17.7: Chemical Potential, Pressure, Fugacity

Equation 12.9.11 told us how to calculate the change in the Gibbs function of a mole of an ideal gas going from one state to another. For N moles it would be

$$\Delta G=N\int C_P dT-NT_2\int C_P d(\ln T)+NRT_2\ln\left(\frac{P_2}{P_1}\right)-NS\left(T_2-T_1\right), \tag{17.7.1}$$

where C_P and S are molar, and G is total.

Since we know now how to calculate the absolute entropy and also know that the entropy at $T = 0$ is zero, this can be written

$$G(T,P)=N(RT\ln P+\text{ constant }) \tag{17.7.2}$$

The "constant" here depends on the temperature, but is not a function of the pressure, being in fact the value of the molar Gibbs function extrapolated to the limit of zero pressure. Sometimes it is convenient to write Equation 17.7.2 in the form

$$G=NRT(\ln P+\phi) \tag{17.7.3}$$

where φ is a function of temperature.

If we have a mixture of several components, the total Gibbs function is

$$G(T,P)=\sum_i N_i\left(RT\ln p_i+\text{ constant }\right) \tag{17.7.4}$$

We can now write this in terms of the partial molar Gibbs function of the component i – that is to say, the chemical potential of the component *i*, which is given by $\mu_i=(\partial G/\partial N_i)_{P,T,N_{j\neq 1}}$, and the *partial pressure* of component *i*. Thus we obtain

$$\mu_i=\mu_i^0(T)+RT\ln p_i \tag{17.7.5}$$

and

$$\mu_i=RT\left(\ln p_i+\phi_i\right) \tag{17.7.6}$$

Here I have written the "constant" as 0 μ_i^0 (T), or as $RT\varphi_i$. The constant μ_i^0 (T) is the value of the chemical potential at temperature T extrapolated to the limit of zero pressure. If the system consists of a mixture of ideal gases, the partial pressure of the *i*th component is related to the total pressure simply by *Dalton's law of partial pressures*:

$$p_i=n_iP, \tag{17.7.7}$$

where n_i is the mole fraction of the *i*th component. In that case, equation 17.7.4 becomes

$$\mu_i=\mu_i^0(T)+RT\ln n_i+RT\ln P. \tag{17.7.8}$$

and equation 17.7.5 becomes

$$\mu_i=RT\left(\ln n_i+\ln P+\phi_i\right). \tag{17.7.9}$$

However, in a common deviation from ideality, volumes in a mixture are not simply additive, and we write equation 17.7.4 in the form

$$\mu_i=\mu_i^0(T)+RT\ln f_i, \tag{17.7.10}$$

or equation 17.7.5 in the form

$$\mu_i=RT\left(\ln f_i+\phi_i\right). \tag{17.7.11}$$

where f_i is the *fugacity* of component *i*.