

6.3: Chemical Potential

In much the same fashion as the partial molar volume is defined, the **partial molar Gibbs function** is defined for compound i in a mixture:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{p,T,n_j \neq i} \quad (6.3.1)$$

This particular partial molar function is of particular importance, and is called the **chemical potential**. The chemical potential tells how the Gibbs function will change as the composition of the mixture changes. And since systems tend to seek a minimum aggregate Gibbs function, the chemical potential will point to the direction the system can move in order to reduce the total Gibbs function. In general, the total change in the Gibbs function (dG) can be calculated from

$$dG = \left(\frac{\partial G}{\partial p} \right)_{T,n_i} dp + \left(\frac{\partial G}{\partial T} \right)_{p,n_i} dT + \sum_i \left(\frac{\partial G}{\partial n_i} \right)_{T,n_j \neq i} dn_i$$

Or, by substituting the definition for the chemical potential, and evaluating the pressure and temperature derivatives as was done in Chapter 6:

$$dG = V dp - S dT + \sum_i \mu_i dn_i$$

But as it turns out, the chemical potential can be defined as the partial molar derivative any of the four major thermodynamic functions U , H , A , or G :

Table 6.3.1: Chemical potential can be defined as the partial molar derivative any of the four major thermodynamic functions

$dU = TdS - pdV + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j \neq i}$
$dH = TdS - VdT + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial H}{\partial n_i} \right)_{S,p,n_j \neq i}$
$dA = -pdV - TdS + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial A}{\partial n_i} \right)_{V,T,n_j \neq i}$
$dG = Vdp - SdT + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{p,T,n_j \neq i}$

The last definition, in which the chemical potential is defined as the partial molar Gibbs function is the most commonly used, and perhaps the most useful (Equation 6.3.1). As the partial most Gibbs function, it is easy to show that

$$d\mu = V dp - S dT$$

where V is the molar volume, and S is the molar entropy. Using this expression, it is easy to show that

$$\left(\frac{\partial \mu}{\partial p} \right)_T = V$$

and so at constant temperature

$$\int_{\mu^o}^{\mu} d\mu = \int_{p^o}^p V dp \quad (6.3.2)$$

So that for a substance for which the molar volume is fairly independent of pressure at constant temperature (i. e., κ_T is very small), therefore Equation 6.3.2 becomes

$$\begin{aligned} \int_{\mu^o}^{\mu} d\mu &= V \int_{p^o}^p dp \\ \mu - \mu^o &= V(p - p^o) \end{aligned}$$

or

$$\mu = \mu^o + V(p - p^o)$$

Where p^o is a reference pressure (generally the standard pressure of 1 atm) and μ^o is the chemical potential at the standard pressure. If the substance is highly compressible (such as a gas) the pressure dependence of the molar volume is needed to complete the integral. If the substance is an ideal gas

$$V = \frac{RT}{p}$$

So at constant temperature, Equation 6.3.2 then becomes

$$\int_{\mu^o}^{\mu} d\mu = RT \int_{p^o}^p \frac{dp}{p} \quad (6.3.3)$$

or

$$\mu = \mu^o + RT \ln\left(\frac{p}{p^o}\right)$$

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