

AP Chemistry

1 Moles and Molar Mass

Drawing reaction diagrams: formation of precipitate, relative size of ions, relative number of ions.

Gravimetric analysis determines the water content of a sample, from the difference in mass before and after repeated rounds of heating, until constant mass on consecutive weightings.

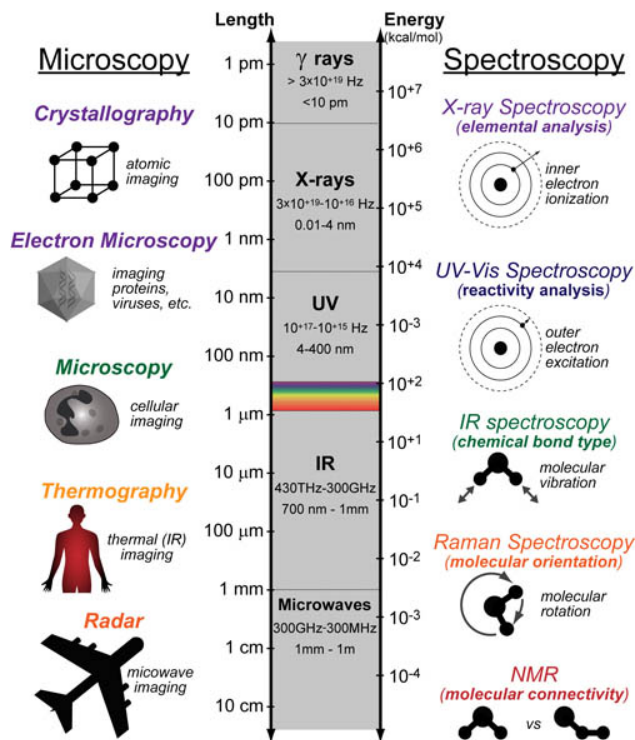
- (a) Explain what the student can correctly conclude after the third heating of the hydrate in the experiment.
- Since the mass of the sample and container remains approximately constant after the second and third heating, all the water of crystallisation in the hydrated salt has evaporated
- (b) Mass of $\text{MgCl}_2 = m_{\text{final}} - m_{\text{container}}$, mass of $\text{H}_2\text{O} = m_{\text{initial}} - m_{\text{final}}$
- Give mass to 3dp (or dp used in question), ratio to nearest whole number
- (c) What effect would spattering of the hydrate have on the calculated mass of the water lost?
- The calculated mass of the water lost is larger because the mass of solid that spattered out is taken as the mass of water evaporated.

2 Mass and Photoelectron Spectroscopy

The size of atoms is much smaller than the wavelengths of visible light, hence they do not change how light is reflected, thus they cannot be observed with an optical microscope.

Photoelectron spectroscopy determines the ionisation energy of an electron based on the frequency of incident light and KE of ejected electron.

- (a) H and He has only 1 ionisation energy, even though He has 2 electrons
- The 2 electrons in He must be the same distance from the nucleus (or in the same shell).
- (b) 1st IE of He is approximately double that of H
- He nucleus has 2 protons, hence has a nuclear charge twice that of H
- (c) What does the Ionisation Energy data of H and He suggest about the number of electrons that can occupy the shell closest to the nucleus ($n = 1$); and about the distance of the $n = 1$ shell in He compared to $n = 1$ shell in H?
- Since there is only 1 IE value for He (and 2 IE values for Li), it indicates the $n = 1$ shell can hold 2 electrons. The energy of the $n = 1$ shell in H is lower than in He, suggesting the shell in He is closer to the nucleus.
- (d) Large difference in magnitude in the 2 IE of Be
- The 3rd and 4th electrons are in a different shell from the first two electrons, and are much farther from the nucleus



Mass spectroscopy shows that an element can have isotopes which are atoms of the same element but have different masses (due to the different number of neutrons in the nuclei).

3 Periodic Trends

Electron shielding: across the period, actual nuclear charge increases with increase in number of protons while screening effect remain constant as number of core e^- [inner electron shells] remain the same. Thus, effective nuclear charge increases, and valence e^- are held more tightly to the nucleus, resulting in smaller atomic radius. Down a group, the principal quantum number increases [increase in number of electron shells], thus the probability of finding e^- further away from the nucleus is greater, greater atomic radius.

Oxygen atom gains two e^- to form oxide ion, O^{2-} . The same nuclear charge is now holding to more e^- , hence e^- in valence shell is less tightly held, resulting in larger radius of the anion; aluminium atom loses three e^- to form Al^{3+} ion, as Al^{3+} ion has 1 quantum shell less than Al atom [from loss of valence shell], the same nuclear charge is now holding to less e^- . Hence, e^- in the outer shell are more tightly held, resulting in smaller radius of the cation.

Isoelectric series: similar electron configuration, ionic radius decreases with increasing nuclear charge.

Coulomb forces: the last e^- is experiencing the full nuclear charge of n protons without any e^- screening/found in the first orbital [1s] of principal quantum number 1 so the average distance [d] in between e^- and nucleus is very small, hence the last ionisation requires greatest energy to overcome largest attractive force.

X^{n+} has the same e^- configuration as N [noble gas] following the n^{th} reaction, hence the following reaction need to remove a e^- from a lower shell that is at a closer average distance [d], increase in energy required for ionisation.

Energy level of subshells: e^- removed from Si^+ is from the 3p-subshell which is of higher energy as compared to the 3s-subshell for Al^{3+} , thus the valence electron is less tightly held by the nucleus.

Electron repulsion: inter-electron repulsion between the paired e^- in the 3p orbital for Cl reduces energy required to remove the e^- , resulting in a lower 2nd ionization energy.

By acquiring an extra e^- carbon gain a half-filled p orbital that increase stability, thus C easily gains one extra e^- , N already has a half-filled p orbital, the new e^- occupies an orbital which already has an e^- which results in electron-electron repulsion and add instability, thus does not easily gain an extra e^- .

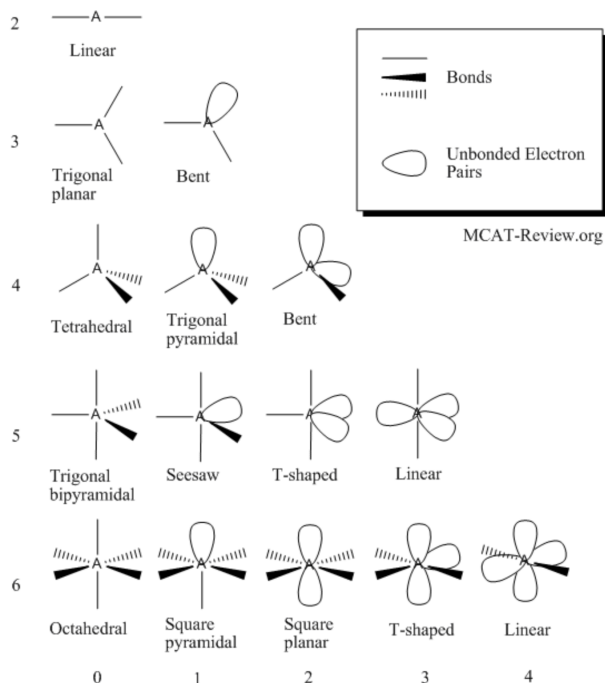
4 Covalent Molecules

(a) **Lewis structure model:** assumes each atom has an octet structure in its valence shell.

(b) **resonance structures:** actual structure is a resonance hybrid of the equivalent structures, thus each N-O bonds is identical, **bond order** changes

(c) **formal charge:** charge assigned to an atom in a molecule, assuming that electrons in a chemical bond are shared equally between atoms, regardless of relative electronegativity

- formal charge = no. of valence electron around a free atom — no. of valence electron around bonded atom
 - oxidation number: number of electron exchanged between atoms during formation of the molecule
- most preferred structure is one with no formal charge, or one where negative formal charge is placed on the more electronegative atom
- presence of formal charge indicates a dative bond is formed between the electron-pair donor and acceptor



Valence Bond Theory: Both C-O σ bonds are formed by end-to-end overlap of a sp -hybridised orbital of C with sp^2 -hybrid orbital of O; C-O π bond is formed from the sideways overlap of the unhybridized 2p-atomic orbital of C with unhybridized 2p-atomic orbital of O; other sp^2 -hybrid orbitals of O contain lone pair of electrons.

Intermolecular forces: Ion-Dipole Force, Hydrogen Bonding (between polar molecules with highly-polar N/O/F-H bonds), Dipole-Dipole Force, Ion/Dipole-Induced Dipole, London Dispersion Force (arises from distortion of electron cloud resulting in a temporary dipole, strength depends on size/polarisability of electron cloud (size of induced dipole), and surface area of contact (less interactions between spherical, branched, compact molecules)).

Structure: *giant ionic structure* (oppositely-charged ions held by strong ionic bonds, strength depends on coulombic force of attraction), *giant metallic structure* (positive ions held by strong metallic bonds in sea of delocalized valence e^-), *giant covalent network* (atoms held in rigid, 3D network structure by strong covalent bonds), *simple molecular structure* (discrete covalent molecules held by IMF, less energy required to overcome weaker bonds).

In HClO_3 , the Cl atom is bonded to 2 electronegative O atoms which attract the e^- density away from Cl atom. This inductive effect causes the O-H bond to be more polarized (weaker), ionises more readily to produce H^+ in solution and is more acidic compared to HOCl , where the Cl atom is not bonded to any other electronegative atom.

Graphite is slippery as the macromolecular layers are held together by weak LDF which are easily overcome and can slide easily. Graphite is an electrical conductor, as each C atom only uses 3 of its valence e^- to form covalent bonds, hence each atom contributes an e^- to form a cloud of delocalised electrons that is mobile in an electric field.

Interstitial alloys form from atoms of different radius, *density is higher* as Carbon atoms occupy the interstitial spaces between Iron atoms, thus mass of the alloy increases but not the volume; *malleability and ductility is reduced* as Iron atoms in the interstitial spaces prevent the layers of Fe atoms from sliding to form a new shape when a physical force is applied. **Substitutional alloys** form from atoms of comparable radius, *density* depends on composition of the alloy, *malleability* is minimally affected as layers can slide past each other.

5 Kinetic Molecular Theory and Ideal Gas Law

Increasing the temperature increases the average kinetic energy, resulting in greater translational and vibrational motion of the gaseous molecules. Hence, the molecules collide against the walls of the container with greater force and with higher frequency, resulting in an increase in pressure.

**Maxwell-Boltzmann distribution curve shift right, show wider spread of molecular speeds*

Assumptions of Kinetic Molecular Theory: (1) There are negligible intermolecular forces between the particles. (2) The particles are point masses that have negligible volume compared to the volume occupied by the gas. Most gases behave like an ideal gas only at low pressures and high temperatures.

van der Waals equation: V adjusted down, account for V occupied by particles [$b \propto$ molecular size], P adjusted up, account for attractive IMF between particles that reduce P [$a \propto$ attractive IMF].

For real gases, repulsion forces between electron clouds become significant when molecules come very close to each other, hence the minimum volume that the real gas molecules can occupy is larger than for ideal gas molecules.

Dalton's Law of partial pressures: $P_{\text{total}} = P_A + P_B + P_C + \dots$, where $P_A = \chi_A \times P_{\text{total}}$

Graham's Law of effusion [molecules escape through orifice smaller than mean free path]: rate of effusion $\propto \frac{1}{\sqrt{M}}$

6 Solutions and Mixtures

In a closed system, dynamic equilibrium is reached between a liquid and its vapour when rate of evaporation of liquid equals rate of condensation of vapour, and $P = P_{\text{vapour}}$. *Boiling happens when $P_{\text{external}} = P_{\text{vapour}}$*

Higher temperature: more molecules escape the intermolecular attraction with other molecules in the liquid to vapourise, P_{vapour} increase. **Higher density** suggests stronger IMF, less molecules can escape intermolecular attractions, P_{vapour} decrease. **Larger surface area:** equilibrium is reached faster, P_{vapour} is unchanged.

In a solution, the solute and solvent cannot be separated by filtration, and there are no components large enough to scatter light (unlike colloids); components can be separated with **paper/column chromatography** [on the basis of their differential strength of IMF between the stationary phase (paper or column packed with silica) and the solvent mobile phase], and **distillation** [different boiling points which depend on their differential strength of IMF between each other and the effects these interactions have on their vapor pressures].

Substances with stronger (or similar) intermolecular interactions tend to be miscible or soluble in one another to form homogeneous mixtures. **Ionic compounds** form numerous ion-dipole interactions with polar water molecules which cumulatively releases sufficient energy to overcome the ionic bonds in the ionic solid, hence are soluble in water. **Polar covalent compounds** form hydrogen bonds with each other or with water which are similar in strength with the hydrogen bonds between polar water molecules, hence are soluble in water. **Non-polar covalent compounds** are insoluble in water since the solute-solvent interactions are usually dipole-induced dipole interactions which are weaker than the hydrogen-bonds between the water molecules.

$$\text{retention factor } R_f = \frac{\text{distance moved by dye}}{\text{distance moved by solvent}}$$

7 Chemical Reactions

For a reaction $2A + B \rightarrow 3C$,

$$\text{reaction rate} = -\frac{1}{2} \frac{d[A]}{dt} = -\frac{d[B]}{dt} = +\frac{1}{3} \frac{d[C]}{dt}$$

The probability of 3 particles colliding with sufficient energy and correct orientation in a single step is low, thus it is unlikely to proceed in a single step. **Reaction mechanism:** *series of elementary steps.*

A **homogeneous catalyst** participates in the reaction, reacting with one reactant to form an intermediate. The intermediate then reacts with the other reactant to form the products and regenerate the catalyst.

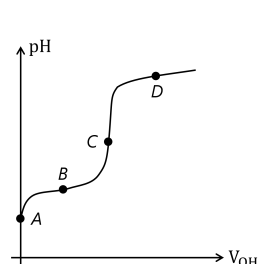
Chemical equilibria: [homogeneous equilibria] gas phase equilibrium, acid-base equilibrium, solubility equilibrium. [heterogeneous equilibria] solid/gas equilibrium. Equilibrium constant K_{eq} is constant at a certain temperature.

$$K_p = K_c(RT)^{\Delta n}, \quad \Delta n = n_{\text{gaseous product}} - n_{\text{gaseous reactant}}$$

Le Chatelier's Principle: When **temperature is increased**, the position of equilibrium shifts in the direction of the endothermic reaction, to remove the heat added to the equilibrium system. When **pressure is increased**, the position of equilibrium of a gaseous reaction shifts in the direction with a smaller total number of moles (lower volume) to relieve the pressure applied to the equilibrium system. When a **catalyst** is added, it increases the rates of both the forward and reverse reaction by the same extent, hence has no effect on the equilibrium system.

Reaction quotient: If $Q > K$, there are more products to reactants as compared to the equilibrium system, hence the reverse reaction is favoured. This will lower [product] and increase [reactant] until equilibrium is reached.

8 Introduction to Titration

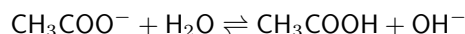


Point A: weak acid only (CH_3COOH).

Point B: [midpoint/half-equivalence point] buffer of weak acid and conjugate base ($[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$), point of maximum buffering capacity, $\text{pH} = \text{p}K_a$.

Point C: [equivalence point] conjugate base only (CH_3COO^-)

$\text{CH}_3\text{COO}^- \text{Na}^+$ undergoes a hydrolysis reaction, producing OH^- which cause $\text{pH} > 7$.



Point D: mixture of excess strong alkali and conjugate base (OH^- , CH_3COO^-)

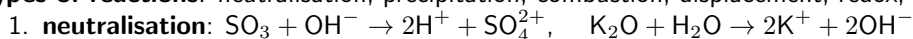
The presence of the strong OH^- alkali suppresses the hydrolysis reaction of CH_3COO^- , by LCP, equilibrium position lies left. The pH is due solely to the excess OH^- present.

9 Types of Chemical Reactions

The **strong acids** are H_2SO_4 , HNO_3 , HCl , HBr , HI , and HClO_4 : written as H^+ in ionic equations.

Weak acids are written as undissociated acid molecules, with H^+ that can be ionised in front.

Types of reactions: neutralisation, precipitation, combustion, displacement, redox, decomposition, ...



- The total energy released when new bonds in the products formed is greater than the total energy required to break the bonds in the reactants. There is a net release of energy resulting in an **exothermic reaction**.

If $Q > K_{sp}$, the product of ion concentrations exceeds what the solution can hold at equilibrium, hence precipitation occurs. If $Q = K_{sp}$, the solution is saturated. If $Q < K_{sp}$, no precipitate forms. **Factors affecting solubility:** temperature (solubility of gas decreases with temperature), common ion effect, pH, complex-ion formation.

Soluble Salts		Insoluble Salts	
Rule	Exception	Rule	Exception
1. Group 1, NH_4^+ salts, nitrates, acetates, chlorates, perchlorates	-	Hydroxides	Group 1, Group 2 hydroxides ($\text{Sr}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$)
2. Halides	Silver, lead halides	Carbonates	G1, NH_4^+ carbonates
3. Sulfates	Ca, Sr, Ba, Pb, Ag sulfates		

10 Enthalpy and Entropy

In **exothermic** reactions, reactants have higher potential energy (weaker bonds) than the products. The excess potential energy is transferred to the surrounding as heat, such that kinetic energy of particles in the surrounding increases and temperature of surrounding increase.

Hess's Law: in going from a particular set of reactants to a particular set of products, the change in enthalpy is the same whether the reaction take place in one step or in a series of steps.

Standard enthalpy of reaction: relatively independent of pressure (ideal gas assumption), standard state (1atm pressure for gas, 1M concentration for aqueous solution, pure liquid and solid) at a specified temperature.

Standard enthalpy of neutralisation: **Strong acids/bases** ionizes completely in the solution, the neutralization reaction involves only the H^+ and OH^- ions, the rest are spectator ions. Thus, regardless of the SA/SB used to form water, ΔH is the same. **Weak acid/bases** only partially ionize in aqueous solution, energy needed to convert HA or BOH into ions, thus the enthalpy change of neutralization is less exothermic.

Spontaneous reaction occurs of its own accord without continuous external intervention, in a definite direction; initial trigger may be needed. **Non-spontaneous reaction** will not occur without continuous external action. Reactions with negative ΔG° may not occur to a measurable extent as they are kinetically unfavorable: activation energy of reaction is too high, few reactant particles can overcome activation energy barrier, slow rate of reaction.

11 Galvanic (Voltaic) and Electrolytic Cells

Electrochemical/Galvanic cell: connected to bulb, chemical energy to electrical energy. Electrons released at anode (-). **Electrolytic cell:** connected to DC source: electricity drives chemical reaction to take place. Anions attracted to anode (+). **Electron flow** [through external wiring]: from anode to cathode

Electrolytes: conducts electricity in molten or aqueous state, due to presence of mobile ions which are charge carriers. strength depends on extent of ionization in solution (or molten).

Electrode: electrical conductor used to make contact with a non-metallic part of a circuit (electrolyte). **Reactive electrode:** acts as conductor of electricity, and takes part in redox reaction (not platinum, C).

Salt bridge: [contains strong electrolyte, similar transport numbers between cations and anions] prevents direct mixing of the 2 solutions, but allows the passage of ions between the 2 half cells, to complete the circuit, helps maintain the electrical neutrality in each half cell.

Electrode/reduction potential: potential difference between electrode and aqueous solution of its ions under std, relative to standard hydrogen electrode, whose electrode potential is assigned to be zero. **Standard conditions:** 1M concentration of aqueous ions, 1 atm partial pressure of gas, Pt electrode if half-cell does not include a metal.

Spontaneity of reaction: $E_{\text{cell}}^\circ = \frac{RT}{nF} \ln K > 0$ indicates reaction is thermodynamically favorable.