5.4: Closed Systems

In order to find expressions for the total differentials of H, A, and G in a closed system with one component in one phase, we must replace $\mathrm{d}U$ in Eqs. 5.3.4–5.3.6 with

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V \tag{5.4.1}$$

to obtain

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p \tag{5.4.2}$$

$$\mathrm{d}A = -S\,\mathrm{d}T - p\,\mathrm{d}V \tag{5.4.3}$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p \tag{5.4.4}$$

Equations 5.4.1–5.4.4 are sometimes called the **Gibbs equations**. They are expressions for the total differentials of the thermodynamic potentials U, H, A, and G in closed systems of one component in one phase with expansion work only. Each equation shows how the dependent variable on the left side varies as a function of changes in two independent variables (the natural variables of the dependent variable) on the right side.

By identifying the coefficients on the right side of Eqs. 5.4.1–5.4.4, we obtain the following relations (which again are valid for a closed system of one component in one phase with expansion work only):

from Eq. 5.4.1:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{5.4.5}$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \tag{5.4.6}$$

from Eq. 5.4.2:

$$\left(\frac{\partial H}{\partial S}\right)_p = T \tag{5.4.7}$$

$$\left(\frac{\partial H}{\partial p}\right)_S = V \tag{5.4.8}$$

from Eq. 5.4.3:

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \tag{5.4.9}$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -p \tag{5.4.10}$$

from Eq. 5.4.4:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \tag{5.4.11}$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V \tag{5.4.12}$$

This e-book now uses for the first time an extremely useful mathematical tool called the **reciprocity relation** of a total differential (Sec. F.2). Suppose the independent variables are x and y and the total differential of a dependent state function f is given by

$$\mathrm{d}f = a\,\mathrm{d}x + b\,\mathrm{d}y \tag{5.4.13}$$

where a and b are functions of x and y. Then the reciprocity relation is

$$\left(\frac{\partial a}{\partial y}\right)_x = \left(\frac{\partial b}{\partial x}\right)_y \tag{5.4.14}$$

The reciprocity relations obtained from the Gibbs equations (Eqs. 5.4.1–5.4.4) are called **Maxwell relations** (again valid for a closed system with $C\!=\!1$, $P\!=\!1$, and $đw'\!=\!0$):

from Eq. 5.4.1:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \tag{5.4.15}$$

from Eq. 5.4.2:

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \tag{5.4.16}$$

from Eq. 5.4.3:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \tag{5.4.17}$$

from Eq. 5.4.4:

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p \tag{5.4.18}$$