5.5: Open Systems

An open system of one substance in one phase, with expansion work only, has three independent variables. The total differential of U is given by Eq. 5.2.5:

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}n \tag{5.5.1}$$

In this open system the natural variables of U are S, V, and n. Substituting this expression for $\mathrm{d}U$ into the expressions for $\mathrm{d}H$, $\mathrm{d}A$, and $\mathrm{d}G$ given by Eqs. 5.3.4–5.3.6, we obtain the following total differentials:

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \mu\,\mathrm{d}n \tag{5.5.2}$$

$$\mathrm{d}A = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}n \tag{5.5.3}$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\,\mathrm{d}n \tag{5.5.4}$$

Note that these are the same as the four Gibbs equations (Eqs. 5.4.1–5.4.4) with the addition of a term $\mu\,\mathrm{d}n$ to allow for a change in the amount of substance.

Identification of the coefficient of the last term on the right side of each of these equations shows that the chemical potential can be equated to four different partial derivatives:

$$\mu = \left(\frac{\partial U}{\partial n}\right)_{S,V} = \left(\frac{\partial H}{\partial n}\right)_{S,p} = \left(\frac{\partial A}{\partial n}\right)_{T,V} = \left(\frac{\partial G}{\partial n}\right)_{T,p} \tag{5.5.5}$$

All four of these partial derivatives must have the same value for a given state of the system; the value, of course, depends on what that state is.

The last partial derivative on the right side of Eq. 5.5.5, $(\partial G/\partial n)_{T,p}$, is especially interesting because it is the rate at which the Gibbs energy increases with the amount of substance added to a system whose intensive properties remain constant. Thus, μ is revealed to be equal to G_{m}, the molar Gibbs energy of the substance.

Suppose the system contains several substances or species in a single phase (a mixture) whose amounts can be varied independently. We again assume the only work is expansion work. Then, making use of Eq. 5.2.6, we find the total differentials of the thermodynamic potentials are given by

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \sum_i \mu_i\,\mathrm{d}n_i \tag{5.5.6}$$

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \sum_i \mu_i\,\mathrm{d}n_i \tag{5.5.7}$$

$$\mathrm{d}A = -S\,\mathrm{d}T - p\,\mathrm{d}V + \sum_i \mu_i\,\mathrm{d}n_i \tag{5.5.8}$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \sum_i \mu_i\,\mathrm{d}n_i \tag{5.5.9}$$

The independent variables on the right side of each of these equations are the natural variables of the corresponding thermodynamic potential. Section F.4 shows that all of the information contained in an algebraic expression for a state function is preserved in a Legendre transform of the function. What this means for the thermodynamic potentials is that an expression for any one of them, as a function of its natural variables, can be converted to an expression for each of the other thermodynamic potentials as a function of its natural variables.

Willard Gibbs, after whom the Gibbs energy is named, called Eqs. 5.5.6–5.5.9 the *fundamental equations* of thermodynamics, because from any single one of them not only the other thermodynamic potentials but also all thermal, mechanical, and chemical properties of the system can be deduced (J. Willard Gibbs, in Henry Andrews Bumstead and Ralph Gibbs Van Name, editors, *The Scientific Papers of J. Willard Gibbs*, Vol. I, Ox Bow Press, Woodbridge, Connecticut, 1993, p. 86). Problem 5.4 illustrates this useful application of the total differential of a thermodynamic potential.

In Eqs. 5.5.6–5.5.9, the coefficient μ_i is the chemical potential of species i. The equations show that μ_i can be equated to four different partial derivatives, similar to the equalities shown in Eq. 5.5.5 for a pure substance:

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_{j\neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}} = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} \tag{5.5.10}$$

The partial derivative $(\partial G/\partial n_i)_{T,P,n_{j\neq i}}$ is called the *partial molar Gibbs energy* of species i, another name for the chemical potential as will be discussed in Sec. 9.2.6.