

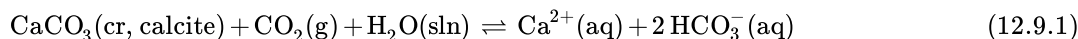
12.9: Reaction Equilibria

The definition of the thermodynamic equilibrium constant of a reaction or other chemical process is given by Eq. 11.8.9:

$$K = \prod_i (a_i)_{\text{eq}}^{\nu_i} \quad (12.9.1)$$

The activity a_i of each reactant or product species is based on an appropriate standard state. We can replace each activity on the right side of Eq. 12.9.1 by an expression in Table 12.2.

For example, consider the following heterogeneous equilibrium that is important in the formation of limestone caverns:



If we treat H_2O as a solvent and Ca^{2+} and HCO_3^{-} as the solute species, then we write the thermodynamic equilibrium constant as follows:

$$K = \frac{a_+ a_-^2}{a_{\text{CaCO}_3} a_{\text{CO}_2} a_{\text{H}_2\text{O}}} = \Gamma_r \frac{\gamma_+ \gamma_-^2 m_+ m_-^2 / (m^\circ)^3}{(f_{\text{CO}_2}/p^\circ) \gamma_{\text{H}_2\text{O}} x_{\text{H}_2\text{O}}} \quad (12.9.2)$$

The subscripts $+$ and $-$ refer to the Ca^{2+} and HCO_3^{-} ions, and all quantities are for the system at reaction equilibrium. Γ_r is the proper quotient of pressure factors, given for this reaction by

$$\Gamma_r = \frac{\Gamma_+ \Gamma_-^2}{\Gamma_{\text{CaCO}_3} \Gamma_{\text{H}_2\text{O}}} \quad (12.9.3)$$

Unless the pressure is very high, we can with little error set the value of Γ_r equal to unity.

The product $\Gamma_+ \Gamma_-^2$ in the numerator of Eq. 12.9.3 is the pressure factor $\Gamma_{m,B}$ for the solute $\text{Ca}(\text{HCO}_3)_2$ (see Eq. 10.3.11).

Equation 12.9.2 is an example of a “mixed” equilibrium constant—one using more than one kind of standard state. From the definition of the mean ionic activity coefficient (Eq. 10.3.7), we can replace the product $\gamma_+ \gamma_-^2$ by γ_{\pm}^3 , where γ_{\pm} is the mean ionic activity coefficient of aqueous $\text{Ca}(\text{HCO}_3)_2$:

$$K = \Gamma_r \frac{\gamma_{\pm}^3 m_+ m_-^2 / (m^\circ)^3}{(f_{\text{CO}_2}/p^\circ) \gamma_{\text{H}_2\text{O}} x_{\text{H}_2\text{O}}} \quad (12.9.4)$$

Instead of treating the aqueous Ca^{2+} and HCO_3^{-} ions as solute species, we can regard the dissolved $\text{Ca}(\text{HCO}_3)_2$ electrolyte as the solute and write

$$K = \frac{a_{m,B}}{a_{\text{CaCO}_3} a_{\text{CO}_2} a_{\text{H}_2\text{O}}} \quad (12.9.5)$$

We then obtain Eq. 12.9.4 by replacing $a_{m,B}$ with the expression in Table 12.2 for an electrolyte solute.

The value of K depends only on T , and the value of Γ_r depends only on T and p . Suppose we dissolve some NaCl in the aqueous phase while maintaining the system at constant T and p . The increase in the ionic strength will alter γ_{\pm} and necessarily cause a compensating change in the solute molarity in order for the system to remain in reaction equilibrium.

An example of a different kind of reaction equilibrium is the dissociation (ionization) of a weak monoprotic acid such as acetic acid



for which the thermodynamic equilibrium constant (the *acid dissociation constant*) is

$$K_a = \Gamma_r \frac{\gamma_+ \gamma_- m_+ m_-}{\gamma_{m,\text{HA}} m_{\text{HA}} m^\circ} = \Gamma_r \frac{\gamma_{\pm}^2 m_+ m_-}{\gamma_{m,\text{HA}} m_{\text{HA}} m^\circ} \quad (12.9.6)$$

Suppose the solution is prepared from water and the acid, and H^+ from the dissociation of H_2O is negligible compared to H^+ from the acid dissociation. We may then write $m_+ = m_- = \alpha m_B$, where α is the degree of dissociation and m_B is the overall molality of the acid. The molality of the undissociated acid is $m_{\text{HA}} = (1 - \alpha)m_B$, and the dissociation constant can be written

$$K_a = \Gamma_r \frac{\gamma_{\pm}^2 \alpha^2 m_B / m^{\circ}}{\gamma_{m,HA} (1 - \alpha)} \quad (12.9.7)$$

From this equation, we see that a change in the ionic strength that decreases γ_{\pm} when T , p , and m_B are held constant must increase the degree of dissociation (Prob. 12.17).

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