

18.1: Partial Molar Quantities

Because they are easy to control in typical laboratory experiments, pressure, temperature, and the number of moles of each component are the independent variables that we find useful most often. Partial derivatives of thermodynamic quantities, taken with respect to the number of moles of a component, **at constant pressure and temperature**, are given a special designation; they are called **partial molar quantities**. That is,

$$\left(\frac{\partial U}{\partial n_i} \right)_{P,T,n_{j \neq i}} \quad (18.1.1)$$

is the partial molar energy of component i ,

$$\left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_{j \neq i}} \quad (18.1.2)$$

is the partial molar Gibbs free energy, etc. All partial molar quantities are intensive variables.

Because partial molar quantities are particularly useful, it is helpful to have a distinctive symbol to represent them. We use a horizontal bar over a thermodynamic variable to represent a partial molar quantity. (We have been using the horizontal over-bar to mean simply per mole. When we use it to designate a partial molar quantity, it means per mole of a specific component.) Thus, we write

$$\left(\frac{\partial U}{\partial n_i} \right)_{P,T,n_{j \neq i}} = \bar{U}_i \quad (18.1.3)$$

$$\left(\frac{\partial V}{\partial n_i} \right)_{P,T,n_{j \neq i}} = \bar{V}_i \quad (18.1.4)$$

$$\left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_{j \neq i}} = \bar{G}_i \quad (18.1.5)$$

etc.

In Sections 14.1 and 14.2, we introduce the chemical potential for substance i , μ_i , and find that the chemical potential of substance i is equivalently expressed by several partial derivatives. In particular, we have

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_{j \neq i}} = \bar{G}_i \quad (18.1.6)$$

that is, **the chemical potential is also the partial molar Gibbs free energy**.

It is important to recognize that the other partial derivatives that we can use to calculate the chemical potential are not partial molar quantities. Thus,

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_{j \neq i}} \neq \left(\frac{\partial U}{\partial n_i} \right)_{P,T,n_{j \neq i}} \quad (18.1.7)$$

That is, $\mu_i \neq \bar{U}_i$. Similarly, $\mu_i \neq \bar{H}_i$, $\mu_i \neq \bar{A}_i$, and $\mu_i \neq -T\bar{S}_i$.

We can think of a thermodynamic variable as a manifold—a “surface” in a multidimensional space. If there are two independent variables, the dependent thermodynamic variable is a surface in a three-dimensional space. Then we can visualize the partial derivative of the dependent thermodynamic variable with respect to an independent variable as the slope of a line tangent to the surface. This tangent lies in a plane in which the other independent variable is constant. If the independent variables are pressure, temperature, and compositions, the slope of the tangent line at $(P, T, n_1, n_2, \dots, n_\omega)$ is the value of a partial molar quantity at that point.

A more concrete way to think of a partial molar quantity for component i is to view it as the change in that quantity when we add one mole of i to a very large system having the specified pressure, temperature, and composition. When we add one mole of i to this system, the relative change in any of the system’s properties is very small; for example, the ratio of the final volume to the initial volume is essentially unity. Nevertheless, the volume of the system changes by a finite amount. This amount approximates

the partial molar volume of substance i . This approximation becomes better as the size of the system becomes larger. We expect the change in the volume of the system to be approximately equal to the volume of one mole of pure i , but we know that in general it will be somewhat different because of the effects of attractive and repulsive forces between the additional i molecules and the molecules comprising the original system.

Partial molar quantities can be expressed as functions of other thermodynamic variables. Because pressure and temperature are conveniently controlled variables, functions involving partial molar quantities are particularly useful for describing chemical change in systems that conform to the assumptions that we introduce in §1. Because the chemical potential is the same thing as the partial molar Gibbs free energy, it plays a prominent role in these equations.

To use these equations to describe a real system, we must develop empirical models that relate the partial molar quantities to the composition of the system. In general, these empirical models are non-linear functions of the system composition. However, simple approximations are sometimes adequate. The simplest approximation is a case we have already considered. If we can ignore the attractive and repulsive interactions among the molecules comprising the system, the effect of increasing n_i by a small amount, dn_i , is simply the effect of adding dn_i moles of pure component i to the system. If we let \bar{U}_i^* be the energy per mole of pure component i , the contribution to the energy of the system, at constant temperature and pressure, is

$$\left(\frac{\partial U}{\partial n_i}\right)_{P,T,n_{j \neq i}} dn_i = \bar{U}_i^* dn_i \quad (18.1.8)$$

In [Chapter 12](#), we apply the thermodynamic criteria for change to the equilibria between phases of a pure substance. To do so, we use the Gibbs free energies of the pure phases. In [Chapter 13](#), we apply these criteria to chemical reactions of ideal gases, using the Gibbs free energies of the pure gases. In these cases, the properties of a phase of a pure substance are independent of the amounts of any other substances that are present. That is, we use the approximation

$$\left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j \neq i}} dn_i = \bar{G}_i^* dn_i \quad (18.1.9)$$

albeit without using the over-bar or the bullet superscript to indicate that we are using the partial molar Gibbs free energy of the pure substance. In [Section 14.1](#), we develop the principle that $\sum_{i=1}^N \mu_i dn_i \leq 0$ are general criteria for change that are applicable not only to closed systems but also to open systems composed of homogeneous phases.

Thus far in this chapter, we have written each partial derivative with a complete list of the variables that are held constant. This is typographically awkward. Clarity seldom requires that we include the work-related variables and composition variables, n_i , in this list. From here on, we usually omit them.

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