Why?
Most chemical reactions are reversible. This means that once products are formed, they can react to reform the reactants. If we allow a reaction to run long enough, it may reach a state where the rate of the forward reaction (forming products) is equal to the rate of the reverse reaction (reforming reactants). When this occurs, the reaction is said to be in equilibrium. At equilibrium reactant and product amounts do not change over time and maintain a fixed ratio, which can be expressed as an equilibrium constant. The concept of the equilibrium constant is one of the most powerful in chemistry, allowing us to calculate amounts of products and remaining reactants in real reaction mixtures.

Learning Objectives
• Understand the meaning of dynamic equilibrium
• Understand how the differential rate expressions for the forward and reverse processes lead to the definition of the equilibrium constant, \( K \), for the reaction
• Understand how the equilibrium constant, \( K \), is defined from a balanced chemical equation for a reaction
• Understand how to assess changes in reactant and product amounts and to set up calculations of amounts present at equilibrium

Success Criteria
• Be able to write the \( K_c \) expression for any balanced reaction equation
• Be able to calculate the value of \( K_c \) from equilibrium concentration data and stoichiometry
• Be able to use the stoichiometry of a balanced equation to write algebraic expressions for concentrations of reactants and products at equilibrium
• Be able to calculate equilibrium concentrations, given the value of \( K_c \) and initial amounts of reactants and/or products.

Prerequisite
Have read sections 15.1 through 15.6
Key Question (Review & Preparation)

1. Consider the gas phase reaction

\[ 2 \text{N}_2\text{O}_5 \rightarrow 4 \text{NO}_2 + \text{O}_2 \]

for which the observed rate law expression is

\[ \text{Observed Rate} = k[\text{N}_2\text{O}_5] \]

The following mechanism has been proposed:

\[
\begin{align*}
\text{N}_2\text{O}_5 & \rightleftharpoons \text{NO}_2 + \text{NO}_3 & k_1 (\rightarrow), k_{-1} (\leftarrow) & \text{fast equilibrium} \\
\text{NO}_3 + \text{NO}_2 & \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2 & k_2 & \text{slow} \\
\text{NO}_3 + \text{NO} & \rightarrow 2\text{NO}_2 & k_3 & \text{fast}
\end{align*}
\]

Carry out the following steps to show that this is a plausible mechanism.

i. Show that this series of steps adds to give the overall stoichiometry of the reaction. [Hint: One step needs to be multiplied by an integer factor.]

ii. Write the rate law for each step. The first step is reversible, so you will need to write two rate law expressions, one for each direction.

iii. Which step is rate determining. Write its rate law expression.

iv. What species are reaction intermediates?

v. Your rate expression, based on the rate expression for the rate-determining step, contains a concentration term for an unobservable reaction intermediate. We need to express the rate law for the rate determining step in terms of observable starting materials. Note that the first step is a rapidly established equilibrium, which means its rate in the forward direction is exactly the same as in the reverse direction. Write an equality between your two expressions for the two directions, and rearrange it to solve for \([\text{NO}_3] \).

vi. Substitute your expression for \([\text{NO}_3] \) into your expression for the rate law of the rate determining step. Does this agree with the experimentally observed rate law expression?
Information (Dynamic Equilibrium and the Equilibrium Constant)

As a chemical reaction runs to convert reactants into products, the build-up of products increases the likelihood that they will react with each other to reform the reactants. In other words, most real reactions do not run "to completion," meaning total conversion of reactants into products. In the early stages of a chemical reaction, the product concentrations are small and the rate of the reverse reaction is slow. But as product amounts increase, so too does the rate of the reverse reaction. Eventually, there comes a point at which the rate of the forward reaction exactly equals the rate of the reverse reaction. This is the point of *dynamic equilibrium*. The equilibrium state is dynamic, because both the forward and reverse processes are still taking place. Nonetheless, at equilibrium the amounts of reactants and products in the reaction mixture do not change over time. At equilibrium, as soon as a product is formed it reacts by the reverse reaction to reform reactant. Because the amounts of reactants and products do not change over time, there exists a fixed ratio between their amounts. We can define this ratio, called the equilibrium constant, *K*, in such a way that there is a connection between its form and the stoichiometry of the balanced equation. If the amounts of all species are stated in concentrations of mol/L, we call this constant *Kc*. The following steps will take you though the definition of an equilibrium constant for a simple reaction and show you the relationship between its form and the stoichiometry of the balanced equation.

**Key Questions**

2. Consider the following reversible reaction, which is believed to proceed by a one-step mechanism in each direction:

\[
2\text{NO}_2 \xrightleftharpoons{k_f}{k_r} \text{N}_2\text{O}_4
\]

   a. Write the rate expression for each direction.

   b. At equilibrium, the net rate of the reaction is zero, because the rate of the forward reaction is exactly equal to that of the reverse reaction. Set your two rate expressions equal to each other, and solve the equality for *k/fk*. This ratio of constants is itself a constant, which we call the *equilibrium constant*, *Kc*.

Information (Defining the Form of *Kc* from a Balanced Equation)

Note that the expression you have derived for *Kc* is the ratio of the concentration of product, \([\text{N}_2\text{O}_4]\), over the concentration of reactant, \([\text{NO}_2]\), at equilibrium:

\[
K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}
\]
Moreover (and most importantly), each concentration term is raised to a power that is its stoichiometric coefficient in the balanced reaction equation (here, an unwritten 1 for \([\text{N}_2\text{O}_4]\) and a written 2 for \([\text{NO}_2]\)). We will not prove it here, but for a general reaction of the form

\[ aA + bB \rightarrow cC + dD, \]

where the lower case letters represent the stoichiometric coefficients, at equilibrium the concentrations of all species will have specific values that define a constant of the form

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

regardless of the number of steps in the mechanism. Thus, we can write down the form of \(K_e\) by simply noting the stoichiometry of the balanced equation. In doing this, the following conventions are observed:

- For \(K_e\), all concentrations are the values \textit{at equilibrium} in mol/L.
- \(K_e\) is defined as the ratio of equilibrium concentrations of reactants over products, each raised to powers equal to their stoichiometric coefficients in the balanced reaction equation.
- All solids and neat liquids (not solutions) behave as if they have unit concentration and do not appear in the expression for \(K_e\).
- For solutions, solutes appear in the expression for \(K_e\), but solvents are usually omitted, unless the solvent’s concentration could change significantly through active participation in the reaction.
- Non-reactive species, such as spectator ions, are omitted from \(K_e\).
- \(K_e\) is defined for the reaction proceeding in the usual left-to-right manner, as written. The value of \(K_e\) for the reverse reaction is the inverse of that for the forward reaction. For example

\[ 2\text{NO}_2 \leftrightarrow \text{N}_2\text{O}_4 \quad K_e = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} \]

\[ \text{N}_2\text{O}_4 \leftrightarrow 2\text{NO}_2 \quad K'_e = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{1}{K_e} \]
Key Questions

3. Write the expressions for the equilibrium constant, $K_c$, for the following reactions.

a. $N_2(g) + 3H_2(g) ⇌ 2NH_3(g)$

b. $Cu(NO_3)_2(aq) + Zn(s) = Cu(s) + Zn(NO_3)_2(aq)$ [Hint: Write the net ionic equation first.]

c. $CaO(s) + CO_2(g) = CaCO_3(s)$

d. $CaCO_3(s) = CaO(s) + CO_2(g)$
   How does this compare to the expression you wrote for the reverse reaction in part c?

e. $HF(aq) + H_2O(l) ⇌ H_3O^+(aq) + F^-(aq)$ [Hint: H$_2$O(l) is a solvent.]

Information (Setting Up an Equilibrium Calculation)

Very often we use $K_c$ as a basis for calculating amounts of reactants and products present at equilibrium, starting from some initial concentrations. Alternately, we may use information about how initial concentrations change to their values at equilibrium as a means of calculating the value of $K_c$ for the reaction. In either case, it is generally helpful to set up a table, listing initial concentrations, changes to reach equilibrium, and values at equilibrium. Depending on the nature of the problem, some of the entries in this table might be specific numbers, while others may need to be algebraic expressions, based on the stoichiometry of the reaction.

Key Questions

4. Consider the equilibrium

$$HF(aq) + H_2O(l) ⇌ H_3O^+(aq) + F^-(aq)$$

and its $K_c$ as you defined it in Key Question 3.e. A solution of hydrofluoric acid is prepared by dissolving 0.100 mol HF in enough water to make a liter of solution. Once equilibrium is established, the concentration of hydronium ion is found to be $[H_3O^+] = 7.91 \times 10^{-3}$ M.

a. What is the concentration of undissociated HF in the solution? To answer this question, fill in the values in the following table.

<table>
<thead>
<tr>
<th></th>
<th>[HF]</th>
<th>[H$_3$O$^+$]</th>
<th>[F$^-$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start</td>
<td>0.100 M</td>
<td>~0 M</td>
<td>0 M</td>
</tr>
<tr>
<td>Change</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
<td>+7.91 x 10$^{-3}$ M</td>
<td></td>
</tr>
</tbody>
</table>
b. What is the value of $K_c$ for HF?

c. What is the concentration of undissociated HF in a hydrofluoric acid solution in which $[\text{H}_3\text{O}^+] = [\text{F}^-] = 0.0100 \text{ M}$?

d. How many moles per liter of HF were added to make the solution in part c?

**Information (Defining $K$ in Pressure Units)**

We have been discussing the equilibrium constant $K_c$, in which the concentrations are expressed in units of mol/L. If all components that would appear in the expression for the equilibrium constant are gases at constant temperature and volume, it may be more convenient to express the amounts of reactants and products in terms of their partial pressures. This is an application of Gay-Lussac's Law of Combining Gas Volumes, based on the relationship $P = gn$.

Consider the Haber process at equilibrium:

$$\text{N}_2(g) + 3 \text{H}_2(g) \leftrightarrow 2 \text{NH}_3(g)$$

We could define the equilibrium constant for this gas-phase reaction either in terms of concentrations ($K_c$) or in terms of pressures ($K_p$). If we chose units of mol/L we would define $K_c$ as

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

In terms of partial pressures, we could define the equilibrium constant $K_p$ as

$$K_p = \frac{(p_{\text{NH}_3})^2}{(p_{\text{N}_2})(p_{\text{H}_2})^3}$$

Will $K_p$ and $K_c$ have the same numerical value for this reaction? Except in special cases, the answer is “no.” To see why there is a difference, let us convert pressures in $K_p$ to moles per liter using the relationship

$$p = (n/V)RT$$

Recognizing that $n/V$ is mol/L, for each component we have an expression of the form

$$p_A = (n_A/V)RT = [A]RT$$

Substituting into the expression for $K_p$, we obtain

$$K_p = \frac{(p_{\text{NH}_3})^2}{(p_{\text{N}_2})RT(p_{\text{H}_2})^3} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}(RT)^{-2}$$

The first part of this is just $K_c$, so we may write
\[ K_p = K_c (RT)^{\Delta n} \]

Notice that the exponent on the \(RT\) term is the difference between the sum of coefficients on gas products minus the sum of coefficients on gas reactants:

\[ \Delta n = (2) - (1 + 3) = -2 \]

As this specific example shows, the general relationship between \(K_c\) and \(K_p\) is expressed by the equation

\[ K_p = K_c (RT)^{\Delta n} \]

The following examples illustrate:

1. \(2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)\)
   \[ \Delta n = 1 - 2 = -1 \quad K_p = K_c (RT)^{-1} \]

2. \(\text{H}_2(g) + \text{I}_2(g) = 2 \text{HI}(g)\)
   \[ \Delta n = 2 - 2 = 0 \quad K_p = K_c \quad \text{Note!} \]

3. \(\text{CaO}(s) + \text{CO}_2(g) = \text{CaCO}_3(s)\)
   \[ \Delta n = 0 - 1 = -1 \quad K_p = K_c (RT)^{-1} \]

Notice in the second example that \(K_p = K_c\). This will only be true when the sum of gas coefficients for reactants and products are the same. Otherwise, \(K_p \neq K_c\). In the last example, notice that only coefficients of gas species are counted in calculating \(\Delta n\). The solids are not in the defining expression of either \(K_p\) or \(K_c\).

**Key Question**

5. At 1000 K, the value of \(K_c\) is 4.08 \times 10^{-3} for the equilibrium

   \[ 2 \text{SO}_3(g) \rightleftharpoons 2 \text{SO}_2(g) + \text{O}_2(g) \]

   What is the value of \(K_p\)? [\(R = 0.0821 \text{ L·atm/K·mol}\)]

6. At 800K, the value of \(K_p\) is 4.55 \text{ atm}^{-1} for the equilibrium

   \[ \text{CaO}(s) + \text{CO}_2(g) \rightleftharpoons \text{CaCO}_3(s) \]

   What is the value of \(K_c\)?