Mr SGs Chemistry ATAR Unit 3 Course Summary

Equilibrium Systems

Collision theory: For a chemical reaction to occur, the following needs to happen

-Reactant particles need to collide

-In the correct orientation

-With enough kinetic energy to overcome the E_A barrier

-All factors affecting the rate of a reaction (or the balance of an equilibrium) can be explained by their effect on the rate of collisions or the proportion of collisions where $E_k > E_A$

Factors $\uparrow$ rate of collisions: $\uparrow P, \downarrow V, \uparrow conc/pp, \uparrow T, \uparrow$ state of subdivison

Factors $\uparrow$ proportion of successful collisions: $\uparrow$ temp, catalyst

A system is at equilibrium when:

-Rates of forward and reverse reactions are equal

-Concentrations of all reactants and products are constant

-Macroscopic properties of the system are constant

-**Le Chatelier's Principle** (LCP) can be used to predict how a system will respond to an applied change

If a system at equilibrium is subjected to a change in conditions it will act to partially counteract the change

-**Equilibrium Constant (K)/ Reaction Quotient (Q)**

For the reaction $aA + bB \longleftrightarrow cC + dD$, $K = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

-The expression represents K at equilibrium and Q when not at equilibrium

-K is constant for a system at equilibrium for a particular temperature

-Only changes in the concentration of a gas or aqueous substance can alter the value of Q

-Only a change in temperature can alter the numerical value of K

Changes to equilibrium

To determine (or to graph) how a system will respond to an applied change:

-Determine whether the applied change will cause an immediate change in any concentrations

-Use LCP to predict how the system can partially counteract the change

-Determine whether the forward or reverse reaction will be temporarily favoured in order to partially counteract the change

-If asked to explain the change, use collision theory to explain why the rates of the forward and reverse reactions change

- The forward and reverse reaction rates will then converge until equilibrium is re-established

-As the system moves towards the new equilibrium, the concentrations of substances will change in proportion with their coefficients

Rate and Equilibria considerations in industry

-**Rate** (how quickly the reaction reaches equilibrium) can be maximised by using high temperatures and pressures and an appropriate catalyst

-**Yield** can be maximised by using a pressure and temperature that favours the forwards reaction, constantly removing products and adding at least one (preferably cheap) reactant in excess

-**Cost** can be minimised by using low temperatures and pressures

Equilibria involving atmospheric and oceanic CO_2

1) $\quad\quad\quad CO_{2(g)} \longleftrightarrow CO_{2(aq)}$

2) $\quad\quad CO_{2(aq)} + H_2O_{(l)} \longleftrightarrow H_2CO_{3(aq)}$

3) $\quad H_2CO_{3(aq)} + H_2O_{(l)} \longleftrightarrow HCO_{3\ (aq)}^- + H_3O^+_{\ (aq)}$

4) $\quad H_2CO_{3(aq)} + H_2O_{(l)} \longleftrightarrow HCO_{3\ (aq)}^- + H_3O^+_{\ (aq)}$

5) $\quad HCO_{3\ (aq)}^- + H_2O_{(l)} \longleftrightarrow CO_{3\ (aq)}^{2-} + H_3O^+_{\ (aq)}$

-↑ atmospheric CO_2 concentrations result in acidification due to reactions 1-3

-↑ acidity (↑ $[H_3O^+]$) causes ↓ $[CO_3^{2-}]$ by shifting equilibrium 5 to the left

-Equilibrium 5 also acts to buffer pH in human blood

Acids and Bases
-The Bronsted Lowry theory defines acids as proton donors and bases as proton acceptors

Acidity Constants (K_A)
-For the reaction: $\quad\quad\quad HA + H_2O \longleftrightarrow A^- + H_3O^+ \quad\quad\quad K_A = \dfrac{[A^-][H_3O^+]}{[HA]}$

-As acid strength is determined by the degree of ionisation, it can be measured with K_A
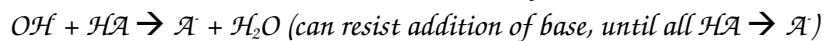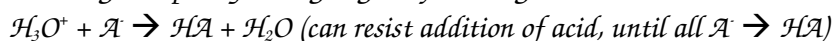

Acidity/Basicity of Salts
-Salts will be acidic or basic, if they can react with water in a hydrolysis reaction to produce H_3O^+ or OH^- ions

Acidic	Basic	Neutral
Conjugate acids of weak bases	Conjugate bases of weak acids	Conjugate bases of strong monoprotic acids
Transition metal ions	HCO_3^-, CO_3^{2-}, HPO_4^{2-}, PO_4^{3-}	Conjugate acids of strong bases

HSO_4^-, $H_2PO_4^-$		

Buffers

-Buffers are solutions that contain a weak acid (HA) and it's conjugate base (A^-)

-They resist changes in pH by undergoing the following reactions:

$H_3O^+ + A^- \rightarrow HA + H_2O$ (can resist addition of acid, until all $A^- \rightarrow HA$)

$OH^- + HA \rightarrow A^- + H_2O$ (can resist addition of base, until all $HA \rightarrow A^-$)

pH

-Water self ionises according to: $H_2O + H_2O \leftrightarrow H_3O^+ + OH^-$

$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{14}$ at 25°C $\qquad pH = -log[H_3O^+] \qquad [H_3O^+] = 10^{-pH}$

Indicators

-Indicators are weak acids where the acid (HInd) and its conjugate base (Ind^-) are different colours

-Changes in pH change their colour, by altering the equilibrium

$HInd + H_2O \leftrightarrow Ind^- + H_3O^+$
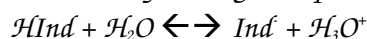
-Indicators will change colour close to their pK_a (the pH at which [HInd] = [Ind^-])

- $pK_a = -log_{10}K_a$

Volumetric Analysis (titrations)

-In an acid base titration, an acid/base of unknown concentration has its concentration determined by measuring the volume of a standard solution required to react with it

-**Standard solutions** are those with a known concentration

-**Primary Standards** have the following characteristics:

-Known formula, high purity, chemically stable (not deliquescent or hygroscopic), high formula mass

-Common primary standards include anhydrous sodium carbonate and oxalic acid

-**Secondary Standards** have their concentration measured by titration against a primary standard

Equipment	Rinsed with….
Burette	Solution it will be filled with
Pipette	Solution it will be filled with
Conical Flask	Water

-The progress of the reaction is usually measured by using an indicator that changes colour during the large pH change associated with the completion of the reaction

Equivalence point: The point at which stoichiometric quantities of reactants have been added

End point: The point at which the indicator will change colour

-An indicator is suitable for a titration if its end point occurs at the equivalence point (eg if its $pK_a \approx pH$ at equivalence point)

Acid	Base	pH at equivalence point	Suitable indicators
Strong	Strong	~7	methyl orange, phenylphthalein
Strong	Weak	<7	methyl orange
Weak	Strong	>7	phenylphthalein
Weak	Weak	~7	pH meter only

-Calculations from a titration are made based on concordant titres only (those within 0.1 mL)

Redox

-At the **AN**ode, **O**xidation **I**s **L**oss of electrons, **R**eduction **I**s **G**ain of electrons at the **CAT**hode (AN OIL RIG CAT)

-Oxidation can also be defined as an increase in oxidation number and reduction as a decrease in oxidation number

Determining oxidation number (O.N.):

-elements have an O.N. of O

-monoatomic ions have an O.N. equal to their charge

-oxygen has an O.N. of -2 in compounds, except in F_2O (+2) and peroxides (-1)

-hydrogen has an O.N. of +1 in compounds except metal hydrides (-1)

-the sum of oxidation numbers in a compound/polyatomic ion is equal to its charge

Writing redox half equations:

1) determine the substances being oxidised and reduced, using oxidation numbers
2) write down the oxidant or reductant and its product
3) balance the atoms undergoing oxidation or reduction
4) balance the oxygen atoms by adding water to one side
5) balance the hydrogen atoms by adding hydrogen ions to one side (acidic conditions)
6) balance charges by adding electrons
7) add state symbols

Combining half equations into a redox equation

1) multiply both half equations by a coefficient so that they contain the same number of electrons
2) combine the equations by writing all reactants from both half equations on the left and all products from both half equations on the right
3) simplify by cancelling out electrons and substances that appear on both sides of the equation

-The **Electromotive force** (emf) of a redox reaction can be used to determine the voltage of a cell, or whether a reaction will occur spontaneously (eg if $E°_{cell} > 0$)

$$E°_{cell} = E°_{oxidation} + E°_{reduction}$$

Galvanic (electrochemical) cells convert chemical potential energy into electrical energy

Zn(s) → Zn^{2+} + 2e$^-$ Cu^{2+} + 2e$^-$ → Cu(s)
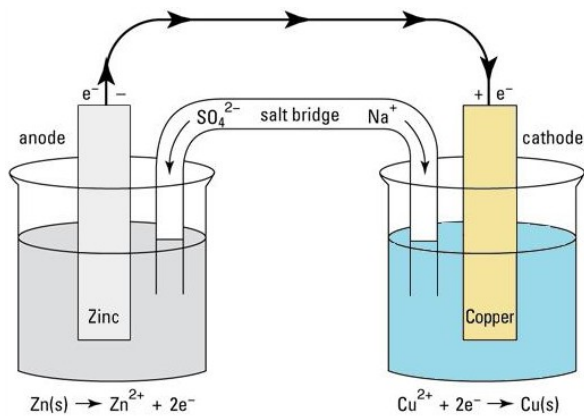
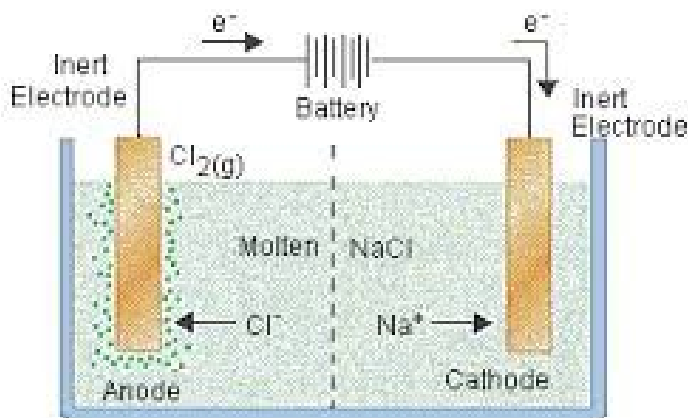*Anode: site of the oxidation half reaction, negative terminal of the cell*

External circuit: allows electrons to flow from anode to cathode, performing work

Cathode: site of reduction half equation, positive terminal

Electrolyte: Allows current to flow from cathode to anode as ions (cations to cathode, anions to anode)

Salt Bridge: Contains unreactive, highly soluble ions, allowing current to flow between half cells

Electrolytic cells *use electrical energy to drive a non-spontaneous redox reaction*

Power supply: Supplies the electrical energy required, provides electrons to cathode

Cathode: Site of reduction half equation, negative terminal of the cell

Electrolyte: Allows charge to flow from cathode to anode as ions, can contain reactants for the redox reaction
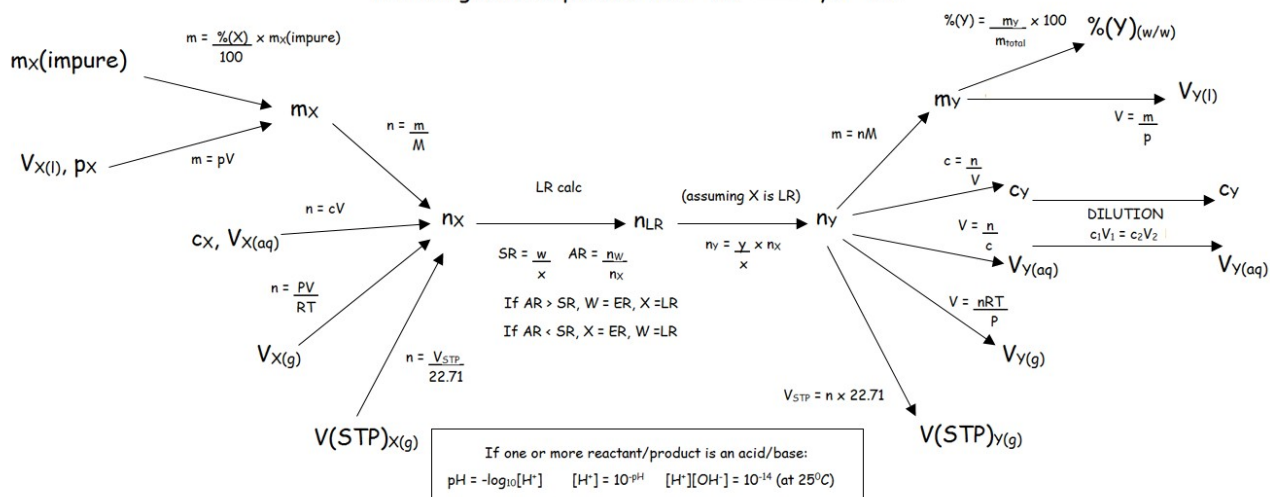
Anode: Site of oxidation half equation, positive terminal of the cell

-In **fuel cells**, *the reactants must be continually added to the cell*

Calculations

REACTION STOICHIOMETRY

For the general equation: wW + xX ⟶ yY + zZ

$m = \frac{\%(X)}{100} \times m_X(\text{impure})$

$m_X(\text{impure})$

$V_{X(l)}, \rho_X$

$m = \rho V$

m_X

$n = \frac{m}{M}$

$\%(Y) = \frac{m_Y}{m_{total}} \times 100$ $\%(Y)_{(w/w)}$

m_Y

$V_{Y(l)}$

$V = \frac{m}{\rho}$

$m = nM$

$c_X, V_{X(aq)}$

$n = cV$

n_X

LR calc

(assuming X is LR)

n_Y

$c = \frac{n}{V}$

c_Y

DILUTION
$c_1V_1 = c_2V_2$

c_Y

n_{LR}

$V = \frac{n}{c}$

$V_{Y(aq)}$

$V_{Y(aq)}$

$n = \frac{PV}{RT}$

$SR = \frac{w}{x}$ $AR = \frac{n_W}{n_X}$

$n_Y = \frac{y}{x} \times n_X$

$V = \frac{nRT}{P}$

$V_{X(g)}$

If AR > SR, W = ER, X = LR

If AR < SR, X = ER, W = LR

$V_{Y(g)}$

$n = \frac{V_{STP}}{22.71}$

$V_{STP} = n \times 22.71$

$V(STP)_{X(g)}$

If one or more reactant/product is an acid/base:

$pH = -\log_{10}[H^+]$ $[H^+] = 10^{-pH}$ $[H^+][OH^-] = 10^{-14}$ (at 25^0C)

$V(STP)_{Y(g)}$

-For reactions that are not 100% efficient, $m(\text{product})_{actual} = m(\text{product})_{max} \times (^{\%efficiency}/_{100})$

NOTE: This document covers Year 12 content only. The Year 12 Syllabus assumes that you are familiar with content taught in Year 11. Year 11 content that may need to be revised include, general reaction types, ionic and molecular equations, observations, ionic charges and solubility rules