
Lecture 5: Computation of Phase Diagrams

The theory we have covered in the earlier lectures helps understand solutions and has been used extensively in modelling their behaviour. The theory is, nevertheless, too complicated mathematically and too simple in its representation of real solutions. It fails as a general method of phase diagram calculation, where it is necessary to implement calculations over the entire periodic table, for any concentration, and in a seamless manner across the elements. There have been many review articles on the subject (*e.g.* Kaufman, 1969; Chart *et al.*, 1975; Hillert, 1977; Ansara, 1979; Inden, 1981). A recent book deals with examples of applications (edited by Hack, 1996). We shall focus here on the models behind the phase diagram calculations with the aim of illustrating the remarkable efforts that have gone into creating a general framework.

One possibility is to represent thermodynamic quantities by a series expansion with sufficient adjustable parameters to adequately fit the experimental data. There has to be a compromise between the accuracy of the fit and the number of terms in the expansion. However, such expansions do not generalise well when dealing with complicated phase diagram calculations involving many components and phases. Experience suggests that the specific heat capacities at constant pressure, C_P, for the pure elements are better represented by a polynomial with a form which is known to adequately describe most experimental data:

$$C_P = b_1 + b_2T + b_3T^2 + \frac{b_4}{T^2} \tag{1}$$

where b_i are empirical constants. Where the fit with experimental data is found not to be good enough, the polynomial is applied to a range over which the fit is satisfactory, and more than one polynomial is used to represent the full dataset. A standard element reference state is defined with a list of the measured enthalpies and entropies of the pure elements at 298 K and one atmosphere pressure, for the crystal structure appropriate for these conditions. With respect to this state, and bearing in mind that $\Delta H = \int\limits_{T_1}^{T_2} C_P \, dT$ and $\Delta S = \int\limits_{T_1}^{T_2} \frac{C_P}{T} dT$, the Gibbs free energy is obtained by integration to be:

$$G = b_5 + b_6T + b_7T\ln\{T\} + b_8T^2 + b_9T^3 + \frac{b_{10}}{T} \tag{2}$$

Allotropic transformations can be included if the transition temperatures, enthalpy of transformation and the C_P coefficients for all the phases are known.

Any "exceptional" variations in C_P, such as due to magnetic transitions, are dealt with separately, as are the effects of pressure. Once again, the equations for these effects are chosen carefully in order to maintain generality.

The excess Gibbs free energy for a binary solution with components A and B is written:

$$\Delta_e G_{AB} = x_A x_B \sum_{i=0}^{j} L_{AB,i}(x_A - x_B)^i \tag{3}$$

For $i = 0$ this gives a term $x_A x_B L_{AB,0}$ which is familiar in regular solution theory, where the coefficient $L_{AB,0}$ is, as usual, independent of chemical composition, and to a first approximation describes the interaction between components A and B. If all other $L_{AB,i}$ are zero for $i > 0$ then the equation reduces to the regular solution model with $L_{AB,0}$ as the regular solution parameter. Further terms ($i > 0$) are included to allow for any composition dependence not described by the regular solution constant.

As a first approximation, the excess free energy of a ternary solution can be represented purely by a combination of the binary terms in equation 3:

$$\begin{aligned}\Delta_e G_{ABC} =& x_A x_B \sum_{i=0}^{j} L_{AB,i}(x_A - x_B)^i \\ &+ x_B x_C \sum_{i=0}^{j} L_{BC,i}(x_B - x_C)^i \\ &+ x_C x_A \sum_{i=0}^{j} L_{CA,i}(x_C - x_A)^i\end{aligned} \tag{4}$$

We now see that the advantage of the representation embodied in equation 4 is that for the ternary case, the relation reduces to the binary problem when one of the components is set to be identical to another, *e.g.* $B \equiv C$ (Hillert, 1979).

There might exist ternary interactions, in which case a term $x_A x_B x_C L_{ABC,0}$ is added to the excess free energy. If this does not adequately represent the deviation from the binary summation, then it can be converted into a series which properly reduces to a binary formulation when there are only two components:

$$
\begin{aligned}
x_A x_B x_C \big[L_{ABC,0} &+ \frac{1}{3}(1 + 2x_A - x_B - x_C) L_{ABC,1} \\
&+ \frac{1}{3}(1 + 2x_B - x_C - x_A) L_{BCA,1} \\
&+ \frac{1}{3}(1 + 2x_C - x_A - x_B) L_{CAB,1} \big]
\end{aligned}
$$

It can be seen that this method can be extended to any number of components, with the great advantage that very few coefficients have to be changed when the data due to one component are improved. The experimental thermodynamic data necessary to derive the coefficients may not be available for systems higher than ternary so high order interactions are often set to zero.

References

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