curves mark the intersection of a surface of one phase with a plane tangent to two others.

The features of multicomponent phase diagrams can be readily imagined to originate from free energy surfaces of various phases that evolve and shift relative to each other with changing temperature and pressure. It is seen that the metastable continuation of a stable equilibrium involves only the free energy curves of the participating phases and should be unaffected by the new phase whose free energy surface happened to move through the tangent plane. Thus, all stable equilibria can again be extended to depict the metastable equilibria between the same phases. The qualitative evolution of the metastable portion of Fig. 6 can be understood by the more rapid rise in Fig. 5 of the liquid free energy relative to that of the two solids with decreasing temperature. These free energy curves could be obtained quantitatively by a number of methods and then extrapolated to allow determination of the metastable

Fig. 5 Two-Component Free Energy Curves for Various Phases at Constant Temperature
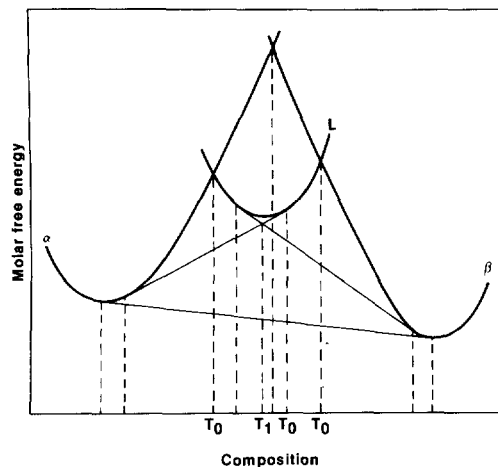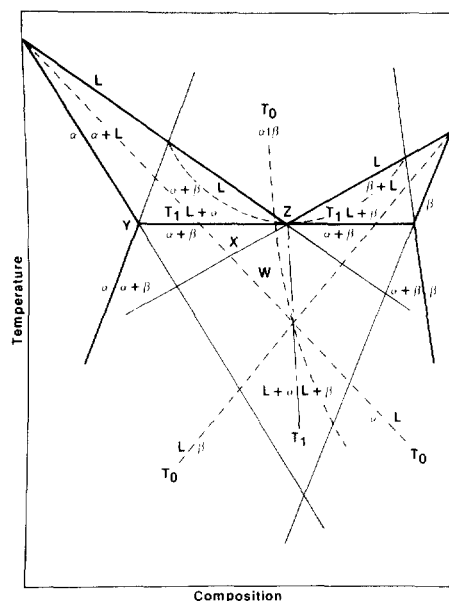

The left and right portions of the curves for α and β respectively, and the tangent between them represent the stable equilibrium. Several metastable equilibria are depicted by other tangents. The crossing of free energy curves represent points on the T_0 curves, while the crossing of tangents represent T_1 curves. Within each region of composition separated by the vertical lines, a given phase-equilibrium hierarchy holds.

diagram. For some of the curves it seems far simpler and probably more accurate to extrapolate the portions of a measured stable (or metastable) phase diagram. As for the single component, wherever a liquid undergoes a glass transition the curves will be continuous with only a rapid change of slope.

It should be immediately pointed out that no simple hierarchy of phases exists. A system at a point in region X in Fig. 6 is in equilibrium when α and β are present as the stable phases, and the liquid is metastable. Yet when stable β is brought into contact with liquid in X under conditions where α does not nucleate, stable β will dissolve in metastable liquid. Such a reaction in which a stable phase dissolves in a metastable one is impossible in single component systems, but quite common in multicomponent ones. Only when α finally nucleates can β reappear. This disappearance and reappearance of a phase in spontaneous processes indicates that there can be no hierarchical listing of phases.

This can also be indicated by listing the metastable hierarchies in region X. Because X lies outside the β + L field, no equilibrium between β and L is possible. The remaining five equilibria are ranked as follows: single-phase β is highest in free energy, followed by single-phase α, single-phase liquid, two-phase α + L, and equilibrium is reached with two-phase α + β. In region W, the sequence β + L is inserted between L and α + L. In such metastable sequences phases can appear,

Fig. 6 Binary-Eutectic Diagram at Constant Pressure

Composition

With metastable extension of all curves and the T_0 and T_1 curves. Because metastable liquid at point X will dissolve small amounts of the stable phase β no stability hierarchy based on phases per se can exist.

In solidification, thermodynamics put bounds on the solid composition that can form from liquid given the composition and temperature of the liquid at the interface (1). The T_0 curves pertaining to liquid with a given solid form an upper bound to the solid composition that can form from liquid of any composition at that temperature. Because the T_0 lies between the liquidus and solidus, systems in which the extrapolated solidus appears to span the entire composition range are good candidates for segregationless solidification to that particular phase. Systems with retrograde solidi (stable or metastable), even where the corresponding liquidi sweep across the composition axis, can be shown to have T_0 curves which are bounded in composition. Compositions beyond this bound, which is approximately the liquidus composition at the retrograde temperature,[8] can not undergo segregationless solidification to that crystalline phase at any temperature. Because crystallization involving segregation is much slower, retrograde systems might be good candidates for glass formers.

Two T_1 curves in Fig. 6 intersect at the eutectic point Z. The eutectic horizontal is a stable T_1, the other moving downward in temperature is metastable and defines bounds to conditions where it is impossible for one metastable two-phase equilibrium to follow another. A T_2 curve (not shown) also goes through point Z. It indicates the temperature where eutectic solidification in the absence of a proeutectic reaction first becomes thermodynamically possible although unlikely.

Because of the segregation accompanying most solidification and the slowness of diffusion in the solid state, most solidification processes yield solids in which the individual phases are not homogeneous. The hierarchy diagrams rank equilibria, and homogeneity of a phase is, apart from minor gravitational and defect segregation phenomena, a necessary condition for equilibrium whether stable or metastable. These segregation effects can bring the system into a state where it contains phases that it would not contain in any metastable sequence.

This can be illustrated by an example. A liquid cooled to a point in region Y could at no temperature during its cooling path reach any equilibria other than α, L, L + α. Yet during conventional cooling, segregation will lead to the formation of β and the system as a whole will not reach equilibrium until all the β has disappeared. The hierarchy diagrams can only be used for conventional solidification on a local equilibrium basis. They are more useful for the solid state sequences following a segregationless solidification or a homogenized solid formed by rapid solidification.

The usefulness of metastable equilibrium diagrams lies in the fact that like stable diagrams there are rules for their construction which guide measurement and permit our experience to be organized. The ability to extrapolate and interpolate is one aspect which lets us make rapid strides in sketching in the main feature of such a diagram. When metastable equilibria is reached, thermodynamics can make its full range of predictions. For single components a sequence of equilibria are likely. The possibility of segregation makes it difficult for us to bring in strong predictions about multicomponent systems, except in rapid solidification and on a local level in conventional solidification.

disappear, reappear with a different composition and disappear again. Once a particular phase equilibrium has disappeared it can not reappear unless the system is reprocessed.

The inability of β to form from liquid in X unless α has also appeared is an example of a thermodynamically required precursor reaction.[7] Such requirements do not occur in single component systems, because any of the more stable phases can appear at any time. Consider a multicomponent system in metastable equilibrium of one or more (m) phases. The composition must lie within that m-phase field on the metastable phase diagram. The addition of a new phase can occur only if the composition lies also beyond where the metastable ($m + 1$)–phase field first intercepts the m-phase field. In Fig. 6, β can form from liquid in W but not in X, while α can form in either. This places a strong and easily formulated constraint on the phase-sequences that can occur in a given hierarchy which can be locally applied even if the system has only reached local equilibrium.

During such isothermal sequences the free energy is monotonically decreasing, but chemical potentials can increase as well as decrease. In the graphical construction of Fig. 5, the chemical potentials of the two components are the intercept with the component axes of a tangent to the single phase curve at the system composition or of the common tangent in a multiphase equilibrium. These ups and downs of chemical potentials of a component go hand in hand with the appearance or disappearance of a phase enriched in that component.

Acknowledgments

References

1. J. C. Baker and J. W. Cahn, Thermodynamics of Solidification, in *Solidification*, p 23–58, American Society for Metals (1971).
2. T. P. Seward, III, Metastable Phase Diagrams and Their Applications to Glass-Forming Ceramic Systems, *Phase Diagrams, Materials Science and Technology*, A. M. Alper, Ed., Vol 1, p 295–338, Academic Press, New York (1970).
3. J. W. Cahn, Thermodynamics of Metastable Equilibria, *Proc. Second Intl. Conf. Rapid Solidification Processing: Principles and Technologies*, R. Mehrabian, B. H. Kear and M. Cohen, Eds., Claitor's Publishing Division, Baton Rouge, La., p 24–34 (1980).
4. W. Kauzmann, *Chem. Rev., 43*, p 219 (1948).
5. C. A. Angell and W. Sichina, in *Glass Transition and the Nature of the Glass State*, M. Goldstein and R. Simha, Eds., New York Academy of Science (1976).
6. R. B. Stephens, *J. Appl. Phys., 49*, p 5855 (1978); *J. Non-Cryst. Solids, 20*, p 75 (1976).
7. J. W. Cahn, *J. Am. Ceram. Soc., 52*, p 118 (1969).
8. J. W. Cahn, S. R. Coriell and W. J. Boettinger, Rapid Solidification, in *Laser and Electron Beam Processing of Materials*, C. W. White and P. S. Peercy, Eds., Materials Research Society (1979).

The Binary Phase Diagram Evaluation Program

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The availability of compiled and evaluated information on phase diagrams fulfills many needs in scientific, technological and commercial applications. The well-known compilations published during the late 1950's and 1960's have been in constant use, but a formal compilation and evaluation program which would update and extend these compilations has been lacking, with the result of an ever-increasing gap between published and evaluated data. The Binary Phase Diagram Evaluation Program is intended to rectify this situation during the next several years.

Fortunately, the potential number of binary phase diagrams is reasonably finite, and consequently, when Hansen[1] attempted his first alphabetical compilation during the 1930's, the job must have appeared to be quite manageable, and so it proved to be. Hansen's original German volume published in 1936 contained some 450 binary phase diagrams in evaluated reviews of more than 800 systems. The major emphasis was on phase boundary information, accompanied by some crystal structure data. Metastable solubilities and phases were not included (except perhaps for Fe-C), nor was any thermodynamic data. Hansen made his own authoritative decisions about phase nomenclatures and crystal structure designations, and probably many other features as well, such as whether or not to use the centigrade scale, atomic percentages, stoichiometric ratios, etc. The postwar English language enlarged edition of Hansen, published in collaboration with Kurt Anderko[2] in 1958, and the subsequent volumes by R. P. Elliott[3] and F. A. Shunk,[4] which followed Hansen's general scheme, are probably the most widely used publications of

evaluated binary phase diagrams today. In addition to these volumes, however, a large number of other publications have now appeared, or are being produced; these present partially evaluated binary diagrams to a varying degree of detail and scope, from a mere recording of phase boundaries to attempted calculated predictions of diagrams that have not yet been explored experimentally. Such compilations, taken together, now include thousands of systems.[5,6]

Perhaps the first major step that affected plans for binary phase diagram compilation under the present NBS/ASM program was the recognition that, with the mushrooming amount of phase diagram information, an alphabetical, single volume, Hansen-like scheme, under the control of one author, or even several authors, is no longer feasible, or practical. A single author may be willing (and have time and resources) to review in depth perhaps 20 to 100 diagrams, but not thousands. He may be familiar with systems based on a single metal (for example, copper), or a group of metals (for example, the actinide metals), but not familiar, or interested, in