12.3: Binary Mixture in Equilibrium with a Pure Phase

This section considers a binary liquid mixture of components A and B in equilibrium with either pure solid A or pure gaseous A. The aim is to find general relations among changes of temperature, pressure, and mixture composition in the two-phase equilibrium system that can be applied to specific situations in later sections.

In this section, *[Math Processing Error]* is the chemical potential of component A in the mixture and *[Math Processing Error]* is for the pure solid or gaseous phase. We begin by writing the total differential of *[Math Processing Error]* with *[Math Processing Error]*, *[Math Processing Error]*, and *[Math Processing Error]* as the independent variables. These quantities refer to the binary liquid mixture, and we have not yet imposed a condition of equilibrium with another phase. The general expression for the total differential is *[Math Processing Error]* With substitutions from Eqs. 9.2.49 and 12.1.3, this becomes *[Math Processing Error]*

Next we write the total differential of *[Math Processing Error]* for pure solid or gaseous A. The independent variables are *[Math Processing Error]* and *[Math Processing Error]*; the expression is like Eq. 12.3.2 with the last term missing: *[Math Processing Error]*

When the two phases are in transfer equilibrium, *[Math Processing Error]* and *[Math Processing Error]* are equal. If changes occur in *[Math Processing Error]*, *[Math Processing Error]*, or *[Math Processing Error]* while the phases remain in equilibrium, the condition *[Math Processing Error]* must be satisfied. Equating the expressions on the right sides of Eqs. 12.3.2 and 12.3.3 and combining terms, we obtain the equation *[Math Processing Error]* which we can rewrite as *[Math Processing Error]* Here *[Math Processing Error]* is the molar differential enthalpy of solution of solid or gaseous A in the liquid mixture, and *[Math Processing Error]* is the molar differential volume of solution. Equation 12.3.5 is a relation between changes in the variables *[Math Processing Error]*, *[Math Processing Error]*, and *[Math Processing Error]*, only two of which are independent in the equilibrium system.

Suppose we set *[Math Processing Error]* equal to zero in Eq. 12.3.5 and solve for *[Math Processing Error]*. This gives us the rate at which *[Math Processing Error]* changes with *[Math Processing Error]* at constant *[Math Processing Error]*: *[Math Processing Error]* We can also set *[Math Processing Error]* equal to zero in Eq. 12.3.5 and find the rate at which *[Math Processing Error]* changes with *[Math Processing Error]* at constant *[Math Processing Error]*: *[Math Processing Error]*

Equations 12.3.6 and 12.3.7 will be needed in Secs. 12.4 and 12.5.