property (right-hand side), it is as if the total number of moles can be "factored" out of all the terms that contain it. This expresses mathematically the fact that the properties of mixture depend on the *relative* amounts (i.e., mole fractions) of each component. The actual number of moles n makes a simple multiplicative contribution. In math language, the "factorization" of n means that extensive properties are *homogeneous* functions of number of moles n_i of component i. The homogeneity of thermodynamic properties leads to an important theoretical results, the Gibbs-Duhem equation, which discussed later on page 406.

9.2 Mathematical Treatment of Mixtures

Now we consider the mathematical problem of how to express properties as functions of pressure, temperature, *and* composition. We will develop equations for the generic extensive property F^{tot}, which will stand in for enthalpy, entropy, volume, and the like. This is a mathematical function of T, P, and the moles of all components:

$$F^{\text{tot}} = F^{\text{tot}}(T, P, n_1, n_2, \cdots).$$

By standard calculus the differential of this expression is

$$dF^{\text{tot}} = \left(\frac{\partial F^{\text{tot}}}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial F^{\text{tot}}}{\partial P}\right)_{T,n_i} dP + \sum_i \left(\frac{\partial F^{\text{tot}}}{\partial n_i}\right)_{P,T,n_j} dn_i.$$

This expression contains the partial derivatives with respect to every variable and each derivative is multiplied by the differential of the corresponding variable. In these derivatives, all variables except one are held constant. In the derivatives with respect to T or P, all n_i are held constant. This is indicated by the subscript n_i. In derivatives with respect to n_i, pressure, temperature, and all other moles $(n_j \neq i)$ are held constant. This is indicated by the subscript n_j that appears in the derivative. We define the *partial molar property*, $\bar{F}_i$, as

n_j

replace j by
n subscript j

$$\bar{F}_i = \left(\frac{\partial F^{\text{tot}}}{\partial n_i}\right)_{P,T,n_j}. \tag{9.7}$$

With this definition, the differential of an extensive property is written in the more compact form,

$$dF^{\text{tot}} = \left(\frac{\partial F^{\text{tot}}}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial F^{\text{tot}}}{\partial P}\right)_{T,n_i} dP + \sum \bar{F}_i \, dn_i. \tag{9.8}$$

This differential expresses the change in property F^{tot} upon a change of state by $(dT,\ dP,\ dn_1,\ \cdots)$.