

H2 Chemistry

Physical Chemistry

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Abstract

This book is written with the intention to provide readers with a brief summary of each topic in the Singapore GCE A-Level Chemistry at the H2 Level. The full syllabus can be found [here](#).

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§1 Mole Concept and Stoichiometry

§1.1 Relative masses

Definition 1.1: Relative isotopic mass

Mass of one atom of isotope of element relative to $\frac{1}{12}$ of mass of C-12 atom.

Definition 1.2: Relative atomic mass A_r

Average mass of atoms of element in isotopic mixture relative to $\frac{1}{12}$ of mass of C-12 atom.

Given i isotopes, A_r is the weighted average of all isotopes (so it is usually not an integer).

$$A_r = \frac{\sum_i m_i \times \text{Abundance}_i}{\sum_i \text{Abundance}_i} \quad (1)$$

Definition 1.3: Relative molecular mass M_r

Average mass of one molecule relative to $\frac{1}{12}$ of mass of C-12 atom.

M_r is the sum of the A_r of the atoms shown in the molecular formula.

$$M_r = \sum_i (A_r)_i \quad (2)$$

Definition 1.4: Relative formula mass M_r

Average mass of one formula unit of substance relative to $\frac{1}{12}$ of mass of C-12 atom.

Remark. A formula unit is the smallest collection of atoms from which the formula of an ionic compound can be established. It is equal to the sum of the A_r of the atoms shown in the formula unit.

Exercise 1.1

Determine the A_r of chlorine given that there exist two isotopes, ^{35}Cl and ^{37}Cl , with percentage isotopic abundance 75% and 25%, respectively.

Solution. To calculate A_r , we need to consider the relative amount of each isotope. To calculate a weighted average,

$$A_r \text{ of chlorine} = \frac{75(35) + 25(37)}{75 + 25} = \boxed{35.5}$$

□

§1.2 Mole

Definition 1.5: Mole

One mole contains exactly 6.02×10^{23} (or Avogadro constant) elementary entities.

Avogadro constant $L = 6.02 \times 10^{23} \text{ mol}^{-1}$

Definition 1.6: Molar mass

Mass of one mole of substance.

Definition 1.7: Avogadro's Law

Equal volumes of all gases, under same conditions of temperature and pressure, contain same number of molecules/ atoms.

Definition 1.8: Molar volume

Volume occupied by one mole of gas.

Molar volume at r.t.p. = $24.0 \text{ dm}^3 \text{ mol}^{-1}$

Molar volume at s.t.p. = $22.7 \text{ dm}^3 \text{ mol}^{-1}$

Definition 1.9: Standard solution

Solution which contains known amount of solute in given volume of solution (i.e. one with a known concentration).

Dilution:

$$C_0 V_0 = C_d V_d \quad (3)$$

§1.3 Oxidation number

Rules to assign oxidation number

1. ON of element = 0
2. ON of H in compound = +1 (except in metal hydrides)
3. ON of O in compound = -2 (except in peroxides, superoxides)
4. ON of more electronegative atom = -ve
5. ON of less electronegative atom = +ve
6. ON of uncharged compound = sum of individual ON = 0

§1.4 Redox reactions

To construct a redox equation in acidic medium,

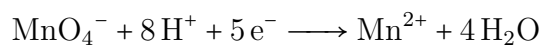
1. Construct unbalanced oxidation and reduction half-equations
2. Balance all elements except H and O
3. Balance O atoms by adding H₂O
4. Balance H atoms by adding H⁺ ions
5. Balance charges by adding electrons
6. Add both half-equations

To construct a redox equation in alkaline medium,

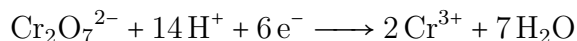
7. Neutralise H⁺ ions by adding OH⁻ ions, combine H⁺ and OH⁻ to form H₂O

§1.4.1 Half equations

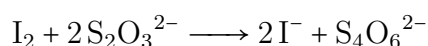
Manganate(VII) as oxidising agent



Dichromate(VI) as oxidising agent



Thiosulfate as reducing agent

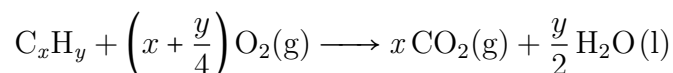


Calculate empirical and molecular formulae

Back-titration

§1.5 Combustion

Complete combustion of hydrocarbon:



§2 Atomic Structure

§2.1 Subatomic particles

particle	charge	mass	angle of deflection
proton	+1	1	small
electron	-1	≈ 0	large
neutron	0	1	none

Table 1: Subatomic particles

§2.1.1 Behaviour in an electric field/magnetic field

Deflection of subatomic particles in electric field:

$$\angle \propto \frac{q}{m} \iff \angle = k \frac{q}{m} \quad (4)$$

Remark. Constant of proportionality k remains the same under the same experimental conditions.

Remark. Note the sign of charge q : electrons and protons are deflected in opposite directions.

A beam of charged particles passing through an electric field is deflected.

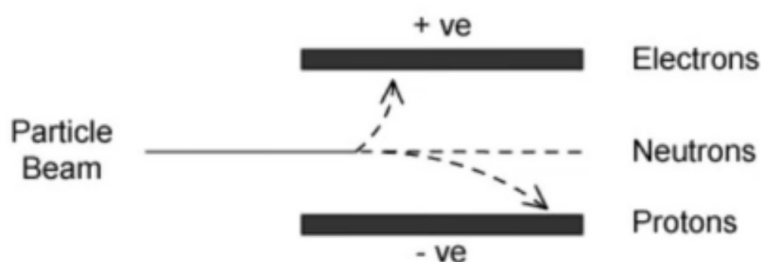


Figure 1: Deflection of subatomic particles in electric field

§2.1.2 Isotopes

Definition 2.1: Isotope

Atom of same element with same number of protons but different number of neutrons.

Isotopes have similar chemical properties since they have the same number of protons and hence the same number of electrons.

However, their physical properties differ since they have different numbers of neutrons and hence different masses.

To distinguish among the isotopes present, a classification system has been devised. In this system, the nuclide of an element is represented as such:



where X denotes atomic symbol of the element in the periodic table, Z denotes the atomic number/proton number (number of protons in the nucleus), A denotes mass number/nucleon number (number of protons and neutrons in the nucleus).

§2.2 Electronic structure

Definition 2.2: Orbital

Region in space where there is high probability of finding an electron.

§2.3 Electronic configuration

Ground state: electron occupy orbitals of lowest available energy levels

Excited state: electron absorbs energy, promoted to higher energy level. Such atoms are unstable, release energy to return to ground state

Rules of orbital filling

1. Aufbau principle

Electrons occupy lowest energy orbitals first before higher energy orbitals – filled in the order of increasing orbital energy. (4s filled before, removed before 3d)

2. Hund's rule

Electrons added into orbitals singly first with parallel spins before pairing. (electrons positioned as far apart as possible to minimise inter-electronic repulsion)

3. Pauli exclusion principle

Each orbital holds max 2 electrons in opposite spins.

Exceptions¹:

- **Chromium:** $[\text{Ar}] 3d^5 4s^1$ instead of $[\text{Ar}] 3d^4 4s^2$
to minimise inter-electronic repulsion
- **Copper:** $[\text{Ar}] 3d^{10} 4s^1$ instead of $[\text{Ar}] 3d^9 4s^2$
fully filled 3d shells are stable due to symmetrical charge distribution

¹You need to know these!

§2.4 Atomic trends

Definition 2.3: First ionisation energy

Energy required to remove 1 mole of electrons from 1 mole of gaseous atoms of the element to form 1 mole of singly charged gaseous cations.

Definition 2.4: Second ionisation energy

Energy required to remove 1 mole of electrons from 1 mole of singly positively charged gaseous ions to form 1 mole of doubly charged gaseous cations.

Definition 2.5: Nuclear charge

Electrostatic attraction of protons in nucleus on surrounding electrons.

Definition 2.6: Shielding effect

Partial decrease in electrostatic attraction of nucleus on valence electrons due to repulsive forces from other electrons.

Definition 2.7: Effective nuclear charge

Net electrostatic attraction of protons in nucleus on valence electrons.

§3 Chemical Bonding

§3.1 Types of Bonding

Type	Description	Factors affecting bond strength
Ionic bond	Electrostatic forces of attraction b/w oppositely charged ions in giant ionic structure	Lattice energy $\propto \frac{q^+ \cdot q^-}{r^+ + r^-}$
Metallic bond	Electrostatic forces of attraction b/w lattice of cations & sea of delocalised electrons in giant metallic structure	No. of valence electrons available for delocalisation per atom Size of metal cation (cationic radius)
Covalent bond	Electrostatic forces of attraction b/w positively charged nuclei of two atoms & shared pair of electrons in simple/-giant molecular structure (formed due to orbital overlap)	Bond dissociation energy, affected by: Bond order (no. of bonds) Effectiveness of orbital overlap: larger orbital is more diffused \rightarrow orbital overlap less effective \rightarrow shorter bond length \rightarrow weaker bond strength Bond length: sigma bond vs pi bond Polar VS non-polar bond
Dative bond	Electrostatic forces of attraction b/w positively charged nuclei of donor and acceptor atom & shared pair of electrons <ul style="list-style-type: none"> • Donor: lone pair of electrons available for donation (electron-rich) • Acceptor: vacant low-lying orbital to accept electron pair (electron-deficient) 	

Definition 3.1: Electronegativity

Ability of atom to attract shared pair of electrons towards itself in a covalent bond.

Intermediate bond types

§3.2 Covalent Bonds

§3.2.1 Overlap of orbitals

§3.2.2 Polarity

- Bond polarities and polarity of molecules

§3.2.3 Octet rule

§3.2.4 Valence Shell Electron Pair Repulsion (VSEPR) theory

- Shapes of simple molecules and bond angles

§3.3 Intermolecular Forces

Definition 3.2: Instantaneous dipole-induced dipole interaction

Electrostatic forces of attraction b/w oppositely charged poles ($\delta+$ and $\delta-$) of temporary dipoles in molecules.

Definition 3.3: Permanent dipole-permanent dipole interaction

Electrostatic forces of attraction b/w oppositely charged poles ($\delta+$ and $\delta-$) of permanent dipoles in polar molecules

Definition 3.4: Hydrogen bond

Electrostatic forces of attraction b/w molecules in simple molecular substances involving hydrogen atom from H-F/O/N covalent bond & lone pair from F/O/N of another molecule

§3.4 Physical Properties

§4 Gaseous State

§4.1 Gas Laws

The gas laws are given by

- **Boyle's Law:** $p \propto \frac{1}{V}$ at constant T and n
- **Charles' Law:** $V \propto T$ at constant p and n
- **Gay-Lussac's Law:** $p \propto T$ at constant V and n
- **Avogadro's Law:** $V \propto n$ at constant p and n

Remark. Remember to take note which quantities are *variables* and *constants*!

Remark. SI units must be used for calculations: p (in Pa), T (in K), V (in m^3), n (in mol)

Note that $1 \text{ atm} = 101325 \text{ Pa}$, $1 \text{ bar} = 10^5 \text{ Pa}$, $T \text{ (K)} = T \text{ (}^\circ\text{C)} + 273$

§4.1.1 Ideal gas equation

The **ideal gas equation** is given by

$$pV = nRT \quad (5)$$

where molar gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$

From eq. (5) we can derive the expression for **molar mass** of gas:

$$M_r = \frac{mRT}{pV} \quad (6)$$

and also the expression for **density** of gas:

$$\rho = \frac{pM_r}{RT} \quad (7)$$

§4.1.2 Partial pressure

Definition 4.1: Dalton's Law

In a mixture of inert gases at constant volume and temperature, total pressure of mixture is the sum of partial pressures of constituent gases.

$$p_{\text{gas}} = \frac{n_{\text{gas}}}{n_T} p_T \quad (8)$$

§4.2 Kinetic theory of gases

Basic assumptions:

1. Small particles of negligible volumes, as compared to container
2. Negligible intermolecular forces of attraction
3. Perfectly elastic collisions between gas particles and walls of container

All gases are non-ideal; they are real gases.

Approach ideality	Deviate from ideality
High temperature: gas particles able to overcome most of the intermolecular forces of attraction	Low temperature: molecules move more slowly, intermolecular forces of attraction become less negligible
Low pressure: volume of gas particles becomes negligible as compared to volume occupied by gas	High pressure: intermolecular distances become less negligible
	Strong intermolecular forces of attraction Large size of gas molecule

Definition 4.2: Compressibility

Ratio of measured molar volume V_m to molar volume of ideal gas V_m° at same temperature and pressure.

$$Z = \frac{V_m}{V_m^\circ} = \frac{pV_m}{RT} \quad (9)$$

§4.2.1 Compressibility against pressure

[graph]

At low pressure, $Z < 1$. Reason: Attractive forces between molecules, molar volume V_m is smaller than that of ideal gas V_m° .

At high pressure, $Z > 1$. Reason: Repulsive forces between molecules, molar volume V_m is larger than that of ideal gas V_m° .

§4.2.2 Compressibility against temperature

[graph]

Temperature decreases, deviation from ideality increases Average kinetic energy of gas particles decreases Gas particles closer together, intermolecular forces of attraction become significant V_m smaller than that of ideal gas

§5 Chemical Energetics

§5.1 Thermochemistry

Definition 5.1: Enthalpy change of reaction ΔH

Energy change when molar quantities of reactants as specified by the chemical equation react to form products.

Definition 5.2: Hess' Law

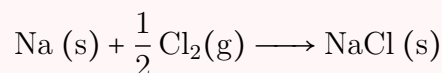
Enthalpy change accompanying a chemical reaction is the same regardless of the route by which the chemical change occurs, provided the initial and final states are the same.

Definition 5.3: Standard enthalpy change of reaction ΔH°

Energy change when molar quantities of reactants as specified by the chemical equation react to form products at standard conditions.

Definition 5.4: Standard enthalpy change of formation ΔH_f°

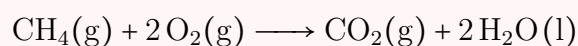
Energy change when one mole of the substance is formed from its constituent elements under standard conditions.



$$\Delta H = \sum H_f (\text{products}) - \sum H_f (\text{reactants}) \quad (10)$$

Definition 5.5: Standard enthalpy change of combustion ΔH_c°

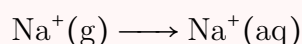
Energy evolved when one mole of the substance is completely burnt in oxygen under standard conditions.



$$\Delta H = \sum H_c (\text{reactants}) - \sum H_c (\text{products}) \quad (11)$$

Definition 5.6: Standard enthalpy change of hydration $\Delta H_{\text{hyd}}^\circ$

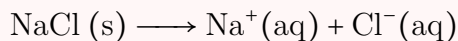
Energy evolved when one mole of gaseous ions is hydrated under standard conditions. Standard enthalpy change of solution.



$$\Delta H_{\text{hyd}}^{\ominus} \propto \frac{q^+}{r^+} \quad (12)$$

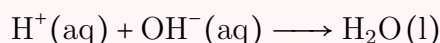
Definition 5.7: Standard enthalpy change of solution $\Delta H_{\text{soln}}^{\ominus}$

Energy change when one mole of substance is completely dissolved in a solvent to form an infinitely dilute solution under standard conditions.



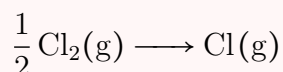
Definition 5.8: Standard enthalpy change of neutralisation ΔH_n^{\ominus}

Energy evolved when one mole of water is formed from the neutralisation between acid and base under standard conditions.



Definition 5.9: Standard enthalpy change of atomisation $\Delta H_{\text{atom}}^{\ominus}$

Energy absorbed when one mole of gaseous atoms is formed from the element under standard conditions.



Definition 5.10: Bond dissociation energy

Energy required to break one mole of covalent bond in a specific molecule in the gaseous state to form gaseous atoms.

Definition 5.11: Bond energy

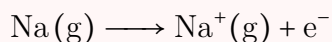
Average energy absorbed to break one mole of covalent bond in the gaseous state to form gaseous atoms under standard conditions.

$$\Delta H^{\ominus} = \sum \text{BE (bonds broken)} - \sum \text{BE (bonds formed)} \quad (13)$$

$$\text{BE (A}_2) = 2\Delta H_{\text{atom}}^{\ominus} (\text{A}_2) \quad (14)$$

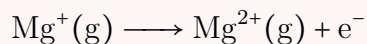
Definition 5.12: First ionisation energy

Energy absorbed when one mole of gaseous atoms loses one mole of electrons to form one mole of singly charged gaseous cations.

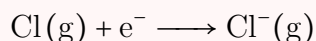


Definition 5.13: Second ionisation energy

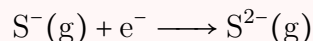
Energy absorbed when one mole of singly charged gaseous cations loses one mole of electrons to form one mole of doubly charged gaseous cations.

**Definition 5.14: First electron affinity**

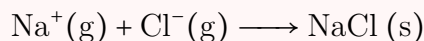
Energy evolved when one mole of gaseous atoms acquires one mole of electrons to form one mole of singly charged gaseous anions.

**Definition 5.15: Second electron affinity**

Energy absorbed when one mole of singly charged gaseous anions acquires one mole of electrons to form one mole of doubly charged gaseous anions.

**Definition 5.16: Lattice energy**

Energy evolved when one mole of the solid ionic compound is formed from its constituent gaseous ions under standard conditions.



$$\text{LE} \propto \frac{q^+ \cdot q^-}{r^+ + r^-} \quad (15)$$

$$\Delta H_{\text{soln}}^\circ = \sum \Delta H_{\text{hyd}}^\circ - \text{LE} \quad (16)$$

Remark. Take note of the following when writing equations:

1. State symbols
2. Stoichiometric coefficients
3. Sign for ΔH

Values

- Standard conditions: 298 K, 1 bar
- Standard temperature and pressure (s.t.p.): 273 K, 1 atm
- Room temperature: 20°C
- Specific heat capacity of water: 4.18 kJ.kg.⁻¹.K⁻¹ (or 4.18 J.g⁻¹.K⁻¹)

Refer to Data Booklet for bond energies, ionisation energies.

§5.1.1 Heat change

$$Q = mc\Delta T \quad (17)$$

$$\Delta H = \pm \frac{Q}{n} \quad (18)$$

§5.2 Thermodynamics

Definition 5.17: Entropy S

Degree of disorder or randomness in a system.

Factors affecting entropy change ΔS :

- **Temperature**

At higher temperature, average kinetic energy of particles increases. More ways to distribute greater amount of energy among particles. Entropy increases.

- **Phase**

Particles move about more freely and with greater speeds. More ways to distribute particles and energy. Entropy increases.

- **Number of particles**

More particles moving randomly. More ways to distribute particles and energy. Entropy increases.

- **Expansion of volume** (gaseous system)

Larger volume. More ways to distribute particles and energy. Entropy increases.

- **Mixing of particles**

When gases are mixed, each gas expands to occupy the whole container. More ways to distribute particles and energy in a larger volume. Entropy increases.

§5.2.1 Spontaneity

Gibbs free energy change ΔG is given by

$$\Delta G = \Delta H - T\Delta S \quad (19)$$

Remark. Note that since the units of ΔS is usually given in $\text{J mol}^{-1} \text{K}^{-1}$, so it has to be converted to $\text{kJ mol}^{-1} \text{K}^{-1}$ for calculations of ΔG .

Standard Gibbs free energy change, at standard conditions, is given by

$$\Delta G^\circ = \Delta H^\circ - T\Delta S$$

The spontaneity of a reaction can be determined from the value of ΔG :

$\Delta G < 0$	Reaction is spontaneous
$\Delta G > 0$	Reaction is non-spontaneous
$\Delta G = 0$	Reaction is at equilibrium (phase change)

To determine the change in spontaneity of reaction with temperature, use the **signs** of ΔH and $-T\Delta S$ to determine change in ΔG .²

ΔH	ΔS	$-T\Delta S$	ΔG	Spontaneity
-	+	-	always negative	Spontaneous at ALL temperatures
+	-	+	always positive	Non-spontaneous at ALL temperatures
+	+	-	negative if $ T\Delta S > \Delta H $	Spontaneous at HIGH temperatures
-	-	+	negative if $ \Delta H > T\Delta S $	Spontaneous at LOW temperatures

Limitations in the use of ΔG to predict spontaneity:

- Kinetic feasibility

Some reactions are energetically feasible (also known as thermodynamically feasible) since ΔG is negative, but kinetically not feasible since it occurs very slowly due to high activation energy. Such reactions are spontaneous but very slow.

- Non-standard conditions

ΔG° can only be used to predict the spontaneity of a reaction under standard conditions. Under non-standard conditions, ΔG must be calculated.

²sketch out graph to visualise better

§6 Chemical Equilibria

§6.1 Dynamic equilibrium

Definition 6.1: Dynamic equilibrium

The state of a reversible process at which the rates of forward and backward reactions are equal, but not equal to zero.

No change in concentrations of reactants and products, i.e. $k_f = k_b$.

§6.2 Equilibrium Law and Equilibrium Constants

§6.2.1 Equilibrium constants

For a reaction with equation $aA + bB \rightleftharpoons cC + dD$, the equilibrium constant, in concentrations, is given by

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (20)$$

In pressures, the equilibrium constant is given by

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b} \quad (21)$$

$$K_C = \frac{k_f}{k_b} \quad (22)$$

Recall that the partial pressure of gas is given by

$$P_A = \frac{n_A}{n_T} P_T \quad (23)$$

Degree of dissociation of A

$$\alpha = \frac{n_{A,\text{dissociated}}}{n_{A,\text{initial}}} \quad (24)$$

The position of equilibrium is related to K_C .

$K_C > 1$	More products at equilibrium, reaction proceeds in forward direction to larger extent, POE lies to the right.
$K_C < 1$	More reactants at equilibrium, reaction proceeds in backward direction to larger extent, POE lies to the left.

To do calculations, use the **ICE table**.

	A	B	C	D
Initial moles / mol				
Change in moles / mol				
Equilibrium moles / mol				

Remark. Note when to use moles, concentration, or partial pressure; use moles when total pressure is not constant.

Gibbs free energy change

$\Delta G < 0$	Forward is spontaneous $K > 1$, POE lies to right
$\Delta G = 0$	Equilibrium $K = 1$
$\Delta G > 0$	Backward is spontaneous $K < 1$, POE lies to left

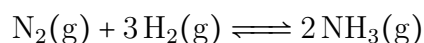
§6.3 Le Chatelier's Principle

Definition 6.2: Le Chatelier's Principle

If a system at dynamic equilibrium is subjected to a change which disturbs the equilibrium, the system responds in such a way so as to counteract the effect of the change to re-establish equilibrium.

Change in concentration Change in pressure Change in temperature Addition of catalyst

§6.4 Haber Process



Temperature	Pressure
Expectation: reaction is favoured by low temperature	Expectation: reaction is favoured by high pressure
Reality: High temperature used for higher rate of reaction, economical production	Reality: Low pressure used, as high cost of maintaining equipment for high pressure

§7 Chemistry of Aqueous Solutions

§7.1 Theories of Acids and Bases

Theory	Acid	Base
Arrhenius	hydrogen-containing substance, ionises and releases H^+ ions in aq solution	hydroxide-containing substance, ionises and releases OH^- ions in aq solution
Brønsted–Lowry	proton donor	proton acceptor
Lewis	electron pair acceptor (electrophile)	electron pair donor (nucleophile)

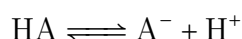
Remark. Let A denote the set of Arrhenius acids and bases, B denote the set of Brønsted–Lowry acids and bases, L denote the set of Lewis acids and bases. Then

$$A \subset B \subset L.$$

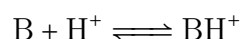
§7.1.1 Conjugate acid-base pair

Conjugate acid-base pair: a pair of compounds or ions which *differ by one proton*

- When acid HA donates proton to base, conjugate base A^- is formed.



- When base B receives proton from acid, conjugate acid BH^+ is formed.



Conjugate acid-base pairs: HA and A^- , B and BH^+

§7.1.2 Lewis acids

Types of species which can act as Lewis acids

- Electron-deficient molecules
Less than an octet of electrons around one atom. Dative bond formed in adduct³.
- Molecules with central atom that can expand octet
Low-lying vacant orbitals to accept lone pairs of electrons.

³compound that contains a dative bond between the Lewis acid and the Lewis base

- Molecules with multiple bonds that has atom with partial positive charge
Lewis base donates lone pair of electrons to form bond with central atom, one pair of electrons displaced from multiple bond to become lone pair on terminal atom.
- Metal cations
Accept lone pair of electrons via dative bond to form complex ions.

§7.2 Acid–Base Equilibria

§7.2.1 Strength of acids and bases

Strength is a measure of extent of dissociation to give ions in solution. (independent of concentration)

	Strong	Weak
Definition	Complete dissociation in aq solution	Partial dissociation in aq solution
Extent of dissociation	100%	<< 100%
Arrow	\longrightarrow	\rightleftharpoons
Equilibrium constant	–	K_a, K_b

§7.2.2 Acid and base dissociation constants

Power of hydrogen:

$$pH = -\lg[H^+] \quad (25)$$

Power of hydroxide:

$$pOH = -\lg[OH^-] \quad (26)$$

Acid dissociation constant: measure of strength of *weak* acid⁴

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (27)$$

$$pK_a = -\lg K_a \quad (28)$$

Base dissociation constant: measure of strength of *weak* base

$$K_b = \frac{[BH^+][OH^-]}{[B]} \quad (29)$$

$$pK_b = -\lg K_b \quad (30)$$

Acidic, basic & neutral solutions

Solution	Meaning
acidic	$[H^+] > [OH^-]$
basic	$[H^+] < [OH^-]$
neutral	$[H^+] = [OH^-]$

⁴equilibrium constant

§7.2.3 Ionic product of water

Self-ionisation of water can be simplified to $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$.

Ionic product of water:

$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ at } 298 \text{ K} \quad (31)$$

By manipulation we have

$$pH + pOH = pK_w = 14 \text{ at } 298 \text{ K} \quad (32)$$

The following relationship holds for a conjugate acid-base pair:

$$K_w = K_a K_b \quad (33)$$

This suggests a reciprocal strength relationship: the stronger the acid, the weaker its conjugate base (and vice versa).

§7.2.4 Salt solutions

Salts undergo hydration to form solutions. Then cations / anions undergo hydrolysis to form acidic / alkaline solutions.

Acidic salt solution	Alkaline salt solution
cation: conjugate acid of WB hydrolyses partially in water to give H_3O^+	anion: conjugate base of WA hydrolyses partially in water to give OH^-
$\text{BH}^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{B}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$	$\text{A}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HA}(\text{aq}) + \text{OH}^-(\text{aq})$

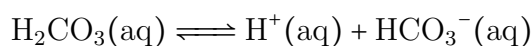
§7.2.5 Buffer solutions

Definition 7.1: Buffer solution

A solution capable of maintaining a fairly constant pH (by resisting pH change) when small amounts of acid or base are added to it.

Acidic buffer solution	Basic buffer solution
weak acid + salt of conjugate base (HA and A^-)	weak base + salt of conjugate acid (B and BH^+)
On addition of acid: $A^-(aq) + H^+(aq) \longrightarrow HA(aq)$	On addition of acid: $B(aq) + H^+(aq) \longrightarrow BH^+(aq)$
On addition of base: $HA(aq) + OH^-(aq) \longrightarrow A^-(aq) + H_2O(l)$	On addition of base: $BH^+(aq) + OH^-(aq) \longrightarrow B(aq) + H_2O(l)$
Large reservoir of HA and A^- present is able to cope with small amount of H^+ and OH^- added.	Large reservoir of B and BH^+ present is able to cope with small amount of H^+ and OH^- added.

Buffer solutions are used in systems where pH must not deviate widely. H_2CO_3 / HCO_3^- buffer pair is used to control pH of blood:



- On addition of acid: $HCO_3^-(aq) + H^+(aq) \longrightarrow H_2CO_3(aq)$
- On addition of base: $H_2CO_3(aq) + OH^-(aq) \longrightarrow HCO_3^-(aq) + H_2O(l)$

§7.2.6 Titration

Titrate titrant against analyte / Analyte titrated against titrant

Equivalence point: stoichiometric amounts of acid & base react together

End-point: when indicator first changes colour permanently

Choice of pH indicator is considered appropriate if its pH transition range lies within range of rapid pH change over equivalence point.

pH graph sketching

1. initial, equivalence, final pH
2. initial, equivalence, final volume
3. buffer region

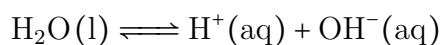
Types of titration

- strong acid–strong base
- strong acid–weak base
- weak acid–strong base
- weak acid–weak base

(d) describe the changes in pH during acid-base titrations and explain these changes in terms of the strengths of the acids and bases (e) explain the choice of suitable indicators for acid-base titrations, given appropriate data

§7.2.7 Calculations

- **Water**



In pure water, $[\text{H}^+] = [\text{OH}^-]$

$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

$$[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ mol dm}^{-3}$$

- **Strong acid**



$$[\text{H}^+] = n \times [\text{H}_n\text{A}]$$

Strong base



$$[\text{OH}^-] = n \times [\text{M}(\text{OH})_n]$$

- **Weak acid** (monobasic)



Since HA is weak acid with small K_a , assume extent of dissociation of HA is negligible, so $[\text{H}^{+}]$ is so small such that $[\text{HA}] \approx [\text{HA}]_{\text{initial}}$.

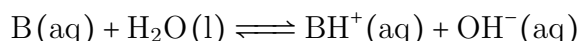
$$K_a = \frac{[\text{H}^{+}][\text{A}^{-}]}{[\text{HA}]} = \frac{[\text{H}^{+}]^2}{[\text{HA}]} \approx \frac{[\text{H}^{+}]^2}{[\text{HA}]_{\text{initial}}}$$

$$\boxed{[\text{H}^{+}] = \sqrt{K_a \times [\text{HA}]_{\text{initial}}}}$$

from which we can calculate pH .

Remark. This formula CANNOT be used to calculate K_a or $[\text{HA}]_{\text{initial}}$! Instead use ICE table.

- **Weak base** (monoacidic)



Since B is weak base with small K_b , assume extent of dissociation of B is negligible, so $[\text{OH}^{-}]$ is so small such that $[\text{B}] = [\text{B}]_{\text{initial}}$.

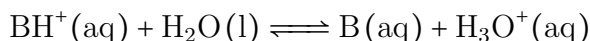
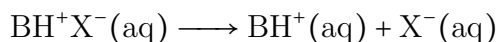
$$K_b = \frac{[\text{BH}^{+}][\text{OH}^{-}]}{[\text{B}]} = \frac{[\text{OH}^{-}]^2}{[\text{B}]} \approx \frac{[\text{OH}^{-}]^2}{[\text{B}]_{\text{initial}}}$$

$$\boxed{[\text{OH}^{-}] = \sqrt{K_b \times [\text{B}]_{\text{initial}}}}$$

from which we can calculate pOH and then pH .

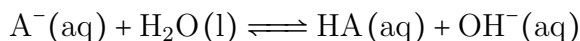
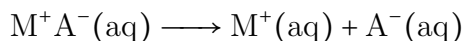
Remark. This formula CANNOT be used to calculate K_b or $[\text{B}]_{\text{initial}}$! Instead use ICE table.

- **Acidic salt solution**



$$\boxed{[\text{H}^{+}] = \sqrt{K_a \times [\text{HA}]_{\text{initial}}}}$$

- **Alkaline salt solution**



$$\boxed{[\text{OH}^{-}] = \sqrt{K_b \times [\text{B}]_{\text{initial}}}}$$

Remark. When solutions are mixed, remember to calculate the new concentrations.

- **Acidic buffer solution**

$$pH = pK_a + \lg \frac{[A^-]}{[HA]}$$

Maximum buffer capacity: $[HA] = [A^-] \implies pH = pK_a$

Basic buffer solution

$$pOH = pK_b + \lg \frac{[BH^+]}{[B]}$$

Maximum buffer capacity: $[B] = [BH^+] \implies pOH = pK_b$

Taking -log on both sides gives us

$$pK_a + pK_b = pK_w \tag{34}$$

At 298 K, $pK_a + pK_b = 14$.

(c) calculate $[H^+(aq)]$ and pH values for strong acids, weak monobasic (monoprotic) acids, strong bases, and weak monoacidic bases [Calculations involving weak acids/bases will not require solving of quadratic equations]

§7.3 Solubility Equilibria

Definition 7.2: Solubility

Maximum mass / amount of solute that can be dissolved per dm^3 of solvent to produce a *saturated solution* at a given temperature.

Definition 7.3: Solubility product K_{sp}

Equilibrium constant which is the product of molar concentrations of dissolved / dissociated ions (each raised to its appropriate power) in a *saturated solution* of salt at a given temperature.

For a sparingly soluble salt MX, $\text{MX (s)} \rightleftharpoons \text{M}^+(\text{aq}) + \text{X}^-(\text{aq})$.

$$K_{sp} = [\text{M}^+]_{\text{satn}}[\text{X}^-]_{\text{satn}} \quad (35)$$

Factors affecting solubility of salt

- **Common ion effect** (addition of cation/anion)

Reduced solubility of a solute in a solution that already contains the same ion.

Saturated sparingly soluble salt solution MX added to soluble salt solution NaX (aq) (containing common ion X^-). $[\text{X}^-]$ increases. By Le Chatelier's Principle, position of equilibrium shifts left to decrease $[\text{X}^-]$, so dissociation of MX suppressed, MX precipitated. Hence solubility decreases in NaX(aq) compared to that in water.

- **Formation of complex ions** (removal of cation)

Suitable base added to saturated sparingly soluble salt solution MX. Formation of complex ions remove cations M^+ , $[\text{M}^+]$ decreases. By Le Chatelier's Principle, position of equilibrium shifts right to increase $[\text{M}^+]$, so dissociation of MX favoured. Hence solubility increases.

$[\text{M}^+]$ decreases, ionic product decreases to below K_{sp} , so MX dissolves.

- **pH of solution** (removal of anion)

H^+ added to saturated sparingly soluble salt solution MOH. $[\text{OH}^-]$ decreases. By Le Chatelier's Principle, position of equilibrium shifts right to increase $[\text{OH}^-]$. Hence solubility increases.

Definition 7.4: Ionic product IP

Product of molar concentrations of constituent ions in solution *at that instant* (each raised to its appropriate power) at a given temperature.

$$\text{IP} = [\text{M}^+][\text{X}^-] \quad (36)$$

Precipitation occurs when $\text{IP} > K_{sp}$.

Condition	Saturation	Precipitation
$IP < K_{sp}$	Below saturation point (unsaturated)	No
$IP = K_{sp}$	At saturation point (saturated)	No
$IP > K_{sp}$	Beyond saturation point (beyond saturation)	Yes

Candidates should be able to: (b) calculate K_{sp} from concentrations and vice versa (c) discuss the effects on the solubility of ionic salts by the following: (i) common ion effect (ii) formation of complex ion, as exemplified by the reactions of halide ions with aqueous silver ions followed by aqueous ammonia (see also Section 13)

§8 Electrochemistry

§8.1 Redox processes

Oxidation: loss of electrons / increase in oxidation state

Reduction: gain of electrons / decrease in oxidation state

§8.2 Electrode potentials

Definition 8.1: Standard electrode (redox) potential E^\ominus

Potential

(i) standard electrode (redox) potentials, E^\ominus ; the redox series (ii) standard cell potentials, E^\ominus_{cell} , and their uses (iii) batteries and fuel cells

§8.3 Electrolysis

(i) factors affecting the amount of substance liberated during electrolysis (ii) the Faraday constant; the Avogadro constant; their relationship (iii) industrial uses of electrolysis

Learning Outcomes Candidates should be able to: (a) describe and explain redox processes in terms of electron transfer and/or of changes in oxidation number (oxidation state) (b) define the terms: (i) standard electrode (redox) potential (ii) standard cell potential (c) describe the standard hydrogen electrode (d) describe methods used to measure the standard electrode potentials of: (i) metals or non-metals in contact with their ions in aqueous solution (ii) ions of the same element in different oxidation states (e) calculate a standard cell potential by combining two standard electrode potential (f) use standard cell potentials to: (i) explain/deduce the direction of electron flow from a simple cell (ii) predict the spontaneity of a reaction (g) understand the limitations in the use of standard cell potentials to predict the spontaneity of a reaction (h) construct redox equations using the relevant half-equations (see also Section 13) (i) state and apply the relationship $\Delta G^\ominus = -nFE^\ominus$ to electrochemical cells, including the calculation of E^\ominus

for combined half reactions (j) predict qualitatively how the value of an electrode potential varies with the concentration of the aqueous ion (k) state the possible advantages of developing other types of cell, e.g. the H₂/O₂ fuel cell and improved batteries (as in electric vehicles) in terms of smaller size, lower mass and higher voltage (l) state the relationship, $F = Le$, between the Faraday constant, the Avogadro constant and the charge on the electron (m) predict the identity of the substance liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential) and concentration (n) calculate: (i) the quantity of charge passed during electrolysis (ii) the mass and/or volume of substance liberated during electrolysis (o) explain, in terms of the electrode reactions, the industrial processes of: (i) the anodising of aluminium (ii) the electrolytic purification of copper