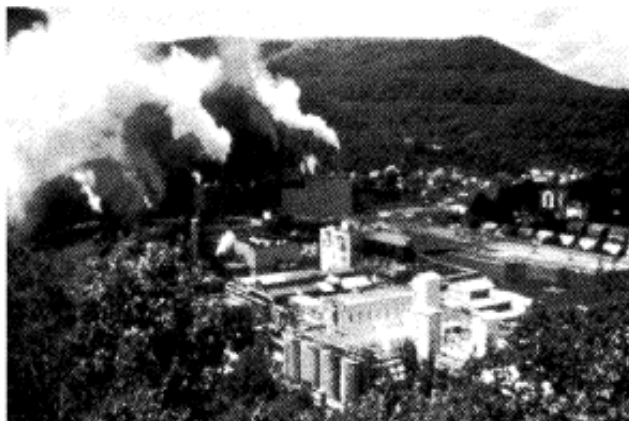


6

Chemical Equilibrium

CHEMICAL EQUILIBRIUM IN THE ENVIRONMENT

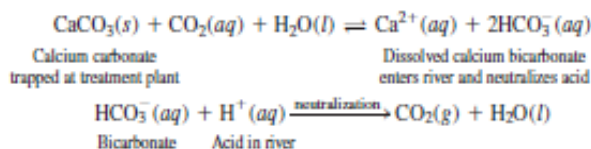


Paper mill on the Potomac River near Westernport, Maryland, neutralizes acid mine drainage in the water. Upstream of the mill, the river is acidic and lifeless; below the mill, the river teems with life. [Photo courtesy C. Dalpra, Potomac River Basin Commission.]



Great Barrier Reef and other coral reefs are threatened with extinction by rising atmospheric CO_2 . [Copyright Jon Arnold Images/Alamy.]

Part of the North Branch of the Potomac River runs crystal clear through the scenic Appalachian Mountains, but it is lifeless—a victim of acid drainage from abandoned coal mines. As the river passes a paper mill and a wastewater treatment plant near Westernport, Maryland, the pH rises from an acidic, lethal value of 4.5 to a neutral value of 7.2, at which fish and plants thrive. This happy “accident” comes about because calcium carbonate exiting the paper mill equilibrates with massive quantities of carbon dioxide from bacterial respiration at the sewage treatment plant. The resulting soluble bicarbonate neutralizes the acidic river and restores life downstream of the plant.¹ In the absence of CO_2 , solid CaCO_3 would be trapped at the treatment plant and would never enter the river.



The chemistry that helps the Potomac River endangers coral reefs, which are largely CaCO_3 . Burning of fossil fuel has increased CO_2 in the atmosphere from 280 ppm when Captain Cook first sighted the Great Barrier Reef in 1770 to 380 ppm today (Figure 0-6). CO_2 in the atmosphere adds CO_2 to the ocean, dissolving CaCO_3 from coral. Rising CO_2 and, perhaps, rising atmospheric temperature from the greenhouse effect threaten coral reefs with extinction.² CO_2 has lowered the average pH of the ocean from its preindustrial value of 8.16 to 8.04 today.³ Without changes in man’s activities, the pH could be 7.7 by 2100.

Chemical equilibrium provides a foundation not only for chemical analysis, but also for other subjects such as biochemistry, geology, and oceanography. This chapter introduces equilibria for the solubility of ionic compounds, complex formation, and acid-base reactions.

6-1 The Equilibrium Constant

For the reaction



we write the **equilibrium constant**, K , in the form

Equilibrium constant:
$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (6-2)$$

where the lowercase superscript letters denote stoichiometry coefficients and each capital letter stands for a chemical species. The symbol $[A]$ stands for the concentration of A relative to its standard state (defined next). By definition, a reaction is favored whenever $K > 1$.

In the thermodynamic derivation of the equilibrium constant, each quantity in Equation 6-2 is expressed as the *ratio* of the concentration of a species to its concentration in its **standard state**. For solutes, the standard state is 1 M. For gases, the standard state is 1 bar ($\approx 10^5$ Pa; 1 atm ≈ 1.01325 bar), and for solids and liquids, the standard states are the pure solid or liquid. It is understood that $[A]$ in Equation 6-2 really means $[A]/(1 \text{ M})$ if A is a solute. If D is a gas, $[D]$ really means (pressure of D in bars)/(1 bar). To emphasize that $[D]$ means pressure of D , we usually write P_D in place of $[D]$. The terms in Equation 6-2 are actually dimensionless; therefore, all equilibrium constants are dimensionless.

For the ratios $[A]/(1 \text{ M})$ and $[D]/(1 \text{ bar})$ to be dimensionless, $[A]$ must be expressed in moles per liter (M), and $[D]$ must be expressed in bars. If C were a pure liquid or solid, the ratio $[C]/(\text{concentration of } C \text{ in its standard state})$ would be unity (1) because the standard state is the pure liquid or solid. If C is a solvent, the concentration is so close to that of pure liquid C that the value of $[C]$ is still essentially 1.

The take-home lesson is this: When you evaluate an equilibrium constant,

1. Concentrations of solutes should be expressed as moles per liter.
2. Concentrations of gases should be expressed in bars.
3. Concentrations of pure solids, pure liquids, and solvents are omitted because they are unity.

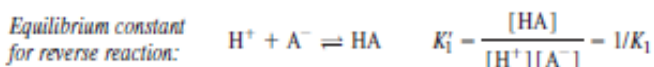
These conventions are arbitrary, but you must use them if you wish to use tabulated values of equilibrium constants, standard reduction potentials, and free energies.

Manipulating Equilibrium Constants

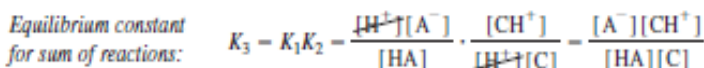
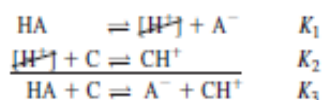
Consider the reaction



If the direction of a reaction is reversed, the new value of K is simply the reciprocal of the original value of K .



If two reactions are added, the new K is the product of the two individual values:



If n reactions are added, the overall equilibrium constant is the product of n individual equilibrium constants.

Equation 6-2, the *law of mass action*, was formulated by the Norwegians C. M. Guldenberg and P. Waage in 1864. Their derivation was based on the idea that the forward and reverse rates of a reaction at equilibrium must be equal.⁴

The equilibrium constant is more correctly expressed as a ratio of activities rather than of concentrations. We reserve the discussion of activity for Chapter 7.

Equilibrium constants are dimensionless.

Equilibrium constants are dimensionless but, when specifying concentrations, you must use units of molarity (M) for solutes and bars for gases.

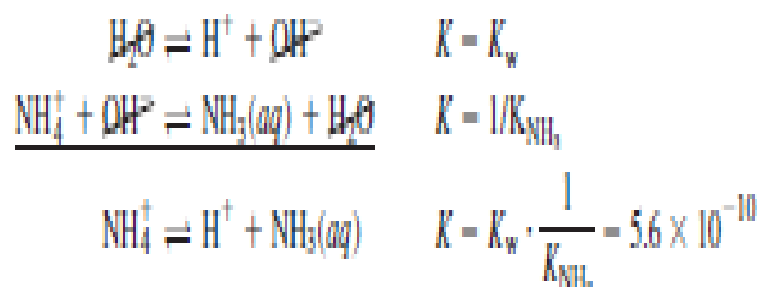
Throughout this book, assume that all species in chemical equations are in aqueous solution, unless otherwise specified.

If a reaction is reversed, then $K' = 1/K$. If two reactions are added, then $K_3 = K_1 K_2$.

EXAMPLE Combining Equilibrium Constants

The equilibrium constant for the reaction $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ is called K_w ($= [\text{H}^+][\text{OH}^-]$) and has the value 1.0×10^{-14} at 25°C . Given that $K_{\text{NH}_4} = 1.8 \times 10^{-5}$ for the reaction $\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$, find K for the reaction $\text{NH}_4^+ \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}^+$.

Solution The third reaction can be obtained by reversing the second reaction and adding it to the first reaction:



Test Yourself For the reaction $\text{Li}^+ + \text{H}_2\text{O} \rightleftharpoons \text{Li}(\text{OH})(\text{aq}) + \text{H}^+$, $K_{\text{Li}} = 2.3 \times 10^{-14}$. Combine this reaction with the K_w reaction to find the equilibrium constant for the reaction $\text{Li}^+ + \text{OH}^- \rightleftharpoons \text{Li}(\text{OH})(\text{aq})$. (Answer: 2.3)