The Influence of Solution-Model Complexity on Phase Diagram Prediction

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In the derivation of phase diagrams using solid- and liquid-solution thermodynamic equilibria, thermodynamic models are used to extrapolate experimental data to a broader range of compositions and temperatures. Such models have historically increased in complexity from the regular-solution formalism, with regard to both temperature and composition dependence of parameters. The regular, quasi-regular, subsubregular, and quasi-subsubregular models have been applied to existing thermodynamic data for four “simple” metallic systems of differing types (Cu-Ni, Pb-Ag, Sn-Zn, and Ge-Mg) to illustrate the effect of more accurate thermodynamic modeling on the resulting predicted phase diagrams. Comparison with the actual phase diagrams demonstrates the relative importance of “nonregularity” in the solution with regard to both composition and temperature in the accuracy of phase diagram prediction.

1. Introduction

One of the intrinsic requirements for the coupling of phase diagrams and solution thermodynamic properties in any system is the specification of a model for representing the latter. Such models allow extrapolation of the available thermodynamic data for the solutions in the system to a range of temperatures and compositions not covered by the original experimental work. This in turn facilitates the determination of multiphase equilibria at those combinations of composition, temperature, and pressure where the chemical potential of the system components is equal in the various conjugate phases (i.e., phase boundaries).

As a result, it seems reasonable to postulate that the choice of solution model can affect the accuracy of a modeling effort, particularly if the needed extrapolation of the available thermodynamic data covers wide ranges of temperature and/or composition. However, little demonstration of the impact of varying solution models on the result of phase diagram prediction has been made. Vijayakumar and Sreeramamurthy1 have illustrated the improvement in calculation of the vanadium-tungsten phase diagram using a subregular rather than regular solution model; the value of using temperature-dependent models in phase diagram prediction has been demonstrated by Brebrick2 and Ji-yu.3 However, these studies have featured limited levels of both solution-model variation and types of phase diagram assessed.

With the development of increasingly sophisticated software for statistical analysis, the degree of complexity of proposed models for describing solution thermodynamic properties has increased as well. The improved ability of these models to deviate from both the composition- and temperature-symmetry assumptions of the regular solution model proposed by Hildebrand4 has made possible a test of the relative importance of solution-model complexity in phase diagram prediction, using three simple types of phase diagram—an isomorphous system (Cu-Ni), two eutectic systems (Pb-Ag and Sn-Zn), and a system featuring a single stoichiometric intermetallic compound (Ge-Mg). Such a test is demonstrated here.

2. Development of Solution Models

As previously mentioned, the solution models used in phase-diagram calculation are generally descendants of the regular-solution model first proposed by Hildebrand.4 This model takes the form (using the notation of Lupis5),

\[ G^{\text{ex}} = X_A X_B \Omega \]  

(Eq 1)

where \( G^{\text{ex}} \) is the excess Gibbs energy of mixing in a binary A-B solution, \( X_A \) and \( X_B \) are the respective mole fractions, and \( \Omega \) is a composition- and temperature-independent constant. The lack of temperature dependence means that the excess entropy of mixing in the system is zero, and so the excess enthalpy of mixing \( H^{\text{ex}} \) is

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equal to $G^{ex}$. Employing the Gibbs-Duhem relation, it can be shown that:

$$RT \ln \gamma_A = \Omega X_B^2$$  \hspace{1cm} (Eq 2)

The composition independence of $\Omega$ implies that $G^{ex}$ at a given temperature will be a symmetrical function of composition, with the greatest magnitude at $X_A = X_B = 0.5$. In real solutions, such is rarely the case. Hardy$^6$ attempted to deal with this by creating a composition-dependent formalism, the subregular solution model:

$$G^{ex} = X_A X_B (A_{BA} X_A - A_{AB} X_B)$$  \hspace{1cm} (Eq 3)

Again, the empirically derived coefficients $A_{BA}$ and $A_{AB}$ are independent of temperature, so that $H^{ex}$ is equal to $C^{ex}$. Gibbs-Duhem integration yields,

$$RT \ln \gamma_A = X_B^2 \left[2X_A A_{BA} + (1 - 2X_A) A_{AB}\right]$$  \hspace{1cm} (Eq 4)

Further ability to mirror thermodynamic data for actual systems stemmed from the proposed subsubregular solution model:$^7$

$$G^{ex} = X_A X_B \left[A_{BA} X_A + A_{AB} X_B + A_{BB} X_A X_B\right]$$  \hspace{1cm} (Eq 5)

$$RT \ln \gamma_A = X_B^2 \left[2X_A A_{BA} + (1 - 2X_A) A_{AB} + X_A (2 - 3X_A) A_{BB}\right]$$  \hspace{1cm} (Eq 6)

As with the regular and subregular solution models, the subsubregular model assumes temperature independence of the model coefficients and, thus, equality between $H^{ex}$ and $G^{ex}$. In systems where only heat of mixing data is available, this assumption has facilitated the calculation of model coefficients, which otherwise would not be extant. Schmid$^8$ also derived a subsubregular equation, based on the convention of Kellogg$^9$ of deriving coefficients as a function of $G^{ex}/RT$ rather than $G^{ex}$; this leads to the expression,$^9$

$$\Delta G^{ex} = RT X_A X_B \left[w_{BA} X_A + w_{AB} X_B - 4 \nu_{AB} X_A X_B\right]$$  \hspace{1cm} (Eq 7)

Deviation from the temperature independence of the regular-solution model is also frequently observed, particularly in highly ordered solutions.$^{11}$ Lupis and Elliott$^{12}$ addressed this problem in 1965 by deriving a “quasi-regular” solution model, in which $\Omega$ is made a linear function of absolute temperature:

$$G^{ex} = X_A X_B \Omega \tau (1 - T/\tau)$$  \hspace{1cm} (Eq 8)

$\tau$ is an empirically derived temperature usually in the range of 1500 to 3500 K; when $T$ is equal to $\tau$, a quasi-regular solution should behave ideally. The higher the value of $\tau$ for a given system, the more closely its behavior matches that of a regular solution.

If a single regular-solution parameter can be made dependent on temperature, subregular and subsubregular parameters can be dealt with similarly, and Chang and coworkers$^{10,13}$ have created such a model. Theirs is based on the Kellogg formalism, meaning that $w_{BA}$, $w_{AB}$, and $\nu_{AB}$ are functions of inverse rather than direct temperature. For the purposes of this work, a “direct-style” quasi-subsubregular solution model will be defined, using the following functions:

$$A_{BA} = B_{BA} (1 - T/\tau_{BA})$$  \hspace{1cm} (Eq 9)

$$A_{AB} = B_{AB} (1 - T/\tau_{AB})$$  \hspace{1cm} (Eq 10)

$$A_{BB} = B_{BB} (1 - T/\tau_{BB})$$  \hspace{1cm} (Eq 11)

As the complexity of solution models has increased, the means of deriving the appropriate parameters have also improved. Most parameters are currently obtained by “back-calculation” from existing thermodynamic data, using either phase boundary compositions or single-phase thermodynamic measurements; the use of least-squares regression analyses to improve the reliability of such back-calculations is well established. However, Fig. 1, an application of modeling to the thermodynamic study of Al-Mg solutions of Tsyplakova and Strelets,$^{14}$ illustrates a further refinement in solution-model parameter derivation of some potential value. The actual data points obtained by Tsyplakova and Strelets representing ln $\gamma_{Mg}$ as a function of composition at 1073 K are heavily concentrated in high-Al alloys; some of these experimental points also show considerable scatter, a common problem with dilute-solution thermodynamic data. While a least-squares routine would to some degree mitigate the effect of this scatter on the reliability of back-calculated solution-model parameters, the relative lack of data from nondilute or high-Mg melts lends an inherent “bias” to a least-squares fit, even if a subregular or subsubregular model is used. The practice of “weighting” data points so that some would have more influence on the regression than others has occasionally been reported,$^{15}$ with the aim of “fea-

![Fig. 1](image-url)