

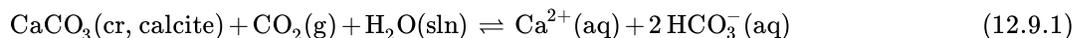
## 12.9: Reaction Equilibria

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  $\text{H}_2\text{O}$  as a solvent and  $\text{Ca}^{2+}$  and  $\text{HCO}_3^{-}$  as the solute species, then we write the thermodynamic equilibrium constant as follows:

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

The subscripts + and – refer to the  $\text{Ca}^{2+}$  and  $\text{HCO}_3^{-}$  ions, and all quantities are for the system at reaction equilibrium.  $\Gamma_{\text{r}}$  is the proper quotient of pressure factors, given for this reaction by

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

Unless the pressure is very high, we can with little error set the value of  $\Gamma_{\text{r}}$  equal to unity.

The product  $\Gamma_+ \Gamma_-^2$  in the numerator of Eq. 12.9.3 is the pressure factor  $\Gamma_{m,\text{B}}$  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  $\gamma_{\pm}^3$ , where  $\gamma_{\pm}$  is the mean ionic activity coefficient of aqueous  $\text{Ca}(\text{HCO}_3)_2$ :

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

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

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

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

The value of  $K$  depends only on  $T$ , and the value of  $\Gamma_{\text{r}}$  depends only on  $T$  and  $p$ . Suppose we dissolve some  $\text{NaCl}$  in the aqueous phase while maintaining the system at constant  $T$  and  $p$ . The increase in the ionic strength will alter  $\gamma_{\pm}$  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

$$K_{\text{a}} = \Gamma_{\text{r}} \frac{\gamma_+ \gamma_- m_+ m_-}{\gamma_{m,\text{HA}} m_{\text{HA}} m^\circ} = \Gamma_{\text{r}} \frac{\gamma_{\pm}^2 m_+ m_-}{\gamma_{m,\text{HA}} m_{\text{HA}} m^\circ} \quad (12.9.6)$$

Suppose the solution is prepared from water and the acid, and  $\text{H}^+$  from the dissociation of  $\text{H}_2\text{O}$  is negligible compared to  $\text{H}^+$  from the acid dissociation. We may then write  $m_+ = m_- = \alpha m_{\text{B}}$ , where  $\alpha$  is the degree of dissociation and  $m_{\text{B}}$  is the overall molality of the acid. The molality of the undissociated acid is  $m_{\text{HA}} = (1 - \alpha)m_{\text{B}}$ , 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  $\gamma_{\pm}$  when  $T$ ,  $p$ , and  $m_B$  are held constant must increase the degree of dissociation (Prob. 12.17).

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