and involves the differentiation of extensive property $F^{\text{tot}}$ with respect to $n_i$. It is convenient to express partial molar property $\overline{F}_i$ as a derivative in terms of $x_i$. In the case of a binary solution, this leads to simple results, as we will see. We begin by obtaining the relationship between derivatives in $n_i$ and in $x_i$. Starting with

$$x_1 = \frac{n_1}{n_1+n_2},$$

multiply by F

we take the derivative with respect to $n_1$ at constant $n_2$:

$$\left(\frac{\partial x_1}{\partial n_1}\right)_{n_2} = \left[\frac{\partial}{\partial n_1}\left(\frac{n_1}{n_1+n_2}\right)\right]_{n_2} = \frac{n_2}{(n_1+n_2)^2} = \frac{x_2}{n_1+n_2}. \tag{12.7}$$

We return to the definition of partial molar and expand the right-hand side by applying the chain rule:

$$\overline{F}_1 = \left(\frac{\partial (n_1+n_2)F}{\partial n_1}\right)_{n_2} = \left(\frac{\partial (n_1+n_2)}{\partial n_1}\right)_{n_1} F + n\left(\frac{\partial F}{\partial n_1}\right)_{P,T,n_2}$$

change 1 to F

$$= \cancel{1} + n\left(\frac{\partial F}{\partial x_1}\right)_{P,T}\left(\frac{\partial x_1}{\partial n_1}\right)_{n_2}.$$

F

Using eq. (12.7) the above results becomes

(this result is correct)

$$\boxed{\overline{F}_1 = F + (1-x_1)\left(\frac{\partial F}{\partial x_1}\right)_{P,T}.} \tag{12.8}$$

The corresponding expression for the partial molar property of component 2 is obtained by symmetry: exchanging subscripts 1 and 2 we obtain

$$\overline{F}_2 = F + (1-x_2)\left(\frac{\partial F}{\partial x_2}\right)_{P,T}.$$

Using $dx_2 = -dx_1$ we obtain $\overline{F}_2$ in the equivalent form

$$\boxed{\overline{F}_2 = F - x_1\left(\frac{\partial F}{\partial x_1}\right)_{P,T}.} \tag{12.9}$$

Here, both partial molar properties are given as derivatives with respect to the mol fraction of component 1. Equations (12.8) and (12.9) apply to any partial molar properties, including excess partial molar. There is a simple graphical interpretation of these equations, as shown in Figure 12-1. In a plot of property $F$ against $x_1$, we draw a tangent line at a mol fraction of interest. The zero intercept of this line is the partial molar property of component 2 and the intercept at $x_1$ is the partial