

Chapter 1.1 – Gases

States of Matter

- A substance may exist in only one state, or it may be present in 2 or 3 states
- **Solid** → particles are locked into a fixed position relative to others in the substance
 - Particles possess vibrational energy
 - When vibrational modes overcome attractive forces, the particles become a liquid
- **Liquid** → some attraction between particles, allowing it to take the shape of its container
- **Gas** → forces that hold particles together are completely overcome, so they escape
 - Much more significant translational energy – change in position
 - “Pressure of gas” – the collisions of gaseous particles within the walls of the container
- Boundaries of the behaviour of gases:
 - The pressure is not too high
 - The temperature is not close to the condensation temperature
- Approximations of gases that developed their boundaries:
 - Atoms/molecules of gas have no volume (negligible compared to volume of container)
 - Atoms/molecules of gas don’t interact with each other

Gas Laws

- **Boyle’s Law** – for a fixed amount of gas at a constant temperature, the gas volume is inversely proportional to the gas pressure
 - $P_1V_1 = P_2V_2$
- **Charles’s Law** – the volume of a fixed amount of gas at a constant pressure is directly proportional to the Kelvin (absolute) temperature
 - $\frac{V_1}{T_1} = \frac{V_2}{T_2}$
- Both laws can be combined for a fixed # of moles of gas: $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$
- **Avagadro’s Law** – equal volumes of different gases, at the same temperature and pressure, contain equal numbers of molecules
 - Therefore, as the # of molecules increases, the volume of gas also increases linearly
 - $\frac{V_1}{n_1} = \frac{V_2}{n_2}$
- **Ideal Gas Law** – $PV = nRT$, where $R = 8.314 \text{ L kPa mol}^{-1} \text{ K}^{-1}$ or $0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$

Chapter 1.2 – The Ideal Gas Law

Molar Volume of a Gas

- For solids and liquids, the mass and volume of one mole of a substance depends on the substance being considered
- Although different gases have different molar masses, Avogadro’s Law states that one mole of any ideal gas always occupies the same volume at a given temp. and pressure
 - **Molar volume** – the volume of one mole of an ideal gas at STP (0°C and 1 atm) is 22.4 L
- **Variations of the Ideal Gas Law:**
 - $d = \frac{(MM)(P)}{RT}$ or $MM = \frac{dRT}{P}$

Dalton's Law of Partial Pressures

- In a mixture of several ideal gases, the total volume, pressure and # of moles of the mixture behave as a single gas with respect to the ideal gas law ($P_{total}V_{total} = n_{total}RT$)
- Each of the constituents in a gas mixture exhibits a **partial pressure**
- **Dalton's Law** – the total pressure exerted by a mixture of gases is the sum of all the partial pressures of these gases ($P_T = P_A + P_B + P_C$)
- **Mole Fraction:** $X_i = \frac{n_i}{n_T}$
 - The sum of all the mole fractions is always 1 ($1 = X_A + X_B + X_C$)
- At a constant temp. and volume, the pressure is directly proportional to moles:
 - $X_i = \frac{P_i}{P_T} = \frac{n_i}{n_T}$, therefore $X_i = \frac{P_i}{P_T}$
 - If gases are expressed in terms of mole fractions: $P_A = X_AP_T, P_B = X_BP_T, P_C = X_CP_T$
- At equilibrium, the rates of evaporation and condensation will be the same, and the pressure of the $H_2O_{(g)}$ will remain constant
 - Total pressure of the gas in the flask would be: $P_T = P_{air} + P_{water\ vapour}$
 - Vapour pressure of water is dependent only on the temperature of water
 - Solvents that are more volatile (have lower boiling points) have higher vapour pressures
 - **Boiling point** – the temperature at which the vapour pressure of a liquid is equal to atmospheric pressure
- **Average Molar Mass of a Mixture:**
 - \overline{MM} is the weighted average of the molar masses of the different components
 - $\overline{MM} = (X_A \times MM_A) + (X_B \times MM_B) + (X_C \times MM_C)$

Gas Reaction Stoichiometry

- **Mole-volume** → reaction is given in moles and the volume of each gaseous component must be determined according to the balanced chemical equation, at the given temp. and pressure
- **Mass-volume** → mass of one component is given and the volume of a gaseous component must be determined at a stated temperature and pressure
 - Convert mass to moles, then use mole ratios
- **Volume-volume** → pressure and temperature are constant, and the stoichiometric coefficients are proportional to volume
- **Pressure-pressure** → pressure is directly proportional to the mole amount at constant volume and temperature

The Kinetic Molecular Theory of Gases

- **Assumptions of the theory:**
 - The size of the molecules is negligible when compared to the space between them and the volume of container
 - Molecules moving through space are considered to be point particles (no vibrational or rotational energy, just translational – kinetic energy)
 - The collisions between molecules and between molecules & the container, are considered to be elastic and at a constant velocity, in a straight line
 - No attractive or repulsive forces between molecules
- Average kinetic energy of the molecules is proportional to the temperature
 - $\overline{E_k} = \frac{1}{2}m\overline{u^2}$, where m is the mass of one molecule and $\overline{u^2}$ is the mean-square speed
 - Not all the molecules are moving at the same speed at the same time

- 3 factors determine the pressure of a gas in a container: mass of each molecule, speed of the molecules, and the frequency of collisions (which is related to the # of molecules, N and the volume of the container)
- Basic equation of the kinetic theory of gases: $P = \frac{1}{3} \frac{N}{V} m \overline{u^2}$, which leads to $\overline{u^2} = \frac{3RT}{MM}$
- At any given moment, some molecules are moving faster and some are moving slower
- **Root-Mean-Square Speed of Gas Molecules:** $u_{rms} = \sqrt{\frac{3RT}{MM}}$, where molar mass is in kg
- The u_{rms} for 2 gases is inversely proportional to the square root ratio of their molar masses:
 - $\frac{u_{rms(A)}}{u_{rms(B)}} = \sqrt{\frac{MM_B}{MM_A}}$

Effusion and Graham's Law

- **Effusion** – flow of gas molecules at low pressures through tiny pores or pinholes
- The rate of effusion of a gas is inversely proportional to the square root of its molar mass
 - Therefore lighter molecules effuse more rapidly than heavier ones
- When 2 gases effuse through a small hole, Graham's Law can be written as:
 - $\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{N_A}{N_B} \sqrt{\frac{MM_B}{MM_A}}$
- The gas that emerges from a container is *enriched* in the lighter component
- The $\sqrt{\frac{MM_B}{MM_A}}$ proportion of Graham's Law is called the enrichment factor, where the heavier MM is the numerator of the fraction
- If a mixture of 2 gases has the same # of moles of each gas, after the mixture effusing for a certain length of time, the mixture that effused would have a proportionally higher ratio of the lighter gas

Chapter 2.1 – Heat, Work and Energy

Thermodynamics

- The study of the energy changes involved in physical and chemical processes
 - *Physical process* → heating and cooling of substances, phase changes, and V/P changes
 - *Chemical process* → chemical reactions
- **Thermochemistry** – investigates the heat flow that occurs during these reactions
 - Rates of most chemical reactions increases as temperature increases

Systems and Surroundings

- **Heat flow** – the transfer of thermal energy in the process being studied
 - Heat always flows from the warmer object to the cooler object
- **System** – the part of the universe that one wants to study
- **Surroundings** – the remaining parts of the universe that can interact (e.g. exchange energy) with a system under study
- In a chemical reaction, the system is the reactants and the surroundings is the vessel (flask) in which the reaction takes place, including the air and any other material making thermal contact with the vessel, such as the solution in which the reaction occurs

- Types of Systems
 - **Open system** – exchanges both matter and energy with its surroundings
 - **Closed system** – exchanges energy, not matter with its surroundings
 - **Isolated system** – exchanges neither matter nor energy with its surroundings

Energy

- **Energy** – the capacity to do work
 - *Heat (thermal energy)* – energy transferred between the system and the surroundings, or from one object to another, as a result of a temperature difference
 - *Kinetic energy* – energy associated with motion
 - *Potential energy* – stored energy or the energy a body possesses due to its position
 - *Chemical energy* – a form of potential energy
- **Work** – the product of a force, acting on an object, and the distance the object moves in response to the force; measured in joules ($w = F \times d$)
- **Pressure-volume (PV)** – the work involved in the expansion or compression of gases; measured in kPa L ($w = -P \times \Delta V$)

Heat Capacity and its Uses

- **Heat capacity (C)** – a measure of how many joules are required to change the temperature of an OBJECT by one degree; measured in J/°C
 - $q = C\Delta T$
- **Specific heat capacity (c)** – a measure of how many joules are required to change the temperature of one mass unit of a SUBSTANCE by one degree; measured in J/kg°C
 - $q = mc\Delta T$
- **Molar heat capacity** – same as above, except moles are used instead of grams (J/mol°C)
- **NOTE:** $\Delta T = T_f - T_i$, and the temperature difference is the same in K and °C
- **Endothermic (+ q)** – when a system absorbs energy from the surrounding (warms up)
- **Exothermic (– q)** – when a system releases energy to the surroundings (cools down)
- **Thermal equilibrium** – the number of joules lost by the warmer object must equal the number of joules gained by the cooler object (both objects therefore reach the same temperature)
 - $-q_{lost} = q_{gained}$

Intensive and Extensive Properties

- **Intensive (intrinsic) property** – physical property that does not depend on the amount of material in the system (e.g. temperature, density, etc.)
 - *Temperature* – the speed of the molecules in a sample (avg. kinetic energy)
- **Extensive (extrinsic) property** – physical property or quantity whose value is proportional to the size of the system it describes (e.g. mass, length, volume, enthalpy, entropy, energy, etc.)
 - *Thermal energy* – the number of molecules in a sample (total kinetic energy)

State Functions

- **State function** – a property whose value depends only on the current state of the system; it does not matter how the state of the system was reached
- Examples → internal energy and enthalpy
- Heat and work are NOT state functions since the work done on or heat transferred to a system by following different paths is different, although the initial and final states of the two paths are identical

First Law of Thermodynamics

- *The total energy of a system and surroundings is conserved*
- **Internal energy (E)** – the sum of all the kinetic and potential energies of all the atoms, ions and molecules in the system
 - Although the absolute internal energy of a system cannot be determined, internal energy changes, ΔE , can be determined
- EXPANSION → the expanding gas (system) is doing work on the surroundings and the value of w is negative (work energy has been used, so it has been removed from the system)
- COMPRESSION → the surroundings are doing work on the system, and the value of w is positive (the system has gained work energy)
- If a process does NOT involve a compression or expansion, there is no volume change ($\Delta V = 0$) and the value of w is zero
- $\Delta E = q + w$
 - If the surroundings do work on, or supply heat to the system, internal energy of the system increases ($\Delta E > 0$)
 - If the system does work on, or supplies heat to the surroundings, internal energy of the system decreases ($\Delta E < 0$)
 - If the system is at a constant volume (zero work), then $\Delta E = q_v$

Chapter 2.2 – Enthalpy

Enthalpy

- **Enthalpy (H)** – the energy content of a system at constant pressure
 - $H = E + PV$, but absolute enthalpy cannot be measured so: $\Delta H = \Delta E + P\Delta V$
 - At constant pressure, the ΔH of a system is equal to the heat (q_p) flowing into or out of a system → $\Delta H = q_p$
- NOTE: The standard conditions used at 1 atm (101.33 kPa) and 25°C (298.15 K)
 - Enthalpy changes under standard conditions are reported as ΔH^0
- Physical Processes and Latent Heat
 - **Latent heat** – the energy change associated with physical processes that involve a change of state (phase)
 - Melting, boiling, and sublimation are endothermic processes
 - Condensation, freezing and deposition are exothermic processes
 - Temperature of the substance remains CONSTANT for any of these processes
 - If the phase changes are carried out at constant pressure, the latent heat values are also ΔH values
 - If the processes are occurring under standard conditions, the ΔH^0 values are slightly different due to the different temperatures

ΔH For Chemical Reactions

- $\Delta H_{rxn}^0 = \sum H^0(\text{products}) - \sum H^0(\text{reactants})$
- Exothermic reactions have $\Delta H < 0$ and endothermic reactions have $\Delta H > 0$
- ΔH for a reaction may be found experimentally by measuring the heat lost or gained when a process is carried out at a constant pressure

Measurement of ΔH

- **Calorimetry** – studies the heat flow of physical and chemical processes
- In an exothermic process, the heat released (q_{sys}) is absorbed by the surroundings (q_{surr}), which causes the calorimeter and its contents to rise in temperature, and vice versa
 - $q_{sys} = -q_{surr}$ a.k.a. $q_{rxn} = -q_{surr}$ where $q_{rxn} = \Delta H_{rxn}$
- In a simple calorimeter, the surroundings consist of both the calorimeter assembly (vessel, thermometer, stirrer) and the solution contained within the vessel
 - The system consists of just the reactants used
- **Molar enthalpy of reaction** – expressing ΔH in terms of the amount of a key reactant (or product) in the reaction; expressed as some amount of energy in KJ/mol of that reactant
- $q_{rxn} = -(q_{cal} + q_{solution}) = -(C_{cal}\Delta T + m_s c_s \Delta T)$
- To determine C_{cal} , you have to do a calorimeter calibration, using one of 2 methods:
 - Add a known amount of hot water with a known initial temperature to the calorimeter and then measure the temperature at equilibrium ($q_{hot\ water} = -q_{cal}$)
 - No chemical reaction is taking place
 - Carry out a reaction with a known ΔH_{rxn} , inside a bomb calorimeter, where no solution is present ($q_{rxn} = -q_{cal}$)
- **Bomb calorimeter** – usually involved in measuring the heat liberated from gaseous or combustion reactions
 - Unlike a simple calorimeter (which takes place at constant pressure), reactions in a bomb calorimeter take place under constant volume
 - However, for combustion reactions, we can assume constant pressure as well

Standard Enthalpy of Formation (ΔH_f°)

- This is the enthalpy change that occurs when one mole of a substance is formed from its constituent elements in their standard states
- ΔH_f° (element in standard state) = 0
- **Formation reaction:** *elements (standard state) \rightarrow 1 mole of a substance*

Hess's Law of Thermochemistry

- **Hess's Law** – the enthalpy change for a reaction is the sum of the enthalpy changes for the individual steps of the reaction
- $\Delta H_{rxn}^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$
 - Note that the stoichiometric coefficients are essential in the equation
- Any set of ΔH° values can be combined, not just ΔH_f°
- **Heat of combustion (ΔH_c°)** – the energy released when one mole of a fuel in its standard state undergoes complete combustion with oxygen to form $H_2O_{(l)}$ and $CO_{2(g)}$

Bond Enthalpy

- **Bond Enthalpy (BE)** – the energy required to break one mole of a specific type of bond (single, double or triple) between two atoms, providing the reactants and products are both gases
- Bonds broken = energy absorbed (endothermic), therefore BE is always positive
- **Total Bond Enthalpy (TBE)** – the energy required to break all of the bonds in one mole of a gaseous compound
 1. $TBE = \Delta H_{rxn}^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$
 2. TBE = sum of all the enthalpies of all the bonds in the mole, using avg. bond enthalpies

- Both of these methods give slightly different values for the TBE because molecular structure has an impact on bond enthalpy (since avg. bond enthalpies are used)
- **Average bond enthalpy** – may be determined from the TBE found using method 1]
 - E.g. TBE of $\text{CH}_4(\text{g}) = 1661.8 \text{ kJ/mol}$, \therefore avg. bond enthalpy of C-H bond = 415.5 kJ/mol
- Bond strength increases with bond order (triple bond is the strongest)
- ΔH of gas phase reactions
 - If a reaction has all its reactants and products in the gas phase, it is possible to estimate the enthalpy change of the gas-phase reaction using average bond enthalpies
 - $\Delta H_{\text{rxn}} = \sum \text{enthalpies of bonds broken} - \sum \text{enthalpies of bonds formed}$

Chapter 23 – Entropy and Spontaneous Change

Spontaneous Processes

- A spontaneous process is one that occurs in the absence of any ongoing outside intervention
- Processes spontaneous in one direction are non-spontaneous in the reverse direction
- A negative ΔE or ΔH are not the only criterion needed for a reaction to occur spontaneously
 - You need to consider **entropy** (S) – measure of the randomness/disorder of a system
 - The higher the # of possible arrangements for a system, the greater the entropy
 - $\Delta S = S_f - S_i$
 - $\Delta S > 0$ is an increase in disorder, and $\Delta S < 0$ is a decrease in disorder
 - States that are highly disordered are generally more probable in nature
- Spontaneity and reaction rate are unrelated
 - Therefore, spontaneous processes don't have to be necessarily fast
- **Standard molar enthalpies** – always greater than zero since entropy increases with temperature
 - Reported in J/molK and refer to standard conditions
 - $\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$
 - $S^\circ = 0$ at 0 K

Effect of Heat and Chemical Reactions on Entropy

- The addition of heat, particularly when associated with a phase change, greatly affects entropy
- Vaporization, melting and sublimation all increase the entropy ($S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$)
- **3rd law of thermodynamics** – the entropy of a perfectly ordered crystalline solid is defined to be zero at a temperature of absolute zero (0 K)
 - At absolute zero, a substance has no translational or rotational motion, but the atoms are still vibrating due to a quantum effect known as *zero-point energy*
 - Increasing temperature of a solid increases only the particles' *vibrational* motion, hence an increase in entropy
 - $\Delta S_{\text{surr}} = \frac{\Delta H_{\text{surr}}}{T} = -\frac{\Delta H_{\text{sys}}}{T}$
- Chemical reactions can affect entropy if they involve reactants/products in the gas phase
 - Increasing the # of molecules in the gas phase also increases the entropy
- **2nd law of thermodynamics** – every spontaneous process increases the entropy of the universe
 - Therefore, $\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$
 - Nature tolerates the creation of order in one part of the universe, as long as this is compensated by the formation of chaos somewhere else

Chapter 2.4 – Free Energy

Gibbs Free Energy

- **Gibbs free energy** – amount of energy available (“free”) to enable spontaneous change to occur
- Every chemical reaction is associated with a free energy change given by:
 - $\Delta G = \sum G_{products} - \sum G_{reactants}$
- **Gibb’s equation:** $\Delta G = \Delta H - T\Delta S$
 - $\Delta G < 0$ Reaction will proceed spontaneously (*favours* formation of products)
 - $\Delta G = 0$ System is at equilibrium; # of moles of reactant/product don’t change
 - $\Delta G > 0$ Reaction will not occur spontaneously (*favours* the reactants)
- **NOTE:** thermodynamics ($\Delta G, \Delta H, \Delta S$) does not determine the rate of a reaction
- According to the Gibb’s equation, all systems tend towards the lowest possible enthalpy and the highest possible entropy

What Drives a Process?

- **The Impact of Temperature and Signs on Gibbs Free Energy:**
 - $+\Delta S$ and $-\Delta H \rightarrow$ enthalpically and entropically driven ($-\Delta G$)
 - $-\Delta S$ and $+\Delta H \rightarrow$ never spontaneous ($+\Delta G$)
 - $-\Delta S$ and $-\Delta H \rightarrow$ enthalpically driven, if spontaneous ($\pm\Delta G$, depending on temp.)
 - $+\Delta S$ and $+\Delta H \rightarrow$ entropically driven, if spontaneous ($\pm\Delta G$, depending on temp.)
- Enthalpically Driven Processes
 - These are exothermic spontaneous processes with $\Delta H \ll 0$ and $\Delta S < 0$
 - The negative entropy is unfavourable
- Entropically Driven Processes
 - Endothermic reactions ($\Delta H > 0$) can only be spontaneous if they are associated with a large entropy increase ($\Delta S \gg 0$)
 - Temperature must be high enough to give a negative Gibbs free energy
 - There is a point where the temperature gives a ΔG of zero
 - This is the melting point temperature (T_m), where $\Delta H = T\Delta S$, since $\Delta G = 0$
- Enthalpically and Entropically Driven Processes
 - These processes are spontaneous because they are associated with favourable enthalpy ($\Delta H \ll 0$) and entropy changes ($\Delta S \gg 0$)

Standard Free Energy Change

- The free energy change under standard conditions is denoted as ΔG°
 - Thus, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
- As with enthalpy, the absolute free energy of a substance cannot be determined
- **Standard free energy of formation (ΔG_f°)** – the standard free energy change that occurs when 1 mol of a compound is made from elements in their standard states
 - The ΔG_f° of any element in its standard state is defined as zero
 - $\Delta G^\circ = \sum \Delta G_f^\circ(products) - \sum \Delta G_f^\circ(reactants)$

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 ΔG° is positive, the equilibrium lies to the LEFT and K is small
- If ΔG° 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 ΔH_{rxn}° 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_{sp}** is an equilibrium constant called the solubility product or the solubility product constant
 - Very soluble compounds have a LARGE K_{sp} value and these dissolutions go to completion
 - Compounds with low solubility have an equilibrium established and a SMALL K_{sp} 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_xB_y, the equilibrium reaction is:
 - $A_xB_y(s) \leftrightarrow xA^{y+}(aq) + yB^{x-}(aq)$
 - The K_{sp} 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_{sp} (system is at equilibrium)
 - When Q < K_{sp}, no solid will be present; all ions will remain in solution (unsaturated)
 - When Q > K_{sp}, 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⁺] concentration in solution (really [H₃O⁺])
- **Bases** – substances that increase hydroxide ion [OH⁻] 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, HNO₃, HClO₄, H₂SO₄
- STRONG BASES → NaOH, KOH, Mg(OH)₂, Ca(OH)₂
- **Arrhenius Theory** – Acids produce H₃O⁺ ions in water, whereas bases produce OH⁻ 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 \rightarrow weak acid and conjugate base
 - BASIC solution \rightarrow 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

Steps for Balancing Redox Reactions

1. Write as two half-reactions
2. Balance the coefficients for all atoms except H and O
3. Add H₂O to the side deficient in O to balance O
4. Add H⁺ to the side deficient in H to balance H
5. For basic conditions → Add an equal # of OH⁻ to both sides to neutralize the H⁺, making H₂O
6. Balance charges by adding electrons to the side deficient in negative charge
7. If half-reactions have different # of electrons, multiply them in order to get same coefficients
8. Add the balanced half-reactions

Disproportionation Reactions

- These are reactions in which a substance in an intermediate oxidation state goes to higher and lower states by electron transfer
- To balance, separate into half-reactions and follow similar steps as above

Chapter 4.2 – Voltaic Cells

Electrochemical Cells

- **Electrochemical cell** (voltaic cell, galvanic cell) – the experimental setup that produces an electric current and does electric work through the use of a redox reaction
- The Daniell Cell:
 - Consisted of zinc and copper metals in oxidized form
 - Based on reaction: $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$
 - To construct this cell, Zn and Cu bars are first immersed in separate beakers filled with aqueous ZnSO₄ and CuSO₄ solutions, and then connected with a wire
 - To compensate for the negative charge loss in the Zn beaker and negative charge gain in the Cu beaker, connect the two sulfate solutions with a *salt bridge*, allowing the negatively charged SO₄²⁻ ions in the Cu beaker to migrate to the Zn beaker
 - *Salt bridge* – filled with an aqueous solution of an inert salt (K₂SO₄)

Electrochemical Cell Notation

- **Half-cell** – the physically separated subsystem where each half-reaction occurs
- **Electrode** – where the half-reaction in each half-cell takes place on
 - The electrode is an electronic conductor that is in contact with an **electrolyte** – a solution or a molten salt
 - When none of the reactants is a solid conductor, a non-reactive metal is used as the electrode instead
 - **Cathode** – the electrode where reduction occurs
 - **Anode** – the electrode where oxidation occurs
- The current always flows from anode to cathode

Cell Diagram

- Anode is written first on the left, followed by other species in the order which they occur in the cell from the anode to cathode
- A phase boundary is represented by a single vertical bar
- The salt bridge is indicated by a double vertical bar
- If two or more reactants are in the same phase, separate them by a comma
- If inert electrodes are involved, they are placed on the anode or cathode end of the diagram as applicable, and separated by a single vertical bar
- Stoichiometric coefficients and species that aren't directly involved in the reaction aren't shown
- EXAMPLE $\rightarrow \text{Zn}(s) | \text{Zn}^{2+} || \text{Cu}^{2+} | \text{Cu}(s)$

Cell Potential

- **Cell potential/voltage** – the electrical energy difference between any two electrodes in an electrochemical cell (can be measured using a voltmeter)
- The voltage measured depends on the nature of the reactants in a cell, their concentrations (or pressures for gaseous reactants) and on the surrounding temperature
- Standard conditions for electrochemical cells \rightarrow 1.0 M and 25°C
- Only the potential of a complete cell can be measured with a voltmeter, not a half-cell
 - The potential for a half-cell can be measured relative to a commonly accepted reference half-cell (*standard hydrogen electrode*)
 - The standard electrode potential (E°) measures the tendency for a reduction process to occur at an electrode
- Stronger oxidizing agents are more easily reduced and have more positive E°_{red} values
- Stronger oxidizing agents form products that are more difficult to oxidize (weak reducing agent)
- To find E°_{cell} for a given redox reaction: $E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}}$

Spontaneity of Redox Reactions

- $\Delta G^\circ = -nFE^\circ_{\text{cell}}$
 - n = # of electrons transferred between the electrodes
 - F = Faraday constant = 96485 C/mol e^-
- If $E^\circ_{\text{cell}} > 0$, then the reaction is spontaneous from left to right
- If $E^\circ_{\text{cell}} < 0$, then the reverse reaction is spontaneous
- If $E^\circ_{\text{cell}} = 0$, then the cell reaction is at equilibrium

Gibbs Free Energy and the Nernst Equation

- To determine the cell potential for a cell in which the reactants are in concentrations other than 1 M $\rightarrow \Delta G = \Delta G^\circ + RT \ln Q$
- Can be rewritten as the Nernst Equation: $E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln Q$
- The Nernst equation can be used to predict the cell potential under non-standard conditions, and to predict the spontaneity of a redox reaction, or to calculate the unknown concentration of a reactant if a cell voltage is known
- It may be required to find the oxidation states of all involved species and take into account the number of moles of electrons involved in the balanced reaction

Chapter 4.3 – Electrolysis and Electrolytic Cells

Electrolysis

- **Electrolysis** – the process by which a non-spontaneous chemical reaction is forced to occur by the application of electrical energy from an external source
- The process of electrolysis is carried out in an **electrolytic cell**, which can be readily constructed from the corresponding voltaic cell
- If a voltage is applied to a voltaic cell from an external power source with an electromotive force greater than E°_{cell} , then the direction of electron flow in the cell will be reversed
 - The anodes and cathodes switch places (but the cell will still go from anode → cathode)
- You don't always have to place the electrodes in separate containers
 - Can have 2 electrodes in a single vessel filled with an electrolyte solution
 - The electrolyte filling can be a pure compound (e.g. water) or a molten salt (aqueous solution of a salt) or a mixture of pure compounds or aqueous solutions
 - A solid ionic compound that isn't melted or dissolved can't be electrolyzed because its ions are immobilized and cannot travel to the electrodes
- Electrolysis of Neutral Water
 - Pure water contains no ions to conduct electricity and so is very difficult to electrolyze
 - In order to decrease water's conductivity, you add a non-reacting, readily ionizing salt such as Na_2SO_4
 - Electrolysis of water is different from electrolysis of salts since individual H_2O molecules don't dissociate into cations and anions that migrate to the anode and cathode
 - Rather, some H_2O molecules are reduced at the cathode
 - $2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$
 - While others are oxidized at the anode
 - $2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^-$
 - Overall reaction: $2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + \text{H}_2(g)$
 - Note that every time two moles of water react, 4 moles of electrons are involved

Voltage Needed for Electrolysis

- The minimum standard voltage required to force a non-spontaneous redox reaction to occur is:
 $E^\circ_{\text{electrolysis}} = -E^\circ_{\text{cell}}$
- **Electrolysis of Water in Acidic Solution** – abundance of H^+ ions in aqueous acid which can undergo reduction at the cathode ($E^\circ_{\text{electrolysis}} = +1.23 \text{ V}$)
- **Electrolysis of Water in Basic Solution** – abundance of OH^- ions in the solution which can undergo oxidation at the anode ($E^\circ_{\text{electrolysis}} = +1.23 \text{ V}$)
- **Overpotential** – the additional voltage required to force a non-spontaneous reaction to occur
 - Arises from kinetic factors such as the activation barrier for the reactions taking place at the surface of the electrode
 - This is why the voltage of a battery charger must be higher than the output voltage
 - The magnitude of the overpotential depends on the surface structure of the electrodes and the type of chemical reaction at the surface

Predicting Electrolysis Products of Aqueous Solutions

- If the electrolytic cell contains a mixture of compounds, then more than one variation is possible at each electrode (usually one reaction favoured over the others)

- We can predict the actual products of electrolysis based on the ability of reactants to give up or attract electrons (compare E°_{red} for all possible half-reactions)
- **For the reduction half-rxn at cathode:** the higher the E°_{red} , the more favourable the reaction
- **For the oxidation half-rxn at anode:** the higher the E°_{ox} , the more favourable the reaction

Quantitative Determination of Electrolysis Products

- **Faraday's Law** – the # of moles of products reduced or oxidized by the passage of an electric current through an electrolytic cell is stoichiometrically equivalent to the # of moles of electrons supplied
- The charge (Q) of n moles of electrons can be written as: $Q = n_e F$
- Electric current (I) is defined as the flow of charge per unit time: $Q = It$

The Chlor-Alkali Process

- This is when an aqueous NaCl solution (brine) is electrolyzed to produce NaOH, $\text{H}_{2(g)}$ and $\text{Cl}_{2(g)}$
- The current used in this process is extremely high, but the applied voltage is only a few volts
- An ion-exchange membrane allows Na^+ ions to flow through but not Cl^-

Chapter 4.4 – Batteries

Batteries

- **Battery** – device that converts the chemical energy stored in its active materials into electrical energy, thus providing a source of power
 - **PRIMARY** – can be used only once because the chemical reactions that supply the electrical current are irreversible
 - **SECONDARY** – can be used, recharged, and reused since the chemical reactions that supply electrical current are easily reversed so that the battery can regain its charge
- **Discharging** – electrons from the anode migrate through an external circuit to the cathode
 - This is a spontaneous process that can only continue until the cell is completely dead
 - Dead batteries have zero cell potential since its reactants and products have attained equilibrium (limiting reagent may still be present)

Electrolytic Cells

- If a dead cell can be recharged by an external source, it becomes an electrolytic cell
- The external voltage required to force this non-spontaneous cell reaction is greater than the voltaic cell voltage
- Since the negative terminal of the external voltage source is electron rich, electrons flow from this terminal to the cathode
 - The current is sustained by the oxidation at the anode, producing electrons that flow to the positive terminal of the voltage source
 - Note that the cathode and anode have switched places since the direction of the current is reverse of that in the voltaic cell

Lead-Acid Battery

- Comprised of six 2 V cells connected in series
- Overall voltage is the sum of the voltages produced by the individual cells (12 V)
- In the charged state, each cell contains electrodes of Pb and PbO₂ in an electrolyte of H₂SO₄
- As the battery is discharged, both electrodes form PbSO₄ and the [H₂SO₄] is reduced
- Large SA supplied by the plates allows high currents to be generated for short periods of time
- When it charges, an external current is used to provide the energy needed for the non-spontaneous reverse reaction in each of the battery's 6 cells

Other Rechargeable Batteries

- **Nickel-Cadmium (NiCd) Batteries:**
 - Cadmium at the anode and nickel oxide at the cathode
 - Gradually lose their max. energy capacity after repeated recharging ("memory effect")
- **Nickel-Metal Hydride (NiMH) Batteries:**
 - Most popular today, since they don't have any toxic cadmium or a "memory effect"
 - Also able to store more energy than NiCd on a weight-by-weight basis
 - Cheap to manufacture, reliable, and relatively safe
 - The metal hydride is at the anode and nickel oxyhydroxide is at the cathode
- **Lithium-Ion (Li-Ion) Batteries:**
 - Popular due to its high energy-to-weight ratio
 - LiC₆ is at the anode and CoO₂ is at the cathode
 - Li⁺ ions aren't oxidized or reduced to generate a voltage
 - Instead, they migrate to and from the anode and cathode in a process called *intercalation* (possible due to layered structure of electrodes)
 - Although more expensive than NiMH, Li-ion batteries are light, deliver more power and don't suffer from "memory effect"
 - However, they can rupture, ignite or explode when subjected to high temperature or overcharging, and also cannot deliver high currents
- **Lithium-Polymer (Li-Pol) Batteries:**
 - Uses a polymer (solid phase) electrolyte between the two electrodes
 - Electrode material are situated in a spiral inside a cylinder, which prevents electrodes from touching
 - Advantage over a liquid electrolyte is that it allows the materials in the Li-Pol battery to be stacked, with little chance of the two electrodes coming into contact
 - These batteries can therefore be manufactured in virtually any shape

Chapter 5.1 – Reaction Rates and Rate Laws

Reaction Rates

- The speed at which a reaction takes place depends on: what the reactants are and their concentrations, the temperature, and whether or not a catalyst is present
- For any reaction: $aA + bB \rightarrow cC + dD$
 - The rate is expressed as: $\text{Rate} = -\frac{1}{a} \left(\frac{\Delta[A]}{\Delta t} \right) = -\frac{1}{b} \left(\frac{\Delta[B]}{\Delta t} \right) = \frac{1}{c} \left(\frac{\Delta[C]}{\Delta t} \right) = \frac{1}{d} \left(\frac{\Delta[D]}{\Delta t} \right)$

Concentration Effects and Rate Laws

- **Rate laws** – mathematical expressions that link the rate of a rxn with reactant concentration
- In the reaction: $aA + bB \rightarrow \text{products}$
 - The rate of the reaction (rate law) is: $\text{Rate} = k[A]^x[B]^y$
 - k is the specific rate constant for the reaction at a given temperature
 - x and y are the orders for each reactant and can only be found experimentally
- The “order” of a reaction defines how the rate of a reaction is affected by the concentration of the species involved in the reaction
- **Overall order of a reaction** – the sum of all the individual orders
- Experimental Determination of the Exponents
 - The initial rates are observed immediately after the reactants are mixed
 - If there is a graph, the initial slope = instantaneous rate at $t = 0$
 - Between any 2 runs, one of the reactant concentrations must be constant in order to determine the order of the second reactant

First-Order Reactions

- If $A \rightarrow \text{products}$ is a first-order reaction, $\text{Rate} = k[A] = -\left(\frac{\Delta[A]}{\Delta t}\right)$
- Integrated rate law: $\ln\left(\frac{\Delta[A]}{\Delta t}\right) = -k[t]$ or $[A]_t = [A]_0 e^{-kt}$ OR $\ln[A]_t = -kt + \ln[A]_0$
 - $[A]_t$ = concentration of A after time t has elapsed
 - $[A]_0$ = initial concentration
- A plot of $\ln[A]_t$ vs. time yields a straight line with a slope of $-k$ and y-intercept of $\ln[A]_0$
- **Half-life ($t_{1/2}$)** – the amount of time it takes to use up half of the reactant
 - $t_{1/2} = \frac{0.693}{k}$ (it only depends on the rate constant k in first-order reactions)
 - The half-life of a first-order reaction follows an exponential decay
 - Exponential decay plot is not a straight line ($[A]$ vs. time)
 - Graph approaches 0 but never reaches it; thus, the reaction is never complete
 - The fraction of reactant remaining after “ n ” half-lives can be expressed as:
 - $\text{Fraction remaining} = \frac{[A]_t}{[A]_0} = (0.05)^n$
 - $n = \text{number of elapsed half-lives} = \frac{\text{time elapsed}}{\text{length of half-life}}$

Zero-Order Reactions

- If $A \rightarrow \text{products}$ is a zero-order reaction, $\text{Rate} = -\left(\frac{\Delta[A]}{\Delta t}\right) = k[A]^0 = k$
- Integrated rate law: $[A]_t = -kt + [A]_0$
 - A plot of $[A]$ vs. time yields a straight line with a slope of $-k$ and y-intercept of $[A]_0$
- Half-life of zero-order reaction: $t_{1/2} = \frac{[A]_0}{2k}$

Second-Order Reactions

- If $A \rightarrow \text{products}$ is a second-order reaction, $\text{Rate} = -\left(\frac{\Delta[A]}{\Delta t}\right) = k[A]^2$
- Integrated rate law: $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
 - A plot of $1/[A]$ vs. time yields a straight line with a slope of k and y-intercept of $1/[A]_0$
- Half-life of a 2nd order reaction depends on the concentration of the reactant: $t_{1/2} = \frac{1}{k[A]_0}$

Chapter 5.2 – Reaction Mechanisms & the Arrhenius Equation

Thermodynamics and Kinetics

- **Thermodynamics** – net energy difference (ΔE) between reactants and products of a reaction
- **Kinetics** – the rate of the reaction depends on the size of the barrier
- Reaction coordinate diagrams illustrate the energy changes that occur on the route from reactants to products (represents progress along a reaction pathway)
- **Activation Energy** – the amount of energy required to overcome the activation barrier, in order to allow a reaction to proceed (this energy comes from heat, which is measured by temp.)
 - Temperature is a measure of the avg. kinetic energy of a collection of molecules
 - At any given temperature, there is a distribution of kinetic energies for molecules, as represented by a Boltzmann distribution graph
 - At low temperature, none of the reactants have enough energy to overcome barrier
 - As temperature increases, more of the molecules gain enough energy to overcome E_a
- **Collision Theory** – for a reaction to occur, reactants must collide in a proper orientation, with sufficient energy to overcome the activation barrier
- The rate of a reaction is affected by these factors:
 - Reactant concentration (higher concentration = more collisions)
 - Probability factor based on the probabilities of colliding in a particular geometry (steric factor) and continuing to the products at the transition state
 - E_a and temperature (higher temperature = more reactants able to overcome E_a)
- $\text{Rate} = \# \text{ of collisions} \times [\text{probability factor} \times \text{fraction of collisions with enough energy to overcome } E_a]$

The Arrhenius Equation

- $k = Ae^{-\frac{E_a}{RT}}$, where A = Arrhenius probability factor for a specific reaction
- As the value of E_a increases (higher activation barrier), the value of k decreases
 - Therefore, fastest reactions have the smallest activation energy barrier
- **Effect of Temperature on Rate:**
 - For a given reaction, E_a is a constant and can be determined without knowing the probability factor by performing two experiments at different temperatures while maintaining the same reactant concentrations
 - $\text{Rate}_{T_1} = k_{T_1}[A][B]$ at temperature 1
 - $\text{Rate}_{T_2} = k_{T_2}[A][B]$ at temperature 2
 - Therefore, $\ln\left(\frac{\text{Rate}_{T_2}}{\text{Rate}_{T_1}}\right) = \ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
- **Determining Activation Energy Graphically:**
 - The Arrhenius equation can be rearranged as: $\ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right)$
 - E_a can be determined experimentally by measuring a reaction rate at different temperatures, then plotting the graph of $\ln k$ vs. $1/T$
 - A straight line with a slope of $-\frac{E_a}{R}$ and a y-intercept of $\ln A$
- **Effect of a Catalyst on Activation Energy:**
 - A catalyst increases the rate of reaction but is not consumed in the reaction
 - It provides an alternative pathway with a lower E_a , that, in turn, increases k
 - Has no effect on the net enthalpy change (ΔH) of a reaction
 - **Rate enhancement factor** – the ratio of k values for the catalyzed and uncatalyzed reaction ($k_{\text{cat}} / k_{\text{uncat}}$)

- To determine that magnitude of the E_a reduction (ΔE_a) resulting from the introduction of a catalyst: $\ln\left(\frac{\text{Rate}_{cat}}{\text{Rate}_{uncat}}\right) = \ln\frac{k_{cat}}{k_{uncat}} = \frac{E_{a(uncat)} - E_{a(cat)}}{RT} = \frac{\Delta E_a}{RT}$

Reaction Mechanisms

- **Reaction Mechanism** – describes the sequence of steps that occur during a chemical reaction
- Each step is called an **elementary step**
 - Each elementary step has an E_a and a rate constant
 - # of steps = # of transition states
- Species formed and consumed within the reaction mechanism are **reaction intermediates**
 - Unlike transition states, these are real species that can be found in the reaction mixture as the reaction progresses (transition states are short-lived; cannot be found in mixture)
- **Molecularity** – refers to how many species react together in an elementary step
 - **Unimolecular process** – involves only one reactant species (first-order kinetics)
 - **Bimolecular process** – involves two species (second-order)
- ONLY in an elementary step, the coefficients of the reactants become exponents of the rate law
- The overall rate of a reaction is determined by the rate of the slowest or rate-determining step
- Determining Reaction Mechanisms
 - **Proposal A** – reaction occurs in one step
 - Overall reaction is therefore the elementary step
 - Reaction is bimolecular and rate law for the reaction is overall 2nd order
 - **Proposal B** – reaction occurs in two steps
 - First step slow; second step fast
 - Rate law for overall reaction is based on RDS (1st step)
 - Slower step has the higher transition rate
 - **Proposal C** – reaction occurs in two steps, but the slow/fast steps have been swapped
 - First step fast; second step slow
 - Rate law for overall reaction is based on step 2
 - However, since step 2 includes the intermediates (which cannot appear in overall rate law), step 1 must be rearranged and a substitute for the intermediate must be used in the step 2 (RDS) rate expression
- Guidelines for Deriving a Rate Law
 1. Look for the RDS
 2. Write a rate law in terms of concentrations of reactions in the RDS
 3. If there are intermediates, express their concentrations in terms of stable reactants appearing in the overall reaction equation
 - In an equilibrium reaction, forward and reverse rates are equal ($k_{if}[A] = k_{ir}[B]$)
 4. Substitute concentrations of stable reactants for concentrations of intermediates in the rate law
 5. Fast steps following the RDS in the mechanistic sequence may be ignored
 - NOTE: the RDS isn't always the one with the largest activation barrier
 - It is the step whose transition state has the highest overall energy