

# Chapter 3.1 – The Equilibrium Constant

## Chemical Equilibrium

- While some chemical reactions proceed in one direction, many reactions are reversible
  - When these reversible reactions are complete (reach equilibrium), the system contains both reactants and products
- **Equilibrium** – when the rate of the forward reaction is equal to the rate of the reverse reaction
  - Once the system attains equilibrium, the amount of each gas does not change
  - The system is still *dynamic* at the molecular level, since both the forward and reverse processes are still occurring
- For any equilibrium, there is a mathematical relationship between the pressures or concentrations of the reactants and products – **equilibrium constant** ( $K_P$  or  $K_C$ )
- Effect of Temperature
  - Equilibrium constants are temperature dependent
  - Whether the value of  $K$  increases or decreases depends on whether the temperature is increased or decreased, and whether the reaction is endothermic or exothermic
- Homogeneous and Heterogeneous Equilibria
  - **Homogeneous equilibrium** – all components are in the same phase
  - **Heterogeneous equilibrium** – components are in different phases

## The Equilibrium Constant Expression

- A general equilibrium reaction is written as:  **$aA + bB \rightleftharpoons cC + dD$** , and the general form of the equilibrium constant expression for this reaction, using concentrations, is:
  - $K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$  OR, using pressures (atm):  $K_P = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
- NOTE: the concentration of any solid, or of any solvent, is considered to be constant and therefore omitted from the equilibrium constant expression (*only gases included!*)
- **Reversing an equilibrium reaction**  $\rightarrow$  new  $K = 1/K_{original}$
- **Multiplying or dividing an equilibrium reaction by #**  $\rightarrow$  new  $K = (K_{original})^\#$
- **Combining Equilibria (adding reactions)**  $\rightarrow$  new  $K = K_1 \times K_2$
- The magnitude of  $K$  shows how much product or reactant is present at equilibrium
  - $K > 1$  means that the equilibrium lies toward the right (more products)
  - $K < 1$  means that the equilibrium lies toward the left (more reactants)
- Equilibrium constants don't have any units associated with them; they are dimensionless

## The Reaction Quotient, Q

- This number indicates whether the system is at equilibrium, and the direction in which the reaction must proceed to attain equilibrium
- The  $Q$  expression is the same as the  $K$  expression except that the concentrations/pressures used to calculate  $Q$  aren't necessarily at the equilibrium concentrations/pressures
  - $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
- When  $Q = K$ , the system is at equilibrium
- When  $Q < K$ , too much reactants or too little product (reaction must proceed forward)
- When  $Q > K$ , too much products or too little reactants (reaction must proceed in the reverse)

## Le Chatelier's Principle

- If a chemical system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of a participant in the equilibrium, the equilibrium will shift in such a way as to minimize the disturbance
- Concentration Changes
  - Increase [reactants] or decrease [products] → equilibrium shifts to RIGHT
  - Increase [products] or decrease [reactants] → equilibrium shifts to LEFT
- Pressure/Volume Changes
  - Increase pressure (decrease volume) → equilibrium shifts to side with LESS moles
  - Decrease pressure (increase volume) → equilibrium shifts to side with MORE moles
  - Adding an inert gas to the system will result in an increase in total pressure, but no changes to the partial pressures – therefore no change in equilibrium
  - If there are an equal # of moles of gaseous reactants and products, the position of equilibrium is unaltered by pressure/volume changes
  - Systems involving just solids and liquids are not affected by pressure/volume changes
- Relationship between Temperature and K values
  - If the temperature of a system changes, the value of K will change
  - EXOTHERMIC: Increasing temperature → equilibrium shifts to LEFT, decreasing K
    - Decreasing temperature → equilibrium shifts to RIGHT, increasing K
  - ENDOTHERMIC: Increasing temperature → equilibrium shifts to RIGHT, increasing K
    - Decreasing temperature → equilibrium shifts to LEFT, decreasing K

## Gibbs Free Energy and the Equilibrium Constant

- If  $\Delta G^\circ$  is positive, the equilibrium lies to the LEFT and K is small
- If  $\Delta G^\circ$  is negative, the equilibrium lies to the RIGHT and K is large
- $\Delta G^\circ = -RT \ln K$
- $\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$ 
  - When this equation is plotted on a graph ( $\ln K$  vs.  $1/T$ ), it gives a straight line with a slope of  $-\Delta H^\circ/R$  and a y-intercept of  $-\Delta S^\circ/R$
  - Slope is positive for an exothermic reaction

## The van't Hoff Equation

- $\ln \frac{K_2}{K_1} = \frac{-\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$
- Can be used to determine K at a second temperature
- Can also be used to calculate  $\Delta H_{rxn}^\circ$  if K is known at two different temperatures
- Another use is to determine the appropriate temperature at which to carry out a reaction

## Chapter 3.2 – Solubility of Ionic Compounds

### Solubility and Precipitation

- **Solubility** – the amount of a substance that will dissolve in a certain volume of a specific solvent
  - Soluble → more than 10 g can dissolve in a litre of solvent
  - Slightly soluble → 0.1 to 10 g can dissolve in a litre of solvent
  - Insoluble → less than 0.1 g can dissolve in a litre of solvent
- Ionic compounds become more soluble as the temperature increases
- **Solvent** – liquid or gas that dissolves another solid, liquid or gas
  - The substances that dissolve are called **solutes**
- When an ionic solid dissolves in water, it dissociates into hydrated ions
  - As the dissolution proceeds, the concentration of ions increases until eventually no more additional solute would dissolve in the solution
    - At this point, the solution is said to be **saturated** (equilibrium established)
  - If the quantity of a species in solution is less than required for equilibrium with the solid, the solution is said to be **unsaturated**
- **K<sub>sp</sub>** is an equilibrium constant called the solubility product or the solubility product constant
  - Very soluble compounds have a LARGE K<sub>sp</sub> value and these dissolutions go to completion
  - Compounds with low solubility have an equilibrium established and a SMALL K<sub>sp</sub> value
  - This constant is always the same for a given solid at a *given temperature*
- For the dissolution of an ionic solid of composition A<sub>x</sub>B<sub>y</sub>, the equilibrium reaction is:
  - $A_xB_y(s) \leftrightarrow xA^{y+}(aq) + yB^{x-}(aq)$
  - The K<sub>sp</sub> expression is:  $K_{sp} = [A^{y+}]^x [B^{x-}]^y$
  - Doubling surface area doubles the rate of dissolution but also the rate of precipitation, thus there is no effect on the equilibrium position
- **Q** is the reaction quotient, also known as the ion product
  - For a saturated solution, Q = K<sub>sp</sub> (system is at equilibrium)
  - When Q < K<sub>sp</sub>, no solid will be present; all ions will remain in solution (unsaturated)
  - When Q > K<sub>sp</sub>, a precipitate will be formed from ions in solution (supersaturated)
- Sometimes a solution may already contain an ion in common with the dissolving salt
  - **Common Ion Effect** – can significantly reduce the solubility of the solid relative to that in pure water

## Chapter 3.3 – Weak Acids and Bases

### Acid-Base Terminology

- **Acids** – substances that increase hydrogen ion [H<sup>+</sup>] concentration in solution (really [H<sub>3</sub>O<sup>+</sup>])
- **Bases** – substances that increase hydroxide ion [OH<sup>-</sup>] concentration in solution
- Strong acids/bases completely ionize in solution, whereas weak ones don't ionize completely
  - Weak acid and weak base reactions proceed until an equilibrium is achieved between the reactants and products
- STRONG ACIDS → HCl, HBr, HI, HNO<sub>3</sub>, HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>
- STRONG BASES → NaOH, KOH, Mg(OH)<sub>2</sub>, Ca(OH)<sub>2</sub>
- **Arrhenius Theory** – Acids produce H<sub>3</sub>O<sup>+</sup> ions in water, whereas bases produce OH<sup>-</sup> ions in water

- **Bronsted-Lowry Theory** – Acids are proton donors, whereas bases are proton acceptors
  - When weak acids ionize:  $HA_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + A^-_{(aq)}$
  - When weak bases ionize:  $B_{(aq)} + H_2O_{(l)} \leftrightarrow BH^+_{(aq)} + OH^-_{(aq)}$
- **Lewis Acids and Bases** – Acids accept a pair of  $e^-$  from another atom, resulting in the formation of a coordinate covalent bond, whereas bases donate a pair of  $e^-$  to another atom
  - The species formed in this reaction is called an acid-base adduct
  - **Amines** are groups of compounds that behave as Lewis bases (e.g.  $NH_3$ ) as they carry a non-bonding pair of electrons
  - **Metal cations** can act as acids since they form coordination complexes when reacted with Lewis bases (many of these species are highly coloured)
  - **Oxides of non-metals** behave as Lewis acids when reacted with hydroxide (e.g.  $CO_2$  and  $SO_2$  react in this manner to form bicarbonate and bisulfate)

### Equilibrium Constants, pH and Percent Ionization

- $K_a$  is the equilibrium constant for weak acids and  $K_b$  is the equilibrium constant for weak bases
  - $K_a = \frac{[H^+][A^-]}{[HA]}$        $K_b = \frac{[BH^+][OH^-]}{[B]}$
- The larger the K value, the stronger the acid or base and the greater its ionization
- The value of pK becomes smaller as the strength of the acid or base increases
  - $pK_a = -\log K_a$        $pK_b = -\log K_b$
  - $pK_a + pK_b = 14$
- **Weak Acids:**
  - If  $c$  = initial concentration and  $x$  = concentration of  $H^+$  resulting from ionization, then:
    - $K_a = \frac{x^2}{c-x}$ , where  $x$  can be solved using quadratic formula
    - The amount of weak acid ionized is expressed as: % **ionization** =  $\frac{x}{c} \times 100\%$
    - If % ionization is less than 5%, then  $x$  is much smaller than  $c$ , so  $c - x \approx c$ 
      - $K_a \approx \frac{x^2}{c}$ , where  $x$  doesn't have to be solved using quadratic formula
    - If the value of  $\frac{c}{K_a}$  is greater than 400, then the approximation  $c - x \approx c$  is valid
    - If you know what  $x$  is, then use it!!!
- **Weak Bases:**
  - The above principles also apply to bases:  $K_b = \frac{x^2}{c-x}$
  - However, the value of  $x$  gives you  $[OH^-]$
- The more dilute the solution of a weak acid or base, the GREATER the % ionization
  - Because the  $K_a$  or  $K_b$  for the weak acid/base does not change, there must be changes to the concentrations of the products at equilibrium when the initial concentration of acid or base is decreased by dilution
  - As the initial concentration of the acid or base decreases, the % ionization increases, resulting in a greater pH

### Conjugate Species

- When a weak acid loses protons, it produces a **conjugate base**, which will behave like a weak base when in solution:  $A^-_{(aq)} + H_2O_{(l)} \leftrightarrow OH^-_{(aq)} + HA_{(aq)}$  (basic solution)
- When a weak base gains protons, it produces a **conjugate acid**, which will behave like a weak acid when in solution:  $BH^+_{(aq)} + H_2O_{(l)} \leftrightarrow B_{(aq)} + H_3O^+_{(aq)}$  (acidic solution)

### Equilibrium Constant, $K_w$

- The equilibrium constant for the ionization of water:  $H_2O_{(l)} \leftrightarrow H^+_{(aq)} + OH^-_{(aq)}$  is:
  - $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$  (at 25°C)
- For any conjugate-base pair,  $K_a \times K_b = K_w$
- The stronger the weak acid is, the weaker the weak conjugate base will be
- Strong acids have extremely weak conjugate bases (so weak that they're called *spectator ions*)

### Salts

- A salt is an ionic solid containing cations and anions (as it dissolves, cations/anions separate)
- Cations and anions that don't have any effect on pH are **spectator ions**
  - E.g. monovalent and divalent ions such as  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Ba^{2+}$
  - E.g. conjugate bases of strong acids –  $Cl^-$ ,  $Br^-$ ,  $NO_3^-$ ,  $ClO_4^-$ , and  $SO_4^{2-}$
- Some cations that are the conjugate acids of weak bases, act as weak acids (e.g.  $NH_4^+$ )
- Some anions that are the conjugate bases of weak acids, act as weak bases (e.g.  $F^-$ )
- If one of the ions produced is a spectator ion, then the pH will either be basic or acidic depending on whether the reactant with water was a weak base or acid
  - However, sometimes both the cation and anion can affect the pH
  - If  $K_a > K_b \rightarrow$  salt is acidic      and      if  $K_b > K_a \rightarrow$  salt is basic
  - This can be used to decide if an **amphiprotic anion** will be acidic or basic

### Effect of Structure and Bonding on Weak Acid Strength

- Although all weak acids have  $K_a < 1$ , they vary considerably in strength
- The relative strengths of weak acids are primarily determined by the relative thermodynamic stabilities of the conjugate bases
- Conjugate bases with a highly localized charge are high in energy & thermodynamically unstable
- Conjugate bases with a delocalized charge have a reduced energy level & are more stable
  - Species that are more stable are more favourable
- Stronger weak acid = larger  $K_a$  = more stable conjugate base
- Weaker weak acid = smaller  $K_a$  = less stable conjugate base
- What affects the stability of conjugate bases?
  - **Resonance** – delocalizes charge over two or more atoms and increase the ion's stability (more resonance structures = more stable)
  - **Electronegativity of the atom bearing the negative charge** – the more electronegative atom is more favourable and has a higher acidity (only works when comparing atoms across a period, NOT down a group!)
  - **Inductive effect** – the result of one or more electronegative atoms stabilizing a negative charge elsewhere in the ion (more EN atoms = lower electron density = more stable)
    - The closer the EN atom is to the atom with the negative charge, the more stable

### The Common Ion Effect

- In a solution of a weak acid and strong acid, there are 2 sources of the  $H_3O^+$  ion:
  - If the strong acid is added to the weak base, then both produce  $H_3O^+$ , and the  $H_3O^+$  is therefore a common ion
  - When  $H_3O^+$  is added, the equilibrium shifts in the reverse direction and the concentration of the anion is reduced
- Similarly, when a strong base is put in solution with a weak base, the addition of the common ion  $OH^-$  shifts the equilibrium in reverse, away from production of the cation

## Polyprotic Weak Acids

- Some weak acids are **polyprotic** – they contain more than one ionizable hydrogen atom
  - When these acids ionize, they do so in stages, each with a different  $K_a$  value
  - Usually  $K_{a1}$  will be larger than  $K_{a2}$  since the conjugate base from the second ionization is less stable than the first
- This is an example of **simultaneous equilibria** – both reactions happening at the same time
  - As a result, both conjugate bases are present in the equilibrium mixture
  - To determine the equilibrium concentrations of these species, each equilibrium must be analyzed separately
- For weak diprotic acids ( $H_2A$ ) in water with  $K_{a2} \ll K_{a1}$ , the  $[A^{2-}]$  is equal to  $K_{a2}$  and the pH of the solution is determined primarily by the  $H_3O^+$  obtained from the first ionization

## Chapter 3.4 – Buffer Solutions

### Preparation of Buffer Solutions

- **Buffer solution** – when both the weak acid/base and its conjugate base/acid are present in the same solution (in significant amounts), allowing it to withstand changes in pH when small amounts of a strong base or acid are added to it
  - ACIDIC solution → weak acid and conjugate base
  - BASIC solution → weak base and conjugate acid
- **Acid Buffer** – a buffer solution composed of a weak acid and its conjugate base
  - Start with a solution of weak acid and add a salt that contains that conjugate base
  - Simplest method of preparing the buffer is to mix the two required species together
    - OR you could use acid-base reactions:
      - A strong base is used to convert excess of the weak acid (approx. half of it) back into its conjugate base, and then a strong acid is used to convert half of the conjugate base back to its weak acid
- **Basic Buffer** – a buffer solution composed of a weak base and its conjugate acid
  - You could mix the two required species together
  - OR use a strong acid to convert half of the weak base to its conjugate acid, and a strong base to convert half the conjugate acid back to the parent base

### pH of a Buffer Solution

- Usually possible to use mole amounts of the parent and conjugate species instead of concentration units because:
  - The parent and conjugate species are always in the same volume
  - The value of  $x$  is always negligible in a buffer solution due to small % ionization
- However, the  $H_3O^+$  and  $OH^-$  must always be in concentration units
- Thus, for a weak acid buffer, the equilibrium expression is:  $K_a = \frac{[H^+](\text{moles of conjugate base})}{(\text{moles of parent acid})}$ 
  - This shows that the pH of a solution is dependent on the ratio of parent to conjugate species, and also, the volume of the solution is NOT a factor in determining pH
  - Thus, diluting a buffer solution will not change its pH!

## How Buffers Work

- If a small amount of strong acid is added to an acid buffer, it will react with the conjugate base component of the buffer to produce more of the weak acid, resulting in a *small* drop in pH
  - If a small amount of strong base is added to the same buffer, it will react with the weak acid, producing more of the conjugate base, increasing pH
- If a strong acid or base is added to water, it results in the same small increase or decrease in pH

## Acid-Base Titrations

- **Titration** – used to determine the concentration of a base or acid in solution by either adding an acid to neutralize a base OR adding a base to neutralize an acid
- **Equivalence point** – reached when stoichiometric equivalent amounts of acid and base are present in solution (a.k.a. endpoint)
- Strong acid-strong base → At equivalence, a solution of a salt of spectator ions results in a neutral pH
- Weak acid-strong base → At equivalence, a solution of the conjugate base results in a basic pH
- Strong acid-weak base → At equivalence, a solution of the conjugate acid results in an acidic pH
- For any titration involving a weak species and a strong species, an equilibrium will be established between the excess weak species and the just-formed conjugate species
  - At the equivalent point, the only species present is the conjugate, which will then react with water (this reaction ultimately determines the pH)
- **Acid-base indicators** – used to detect the equivalence point in a titration, by a change in colour
  - An indicator is a weak acid ( $HIn$ ) that has a different colour than its conjugate base
    - $HIn_{(aq)} \leftrightarrow H_3O^+_{(aq)} + In^-_{(aq)}$
  - In an acidic solution, the indicator mostly exists in its acid form (colour 1), whereas under basic conditions, it exists in its base form (colour 2)
  - The colour change takes place around the pH value where  $[HIn] = [In^-]$ 
    - When this occurs, then  $K_{HIn} = [H_3O^+]$ , which gives  $pK_{HIn} = pH$
  - At 1 pH unit below this pH or  $pK_a$  value (acidic), the indicator is about 90% in  $HIn$  form
  - At 1 pH unit above this pH or  $pK_a$  value (basic), the indicator is about 90% in  $In^-$  form
  - The indicator is present in a very low concentration, so the value of  $[H_3O^+]$  is driven by the acid-base reaction and is NOT affected by the presence of the indicator
- When an indicator is chosen for a titration, it must change colour close to the pH of the equivalent point, so it is best to have an indicator that has a  $pK_a$  value within one unit of the pH
  - For weak acid-strong base titration → indicator must have  $pK_a$  of 9
  - For strong acid-weak base titration → indicator must have  $pK_a$  of 5
  - For strong acid-strong base titration → almost any indicator may be used (usually  $pK_a$  7)

## Titration Curves

- In the case of a weak/strong titration, the only species present at equivalence point (in addition to water and the spectator ions) is the conjugate species of the original weak acid or base
  - The conjugate species then undergoes a hydrolysis reaction with the water
- **Titration curve** – plots the pH of the solution vs. the volume of base added to the acid
- Strong acid-strong base titration:
  - Initially very acidic pH due to unreacted HCl
  - Approaching the endpoint, very little HCl is left in solution, causing pH to increase
  - pH change is very large at the equivalence point

- pH continues to increase rapidly past the endpoint, then once a basic solution is achieved, it will level off
- Weak acid-strong base titration:
  - Initially an acidic pH, but not as low as a strong acid
  - pH gradually increases as the strong base is added
  - At midpoint of titration (half of volume needed to reach endpoint), the pH of the solution equals the  $pK_a$  of the acid ( $K_a = H^+$ , therefore  $pK_a = pH$ )
  - As the endpoint is reached, pH increases rapidly → solution is basic
  - After the endpoint, the pH will increase and level off until solution is strongly basic
- Strong acid-weak base titration:
  - Initial pH is basic due to presence of weak base
  - As strong acid is added, pH gradually decreases
  - Once all of the weak base is consumed, the solution reaches equivalence point and only the conjugate base is present (pH rapidly decreases)
  - After the endpoint, the pH will decrease and level off until solution is strongly acidic

## Chapter 4.1 – Redox Reactions

### Redox Half Reactions

- **Redox Reaction** – characterized by a change in the oxidation state of one or more elements in the reactants (net transfer of electrons from one reactant to another)
- Consist of 2 half reactions:
  - **Oxidation** – electrons are lost by the reducing agent
  - **Reduction** – electrons are gained by the oxidizing agent
- Oxidation and reduction always occur together (# of electrons lost = # of electrons gained)

### Oxidation States

- Always zero in a pure element
- Is equal to the charge on a monatomic ion (e.g.  $Na^+ = +1$ )
- In a neutral species, the total must equal 0
- In a complex ion, the total must equal the charge on the ion
- When assigning oxidation states to the elements in a COMPOUND:
  - Fluorine is always -1, and other halogens are usually -1
  - Group 1 metals are +1, and group 2 metals are +2
  - Hydrogen is +1 (except when bonded to a metal, where it is -1)
  - Oxygen is usually -2
- Increases when losing electrons, and decreases when gaining electrons
- Oxidation States of Carbon:
  - May be determined by comparing the electronegativity of carbon to the electronegativity of each atom to which the carbon is bonded
  - If the carbon atom is bonded to an atom more electronegative than itself, that bond contributes +1 to the oxidation state of carbon (+1 for each bond)
  - If the carbon atom is bonded to an atom less electronegative than itself, that bond contributes -1 to the oxidation state of carbon