7.4: The Gibbs-Duhem Equation

For a system at **equilibrium**, the Gibbs-Duhem equation must hold:

$$\sum_i n_i d\mu_i = 0 \tag{7.4.1}$$

This relationship places a compositional constraint upon any changes in the chemical potential in a mixture at constant temperature and pressure for a given composition. This result is easily derived when one considers that μ_i represents the partial molar Gibbs function for component i. And as with other partial molar quantities,

$$G_{tot} = \sum_i n_i \mu_i$$

Taking the derivative of both sides yields

$$dG_{tot} = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i$$

But dG can also be expressed as

$$dG = Vdp - sdT + \sum_i \mu_i dn_i$$

Setting these two expressions equal to one another

$$\sum_i n_i d\mu_i + \cancel{\sum_i \mu_i dn_i} = Vdp - sdT + \cancel{\sum_i \mu_i dn_i}$$

And after canceling terms, one gets

$$\sum_i n_i d\mu_i = Vdp - sdT \tag{7.4.2}$$

For a system at constant temperature and pressure

$$Vdp - sdT = 0 \tag{7.4.3}$$

Substituting Equation 7.4.3 into 7.4.2 results in the **Gibbs-Duhem equation** (Equation 7.4.1). This expression relates how the chemical potential can change for a given composition while the system maintains equilibrium. So for a binary system, consisting of components A and B (the two most often studied compounds in all of chemistry)

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A$$