Lecture 7: Quasichemical Solution Models

Introduction

The regular solution model assumes a random distribution of atoms even though the enthalpy of mixing is not zero. In reality, a random solution is only expected at very high temperatures when the entropy term overwhelms any tendency for ordering or clustering of atoms. It follows that the configurational entropy of mixing should vary with the temperature. The *quasi–chemical* solution model has a better treatment of configurational entropy which accounts for a non–random distribution of atoms. The model is so–called because it has a mass–action equation which is typical in chemical reaction theory

Partition Function

The essential problem in the construction of a quasi–chemical model is the partition function.

Consider a total number N of atoms in a system where there are just two energy levels. At any finite temperature a number N_0 of the atoms are in the ground state, whereas a number $N_1 \, (= N - N_0)$ belong to the higher level with an energy E_1 relative to the ground state. The fraction of atoms in the two states at a temperature T and at zero pressure is given by:

$$\frac{N_o}{N} = \frac{g_0}{g_0 + g_1 \exp\left\{\frac{-E_1}{kT}\right\}} \tag{1}$$

$$\frac{N_1}{N} = \frac{g_1 \exp\left\{\frac{-E_1}{kT}\right\}}{g_0 + g_1 \exp\left\{\frac{-E_1}{kT}\right\}}$$

where g_i represents the degeneracy of the ith energy level. The degeneracy gives the number of states with the same energy. In each of these equations, the term in the denominator is called the partition function Ω; in general, for a multi–level system,

$$\Omega = \sum_i g_i \exp\left\{\frac{-E_i}{kT}\right\}$$

where E_i is the energy relative to the ground state.

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The total energy of the assembly for a particular value of N_{AB} is $U_{N_{AB}} = -z(N_A\epsilon_{AA} + N_B\epsilon_{BB} - N_{AB}\omega)$ where $\omega = \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}$. In a non–random solution there are many values that N_{AB} can adopt, each value corresponding to one or more arrangements of atoms with an identical value of U. Each of these energy states is thus associated with a degeneracy $g_{N_{AB}}$ which gives the number of arrangements that are possible for a given value of U. The partition function is therefore the sum over all possible N_{AB}:

$$
\begin{aligned}
\Omega &= \sum_{N_{AB}} g_{N_{AB}} \exp\left\{-\frac{U_{N_{AB}}}{kT}\right\} \\
&= \sum_{N_{AB}} g_{N_{AB}} \exp\left\{\frac{z(N_A\epsilon_{AA} + N_B\epsilon_{BB} - N_{AB}\omega)}{kT}\right\}
\end{aligned}
\tag{2}
$$

For a given value of N_{AB}, the different non–interacting *pairs* of atoms can be arranged in the following number of ways

$$
g_{N_{AB}} \propto \frac{(\frac{1}{2}zN)!}{(\frac{1}{2}z[N_A - N_{AB}])! \, (\frac{1}{2}z[N_B - N_{AB}])! \, (\frac{1}{2}zN_{AB})! \, (\frac{1}{2}zN_{BA})!}
\tag{3}
$$

where the first and second terms in the denominator refer to the numbers of A–A and B–B bonds respectively, and the third and fourth terms the numbers of A–B and B–A pairs respectively. We note also that this not an equality because the various pairs are not independent, as illustrated in (Fig. 1). Another way of stating this is to say that the distribution of pairs is not random. Guggenheim addressed this problem by using a normalisation factor such that the summation of all possible degeneracies equals the total number of possible configurations as follows.
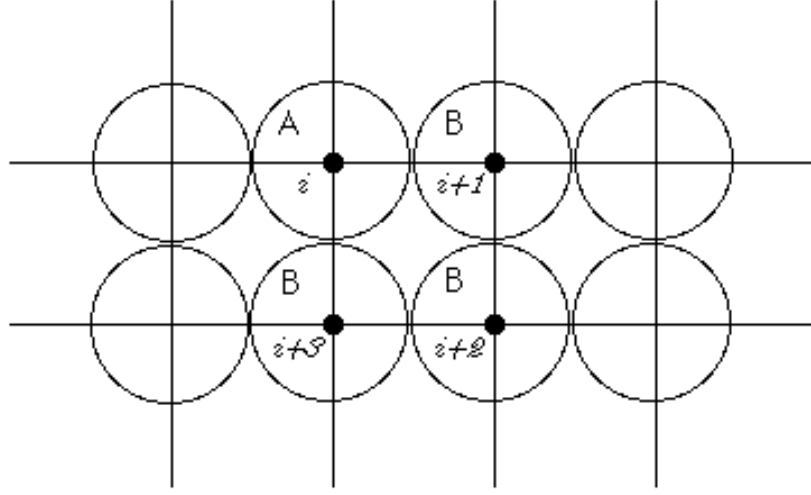
Fig. 1: Diagram showing why pairs of atoms cannot be distributed at random on lattice sites (Lupis, 1983). Once the bonds connecting the coordinates $(i, i+1)$, $(i+1, i+2)$, $(i+2, i+3)$ are made as illustrated, the final bond connecting $(i, i+3)$ is necessarily occupied by a pair AB.

Suppose that we identify with an asterisk, the number of arrangements of pairs of atoms possible in a random solution, then from the proportionality in equation 3, we see that

$$g^* \propto \frac{(\frac{1}{2}zN)!}{(\frac{1}{2}z[N_A - N_{AB}^*])! \, (\frac{1}{2}z[N_B - N_{AB}^*])! \, (\frac{1}{2}zN_{AB}^*)! \, (\frac{1}{2}zN_{BA}^*)!} \tag{4}$$

This again will overestimate the number of possibilities (Fig. 1), but for a random solution we know already that

$$g^* = \frac{N!}{N_A! \, N_B!}. \tag{5}$$

It follows that we can normalize $g_{N_{AB}}$ as

$$g_{N_{AB}} = \frac{(\frac{1}{2}z[N_A - N_{AB}^*])! \, (\frac{1}{2}z[N_B - N_{AB}^*])! \, (\frac{1}{2}zN_{AB}^*)! \, (\frac{1}{2}zN_{BA}^*)!}{(\frac{1}{2}z[N_A - N_{AB}])! \, (\frac{1}{2}z[N_B - N_{AB}])! \, (\frac{1}{2}zN_{AB})! \, (\frac{1}{2}zN_{BA})!} \times \frac{N!}{N_A! \, N_B!} \tag{6}$$

With this, the partition function Ω is defined explicitly and the problem is in principle solved. However, it is usual to first simplify by assuming that the sum in equation 2 can be replaced by its maximum value. This is because the thermodynamic properties that follow from the partition function depend on its logarithm, in which case the

use of the maximum is a good approximation. The equilibrium number N_{AB}^e of A–B bonds may then be obtained by setting $\partial \ln\{\Omega\}/\partial N_{AB} = 0$ (Christian, 1975; Lupis, 1983):

$$N_{AB}^e = \frac{2Nzx(1-x)}{\beta_q + 1} \tag{7}$$

with β_q being the positive root of the equation

$$\beta_q^2 - (1 - 2x) = 4x(1-x)\exp\{2\omega/kT\},$$

so that

$$
\begin{aligned}
N_{AB}^e &= \frac{2Nzx(1-x)}{[1 - 2x + 4x(1-x)\exp\{2\omega/kT\}]^{\frac{1}{2}} + 1} \\
&\equiv \frac{zN}{2(\exp\{2\omega/kT\} - 1)}\left[-1 + [1 + 4x(1-x)(\exp\{2\omega/kT\} - 1)]^{\frac{1}{2}}\right]
\end{aligned}
\tag{8}
$$

The percentage of the different pairs are plotted in Fig. 2. Equation 8 obviously corresponds to the regular solution model if $\beta_q = 1$ with a random arrangement of atoms. As expected, the number of unlike pairs is reduced when clustering is favoured, and increased when ordering is favoured.
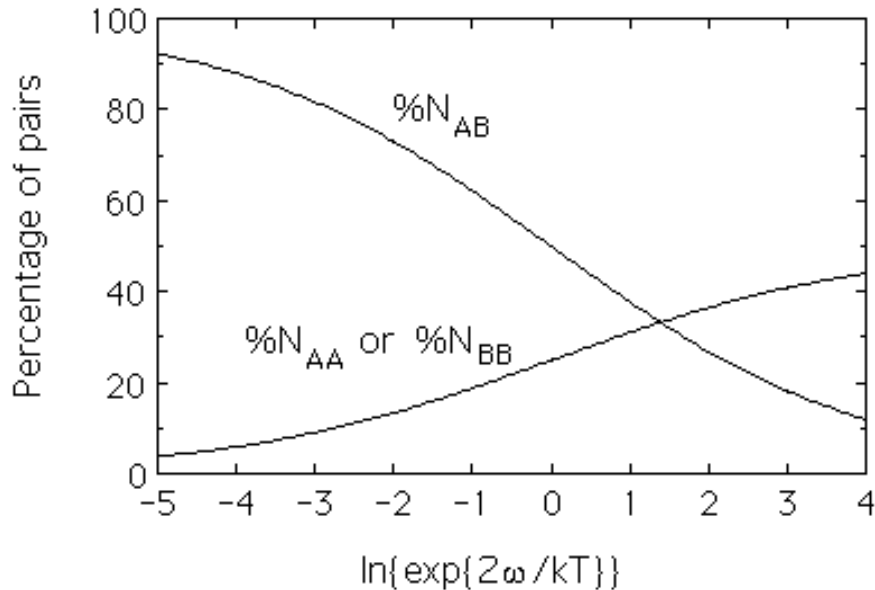

Fig. 2: Calculated percentages of pairs for the quasi–chemical model with $x = (1 - x) = 0.5$. The result is independent of z.

The free energy of the assembly is

$$G = F = -kT \ln\{\Omega\} = U_{N_{AB}^e} - kT \ln g_{N_{AB}^e} \tag{9}$$

so that the free energy of mixing per mole becomes

$$\Delta G_M = z N_{AB}^e \omega - NkT \ln g_{N_{AB}^e}$$

$$= \underbrace{\frac{2z\omega N x(1-x)}{\beta_q + 1}}_{\text{molar enthalpy of mixing}} - RT \ln g_{N_{AB}^e} \tag{10}$$

The second term on the right–hand side has the contribution from the configurational entropy of mixing. By substituting for $g_{N_{AB}^e}$, and with considerable manipulation, Christian has shown that this can be written in terms of β_q so that the molar free energy of mixing becomes:

$$\Delta G_M = \frac{2z\omega N x(1-x)}{\beta_q + 1}$$
$$+ RT\big[(1-x)\ln\{1-x\} + x\ln\{x\}\big] \tag{11}$$
$$+ \frac{1}{2}RTz\left\{(1-x)\ln\frac{\beta_q + 1 - 2x}{(1-x)(\beta_q + 1)} + x\ln\frac{\beta_q - 1 + 2x}{x(\beta_q + 1)}\right\}$$

The second term in this equation is the usual contribution from the configurational entropy of mixing in a random solution, whereas the third term can be regarded as a quasichemical correction for the entropy of mixing since the atoms are not randomly distributed.

It is not possible to give explicit expressions for the chemical potential or activity coefficient since β_q is a function of concentration. Approximations using series expansions are possible but the resulting equations are not as easy to interpret physically as the corresponding equations for the ideal or regular solution models.

The expressions in the quasi–chemical model (or *first approximation*) reduce to those of the regular solution (or *zeroth approximation*) model when $\beta_q = 1$. Although a better model has been obtained, the first approximation relies on the absence of interference between atom–pairs. However, each atom in a pair belongs to several pairs so that better approximations can be obtained by considering larger clusters of atoms in the calculation. Such calculations are known as the "cluster variation"

method. The improvements obtained with these higher approximations are usually rather small though there are cases where pairwise interactions simply will not do.

Finally, it is worth emphasising that although the quasi–chemical model has an excess entropy, this comes as a correction to the configurational entropy. Furthermore, the excess entropy from this model is always negative; there is more disorder in a random solution than in one which is biassed. Therefore, the configurational entropy from the quasi–chemical model is always less than expected from an ideal solution. Thermal entropy or other contributions such as magnetic or electronic are additional contributions.

The procedure in the development of the quasi–chemical models is illustrated in Fig. 3.

References

J. W. Christian, Theory of Transformations in Metals and Alloys, Part I, 2nd edition, 1975, Pergamon Press, Oxford.

C. H. P. Lupis, Chemical Thermodynamics of Materials, North Holland, 1983.

The Quasichemical Approach

Categorise and count the variety of atom-atom or atom-vacancy pairs possible

↓

Estimate the configurational energy arising from the pairwise interactions

↓

Write the configurational partition function

↓

Discover the degeneracy for each configuration

↓

Normalise the degeneracy function to ensure that the grande summation of all degeneracies is the total number of possible configurations

↓

Replace the summation in the partition function by its largest term

↓

Derive required thermodynamic functions from the partition function

↓

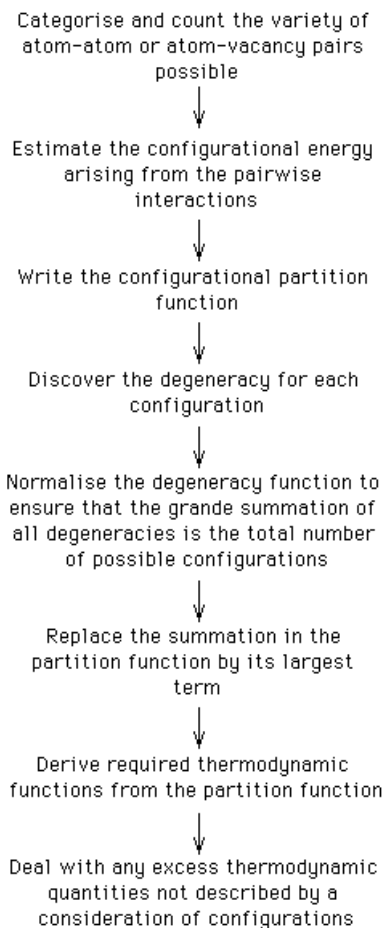Deal with any excess thermodynamic quantities not described by a consideration of configurations

Fig. 3: The steps involved in the construction of a quasichemical solution model.