Big Idea #6
Equilibrium

What is chemical equilibrium?

- Systems that have reached the state where the rates of the forward reaction and the reverse reaction are constant and equal.
- It is a dynamic process where reactants continuously form products and vice versa, but the net amounts of reactants and products remain constant.
- The proportions of products and reactants formed in a system at a specific temperature that has achieved equilibrium is represented by $K$, the equilibrium constant.

LO 6.1: Given a set of experimental observations regarding processes that are reversible, construct an explanation that connects the observations to the reversibility of the underlying chemical reactions or processes.
Manipulating \( Q \) and \( K \)

- \( K \) (equilibrium constant) represents the relative amounts of products to reactants at equilibrium at a given temperature.
- \( Q \) (reaction progress) describes the relative amounts of products to reactants present at any point in the reaction at a given temperature.

\[ K = \frac{[\text{products}]}{[\text{reactants}]} \]

\[ Q = \frac{[\text{products}]}{[\text{reactants}]} \]

\( Q \) and \( K \) only include substances that are gases or in aqueous solutions. No solids or liquids are ever included in these expressions.

Similar reactions will have related \( K \) values at the same temperature.

Kinetics and Equilibrium

- Kinetics examines the rate at which reactions proceed. Rate laws are used to describe how reactant concentrations affect a reaction’s rate. Rate constants (\( k \)) in rate law expressions are determined experimentally at a given temperature.
- Equilibrium describes the state at which the rates of the forward reaction and the reverse reaction are constant and equal.
- If the rates are initially unequal (the system is not at equilibrium), the faster direction depletes its reactants, which feeds back to slow down that direction.
- At the same time, the slower direction accumulates its reactants, speeding up the slower direction.
- These loops continue until the faster rate and the slower rate have become equal.
- In the graph to the right, after equilibrium has been achieved, additional hydrogen gas is added to the system. The system then consumes both \( H_2 \) and \( N_2 \) to form additional \( NH_3 \) molecules, eventually reestablishing equilibrium.

\( Q \) vs. \( K \)

- Equilibrium is reached when the rates of the forward reaction and the rates of the reverse reaction are equal, which is when \( Q \) is equal to \( K \).
- Comparing \( Q \) to \( K \) enables us to determine if a chemical system has achieved equilibrium or will need to move towards reactants or products to reach equilibrium.
  - If \( Q < K \), the reaction will proceed in the forward direction until \( Q = K \)
  - If \( Q > K \), the reaction will proceed in the reverse direction until \( Q = K \)
  - If \( Q = K \), the reaction is at equilibrium, and the concentrations of reactants and products remain constant.

\[ K = \frac{[\text{products}]}{[\text{reactants}]} \]

\[ Q = \frac{[\text{products}]}{[\text{reactants}]} \]

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LO 6.2: The student can, given a manipulation of a chemical reaction or set of reactions (e.g., reversal of reaction or addition of two reactions), determine the effects of that manipulation on \( Q \) or \( K \).

LO 6.3: The student can connect kinetics to equilibrium by using reasoning, such as LeChatelier’s principle, to infer the relative rates of the forward and reverse reactions.

LO 6.4: Given a set of initial conditions and the equilibrium constant, \( K \), use the tendency of \( Q \) to approach \( K \) to predict and justify the prediction as to whether the reaction will proceed toward products or reactants as equilibrium is approached.
Calculating Equilibrium Constants with $K$

- Equilibrium concentrations can be calculated using a $K$ expression, the $K$ constant, and initial concentrations or partial pressures of substances.

Steps:
1. Write an equilibrium expression for the reaction.
2. Set up an ICE table and fill in “initial” quantities.
3. Determine “changes” in the system in terms of $x$ needed for the system to achieve equilibrium.
4. Determine the “equilibrium” values for the system by adding the “initial” and “change” values together.
5. Solve for $x$ using the $K$ expression and the “equilibrium” values.
6. Verify if the change in initial concentrations is negligible using the 5% rule.
7. Determine all equilibrium quantities using the value of $x$.

Example: Given the following reaction at 1373 K: $\text{Cl}_2(g) \rightleftharpoons 2\text{Cl}(g)$, determine the equilibrium partial pressures of all species if 0.500 atm of $\text{Cl}_2$ is present initially. $K = 1.13 \times 10^{-4}$ for the reaction at 1373 K.

LO 6.6: Given a set of initial conditions (concentrations or partial pressures) and $K$, use stoichiometric relationships and the law of mass action ($Q$ equals $K$ at equilibrium) to determine qualitatively and/or quantitatively the conditions at equilibrium for a system involving a single reversible reaction.
LO 6.7: The student is able, for a reversible reaction that has a large or small $K$, to determine which chemical species will have very large versus very small concentrations at equilibrium.

+ **Magnitude of $K$**

- For many reactions involving aqueous solutions, $K$ is either very large (favoring the forward reaction) or very small (favoring the reverse reaction).
- The size of $K$ can be used to describe the relationship between the numbers of reactant and product particles present at equilibrium.

<table>
<thead>
<tr>
<th>Small ($K &lt; 10^{-5}$)</th>
<th>Intermediate ($10^{-5} \leq K \leq 10^{5}$)</th>
<th>Large ($K &gt; 10^{5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mostly reactants</td>
<td>Significant amounts of reactants and products</td>
<td>Mostly products</td>
</tr>
</tbody>
</table>

For many reactions involving aqueous solutions, $K$ is either very large (favoring the forward reaction) or very small (favoring the reverse reaction). The size of $K$ can be used to describe the relationship between the numbers of reactant and product particles present at equilibrium.

LO 6.8: The student is able to use Le Chatelier’s principle to predict the direction of the shift resulting from various possible stresses on a system at chemical equilibrium.

+ **Le Chatelier’s Principle**

- This principle is used to describe changes that occur in a system that has achieved equilibrium. There are three factors that can cause shifts in a system at equilibrium: concentration, pressure, and temperature.

<table>
<thead>
<tr>
<th>Change</th>
<th>Direction System Shifts to Reestablish Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adding a reactant</td>
<td>Shifts towards products</td>
</tr>
<tr>
<td>Adding a product</td>
<td>Shifts towards reactants</td>
</tr>
<tr>
<td>Removing a reactant</td>
<td>Shifts towards reactants</td>
</tr>
<tr>
<td>Removing a product</td>
<td>Shifts towards products</td>
</tr>
<tr>
<td>Increasing pressure (increasing volume)</td>
<td>Shifts towards less gas molecules</td>
</tr>
<tr>
<td>Decreasing pressure (decreasing volume)</td>
<td>Shifts towards more gas molecules</td>
</tr>
<tr>
<td>Decreasing temperature</td>
<td>Exothermic: shifts towards products</td>
</tr>
<tr>
<td>Increasing temperature</td>
<td>Endothermic: shifts towards reactants</td>
</tr>
<tr>
<td>Adding an inert gas</td>
<td>No effect</td>
</tr>
</tbody>
</table>

Systems at equilibrium can be examined using Le Chatelier’s Principle by measuring its properties, including pH, temperature, solution color (absorbance).

LO 6.9: The student is able to use Le Chatelier’s principle to design a set of conditions that will optimize a desired outcome, such as product yield.

+ **Experimentally Examining Le Chatelier’s Principle**

- Systems at equilibrium can be examined using Le Chatelier’s Principle by measuring its properties, including pH, temperature, solution color (absorbance).

Fe$^{3+}$(aq) + SCN$^-$ (aq) $\rightleftharpoons$ FeSCN$^{2+}$(aq)
Changes to $Q$ and $K$ for a System at Equilibrium

<table>
<thead>
<tr>
<th>Change</th>
<th>Direction System Shifts to Reestablish Equilibrium</th>
<th>Effect on $Q$ or $K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adding a reactant</td>
<td>Shifts towards products</td>
<td>$Q$ decreases</td>
</tr>
<tr>
<td>Adding a product</td>
<td>Shifts towards reactants</td>
<td>$K$ increases</td>
</tr>
<tr>
<td>Removing a reactant</td>
<td>Shifts towards reactants</td>
<td>$Q$ increases</td>
</tr>
<tr>
<td>Removing a product</td>
<td>Shifts towards products</td>
<td>$K$ decreases</td>
</tr>
<tr>
<td>Increasing pressure (decreasing volume)</td>
<td>Shifts towards more gas molecules</td>
<td>$Q$ can increase, decrease, or remain constant depending on ratio of gas molecules between reactants and products</td>
</tr>
<tr>
<td>Removing a reactant (increasing volume)</td>
<td>Shifts towards more gas molecules</td>
<td>$Q$ increases</td>
</tr>
<tr>
<td>Adding an inert gas</td>
<td>No effect</td>
<td>$Q$ doesn't change</td>
</tr>
<tr>
<td>Removing a product</td>
<td>Endothermic shifts towards products</td>
<td>$K$ increases</td>
</tr>
<tr>
<td>Increasing the temperature</td>
<td>Endothermic shifts towards reactants</td>
<td>$K$ decreases</td>
</tr>
</tbody>
</table>

Some changes that occur to a system at equilibrium will affect the reaction's current position ($Q$). Others will affect the value of $K$.

Acid/Base Particulates

Strong: Since $K_a = \frac{[H^+][A^-]}{[HA]} > 1$, at equilibrium strong acids are molecules that essentially ionize to completion in aqueous solution, dissociating into $H_3O^+$ and the additional anion.

Weak: Since $K_a = \frac{[H^+][A^-]}{[HA]} < 1$, at equilibrium weak acids are molecules that only partially ionize in aqueous solution, dissociating into few $H_3O^+$ ions and the additional anion.

pH of Weak or Strong Acid

1. This is a particulate picture of a strong acid whose $[HA] = 0.00100M$.
2. Note the 100% ionization of this acid.
3. If similar volumes of both acids above were titrated with the same strong base, the weak acid would require a larger volume of base to reach its equivalence point.

$pH$ of Weak or Strong Acid

Note the similar $pH$ values of both non-protic acids.
LO 6.13: The student can interpret titration data for monoprotic or polyprotic acids involving titration of a weak or strong acid by a strong base (or a weak or strong base by a strong acid) to determine the concentration of the titrant and the pKₐ for a weak acid, or the pKₐ for a weak base.

+ Titrations

LO 6.14: The student can, based on the dependence of K_w on temperature, reason that neutrality requires [H⁺] = [OH⁻] as opposed to requiring pH = 7, including especially the application to biological systems.

+ K_w and Temperature

\[ K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ C \]

As T increases, pH of pure water decreases. The water is NOT becoming more acidic. A solution is only acidic if [H⁺] > [OH⁻].

At 50°C, the pH of pure water is 6.63, which is defined as "neutral," when [H⁺] = [OH⁻]. A solution with a pH of 7 at this temperature is slightly basic b/c it is higher than the neutral value of 6.43.

The dissociation of water is endothermic. An increase of energy will shift the reaction to the right, increasing the forward reaction, and increase the value of K_w.

LO 6.15: The student can identify a given solution as containing a mixture of strong acids and/or bases and calculate or estimate the pH (and concentrations of all chemical species) in the resulting solution.

+ Acid/Base Mixtures and its pH

A 25 mL sample of hydrofluoric acid (HF) is titrated with 25 mL of 0.30M sodium hydroxide (NaOH). At the equivalence point of the titration, what would the pH of the solution be? Justify with a reaction.

a. pH < 7
b. pH = 7
c. pH > 7
d. pH = pK_a

The correct answer is "c" pH>7. At the equivalence point, the moles of acid equal the moles of base. The remaining species would be Na⁺ and F⁻. The conjugate base, F⁻ will hydrolyze with water, producing OH⁻ in solution:

\[ \text{HF}(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{F}^-(\text{aq}) \]

Select the Source link to see more calculations in this titration.
1. Vinegar is 0.50M acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, with a $K_a = 1.8 \times 10^{-5}$. What would be the pH of this solution?

2. Identify and compare the relative strengths of the two acids and the two bases in this neutralization reaction: $\text{OH}^- (\text{aq}) + \text{NH}_4^+ (\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{NH}_3(\text{aq})$.

LO 6.16: The student can identify a given solution as being the solution of a monoprotic weak acid or base (including salts in which one ion is a weak acid or base), calculate the pH and concentration of all species in the solution, and/or infer the relative strengths of the weak acids or bases from given equilibrium concentrations.

LO 6.17: The student can, given an arbitrary mixture of weak and strong acids and bases (including polyprotic systems), determine which species will react strongly with one another (i.e., with $K>1$) and what species will be present in large concentrations at equilibrium.

LO 6.18: The student can design a buffer solution with a target pH and buffer capacity by selecting an appropriate conjugate acid-base pair and estimating the concentrations needed to achieve the desired capacity.
A 50.0 mL sample of 0.50 M HC₂H₃O₂ is titrated to the half equivalence point with 25.0 mL of 0.50 M NaOH. Which of the following options shows the correct ranking of the molarities of the species in solution?

(pKa for HC₂H₃O₂ is 4.7)

- Option A is correct.

At the half equivalence point, the concentrations of the weak acid and its conjugate base are equal because the OH⁻ ion has reacted with half of the original acetic acid. The pH of the buffer is equal to the pKa at that point, so the [H⁺] is 10⁻⁴.₇ which is far lower than the concentrations of the conjugates but far higher than the [OH⁻] which has a value of 10⁻⁹.₃.

Finding the Major Species

A buffer is able to resist pH change because the two components (conjugate acid and conjugate base) are both present in appreciable amounts at equilibrium and are able to neutralize small amounts of other acids and bases (in the form of H₃O⁺ and OH⁻) when they are added to the solution. Take, for example, a fluoride buffer made from hydrofluoric acid and NaF. A model fluoride buffer would contain equimolar concentrations of HF and NaF. Since they are a weak acid and a weak base, respectively, the amount of hydrolysis is minimal and both buffer species are present at, effectively, their initial supplied concentrations.

If a strong acid is added to the HF/F⁻ buffer, then the added acid will react completely with the available base, F⁻. This results in a nearly unchanged [H₃O⁺] and a nearly unchanged pH.

If a strong base is added to the HF/F⁻ buffer, then the added base will react completely with the available acid, HF. This results in a nearly unchanged [H₃O⁺] and a nearly unchanged pH.

Ksp and Solubility Calculations

Question:
What is the maximum number of moles of AgBr that will fully dissolve in 1.0 L of water, if the Ksp value of silver bromide is 4.0 x 10⁻¹²?

- 4.0 x 10⁻¹²
- 2.0 x 10⁻¹²
- 4.0 x 10⁻⁶
- 2.0 x 10⁻⁶

The slight shift in pH after challenge is governed by the hydrolysis equilibrium of HF, based on the new HF and F⁻ concentrations:

HF(aq) + H₂O(ℓ) ⇌ F⁻(aq) + H₃O⁺(aq)

The correct answer is "d" 2.0 x 10⁻⁶.

The question asks for the maximum number of moles of AgBr that will fully dissolve in 1.0 L of water. To determine the solubility of AgBr, we need to determine the maximum concentrations of Ag⁺ and Br⁻ that will equal the equilibrium constant. The Ksp equation is Ksp = [Ag⁺][Br⁻] with [Ag⁺] = [Br⁻] = X, so to solve for X we need to take the square root of 4.0 x 10⁻¹².
LO 6.22: The student can interpret data regarding solubility of salts to determine, or rank, the relevant Ksp values.

Find a Ksp from solubility data

Using a conductivity meter and a pH meter, a student determines the molar solubility of several solutions made by dissolving hydroxides in water. The student’s data is shown in the table below:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>0.12 M</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>6.81 × 10⁻⁵ M</td>
</tr>
<tr>
<td>CO₃⁻</td>
<td>1.3 × 10⁻⁶ M</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>1.1 × 10⁻⁶ M</td>
</tr>
</tbody>
</table>

Which of the hydroxides above has the smaller Ksp value?

a. NaOH   b. Ca(OH)₂  c. CO₃⁻  d. NO₃⁻

Click reveals answer and explanation.

LO 6.23: The student can interpret data regarding the relative solubility of salts in terms of factors (common ions, pH) that influence the solubility.

+ Common Ion Effect

The solubility of a sparingly soluble hydroxide can be greatly increased by the addition of an acid. For example, the hydroxide salt Mg(OH)₂ is relatively insoluble in water:

\[
\text{Mg(OH)₂(s)} \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{OH}^-(aq) \quad \text{K}_\text{sp} = 5.61 \times 10^{-12}
\]

When acid is added to a saturated solution that contains excess solid Mg(OH)₂, the following reaction occurs, removing OH⁻ from solution:

\[
\text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l)
\]

The overall equation for the reaction of Mg(OH)₂ with acid is thus

\[
\text{Mg(OH)₂(s)} + 2\text{H}^+(aq) \rightarrow \text{Mg}^{2+}(aq) + 2\text{H}_2\text{O}(l) \quad (18.7.7)
\]

As more acid is added to a suspension of Mg(OH)₂, the equilibrium shown in Equation 18.7.7 is driven to the right, so more Mg(OH)₂ dissolves.

In contrast, the solubility of a sparingly soluble salt may be decreased greatly by the addition of a common ion. For example, if MgCl₂ is added to a saturated Mg(OH)₂ solution, additional Mg(OH)₂ will precipitate out. The additional Mg²⁺ ions will shift the original equilibrium to the left, thus reducing the solubility of the magnesium hydroxide.

LO 6.24: The student can analyze the enthalpic and entropic changes associated with the dissolution of a salt, using particulate level interactions and representations.

+ Salt dissolution: ΔH and ΔS

The enthalpy (ΔH) of dissolution is dependent upon the intermolecular forces of the solute and solvent.

The entropy (ΔS) of dissolution generally increases the disorder of the system.
The key to understanding the relationship between $\Delta G^\circ$ and $K$ is recognizing that the magnitude of $\Delta G^\circ$ tells us how far the standard-state is from equilibrium. The smaller the value of $\Delta G^\circ$, the closer the standard-state is to equilibrium. The larger the value of $\Delta G^\circ$, the further the reaction has to go to reach equilibrium.

LO 6.25: The student is able to express the equilibrium constant in terms of $\Delta G^\circ$ and $RT$ and use this relationship to estimate the magnitude of $K$ and, consequently, the thermodynamic favorability of the process.