8.3: Criterion for Phase Equilibrium

The thermodynamic criterion for phase equilibrium is simple. It is based upon the chemical potentials of the components in a system. For simplicity, consider a system with only one component. For the overall system to be in equilibrium, the chemical potential of the compound in each phase present must be the same. Otherwise, there will be some mass migration from one phase to another, decreasing the total chemical potential of the phase from which material is being removed, and increasing the total chemical potential of the phase into which the material is being deposited. So for each pair of phases present (α and β) the following must be true:

$$\mu_\alpha = \mu_\beta$$

Gibbs Phase Rule

The **Gibbs phase rule** describes the number of compositional and phase variables that can be varied freely for a system at equilibrium. For each phase present in a system, the mole fraction of all but one component can be varied independently. However, the relationship

$$\sum_i \chi_i = 1$$

places a constraint on the last mole fraction. As such, there are $C-1$ compositional degrees of freedom for each phase present, where C is the number of components in the mixture. Similarly, all but one of the chemical potentials of each phase present must be equal, leaving only one that can be varied independently, leading to $P-1$ thermodynamic constraints placed on each component. Finally, there are two state variables that can be varied (such as pressure and temperature), adding two additional degrees of freedom to the system. The net number of degrees of freedom is determined by adding all of the degrees of freedom and subtracting the number of thermodynamic constraints.

$$
\begin{aligned}
F &= 2 + P(C-1) - C(P-1) \\
&= 2 + PC - P - PC + C \\
&= 2 + C - P
\end{aligned}
\tag{8.3.1}
$$

Equation 8.3.1 is the Gibbs phase rule.

> **✔ Example 8.3.1:**
>
> Show that the maximum number of phases that can co-exist at equilibrium for a single component system is $P = 3$.
>
> **Solution**
> The maximum number of components will occur when the number of degrees of freedom is zero.
>
> $$
> \begin{aligned}
> 0 &= 2 + 1 - P \\
> P &= 3
> \end{aligned}
> $$
>
> Note: This shows that there can never be a "quadruple point" for a single component system!

Because a system at its triple point has no degrees of freedom, the triple point makes a very convenient physical condition at which to define a temperature. For example, the International Practical Temperature Scale of 1990 (IPT-90) uses the triple points of hydrogen, neon, oxygen, argon, mercury, and water to define several low temperatures. (The calibration of a platinum resistance thermometer at the triple point of argon, for example, is described by Strouse (Strouse, 2008)). The advantage to using a triple point is that the compound sets both the temperature and pressure, rather than forcing the researcher to set a pressure and *then* measure the temperature of a phase change, introducing an extra parameter than can introduce uncertainty into the measurement.