

## **LECTURE – 3**

### **Chemical Equilibrium**

**2.1 Reversible Reactions and Chemical Equilibrium**

**2.2 Thermodynamics and Equilibrium Chemistry**

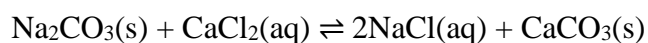
**2.3 Manipulating Equilibrium Constants**

**2.4 Equilibrium Constants for Chemical Reactions**

**2.4.1 Precipitation Reactions**

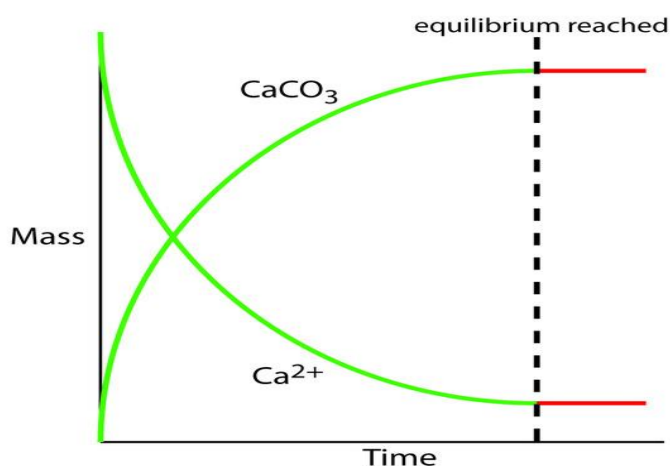
## 1.1: Reversible Reactions and Chemical Equilibrium

For example, the following reaction :



Berthollet's reasoning that reactions are reversible was an important step in understanding chemical reactivity. When we mix together solutions of  $\text{Na}_2\text{CO}_3$  and  $\text{CaCl}_2$  they react to produce  $\text{NaCl}$  and  $\text{CaCO}_3$ . If during the reaction we monitor the mass of  $\text{Ca}^{2+}$  remaining in solution and the mass of  $\text{CaCO}_3$  that precipitates, the result looks something like Figure 6.1.

At the start of the reaction the mass of  $\text{Ca}^{2+}$  decreases and the mass of  $\text{CaCO}_3$  increases. Eventually the reaction reaches a point after which there is no further change in the amounts of these species. Such a condition is called a state of **equilibrium**.



**Figure 2.1** Graph showing how the masses of  $\text{Ca}^{2+}$  and  $\text{CaCO}_3$  change as a function of time during the precipitation of  $\text{CaCO}_3$ . The dashed line indicates when the reaction reaches equilibrium. Prior to equilibrium the masses of  $\text{Ca}^{2+}$  and  $\text{CaCO}_3$  are **changing**; after reaching equilibrium, their masses remain **constant**.

Although a system at equilibrium appears static on a macroscopic level, it is important to remember that the forward and reverse reactions continue to occur. A reaction at equilibrium exists in a **steady-state**, in which the rate at which a species forms equals the rate at which it is consumed.

## 2.2: Thermodynamics and Equilibrium Chemistry

Thermodynamics is the study of thermal, electrical, chemical, and mechanical forms of energy. The study of thermodynamics crosses many disciplines, including physics, engineering, and chemistry. Of the various branches of thermodynamics, the most important to chemistry is the study of the change in energy during a chemical reaction.

Consider, for example, the general equilibrium reaction shown in Equation 2.2.1, involving the species A, B, C, and D, with stoichiometric coefficients  $a$ ,  $b$ ,  $c$ , and  $d$ .



**NOTE :** For obvious reasons, we call the double arrow,  $\rightleftharpoons$ , an equilibrium arrow. By convention, we identify species on the left side of the equilibrium arrow as reactants, and those on the right side of the equilibrium arrow as products. As Berthollet discovered, writing a reaction in this fashion does not guarantee that the reaction of A and B to produce C and D is favorable. Depending on initial conditions, the reaction may move to the left, move to the right, or be in a state of equilibrium. Understanding the factors that determine the reaction's final, equilibrium position is one of the goals of chemical thermodynamics.

The direction of a reaction is that which lowers the overall free energy. At a constant temperature and pressure, typical of many bench-top chemical reactions, a reaction's free energy is given by the **Gibb's free energy** function

$$\Delta G = \Delta H - T\Delta S \quad (2.2.2)$$

where

- T is the temperature in Kelvin and
- $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  are the differences in the Gibb's free energy, the enthalpy, and the entropy between the products and the reactants.

**Enthalpy** is a measure of the flow of energy, as heat, during a chemical reaction. Reactions releasing heat have a negative  $\Delta H$  and are called exothermic. Endothermic reactions absorb heat from their surroundings and have a positive  $\Delta H$ .

**Entropy** is a measure of energy that is unavailable for useful, chemical work. The entropy of an individual species is always positive and tends to be larger for gases than for solids, and for more complex molecules than for simpler molecules. Reactions producing a large number of simple, gaseous products usually have a positive  $\Delta S$ .

The sign of  $\Delta G$  indicates the direction in which a reaction moves to reach its equilibrium position. A reaction is thermodynamically favorable when its enthalpy,  $\Delta H$ , decreases and its entropy,  $\Delta S$ , increases. Substituting the inequalities  $\Delta H < 0$  and  $\Delta S > 0$  into Equation 6.2.2 shows that a reaction is thermodynamically favorable when  $\Delta G$  is negative. When  $\Delta G$  is positive the reaction is unfavorable as written (although the reverse reaction is favorable). A reaction at equilibrium has a  $\Delta G$  of zero.

**NOTE :** Equation 6.2.2 shows that the sign of  $\Delta G$  depends on the signs of  $\Delta H$  and  $\Delta S$ , and the temperature,  $T$ . The following table summarizes the possibilities.

$\Delta H$	$\Delta S$	$\Delta G$
-	+	$\Delta G < 0$ at all temperatures
-	-	$\Delta G < 0$ at low temperatures
+	+	$\Delta G < 0$ at low temperatures
+	-	$\Delta G > 0$ at all temperatures

As a reaction moves from its initial, non-equilibrium condition to its equilibrium position, the value of  $\Delta G$  approaches zero. At the same time, the chemical species in the reaction experience a change in their concentrations. The Gibb's free energy, therefore, must be a function of the concentrations of reactants and products.

As shown in Equation 6.2.3, we can split the Gibb's free energy into two terms.

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (2.2.3)$$

The first term,  $\Delta G^\circ$ , is the change in Gibb's free energy when each species in the reaction is in its **standard state**, which we define as follows: gases with partial pressures of 1 atm, solutes with concentrations of 1 mol/L, and pure solids and pure liquids. The second term, which includes the reaction quotient,  $Q$ , accounts for non-standard state pressures or concentrations. For reaction 6.2.1, the reaction quotient is

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

2.2.4

At equilibrium the Gibb's free energy is zero, and Equation 6.2.3 simplifies to

$$\Delta G^\circ = - RT \ln K \quad (2.2.5)$$

where  $K$  is an **equilibrium constant** that defines the reaction's equilibrium position. The equilibrium constant is just the numerical value of the reaction quotient,  $Q$ , when substituting equilibrium concentrations into Equation 2.2.4 .

Here we include the subscript "eq" to indicate a concentration at equilibrium. Although we usually will omit the "eq" when writing equilibrium constant expressions, it is important to remember that the value of  $K$  is determined by equilibrium concentrations.

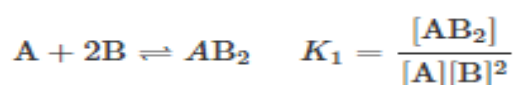
$$K = \frac{[C]_{eq}^c [D]_{eq}^d}{[A]_{eq}^a [B]_{eq}^b}$$

2.2.6

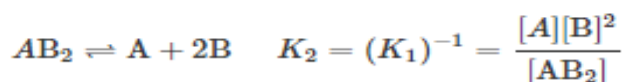
**NOTE :** As written, Equation 6 is a limiting law that applies only to infinitely dilute solutions where the chemical behavior of one species is unaffected by the presence of other species. Strictly speaking, Equation 6 should be written in terms of activities instead of concentrations. We will return to this point in Section 6I. For now, we will stick with concentrations as this convention is already familiar to you.

### 2.3: Manipulating Equilibrium Constants

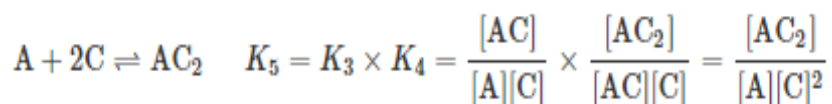
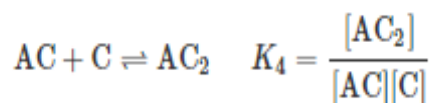
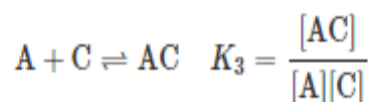
We will take advantage of two useful relationships when working with equilibrium constants. First, if we reverse a reaction's direction, the equilibrium constant for the new reaction is simply the inverse of that for the original reaction. For example, the equilibrium constant for the reaction



is the inverse of that for the reaction

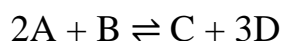


Second, if we add together two reactions to obtain a new reaction, the equilibrium constant for the new reaction is the product of the equilibrium constants for the original reactions.



#### Example 2.1

Calculate the equilibrium constant for the reaction

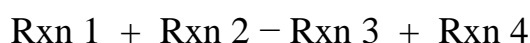


given the following information



### ***Solution***

The overall reaction is equivalent to

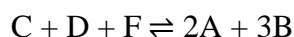


Subtracting a reaction is equivalent to adding the reverse reaction; thus, the overall equilibrium constant is

$$K = \frac{K_1 \times K_2 \times K_4}{K_3} = \frac{0.40 \times 0.10 \times 5.0}{2.0} = 0.10$$

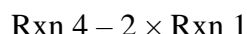
### **Practice Exercise 2.1**

Calculate the equilibrium constant for the reaction



using the equilibrium constants from Example 2.1.

The overall reaction is equivalent to



Subtracting a reaction is equivalent to adding the reverse reaction; thus, the overall equilibrium constant is

$$K = \frac{K_4}{(K_1)^2} = \frac{5.0}{(0.40)^2} = 31.25 \approx 31$$

## **2.4: Equilibrium Constants for Chemical Reactions**

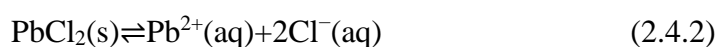
Several types of chemical reactions are important in analytical chemistry, either in preparing a sample for analysis or during the analysis. The most significant of these are: precipitation reactions, acid–base reactions, complexation reactions, and oxidation–reduction (redox) reactions. In this section we review these reactions and their equilibrium constant expressions.

### 2.4.1 Precipitation Reactions

In a precipitation reaction, two or more soluble species combine to form an insoluble **precipitate**. The most common precipitation reaction is a metathesis reaction, in which two soluble ionic compounds exchange parts. For example, if we add a solution of lead nitrate,  $\text{Pb}(\text{NO}_3)_2$ , to a solution of potassium chloride,  $\text{KCl}$ , the result is a precipitate of lead chloride,  $\text{PbCl}_2$ . We usually write a precipitation reaction as a net ionic equation, showing only the precipitate and those ions forming the precipitate. Thus, the precipitation reaction for  $\text{PbCl}_2$  is



When writing an equilibrium constant for a precipitation reaction, we focus on the precipitate's solubility. Thus, for  $\text{PbCl}_2$ , the solubility reaction is



and its equilibrium constant, which we call the **solubility product**,  $K_{\text{sp}}$ , is

$$K_{\text{sp}} = [\text{Pb}^{2+}] [\text{Cl}^{-}]^2 = 1.7 \times 10^{-5} \quad (2.4.3)$$

Even though it does not appear in the  $K_{\text{sp}}$  expression, it is important to remember that equation 2.4.3 is valid only if  $\text{PbCl}_2(\text{s})$  is present and in equilibrium with  $\text{Pb}^{2+}$  and  $\text{Cl}^{-}$ . You will find values for selected solubility products in [Appendix 10](#).

## Example 2.2

How many grams of  $\text{Ba}(\text{IO}_3)_2$  (487 g/mol) can be dissolved in 500 mL of water at 25°C?

The solubility product constant for  $\text{Ba}(\text{IO}_3)_2$  is  $1.57 \times 10^{-9}$  (see Appendix 2). The equilibrium between the solid and its ions in solution is described by the equation



and so

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{IO}_3^-]^2 = 1.57 \times 10^{-9}$$

The equation describing the equilibrium reveals that 1 mol of  $\text{Ba}^{2+}$  is formed for each mole of  $\text{Ba}(\text{IO}_3)_2$  that dissolves. Therefore,

$$\text{molar solubility of } \text{Ba}(\text{IO}_3)_2 = [\text{Ba}^{2+}]$$

Since two moles of iodate are produced for each mole of barium ion, the iodate concentration is twice the barium ion concentration:

$$[\text{IO}_3^-] = 2[\text{Ba}^{2+}]$$

Substituting this last equation into the equilibrium-constant expression gives

$$[\text{Ba}^{2+}](2[\text{Ba}^{2+}])^2 = 4[\text{Ba}^{2+}]^3 = 1.57 \times 10^{-9}$$

$$[\text{Ba}^{2+}] = \left( \frac{1.57 \times 10^{-9}}{4} \right)^{1/3} = 7.32 \times 10^{-4} \text{ M}$$

Since 1 mol  $\text{Ba}^{2+}$  is produced for every mole of  $\text{Ba}(\text{IO}_3)_2$ ,

$$\text{solubility} = 7.32 \times 10^{-4} \text{ M}$$

To compute the number of millimoles of  $\text{Ba}(\text{IO}_3)_2$  dissolved in 500 mL of solution, we write

$$\text{no. mmol } \text{Ba}(\text{IO}_3)_2 = 7.32 \times 10^{-4} \frac{\text{mmol } \text{Ba}(\text{IO}_3)_2}{\text{mL}} \times 500 \text{ mL}$$

The mass of  $\text{Ba}(\text{IO}_3)_2$  in 500 mL is given by

$$\begin{aligned} \text{mass } \text{Ba}(\text{IO}_3)_2 &= \\ & (7.32 \times 10^{-4} \times 500) \text{ mmol } \text{Ba}(\text{IO}_3)_2 \times 0.487 \frac{\text{g } \text{Ba}(\text{IO}_3)_2}{\text{mmol } \text{Ba}(\text{IO}_3)_2} \\ & = 0.178 \text{ g} \end{aligned}$$