

For  $dG^{\text{tot}}$  we substitute eq. (10.4), for  $G^{\text{tot}}$  we substitute  $H^{\text{tot}} - TS^{\text{tot}}$ , and with some straightforward manipulation the result is

$$d\left(\frac{G^{\text{tot}}}{RT}\right) = -\frac{H^{\text{tot}}}{RT^2}dT + \frac{V^{\text{tot}}}{RT}dP + \sum_i \frac{\mu_i}{RT}dn_i. \quad (10.5)$$

This expression is equivalent to eq. (10.4). It has the advantage that it is in dimensionless form and involves the enthalpy, rather than the entropy of the mixture.

### Multicomponent Equilibrium

When a mixture is brought into the two-phase region, it splits into two phases, each with its own composition. The situation is shown schematically in Figure 10-1. On a microscopic basis, molecules of both components pass continuously from one phase to the other. It is this molecular transfer that allows the system to find and maintain its equilibrium composition. When this composition is reached, the net transfer between phases is zero. Molecules continue to cross the interface in such way that the rate of transfer in one direction matches the rate in the reverse direction, so that the average (macroscopic) composition of each phase remains constant. We analyze this situation as follows. We form a mixture by mixing  $n_1$  moles of component 1 with  $n_2$  moles of component 2, and fix the temperature and pressure of the system. Next, we take an arbitrary number  $n_1^V$  moles of component 1 and  $n_2^V$  moles of component 2 and place them in the vapor phase, with the remaining moles placed in the liquid. Out of the infinitely many ways that the two components can be partitioned between the two phases, only one corresponds to the true equilibrium state. To identify the equilibrium state we apply the Gibbs inequality in eq. (10.1): since the Gibbs free energy must be at a minimum, if we transfer as small amount  $\delta n_i$  of component  $i$  from one phase to the other, the Gibbs energy must remain unchanged. That's because this change takes place at the bottom of the Gibbs curve (see Figure 4-7) where its derivative is flat. Suppose that we transfer  $\delta n_i$  mole of component  $i$  from the liquid to the vapor. The change in the Gibbs energy of the liquid is  $-\mu_i^L \delta n_i$

replace "as" with "a"

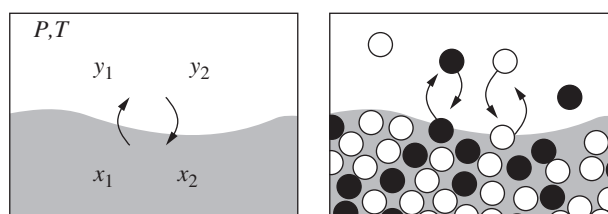


Figure 10-1: Macroscopic and molecular view of vapor-liquid equilibrium.