LEARNING PREREQUISITES – PHASE BEHAVIOR

A phase diagram of a substance shows the regions of pressure and temperature at which its various phases are thermodynamically stable. The boundaries between regions, the phase boundaries, show the value of p and T at which two phases coexist in equilibrium.

A phase is a state of matter that is uniform troughout, not only chemical composition but also in physical state.
By a component it is meant a species present in the system, as for the solute and solvent in a binary solution.

J.W. Gibbs deduced the phase rule, which is a general relation between the variance/ freedom F, the number of components C, and the number of phases at equilibrium P for a system of any composition:

$$F + C = P + 2$$

When two components are present (binary system), C=2 and F = 4- P. For simplicity, the pressure is kept constant (at 1 atm), which uses up one of the degrees of freedom, and it can be written: F' = 3 – P for the remaining variance. One of these remaining degree of freedom is the temperature, the other is the composition.

A binary phase diagram is a temperature - composition map which indicates the equilibrium phases present at a given temperature and composition.
The equilibrium state can be found from the Gibbs free energy dependence on temperature and composition.

Ideal: $\Delta H = 0$ and → $\Delta G_{mix} = nRT\,(x_A \ln x_a + x_B \ln x_B)$

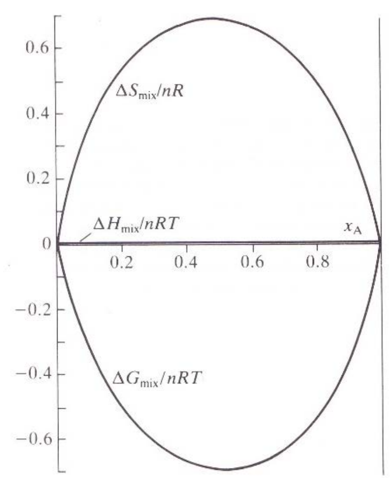

Fig. 7.5 The Gibbs function, enthalpy, and entropy of mixing of an ideal binary mixture, calculated using eqn 13. The entropy is expressed as a multiple of *nR*, the Gibbs function as a multiple of nRT.

To characterize a solution, it is necessary to introduce variables specifying the composition of the different chemical components of the solution. Several composition variables are often used, each having particular advantages in different applications. The first composition variables of importance are the mole numbers. For a system with N components, we will refer to the number of moles of each component i as n_i. When specifying the composition of a multi-component system in a phase diagram, more practical composition variables are mole fraction and weight fraction. The mole fraction of component i, denoted by x_i, refers to the number of mole n_i of i in the solution divided by the total number of mole n_{tot} in the solution. Similarly, the weight fraction, w_i, of component i is the ratio of the weight of component i, W_i, in solution to the total weight of solution, W_{tot}. Weight fractions are often used in practical applications, where a mixture having a particular weight fraction can easily be prepared by weighing the pure components before mixing them. Mole fractions are useful when viewing the solution within a theoretical framework where details of the solution at the atomic level become important. Closely related to mole fraction is the atomic percent of component i which is often denoted by $(at\%)_i$ and equals 100 times the mole fraction x_i. A fourth important composition variable is the concentration C_i of component i, defined as the number of moles of i divided by the volume V of the solution. This variable is often implemented in the study of irreversible processes, since the concentration is a natural variable in Fick's differential equations describing diffusion. As an overview, the four concentration variables are summarized in table 1.

Mole fraction: $x_i \equiv \frac{n_i}{\sum_i n_i}$

Atomic percent: $(at\%) = 100\% \times x_i$

Weight fraction: : $w_i \equiv \frac{W_i}{\sum_i W_i}$

Concentration: $C_i = \frac{n_i}{V}$