

# Thermodynamic modelling of solution phases and phase diagram calculations

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## ABSTRACT

In recent years, the development of phase diagram calculations for multicomponent systems using a thermodynamic approach has proved to be very important in resolving industrial problems. This development is mainly due to the progress in the description of the thermodynamic behaviour of solution phases particularly of alloys and to advances in computer software. Realistic statistical models have been developed to take into account chemical ordering in solution phases.

Moreover, methods of predicting thermodynamic stabilities from fundamental physical calculations have been developed which provide a sounder basis for the thermodynamic description of metastable phases.

The significant progress in the modelling of the thermodynamic properties of solution phases is presented together with some examples of evaluated and assessed phase diagrams.

## INTRODUCTION

The study of phase diagrams has long been an important tool in the development of science and technology. In metallurgy, it has made a major contribution to the design of new alloys, partly due to considerable improvements in experimental techniques which have reached a high level of accuracy. However, with increasing demands of new high technological materials, which are generally complex, it is important that theoretical predictions guide the work of materials scientists. One such possibility is to apply the principles of physical-chemistry in order to compute multicomponent and multiphase equilibria. Such an approach can be very powerful in both planning and also reducing considerably the number of costly experiments.

After the pioneering work of Meijering (ref. 1), followed by the important contributions of Kaufman (ref. 2), great progress has been observed, since the "NBS Workshop on Phase Diagrams", in the application of calculated phase diagram generated from the underlying thermochemical data. This is due mainly to the improvement of models for the solution phases, and an increasing amount of reliable and consistent assessed data is now being generated. The calculation of phase diagrams has been used successfully in a wide range of applications, including crystal growth of semi-conductor materials by liquid phase epitaxy, prediction of phase equilibria for super-alloys, light metal alloys or high speed steels, and chemical vapor deposition. This has been possible because of the development of sophisticated application software, which is now being used in numerous thermochemical computer data banks throughout the world.

A further important aspect of phase diagram calculation is its use in the teaching of thermodynamics and Materials science in general. Very simple computer programs have been used to demonstrate graphically how changing interaction parameters or lattice stabilities affects the phase diagram, while the more powerful application programs used in their simplest modes, can be used to illuminate the deceptive simplicity of concepts such as Gibbs Phase rule.

The calculation of phase diagram requires the knowledge of the thermodynamic properties of the pure components, the compounds and solution phases, in both stable or metastable physical states, and clearly consistency of such data between different phase systems is very important.

## ELEMENTS

### Lattice stabilities

Let us first consider the elements. As many elements can dissolve in a phase which is not a stable for that element itself (e.g. Cr(bcc) dissolves extensively in Ni(fcc)), it is

necessary to estimate the thermodynamic properties of elements in states which are metastable at all temperatures. Kaufman (ref. 2,3) presented sets of estimated parameters for the enthalpy and entropy differences between the bcc and hcp and the fcc and hcp structures of the transition metals applying Richard's rule for the entropy of melting to many of the elements. Later, it was shown that this rule is not satisfactory for refractory metals, whose entropy of fusion increases with increasing melting temperature. However, Kaufman's values of the Gibbs energy differences, also called lattice stabilities, have been extensively used throughout the world in conjunction with solution phase data to compute phase diagrams of metallic systems.

Very recently, Saunders et al (ref. 4), evaluated the lattice stabilities for the metastable fcc(A1), bcc(A2) and hcp (A3) forms of 43 elements. Their results are based on assessed stable phase data, phase boundary extrapolations from binary alloys, extrapolations from pressure-temperature phase diagrams, relationships between the crystal structure, the entropy of fusion and the melting temperature, stacking fault energies and first principle electronic energy calculations.

For the transition metals, the lattice stabilities are now much close in magnitude to ab-initio predictions. This is due mainly to the recent reassessment of stable phase data and the assumption that the entropies of fusion of metastable forms behave in a similar fashion as the stable one, and to advances in electronic energy calculations.

However, most early expressions for lattice stabilities implied that the heat capacities of the two phases involved are the same at all temperatures. This in general is not true for two phases even at their transition temperature and Anderson et al (ref. 5) has described a better, but not perfect, approach used by the Scientific Group Thermodata Europe (SGTE). The heat capacity of the liquid phase of an element is assumed to approach that of the stable form at a temperature of about  $0.5 T_{fus}$ , and similarly, the heat capacities of all solid phases above the melting temperature should approach that of the liquid at higher temperatures. In this assumption, the difference in heat capacities at the melting temperature is taken into account, its effect being less important as the temperature difference with respect to the melting temperature increases. A better estimate of the lattice stability below the melting temperature could certainly be made if a reliable model for the thermodynamics of the transition from liquid to glass were available.

### Magnetic heat capacity

The magnetic contributions to the Gibbs energy for magnetic materials were not, until recently, treated explicitly. It was merely included in the overall expression of the Gibbs energy of transformation with respect to temperature.

Inden (ref. 6) proposed an empirical and approximate analytical formula for the magnetic specific heat which represents the experimental data below and above the critical temperature  $T_c$  by the following equations :

$$\begin{aligned} C_p &= K_1 \cdot R \cdot \ln(1+t^3)/(1-t^3) & \text{for } t = T/T_c < 1 \\ C_p &= K_2 \cdot R \cdot \ln(1+t^{-5})/(1-t^{-5}) & \text{for } t > 1 \end{aligned} \quad (1)$$

$K_1$  and  $K_2$  are constants for an element in its ferromagnetic and paramagnetic states. They can be determined from experimental data and they are related to the total magnetic entropy

$$\Delta S^{mag} = R \ln(\beta + 1) \quad (2)$$

where  $\beta$  is the mean atomic moment expressed in Bohr magnetons.

The expressions of the Gibbs energy obtained by integration are rather lengthy and complicated. Hillert and Jarl (ref. 7) preferred to expand the expression of  $C_p$  in power series and suggested the following expressions :

$$\begin{aligned} C_p &= 2 \cdot K_1 \cdot R \cdot (t^3 + t^9/3 + t^{15}/5) & \text{for } t < 1 \\ C_p &= 2 \cdot K_2 \cdot R \cdot (t^{-5} + t^{-15}/3 + t^{-25}/5) & \text{for } t > 1 \end{aligned} \quad (3)$$

for which the integrations to give S and H give much shorter expressions and represent satisfactorily the experimental data. The magnetic ordering is evaluated with respect to the completely disordered paramagnetic state.

Recently, Chuang et al (ref. 8) have also suggested an expression for the heat capacity due to magnetic ordering which is given by the following equations:

$$\begin{aligned} C_p &= K'_1 t \exp(-4(1-t)) & \text{for } t < 1 \\ C_p &= K'_2 t \exp(8p(1-t)) & \text{for } t > 1 \end{aligned} \quad (4)$$

where  $p = 1$  for bcc lattice and  $p = 2$  for the fcc-lattice.

The quantities  $K'_1$  and  $K'_2$  are related to the entropy of magnetic disordering. Figure 1 compares the magnetic heat capacity calculated from equations 2, 3 and 4 for bcc-iron. The results, in general, are similar except in the vicinity of the critical temperature.

### Pressure dependence

Outside the geological field, rather little work has been undertaken to include the pressure dependence of the Gibbs energy of the pure elements. Fernandez-Guillermot (ref. 9-12) has recently reassessed the thermodynamic properties of iron, molybdenum, cobalt and zirconium while Gustafson reevaluated those of tungsten (ref. 13). Fig.2 shows an assessed pressure-temperature diagram for iron.

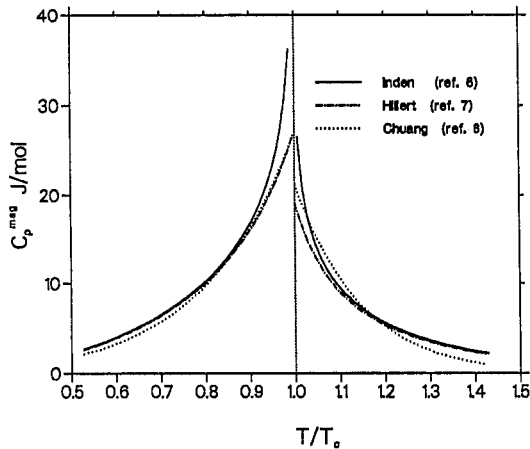


Figure 1 :  
Comparison of the magnetic heat capacity of bcc-iron calculated from equations 1, 3 and 4.

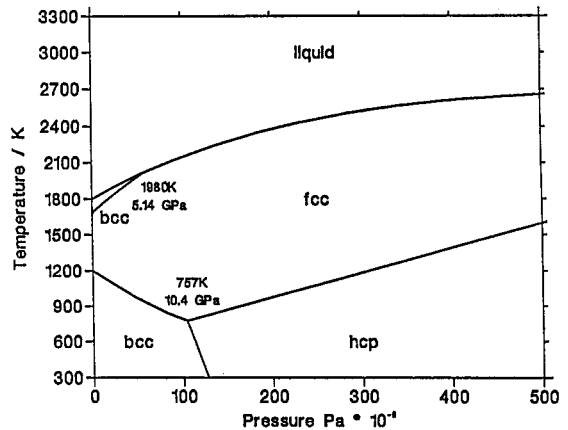


Figure 2 :  
Pressure-temperature diagram for Fe (ref. 9).

## COMPOUNDS

In a series of paper which eventually led to the publication of a book, Miedema et al (ref. 14), developed a semi-empirical approach to treat the energy effects in metallic systems as interfacial energies generated at the contact interfaces between neighbouring atomic cells. For binary alloys, the enthalpy of formation is proportional to the sum of two terms, a negative term proportional to the square of the chemical potential for electronic charge differences of the pure metals,  $X$ , and a positive repulsive contribution which is related to the difference of the electron densities of these elements at the Wigner-Seitz cell boundary  $n_{ws}$ , according to the following equation :

$$\Delta_f H \propto -P (\Delta X)^2 + Q (\Delta n_{ws}^{1/3})^2 \quad (5)$$

$P$  and  $Q$  are constants which are derived from fits to the experimental enthalpies of formation. This expression can be converted to a function of composition and can be applied not only to ordered compounds but also for liquid alloys.

Watson and Bennett (ref. 15) used a simple band theory model to predict the enthalpy of formation of 276 transition metal alloys at the equiatomic composition. Some of the input parameters, namely the bandwidth, the Fermi level position, and the number of electrons in the band are allowed to vary within certain constraints in order to approximate known values of the enthalpy of formation. More recently, Colinet et al (ref. 16) also developed a simple electron band theory model to predict enthalpies of formation of transition metal alloys as a function of composition. They used a tight-binding model considering the moments of the density of states and calculated the enthalpies of formation for 210 binary alloys. They also applied this approach to transition-rare earth metal alloys (ref. 17).

These approaches are very useful to predict the enthalpy of formation of metastable solid alloys of given composition. In the study of multicomponent systems, the knowledge of the enthalpy of formation of metastable as well as stable compounds is needed. For example, the thermodynamic description of  $(Cr,Fe)_{23}C_6$  or  $(Cr,Fe)_7C_3$  carbides using a sub-lattice model requires the enthalpy of formation of  $Fe_{23}C_6$  and  $Fe_7C_3$  which are unstable in normal conditions, and they may be obtained by such methods.

## SOLUTIONS MODELS FOR METALLIC SYSTEMS

Solution theories have also been the subject of great progress and lead now to reasonable representations of the thermodynamic behaviour of multicomponent phases. For many years, simple power series expansions have been used to describe the thermodynamic behaviour of solution phases as well as the quasi-chemical approximation which to a certain extent introduced the concept of ordering in the solution phase. A great variety of empirical equations based on geometrical weighting have been used and have been reviewed by the present author (ref. 18). For most of the substitutional solutions, a simple power series expansion is now preferred because with it allows a very satisfactory representation of the thermodynamic properties of mixing with respect to composition.

### Magnetic contributions

For solutions which are not ferromagnetic at a temperature below the Curie temperature of one of the constituents, the thermodynamic properties are referred to a hypothetical paramagnetic state of the phase where the magnetic moments are completely disordered. Hence, the Gibbs energy of mixing can be expressed by a sum of two terms, one describing the Gibbs energy of mixing and the second describing the ferromagnetic effect for the alloy.

The heat capacity for a solution phase describing the magnetic ordering contribution can be expressed, according to Herzman et al (ref. 19) by an equation identical to (3) but the composition dependence of  $T_C$  and will be expressed by a power series with respect to the molar fraction, for example :

$$T_C = x_A T_{C,A} + x_B T_{C,B} + x_A x_B (T_C^0 + T_C^1 (x_A - x_B)) \quad (6)$$

$$\beta = x_A \beta_A^0 + x_B \beta_B^0 + x_A x_B (\beta_{A,B})$$

The parameters  $T_C^0$ ,  $T_C^1$ ,  $\beta_{A,B}$  are evaluated from experimental information.  $T_{C,A}$ ,  $T_{C,B}$  and  $\beta_A^0$ ,  $\beta_B^0$  are respectively the Curie temperature and the mean atomic moments expressed in Bohr magnetons of the pure elements. Figure 3 illustrates an isothermal section of the Fe-Co-Zn system where the effect of magnetic ordering is taken into account for the calculation of the phase boundaries (ref. 20).

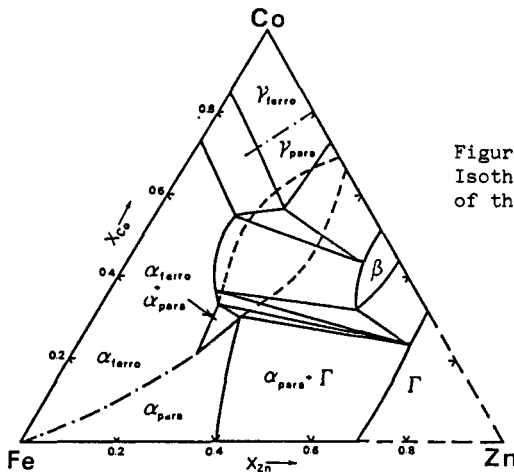
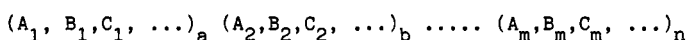


Figure 3 :  
Isothermal section at 1036 K  
of the Fe-Co-Zn system (ref. 20).

### Sub-lattice model

Many binary systems exhibit intermediate phases with a fixed number of sites having a narrow range of non-stoichiometry. In phase diagram calculations, these compounds were generally assumed to be "line compounds". However, it may be necessary to describe the temperature dependence of the composition, when alloying elements are added to these compounds. The sub-lattice model developed by Hillert et al (ref. 21) based on Temkin's model for ionic solution (ref. 22) and extended by Sundman et al (ref. 23) to take into account more than two types of sites which can be represented by the general formula



where a site fraction for each constituent in every sub-lattice is defined, their sum being equal to 1 for each lattice. a, b, ...n represent the number of sites. For example III-V compounds, reciprocal ionic or interstitial solutions respectively of the type (Ga,In)(As,P), (Na<sup>+</sup>,K<sup>+</sup>)(Cl<sup>-</sup>,F<sup>-</sup>) or (Cr,Fe)(C,v) can easily be represented by two sub-lattices.

The number of sub-lattices for solid phases and the elements, including vacancies or ions, which can occupy them, is generally obtained from structural information.

The Gibbs energy of formation of such phases requires the knowledge of the Gibbs energy of formation of the compounds formed by combining a constituent in one sub-lattice with a constituent in the other sub-lattices. It should be noted that to describe the thermodynamic behaviour of the phase  $(Cr,Fe)(C,v)$ , the Gibbs energy of the hypothetical compound  $FeC$  and  $CrC$  are required. These Gibbs energies are generally obtained by means of optimization procedures which will be discussed further on.

Solid phases may have more complex structures such as  $\sigma$  or  $\mu$ -phases, and generally some simplifications are made by reducing the number of sub-lattices to avoid increasing the number of parameters.

The sub-lattice model has also been applied to describe order-disorder transformations in the Al-Ni (ref. 24) and Al-Ti (ref. 25) systems. The ordered phase such as the fcc- $L1_2$  in the Al-Ni can be described by a model with two sub-lattices both of which contain Al and Ni. Mathematical constraints are introduced in order to represent both disordered fcc-Al and ordered fcc- $L1_2$  phases with the same equation. The same model was applied to the  $Al_3Ni_2$  phase which has a  $D5_{13}$  structure. The calculated diagram is shown in figure 4.

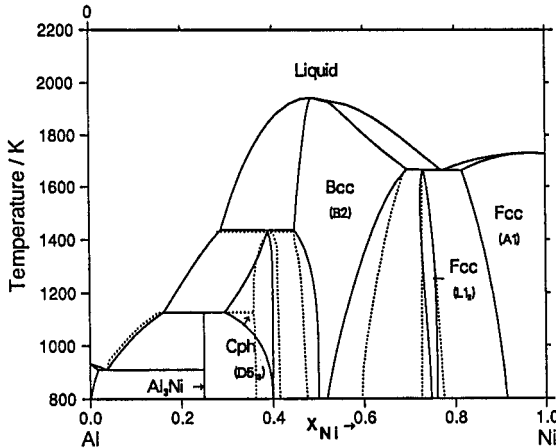


Figure 4 : Comparison between experimental (-----) (ref. 26) and calculated (——) Al-Ni phase diagram.

#### Cluster Variation method

The cluster variation method (CVM) developed by Kikuchi (ref. 27) is now extensively being used to calculate phase diagrams of systems exhibiting ordered phase regions. In this method, the distribution variable is a basic cluster of lattice points. For face-centered-cubic or body-centered-cubic phases, the basic cluster can be a four point tetrahedron. The Gibbs energy of the system is expressed in terms of these basic distribution variables. If the formulation is done using the pair approximation, the entropy of the CVM is equivalent to that of the quasi-chemical model.

De Rooy et al (ref. 28) used that model to calculate the fcc-part of the Cu-Ni-Zn system, the pair-wise interaction potentials being obtained from a pseudo-potential model. This method has also been applied to determine isothermal sections for coherent equilibria in Cu-Ag-Au by De Fontaine (ref. 29) where both clustering equilibria and ordering and their mutual interactions have been calculated from an analysis of the corresponding binary phase diagrams (Fig. 5).

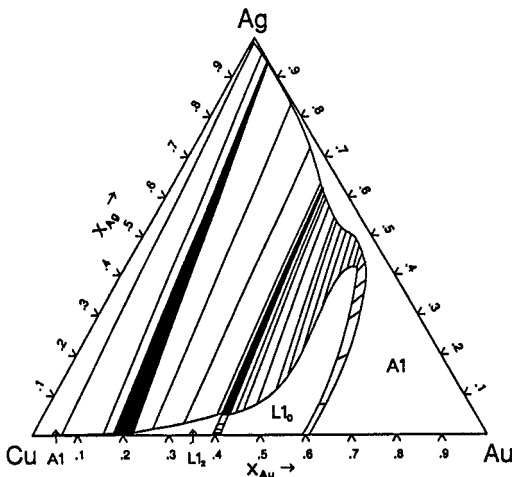


Figure 5 : Isothermal section of Cu-Ag-Au coherent phase diagram at 513 K.

### Monte Carlo simulations

More sophisticated statistical methods are the Monte-Carlo simulations which are also being developed to describe order-disorder phenomena, usually based on the Ising model using pair-interaction energies as phenomenological parameters. In a recent paper, Binder (ref. 30) reviewed the various methods of statistical mechanics which have been applied to describe atomic interactions for binary metallic alloys and compared them to each other, emphasizing the merits as well as the limitations of, for example, the cluster variation method and Monte-Carlo simulation.

### Associate model

An analysis of the experimental results shows that for certain metallic solutions, or even salt systems, the enthalpy of formation as a function of composition presents strongly asymmetrical or even triangular shaped curves. This was attributed to a tendency to form compounds in the melt such as in the group II-VI or IV-VI systems. The associate model was basically developed by Dolezalek (ref. 31) followed by Prigogine et al (ref. 32); more recently Jordan (ref. 33) and Sommer (ref. 34) have both applied it to metallic melts. The model assumes that, in the melt, free atoms of the pure elements coexist with associates and has been very successful in representing the enthalpy of formation of such systems.

The derived expressions introduce a term which corresponds to the enthalpy of formation of the associate, whose value has to be adjusted to experimental results and another which describes the mixing of the different particle types into an associated solution. Similarly, the entropy of mixing contains terms expressing ideal behaviour between the free atoms and the associates, the entropy of formation of the associate and the excess entropy of mixing. The stoichiometry of the associates is generally taken to be the same as a stable solid compound.

### Solution models for oxide systems

In the last few years, an increased effort has been made in modelling the high temperature thermodynamic properties for silica-containing oxide melts. These melts are characterized by a complex ionic structure and little experimental information concerning them is available.

As for associated metallic solutions, the enthalpy of mixing tends to exhibit a negative triangular shaped peak near the composition of maximum ordering while the entropy of mixing has an "m"-shape with a minimum near this composition. Among the numerous models which have been developed, one of the most recent is due to Gaye et al (ref. 35) who uses a cellular model based on Kapoor's (ref. 36) description of the melt.

To account for the high ionization tendency in ionic solutions Hillert et al (ref. 37) extended the sub-lattice model to off-stoichiometric compositions by introducing neutral atoms and charged vacancies into the anion sub-lattice. This model has recently been used in assessments of the thermodynamic properties of the MgO-SiO<sub>2</sub> (ref. 38) and CaO-SiO<sub>2</sub> (ref. 39) systems.

It should be noted that for binary systems, their equation is identical to that of the associate solution model if the stoichiometric number of the anion is taken equal to 1. However, for higher order systems, the two models cannot be made identical.

Pelton et al (ref. 40) used a modified quasi-chemical model, in order to describe molten silicate systems. Their formalism applies to both ordered and disordered systems. They calculated the MnO-SiO<sub>2</sub> (ref. 41) phase diagram over the entire composition range as shown in figure 6. Michels et al (ref. 42) have developed a network model and described the variation of the interaction parameter with composition by assuming a functional dependence of the degree of polymerization of the silicate network. This model was used very recently to describe the thermodynamic behaviour of the CaO-SiO<sub>2</sub>, MgO-SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>-MgO-SiO<sub>2</sub> systems (ref. 43).

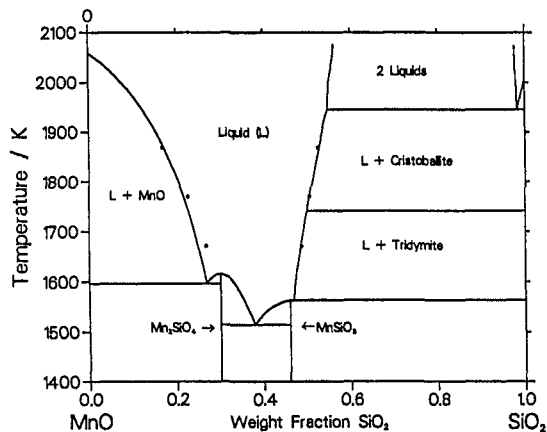


Figure 6 :  
Calculated MnO-SiO<sub>2</sub> phase diagram.  
(● ref.42)

The conformal ionic solution theory, developed by Blander et al (ref. 44-46) has proved to be very successful in calculating the thermodynamic properties for additive and for charge symmetric and asymmetric reciprocal salt ternary systems. Bale et al (ref. 46) extended this theory to reciprocal quaternary systems of the type  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+ || \text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$  or  $\text{Na}^+$ ,  $\text{K}^+ || \text{CO}_3^{2-}$ ,  $\text{OH}^-$ ,  $\text{SO}_4^{2-}$ . The excess Gibbs energy is expressed in terms of equivalent ionic fractions.

## OPTIMIZATION

The need to achieve consistency between phase diagram data and thermodynamic properties of various phases forming a system has led to developments of optimization procedures such as for example those developed by Lukas et al (ref. 47), Pelton et al (ref. 48) and Jansson (ref. 49). These procedures, calculate optimized values of the interaction parameters of the solution models by taking into account all available experimental information such as phase diagram data, enthalpy of mixing, partial Gibbs energies, heat contents, etc., various models for the solution phases being built-in the program. In certain cases, with a limited knowledge of the thermodynamic behaviour of certain phases, missing data may be evaluated when combined with phase boundary information. Fig. (7) shows an example of an thermodynamically assessed binary phase diagram of the Au-In system (ref. 50). Fig. (8) shows an optimized projection of the monovariant lines in the Cu-Li-Mg system (ref. 51), taking into consideration the liquidus temperature obtained by differential thermal analysis, the enthalpies of formation of the different ternary compounds being derived from calorimetric measurement.

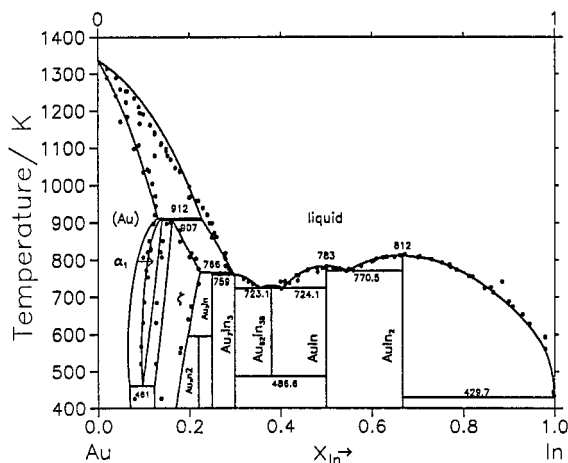


Figure 7 :  
Calculated Au-In phase  
diagram. (● exp. points).

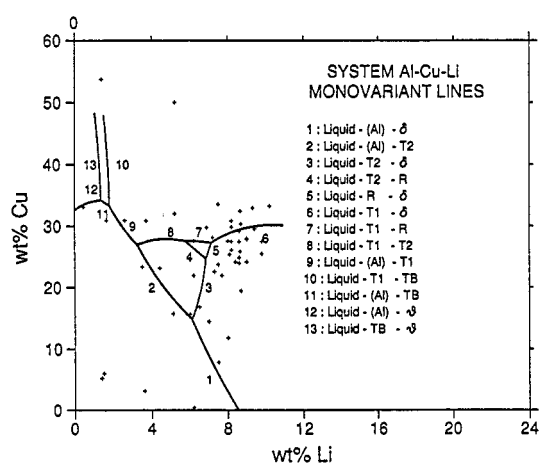


Figure 8 :  
Calculated monovariant lines in  
the Al-Cu-Li system. (+ selected  
alloy compositions).

## CONCLUSION

Pertinent data are now generated in many countries and the tasks of assembling, compiling and collating data on thermochemical properties and phase diagram data is enormous. Much of this task is now being organized among different groups, on an international scale, for instance by the CODATA Task Group of Thermochemical Tables (CTT), the Scientific Group Thermodata Europe (SGTE), the Alloy Phase Diagram International Commission (APDIC), and many other national endeavours. A better coordination of the work of critical evaluation and assessment still has to be organized in order to share on an international scale this important task.

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