

## 14.7: At Constant P and T, $\Delta_r\mu$ is the Change in Gibbs Free Energy

At constant temperature and pressure, the chemical potential of component  $A$  is the contribution that one mole of  $A$  makes to the Gibbs free energy of the system. The Gibbs free energy of the system is the sum of the contributions made by all of its components. The chemical potential change that occurs during a reaction,

$$\Delta_r\mu = \sum_{j=1}^{\omega} \mu_j \nu_j$$

is the same thing as the Gibbs free energy change. To establish these points, we introduce Euler's theorem on homogenous functions. For simplicity, we consider systems in which only pressure-volume work occurs.

A function  $f(x, y, z)$  is said to be homogeneous of order  $n$  if

$$\lambda^n f(x, y, z) = f(\lambda x, \lambda y, \lambda z)$$

Then,

$$\begin{aligned} \frac{d}{d\lambda} [\lambda^n f(x, y, z)] &= n\lambda^{n-1} f(x, y, z) = \left( \frac{\partial f}{\partial (\lambda x)} \right)_{yz} \frac{d(\lambda x)}{d\lambda} + \left( \frac{\partial f}{\partial (\lambda y)} \right)_{xz} \frac{d(\lambda y)}{d\lambda} + \left( \frac{\partial f}{\partial (\lambda z)} \right)_{xy} \frac{d(\lambda z)}{d\lambda} \\ &= x \left( \frac{\partial f}{\partial (\lambda x)} \right)_{yz} + y \left( \frac{\partial f}{\partial (\lambda y)} \right)_{xz} + z \left( \frac{\partial f}{\partial (\lambda z)} \right)_{xy} \end{aligned}$$

Since this must be true for any  $\lambda$ , it must be true for  $\lambda = 1$ . Making this substitution, we have Euler's theorem for order  $n$ :

$$nf(x, y, z) = x \left( \frac{\partial f}{\partial x} \right)_{yz} + y \left( \frac{\partial f}{\partial y} \right)_{xz} + z \left( \frac{\partial f}{\partial z} \right)_{xy}$$

An extensive state function is homogeneous of order one in its extensive variables. In particular, we have

$$\lambda G(P, T, n_A, n_B, n_C, n_D) = G(P, T, \lambda n_A, \lambda n_B, \lambda n_C, \lambda n_D)$$

for any  $\lambda$ . (For, say,  $\lambda = 1/2$ , this says only that, if we divide a homogeneous equilibrium system into two equal portions, all else remaining constant, the Gibbs free energy of each portion will be half of that of the original system. The pressure and temperature are independent of  $\lambda$ .) Taking the derivative with respect to  $\lambda$ , we find

$$\begin{aligned} \frac{d}{d\lambda} [\lambda G(P, T, n_A, n_B, n_C, n_D)] &= G(P, T, n_A, n_B, n_C, n_D) = n_A \left( \frac{\partial G}{\partial (\lambda n_A)} \right)_{PT} + n_B \left( \frac{\partial G}{\partial (\lambda n_B)} \right)_{PT} \\ &\quad + n_C \left( \frac{\partial G}{\partial (\lambda n_C)} \right)_{PT} + n_D \left( \frac{\partial G}{\partial (\lambda n_D)} \right)_{PT} \end{aligned}$$

Since this must be true for any  $\lambda$ , it must be true for  $\lambda = 1$ . We find

$$G(P, T, n_A, n_B, n_C, n_D) = \mu_A n_A + \mu_B n_B + \mu_C n_C + \mu_D n_D$$

The same equation follows from applying Euler's theorem to other state functions. For example, viewing the internal energy as a function of entropy, volume, and composition, we have

$$\lambda E(S, V, n_A, n_B, n_C, n_D) = E(\lambda S, \lambda V, \lambda n_A, \lambda n_B, \lambda n_C, \lambda n_D)$$

so that

$$\begin{aligned} \frac{d}{d\lambda} [\lambda E(S, V, n_A, n_B, n_C, n_D)] &= E(S, V, n_A, n_B, n_C, n_D) = S \left( \frac{\partial E}{\partial (\lambda S)} \right)_V + V \left( \frac{\partial E}{\partial (\lambda V)} \right)_S + n_A \left( \frac{\partial E}{\partial (\lambda n_A)} \right)_{SV} \\ &\quad + n_B \left( \frac{\partial E}{\partial (\lambda n_B)} \right)_{SV} + n_C \left( \frac{\partial E}{\partial (\lambda n_C)} \right)_{SV} + n_D \left( \frac{\partial E}{\partial (\lambda n_D)} \right)_{SV} \end{aligned}$$

Setting  $\lambda = 1$ , we have

$$E(S, V, n_A, n_B, n_C, n_D)$$

$$= TS - PV + \mu_A n_A + \mu_B n_B + \mu_C n_C + \mu_D n_D$$

which we can rearrange to

$$G = E - TS + PV = \mu_A n_A + \mu_B n_B + \mu_C n_C + \mu_D n_D$$

This equation describes any system whose thermodynamic functions are continuous functions of one another. Evidently, we can model the thermodynamic functions of any such system by modeling the chemical potentials of its components. In the remainder of this chapter, we develop this idea.

By definition,  $\Delta_r G$  is the Gibbs free energy change for converting  $a$  moles of  $A$  and  $b$  moles of  $B$  to  $c$  moles of  $C$  and  $d$  moles of  $D$  at constant pressure and temperature and while the composition remains constant at  $n_A$ ,  $n_B$ ,  $n_C$ , and  $n_D$ . That is,

$$\Delta_r G = G(n_A, n_B, n_C + c, n_D + d) - G(n_A + a, n_B + b, n_C, n_D)$$

where  $n_A \gg a$ ,  $n_B \gg b$ ,  $n_C \gg c$ , and  $n_D \gg d$ . Using the relationship we have just found between  $G$  and the  $n_i$ , we have

$$\begin{aligned} \Delta_r G &= [\mu_A n_A + \mu_B n_B + \mu_C (n_C + c) + \mu_D (n_D + d)] \\ &\quad - [\mu_A (n_A + a) + \mu_B (n_B + b) + \mu_C n_C + \mu_D n_D] \\ &= c\mu_C + d\mu_D - a\mu_A - b\mu_B \\ &= \Delta_r \mu \end{aligned}$$

Since any other extensive thermodynamic function is also homogeneous of order one in the composition variables, a similar relationship will exist between the change in the function itself and its partial molar derivatives. For example, expressing the system volume as a function of pressure, temperature, and composition, we have

$$\lambda V(P, T, n_A, n_B, n_C, n_D) = V(P, T, \lambda n_A, \lambda n_B, \lambda n_C, \lambda n_D)$$

and a completely parallel derivation shows that the volume of the system is related to the partial molar volumes of the components by

$$V(P, T, n_A, n_B, n_C, n_D) = \bar{V}_A n_A + \bar{V}_B n_B + \bar{V}_C n_C + \bar{V}_D n_D$$

The volume change for the reaction is given by

$$\Delta_r V = c\bar{V}_C + d\bar{V}_D - a\bar{V}_A - b\bar{V}_B$$

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