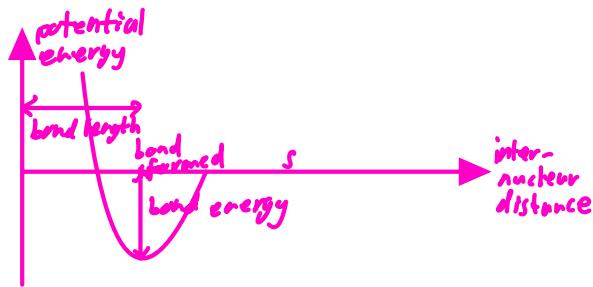


Energetics

Energy change:

Forming of bonds

- atoms approach
- repulsion forces overcome by activation energy
- potential energy very high
- atoms close together, e^- repel
- potential energy become bond energy
- bond formed



Enthalpy change

bond formation: release energy (exothermic)

bond breaking: absorb energy (endothermic)

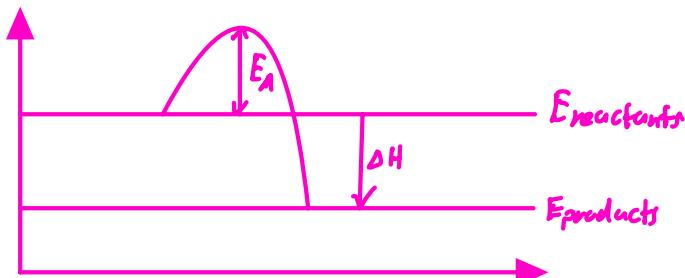
$$\text{enthalpy change} = \Delta H = E_{\text{final}} - E_{\text{initial}}$$

$$\text{activation energy} = E_A$$

Exothermic reaction

$E_{\text{reactants}} > E_{\text{products}}, \Delta H < 0$

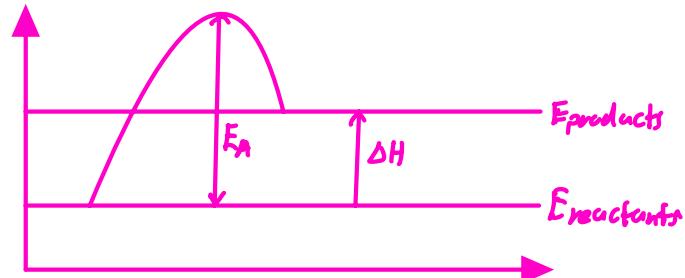
- products more stable than reactants
- energy released to surroundings
- combustion
- respiration
- neutralisation
- diluting concentrated H_2SO_4



Endothermic reaction

$E_{\text{product}} > E_{\text{reactants}}, \Delta H > 0$

- products less stable than reactants
- energy absorbed from surroundings
- photosynthesis
- thermal decomposition



Other enthalpies

standard condition: $25^\circ C$, 1000 mol/m^3 density, 1 atm pressure (denoted sc)

standard enthalpy change (ΔH°): ΔH of 1 mol of reactants (sc)

ΔH° of formation (ΔH_f°): energy to form 1 mol from gaseous elements (sc), 0 for elements

ΔH° of combustion (ΔH_c°): energy released after combusting 1 mol completely (sc), always < 0

ΔH° of neutralisation ($\Delta H_{\text{neutral}}^\circ$): ΔH when acid and base react to form 1 mol of H_2O and some salt (sc)

ΔH° of atomisation ($\Delta H_{\text{atom}}^\circ$): ΔH to form 1 mol of gas atoms from substance (sc), always > 0

Bond dissociation energy: energy needed to break 1 mol of a certain bond (sc) (bond energy)

nth ionisation energy: energy needed to remove n mol of e^- from 1 mol of substance (sc)

nth e^- affinity: energy needed to add n mol of e^- to 1 mol of substance (sc)

Lattice energy: energy needed to form 1 mol of solid ionic compound from constituent ions (sc)

ΔH° of hydration ($\Delta H_{\text{hydr}}^\circ$): ΔH to hydrate 1 mol of gas (sc)

ΔH° of solution ($\Delta H_{\text{soln}}^\circ$): ΔH to completely dissolve 1 mol of substance (sc)

enthalpy laws

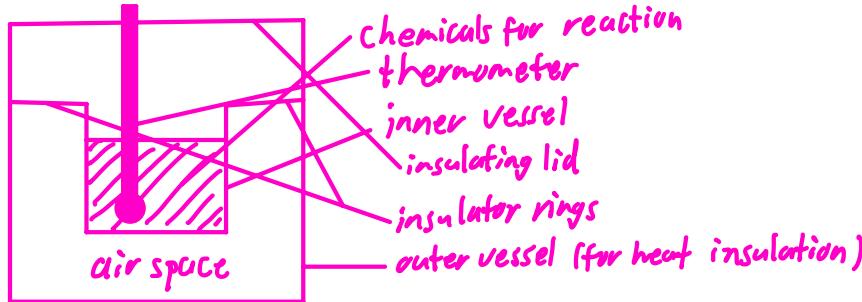
- reverse chemical equation negates enthalpy change
- enthalpy changes proportional to mol of substance used
- enthalpy changes are differences between enthalpies
- enthalpy change independent of reaction route taken

$$\text{enthalpy change} \approx \Delta H = M C T$$

- specific heat capacity given

calorimeter

- measure ΔH
- system thermally isolated
- use equation to calculate from temperature change



Born-Haber Cycles

- to solve questions involving enthalpy change
 - use that ΔH is independent of reaction route
1. form balanced chemical equations
 2. solve for ΔH of partial reactions (individual bonds)
 3. sum all ΔH in partial reactions

Reaction kinetics

Collision theory:

reaction kinetics

- study of reaction rates
- change in amount of products and reactants

$$\text{average rate} = \frac{\text{concentration}}{\text{time}}$$

instantaneous rate = rate at particular time

initial rate = instantaneous rate at $t=0$



$$\text{reaction rate} = -\frac{1}{a} \frac{d[A]}{dt} - \frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} + \frac{1}{d} \frac{d[D]}{dt}$$

where $[N]$ denote concentration of N

Collision theory

- describe collision and reaction of particles
- reactant particles are hard spheres
- no interaction until collision occur
- only collisions with energy $\geq E_A$ will react
 - overcome repulsion of e^-
 - break bonds
 - rearrange atomic structure

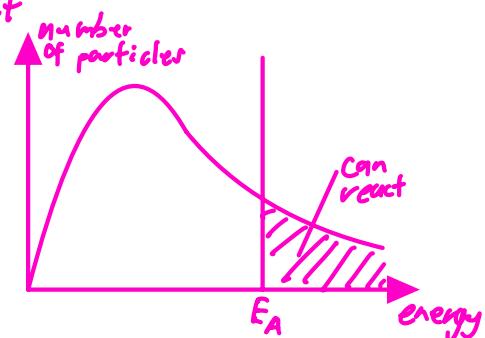
- direction and orientation of particles must be correct

Maxwell-Boltzmann Distribution

- show number of particles with enough energy
- start at zero
- reach energy peak
- approach but do not touch zero
- peak move up and left at lower temperature
- less particles can react

$$\int_0^\infty f(x) dx = \text{total number of particles}$$

$$\int_{E_A}^\infty f(x) dx = \text{particles that can react}$$



reaction rate:

method of isolation

- study effect of $[A]$ on $A + B \rightarrow C$
- B in large excess, $[B]_t \approx [B]_0$
- measure $[A]$ over time to obtain rate

chemical method

- large amount of reactant mixed to react
- small volumes extracted at fixed time
- measured extracted portion
 - add a lot of cold water (quenching agent)/finish 1 reactant to stop reaction
 - mixture cooled and diluted/not enough reactant left

- measure concentration of certain reactant
- attempt getting linear graph, deduce order

physical method

- continuously measure physical property
- data relate to concentration
- indirectly measure concentration

method of initial rate

- measure concentration change
- $\lim_{t \rightarrow 0}$ average rate \approx initial rate
- plot concentration-time graph

clock reaction

- obvious visual change
- vary [reactants] to observe reaction time taken
- time taken inversely proportional to reaction rate

transition states

- maximum energy
- unstable, cannot get in test tube
- not intermediate (can get in test tube)

$[A] \dots [B]^{\ddagger}$ indicate transition state

factors affecting rate

physical state and particle size; surface area to volume ratio

Concentration / pressure of reactants: more particles \rightarrow more collisions

temperature: more energy to overcome E_A

catalysts: decrease E_A

Catalysts

- homogeneous catalysts
 - same state as reactant
 - convert to intermediate, used up
 - intermediate convert to product, regenerated
 - larger E_A replaced by 2 smaller E_A
 - transition metals the best (switch between oxidation states)

- heterogeneous catalysts

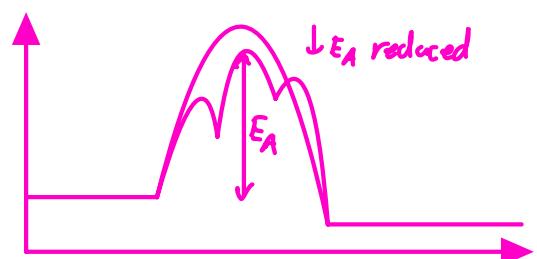
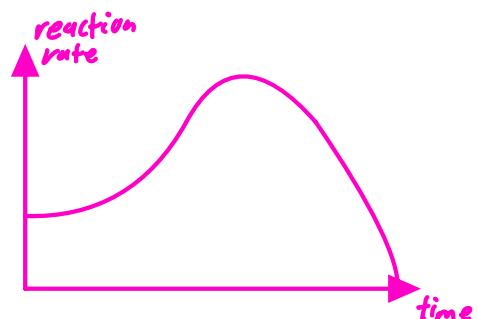
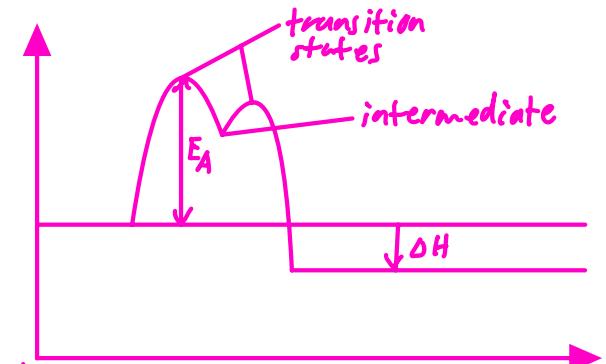
- different state from reactants
- form weak bond with reactants on surface
- weaken intramolecular forces in reactants

- autocatalysts

- product of reaction is a catalyst
- initially slow reaction rate (no catalyst)
- reaction rate accelerate (have catalyst)
- reaction rate then decrease (no more reactants)

- enzymes

- active site fits reactant shape
- lock and key mechanism
- intramolecular bonds weakened at active site
- reaction occur
- shape of product do not fit active site
- product released
- each enzyme catalyse specific reactions
- only 1 E_A needed, not multiple E_A



Reaction order:

reaction rate



where $\text{ord}(N)$ = order of equation with respect to N .

k = constant of proportionality to make equation correct

- measured in $\text{dm}^3 \text{mol}^{-2} \text{s}^{-1}$

- \approx double when temperature increase by 10°C

overall order = $\text{ord}(A) + \text{ord}(B)$

If $[N]$ increase x times, rate increase $x^{[\text{ord}(N)]}$ times

zeroth order equations



rate $\approx k$ (unaffected by $[A]$)

$$[A]_t = [A]_0 - kt$$

first order reactions



rate $\approx k[A]$

- constant half life, independent of $[A]_0$

$$\ln [A]_t = \ln [A]_0 - kt$$

second order reactions



$$\text{rate} = k[A]^2$$

$$[A] \propto t^{-1}$$

pseudo first order reactions

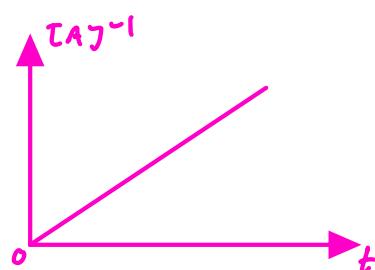
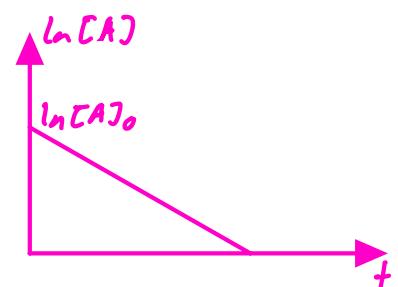
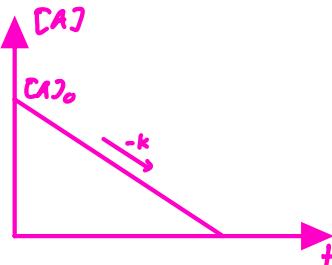
- follow first order rate

- not first order

- 1 reactant in large excess, $[N]_0 \approx [N]_t$

- solvent is a reactant (large excess)

- catalyst used (infinite catalyst supply)



reaction mechanism

- collection of elementary steps

- show how reactant convert to products

- molecularity

- number of molecules involved

- 1, 2, (rarely) 3

- slow steps determine rate

- rate shows which reactants and order of each is involved in rate determining steps

Chemical Equilibrium

Equilibrium:

reversible reactions

- both directions
- will not complete
- mixture of reactants and products obtained

irreversible reactions

- 1 direction only
- will be completed
- 1 reactant used up

static equilibrium

- no reaction

dynamic equilibrium

- rate of forward = rate of backward
- closed system only
- can obtain from both sides

equilibrium ratio



$$\text{instantaneous ratio} = Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- do not include non gases if reaction involve gases

equilibrium ratio = $K_c = Q_c$ at equilibrium

- changes with only temperature

$Q_c < K_c$: favour forward reaction

$Q_c = K_c$: equilibrium

$Q_c > K_c$: favour backward reaction

- K_c does not affect reaction rate

homogeneous equilibrium: all reactants and products same state

heterogeneous equilibrium: some reactants / products different state

partial pressure: concentration of gases

partial pressure of gas X = $P_x = \frac{\text{amount of gas } X}{\text{total amount of gas}}$

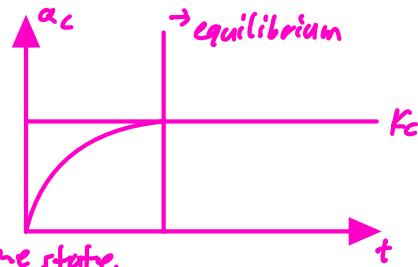
degree of dissociation = $\frac{\text{amount dissociated}}{\text{total amount}}$

initial-change-equilibrium table

	reactant A	reactant B	product C	product D
initial	x	y	0	0
change	-p	-q	+r	+s
equilibrium	x-p	y-q	r	s

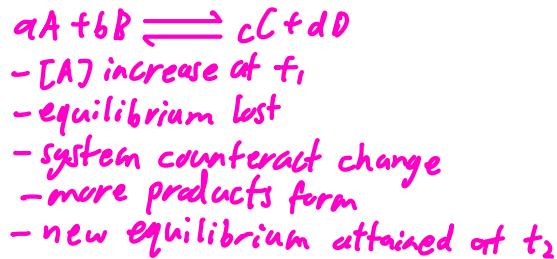
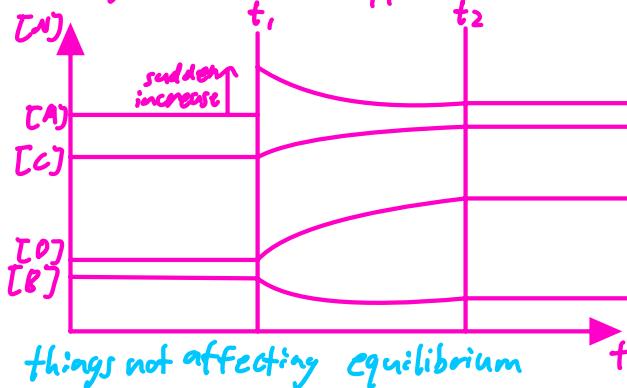


$$K_c = \frac{r^c s^d}{(x-p)^a (y-q)^b}$$



Counter disturbance reactions

- if a system at equilibrium is disturbed, it respond by counteracting the disturbance
- De Châtelier Principle
- equilibrium shift opposite to disturbance



things not affecting equilibrium +

- catalysts
 - increase reaction rate in both directions
 - not in K_c equation
 - reach equilibrium faster
- solvents
 - inert gases, water
 - do not react
 - lower concentration evenly
 - not in K_c equation

Haber Process

- industrial NH_3 production



$$\Delta H^\circ = -92 \text{ kJ/mol} = -92000 \text{ J/g ms}^{-2} \text{ mol}^{-1}$$

- $450^\circ C$

- 200 atm

- continuous removal of NH_3 by condensation

- cool to $-50^\circ C$

- NH_3 boil at $-77^\circ C$

- fast, high yield, minimal cost

Chemical bonding

atomic bonding:

electronegativity

- e^- attracted by p^+
 - measures tendency of atom in a covalent bond to attract e^-
 - most electronegative: O, N, F
 - least electronegative: Cs

Electronegativity of the Elements

ionic covalent spectrum

$$x \div y$$

四

- large electronegativity difference

$-e^-$ held by more electronegative atom

$$x \div y$$

covalent

- same electronegativity

- e⁻ equidistant from both atoms

Lewis diagrams (covalent)

- determine number of valence e^- in each atom
 - less electronegative atom at centre
 - lines represent bonds
 - dots represent e^-
 - determine how many bonds each atom need for octet
 - 1 bond = +1 valence e^-
 - fulfill octet, except following exceptions
 - hypervalency, >8 valence e^- (period 2/3 only)
 - radicals, odd number of valence e^-
 - special chemical reactivity

formal charge

- charge assigned assuming pure covalent bonds
 - number of valence e^- of atom in molecule compared to unbonded atom
 - 2 e^- in each bond shared between 2 atoms, 1 each
 - always zero except for charged molecules or dative bonds

oxidation state

- assuming purely ionic bond
 - both e⁻ in bond allocated to more electronegative atom

- increased by oxidation
- decreased by reduction
- each bond $\equiv \pm 2$ charge

bonding orbitals

- σ bond
 - 2 orbitals overlap head on
 - 1 σ bond between any 2 covalently bonded atoms
- π bond
 - 2 p orbitals overlap side by side
 - all non σ bonds are π bonds

bond strength

- energy required to break bond
- energy released when bond formed
- affected by:
 - number of bonds
 - type of bond (σ or π), or stronger due to higher orbital overlap
 - orbital size (concentration of charge)
 - polarity, electronegativity difference (opposite poles attract)

metallic bond: 80-580 kJ/mol

ionic bond: 120-480 kJ/mol

covalent bond: 120-850 kJ/mol

covalent bond formation

- both atoms have e^- in orbital
- orbitals overlap
- e^- shared
- maximum e^- density between nuclei
- molecular orbital formed

ionic bond formation

- attraction between opposite point charges (ions)
- more covalent if
 - cation (positive) is small and highly charged
 - anion (negative) is large

bond polarity

- bond dipole moment
- partial charges on atoms
- caused by electronegativity difference
- point toward more electronegative atom



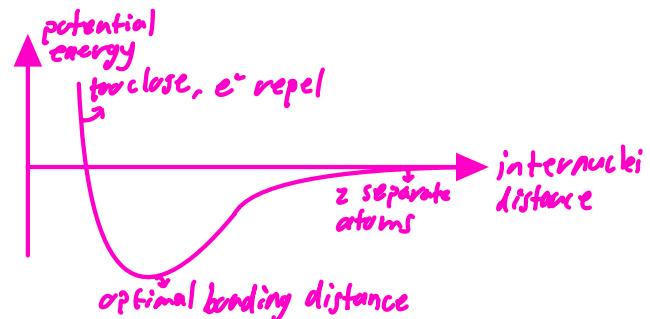
molecule polarity

overall dipole moment = sum of all bond dipole moments

sum = 0: non polar molecule

sum $\neq 0$: polar molecule

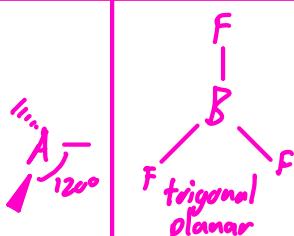
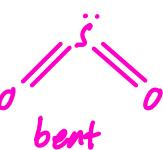
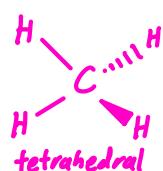
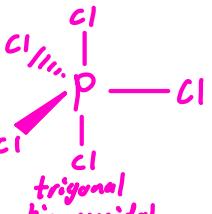
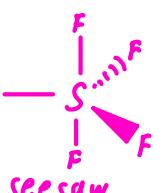
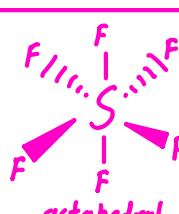
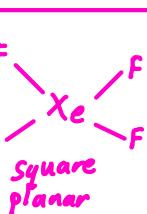
- when subject to electric field, arrange in opposite direction to field
- minimise electrostatic energy



molecular geometry:

- valence e⁻ repulsion theory
- e⁻ pairs around centre atom arranged as far as possible deducing molecular geometry

1. draw Lewis structure
 2. count e⁻ dense regions (lone pairs or set of bonds) around central atom
 3. refer to table
- each lone pair reduces bond angle by 2.5° (more repulsion)
 - bond angle increase for more electronegative central atom

number of e ⁻ dense regions	bond angle	structures (with examples)
0	A	:Ne: single atom
1	A-	H—H linked
2	-A-	O=C=O linear
3	A- 120°	 <p>trigonal planar</p>  <p>bent</p>
4	A- 109.5°	 <p>tetrahedral</p>  <p>trigonal pyramidal</p>  <p>bent</p>
5	A- 120°	 <p>trigonal bipyramidal</p>  <p>seesaw</p>
6	A- 90°	 <p>octahedral</p>  <p>square pyramidal</p>  <p>square planar</p>

Intermolecular forces:

- electrostatic

- affect melting and boiling points

- instantaneous dipole induced dipole

 - not permanent

 - symmetrical e⁻ clouds around molecules

 - randomly broken symmetry

 - partial charges on asymmetricised e⁻ cloud

 - instantaneous dipole formed

 - affect neighbouring e⁻ clouds

 - induce dipoles

 - spread through substance, gets weaker

 - tend to be weak

 - short lived

 - dipoles vanish and reform

 - affected by e⁻ cloud size (interaction surface area)

- permanent dipole permanent dipole

 - polar atoms

 - permanent polarity

 - permanent partial charges

 - opposite partial charges attract

 - intermolecular force formed

 - affect by dipole moment of molecule (strength of partial charges)

 - stronger than id-id

- H-bonds (special pd-pd)

 - very strong pd-pd intermolecular forces

 - between molecules with hydrogen bonded to small and highly electronegative atom (O, N, F)

 - molecules contain lone pairs

 - strong partial positive charge on hydrogen atom

 - H atom is proton like due to strong δ^+

 - highly electronegative atom from nearby molecule allows δ^- to approach proton like H atom

 - electrostatic forces of attraction cause H-bond

 - stronger than other pd-pd

 - deciding factor of strength of intermolecular forces

- strength of intermolecular forces

 - id-id: 0.05 - 40 kJ/mol

 - pd-pd: 5 - 25 kJ/mol

 - H-bonds: 10 - 40 kJ/mol

atomic structure

- lattice bonding

 - ions fixed by very strong ionic bonds

 - ionic bond strength determined by lattice energy

 - attraction between opposite charges

 - lattice energy $\propto \frac{q_1 q_2}{r_1 + r_2}$, where q denote charge and r denote radius

 - strength favours concentrated charge (higher charge, smaller radius)

- giant molecular lattice

 - carbon

πe^- cloud

- delocalised e^- conduct electricity parallel to layer

simple molecular lattice

- molecules attracted by $id-id$ intermolecular forces

- covalent substance in solid state

giant metallic lattice

- strong, non-directed metallic bonds

- depend on valence e^- (more e^- , stronger bond)

- depend on cation size (concentration of charge)

- positive nuclei floating in sea of e^-

summary table

	giant metallic lattice	giant ionic lattice	giant molecular lattice	Simple molecular lattice
component	atoms	ions	atoms	molecules
bonding in solid	strong metallic bonds	strong ionic bonds	strong covalent bonds	weak $id-id$ intermolecular forces
volatility (ability to change state)	no	no	no	yes
state at room temperature	solid	solid	solid	any state
hardness	hard	hard	hard	soft
malleability	yes	no	no	yes
electrical conductivity	good	poor as solid good otherwise	poor	poor
heat conductivity	good	poor as solid good otherwise	poor	poor
possible solvents	liquid metals	polar substances	none	nonpolar substances

Organic Chemistry

molecular arrangement:

why carbon?

- form strong single, double, triple bonds
- 4 covalent bonds formed
- can attach to many atoms
- wide diversity of compounds formed
- kinetically stable
- slow oxidisation
- no lone e^- pairs
- cannot expand valence shell
- strong C-C, C-N bonds

basic hydrocarbon properties

compound	C-C bond	molecular geometry	bond type	bond angle
ethane (alkane)	C-C	tetrahedral	4σ	109.5°
ethene (alkene)	C=C	trigonal planar	$3\sigma, 1\pi$	120°
ethyne (alkyne)	C≡C	linear	$2\sigma, 2\pi$	180°

arrangement of C skeleton

aliphatic

- open chain of C atoms

acyclic

- closed ring of C atoms
- does not contain benzene ring

aromatic

- contain benzene ring

functional group

- atom or group responsible for chemical properties

homologous series (homologues)

- compounds with same functional group
- differ from successive member by CH_2 group
- have general formula
- gradual change in physical properties
- same chemical properties

nth-iary compound (primary/secondary/tertiary)

- n non hydrogen atoms bonded to C atom bonded with functional group

- highest is tertiary

- ≥ 1 bond used for functional group (not counted)

R = any atom or group (not hydrogen or halogen)

X = halogen

homologous series	functional group (skeletal)
alkane	~
alkene	~/\
alkyne	~/\=
phanyl	
benzyl	
alkyl halide	~X
amine	~NH ₂
alcohol	~OH
ether	~OR
thiol	~SH
nitrile	~CN
aldehyde	
ketone	
acid halide	
amide	
carboxylic acid	
ester	

formula types

formula type	example (ethanol, C_2H_6)	description
empirical	CH_3	simplest ratio of atoms
molecular	C_2H_6	number of atoms
condensed Structural	CH_3CH_3	structure + molecular formula
full Structural	$ \begin{array}{ccccc} & H & & H & \\ & & & & \\ H & - C & - C & - H & \\ & & & & \\ & H & & H & \end{array} $	graph of bonds
stereochemical		3D diagram
skeletal	—	connect all non hydrogen atoms in full structural diagram without labelling carbon atoms, make things simpler while maintaining structure

hydrocarbon naming

cyclicity + carbon root + saturation + functional group

cyclicity	name
acyclic	(none)
cyclic	cyclo-

saturation	name
saturated (alkane)	-an-
alkene	-en-
alkyne	-yn-

carbon root (number of C atoms continuously bonded)	name
1	-meth-
2	-eth-
3	-prop-
4	-but-
5	-pent-
6	-hex-
7	-hept-
8	-oct-
9	-non-
10	-dec-

homologue name	functional group	name
carboxylic acid	$\text{—C}(=\text{O})\text{OH}$	-oic acid
ester	$\text{—C}(=\text{O})\text{OR}$	-yl...oate
acid halide	$\text{—C}(=\text{O})\text{X}$	-oyl halide
amide	$\text{—C}(=\text{O})\text{NH}_2$	-amide
nitrile	$\text{—C}\equiv\text{N}$	-nitrile
ketone	>C=O	-one
alcohol	C—OH	-ol
alkane alkene alkyne	C—H	-e

Reaction mechanisms:

bond breaking



electrophile

- e^- pair acceptor
- Lewis acid
- e^- deficit
- possible s^+ charge
- attracted to e^- rich regions
- possibly empty orbital

nucleophile

- e^- pair donor
- Lewis base
- e^- rich
- have lone e^- pairs
- attracted to e^- deficit area (electrophile)

free radical

- contains unpaired e^-
- electrically neutral

oxidation numbers

- for every bond, more electronegative atom gains 1 e^-
- less electronegative atom loses 1 e^-
- if bond between same atoms, no change in e^-
- carbon more electronegative than metals but less than O, N, S, and halogens

addition

- 2 reactants \longrightarrow 1 product
- unsaturated reactants
 - 1 π bond broken to form 2 σ bonds
 - δ bond unbroken
 - can be nucleophilic or electrophilic

substitution

- 2 reactants \longrightarrow 2 products
- group replaced by another group
 - electrophilic, nucleophilic, or free radical

elimination

- 1 reactant \longrightarrow 2 products
- removal of group from hydrocarbon compound
 - unsaturated hydrocarbon formed

oxidation

- add oxygen
- remove hydrogen
- loss of e^-
- oxidation number increase

reduction

- remove oxygen
- add hydrogen
- gain of e^-
- oxidation number decrease

electronic effect

- e^- withdrawing or donating
- through σ bonds due to electronegativity
- delocalisation of lone e^- pairs on atom adjacent to π e^- cloud into cloud

steric effect

- steric hindrance
- presence of substituent hinders approach of reactant
- reactant physically blocked from approach
- reactant hit wrong part of molecule
- lower reactivity
- possibly prevent reaction

S_N1 (nucleophilic substitution)

- old group leaves, then new group enters
- rate = $k [\text{compound}]^0$ $[\text{nd (compound)}]$
- limiting step is old group leaving
- rate dependent only on original molecule (1 reactant, thus S_N1)
- other rate changing factors
 - temperature
 - bond strength of bond to be broken
 - compound stability
- tertiary > secondary > primary
- nucleophile strength does not matter
- solvent used can form H-bond intermolecular forces

S_N2 (nucleophilic substitution)

- nucleophile attack from back, original group leave from front
- stereochemistry inverted
- form racemic mixture
- rate = $k [\text{compound}]^0$ $[\text{nd (compound)}]$ $[\text{nucleophile}]^0$ $[\text{nd (nucleophile)}]$
- depend on both reactants (2 reactants, thus S_N2)
- other rate changing factor
 - temperature
 - strength of original compound (leaving bond)
 - ease of formation of new compound (nucleophile bond)
- limited by stereochemical hindrance
- primary > secondary > tertiary
- must have strong nucleophile
- solvent used cannot form H-bond intermolecular forces

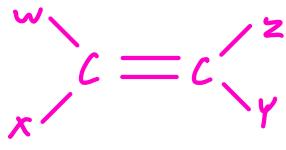
ISOMERS:

- same atoms, different arrangement

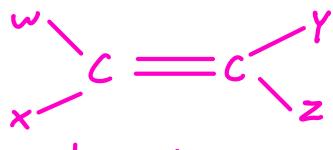
Cis/trans isomers (stereoisomer / spatial isomer)

- restricted rotation about bond due to double bond or ring structure
- each carbon in C=C has 2 groups attached
- attached groups different

For groups w, x, y, z



cis isomer



trans isomer

- similar, not identical property
- react with same reactants
- different reaction rate
- different physical properties
- maximum 2ⁿ cis/trans isomers in compound with n C=C bonds

enantiomers (stereoisomer / spatial isomers)

- non superimposable mirror image
- no plane of symmetry
- contain chiral carbon
 - 4 different groups attached
 - non superimposable mirror image



- identical physical property except
- rotate polarised light in equal but opposite directions
- identical chemical property except
- react differently with another chiral molecule
- different biological property
- maximum 2^n enantiomers in compound with n chiral carbon

functional group isomers (constitutional isomers)

- different functional group
- very different
- isomer by coincidence of atom count

Chain isomers (constitutional isomers)

- differ in atom arrangement
- straight chain vs branched chain

positional isomers (constitutional isomers)

- functional group attached different part of chain
- same functional group

degree of unsaturation

$$\text{degree of unsaturation} = \frac{1}{2}(2C + N - H - x)$$

where C denote the number of atoms I and x indicate any halogen

Alkanes:

general properties

- saturated hydrocarbons
- C-C, C-H bonds only
- all carbon atoms have 4 single bonds
- C_nH_{2n+2} (open) or C_nH_{2n} (loop)
- tetrahedral geometry
- 109.5° bond angle

boiling point

- low
- non polar molecule

- id - id intermolecular forces only
- increase with more carbon atoms
- decrease with more branching

melting point

- affect by molecule distance in solid lattice
- increase with closer molecules
- even carbon atom number have high melting point

solubility

- soluble in non polar solvents only
- insoluble in water
- used as non polar solvent

reactivity

- generally unreactive
- non polar
- unaffected by polar solvents
- saturated hydrocarbon
- no high / low e^- density regions
- strong C-C, C-H bonds

combustion

- produce only CO_2 and H_2O if complete
- otherwise produce other hydrocarbons

free radical substitution with halogens

- need light or heat
- some or all hydrogen replaced with halogens

(let x denote halogen)

1. energy break $x-x$ bonds, form free radical x

2. x replace H in alkane, no change in number of free radicals

3. remaining free radicals collide to combine, form stable products

cracking

- large alkane broken down into small alkane
- thermal cracking at 800°C
- catalytic cracking at $400^\circ\text{C} - 500^\circ\text{C}$ with aluminium or silicon catalyst

classification of atoms

- n degree carbon atom bonded to n other carbon atoms
- n degree hydrogen atom bonded to n degree carbon atom
- no 0 th degree hydrogen

isomers

constitutional: butane onwards

- branching of chain

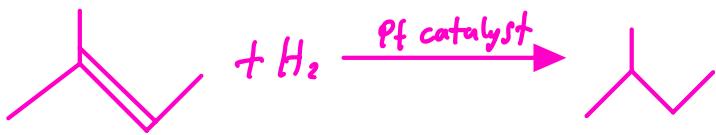
enantiomers: must satisfy conditions

cis/trans isomers: cycloalkanes only

production

wuatz reaction

- synthesis alkanes with even number of carbon atoms



electrolysis

electrolyte = aqueous Na(alkane)

electrode = platinum

- alkane at anode

Alkenes:

general properties

- series of unsaturated hydrocarbons
- aliphatic
- C=C double bond
- physical properties same as alkanes
- trigonal planar geometry
- bond angle 120°

reactivity

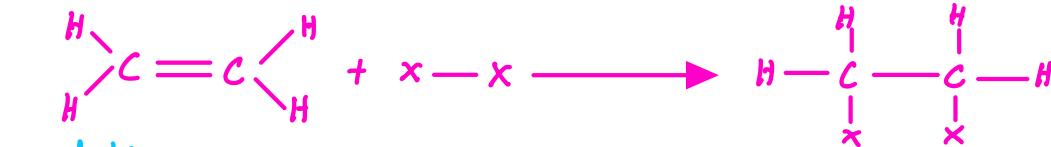
- non polar
- more reactive than alkanes
- C=C double bond
- π bond e^- cloud attract electrophiles
- electrophilic addition
- combustion, oxidation, reduction
- breaking of π bond

drawing reaction mechanisms

1. name reaction
2. draw e^- movement from donor to acceptor
3. show lone e^- pairs
4. indicated partial charges
5. draw formula of intermediates and products

halogenation of alkenes

- π bond broken
- halogen attach to carbon atom
- become halogenised alkane



oxidation

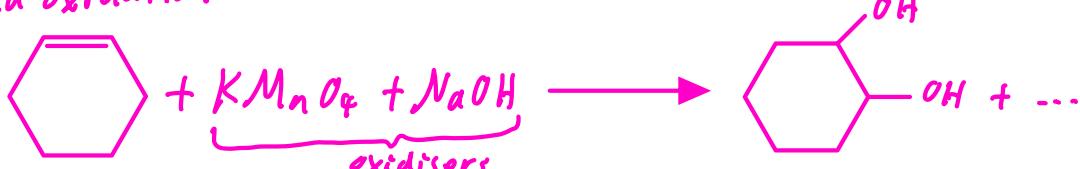
- need oxygen (oxidisers)

Combustion

- same as alkanes

- form CO_2 and H_2O

mild oxidation



strong oxidation

(acidic) alkene + $\text{KMnO}_4 + \text{H}_2\text{SO}_4 \longrightarrow$ carboxylic acid + CO_2

(alkaline) alkene + $\text{NaOH} \longrightarrow$ carboxylate salts + carbonate

reduction

- need catalyst and hydrogen

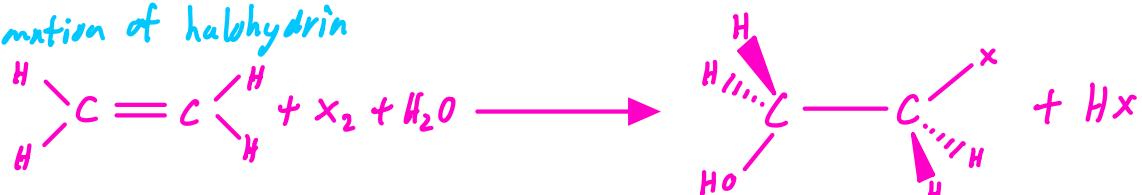
- Ni at 150°C

- Pt at room temperature

- Pd + heat

- C + heat

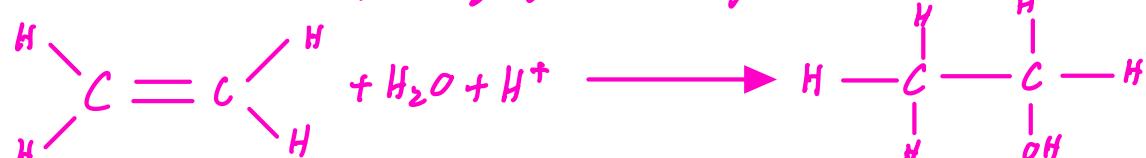
formation of halohydrin



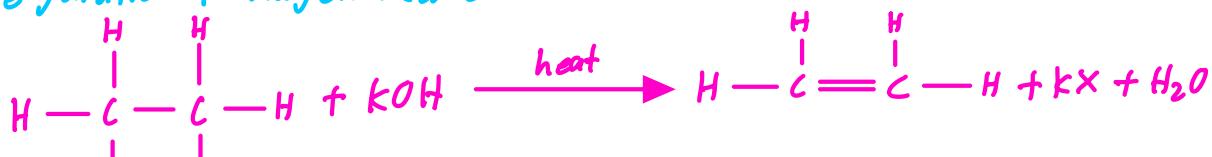
- if alkene is asymmetrical, draw both possible products

formation of alcohols

- add cold concentrated H_2SO_4 followed by warm H_2O



dehydration of halogenalkanes



dehydration of alcohols



- if more than 1 alkene can be formed, more stable one is major product
isomers

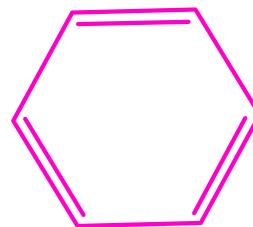
cis/trans isomers

- restricted rotation of $C=C$
- $C=C$ join to 2 groups per carbon atom
- cis less stable due to steric strain

Arenes:

basic properties

- hydrocarbons with benzene ring as structural unit
- aromatic
- special stability
- retains ring after reactions
- only substitution reactions
- entirely planar geometry (regular hexagon)
- cloud of delocalised e^- above and below ring



physical properties

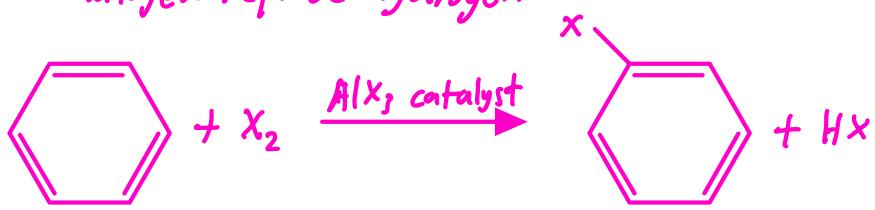
- colourless liquid
- characteristic odour
- non polar
- good organic solvent
- less dense than water
- boiling point $80^\circ C$
- melting point $5.5^\circ C$

electrophilic substitution

- electrophile attack ring, destroy ring structure (slow)
- proton (H^+) lost, restore ring structure
- non arene intermediate

halogenation

- electrophilic substitution with Cl or Br (F impractical), I too unreactive)
- Lewis acid (electrophile) catalyst
- halogen replace hydrogen

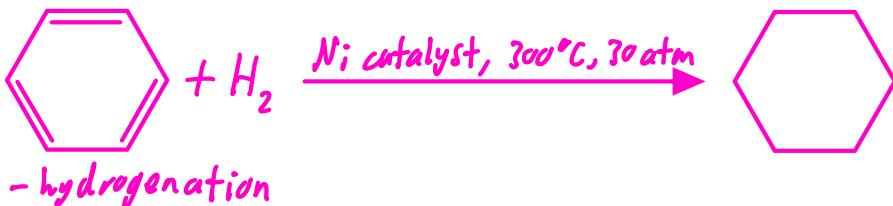


combustion

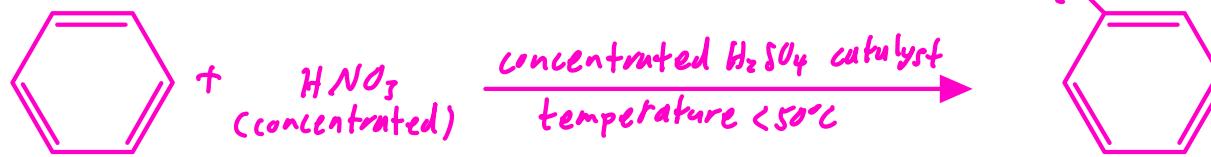


reduction

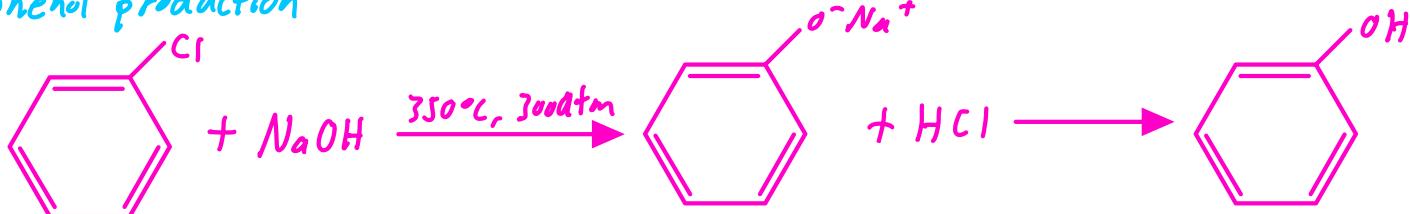
- nickel powder catalyst



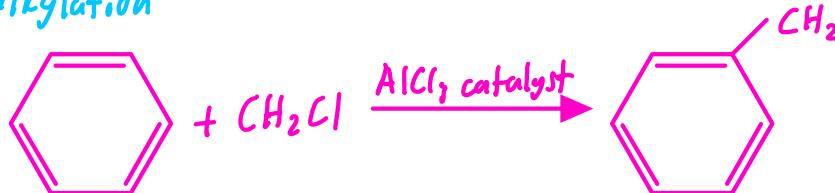
nitration



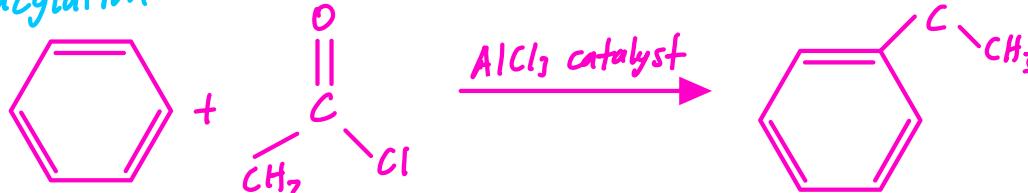
phenol production



alkylation



acylation



sulfonation



effect of leaving groups

-readiness and position of attack

activating groups

- ring less reactive
- increase e^- density in ring
- cause electrophilic attack
- NH_2, OH, CH_3

deactivating groups

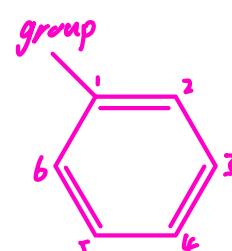
- ring more reactive
- decrease e^- density in ring
- stop electrophilic attack
- $NO_2, COOH, Cl$

directing groups

-direct electrophile to attack certain point

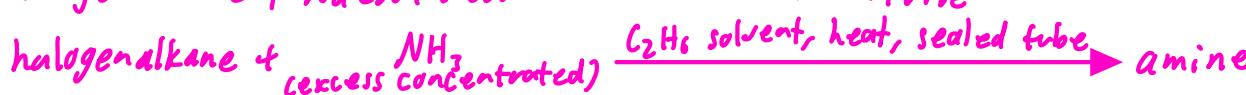
2,4 directing: CH_3, NH_2, OH, Cl

3 directing: $COOH, NO_2, CHO$



Halogenalkanes:

-formed during electrophilic addition to alkanes
nucleophilic substitution





- organic solvents used as water react to form alcohol

elimination

- alkene formation



Alcohols:

general properties

- hydrogen atom in water replaced by carbon
- properties between water and hydrocarbons
- long chain alcohols resemble hydrocarbons
- polar end with functional group
- non polar end with hydrocarbon chain
- same physical properties as alkanes

preparation of alcohols

- electrophilic addition of alkanes
 - add cold concentrated H_2SO_4 then hot H_2O
- nucleophilic substitution of halogenalkanes
 - heat with aqueous NaOH or KOH
- reduction of carboxylic acids or carbonyls
 - mix dry ether with LiAlH_4 at room temperature
 - heat and add water
 - dry ether used to prevent explosion of LiAlH_4

acid-base reactions

- weaker acid than water (in terms of H^+)
- react with reactive metals and their hydrides
- form alkoxide ion



nucleophilic substitution

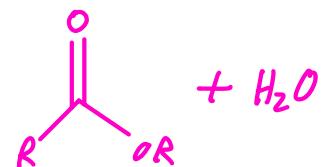
- carbon bonded to oxygen has $+8$ charge
- attract nucleophilic attack
- halogens replace functional group

esterification



dehydration to form alkenes

- reverse of formation
- need catalysts
 - excess concentrated H_2SO_4 at 170°C
 - Al_2O_3 at 400°C
 - H_3PO_4 at 200°C to 250°C



Carboxylic acid:

general property

- both carbonyl and hydroxyl group
- trigonal planar geometry

acid-base reactions

- react with Na, NaOH, Na₂CO₃
- bases + weak acid reactions

acyl chloride formation



oxidation of alcohols

- need oxidiser (K₂Cr₂O₇ or H₂SO₄)
- heat needed
- immediate distillation for aldehyde

alcohol type	alcohol	product of mild oxidation	product of strong oxidation
primary	$\begin{array}{c} \text{OH} \\ \\ \text{R}-\text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{OH} \end{array}$
secondary	$\begin{array}{c} \text{OH} \\ \\ \text{R}-\text{R} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{R} \end{array}$	carbon in functional group removed as CO ₂
tertiary	$\begin{array}{c} \text{OH} \\ \\ \text{R}-\text{R} \\ \\ \text{R} \end{array}$	no reaction	carbon in functional group removed as CO ₂

Carbonyls:

aldehydes

- RCHO
- A can be H, alkyl or acyl group
- at least 1 hydrogen attached to carbon in functional group

ketone

- RCOR'
- R and R' are alkyl or acyl groups
- no hydrogen attached to carbon in functional group

boiling point

- polar molecules
- higher than alkanes
- lower than alcohols

solubility

- oxygen atom has lone pair
- form H-bond with water
- soluble in water
- long chains less soluble in water
- soluble in non polar solvents

nucleophilic addition

- carbon in C=O has +8 charge
 - attract nucleophiles
 - electronic factor
 - e⁻ releasing alkyl or acyl reduce +8 of oxygen atom
 - steric factor
 - bulky hydrocarbon chain hinder nucleophile
 - aldehyde more reactive than ketones

Nitrogen compounds:

general property

- amines
-hydrogen atoms (1 or more) in NH_3 replaced by alkyl or acyl groups

physical property

- polar molecules
 - higher boiling point than alkanes
 - lower boiling point than alcohols
 - boiling point increase from tertiary to primary amines
 - lower members (with less carbon atoms) soluble in water
 - weak bases

basicity

- availability of lone e⁻ pair on nitrogen atom

aromatic < NH_2 < primary < secondary < tertiary

- more e⁻ donating alkyls, nitrogen atom more e⁻ dense, more available lone pair
 - react as nucleophile

Polymers:

Polymer types

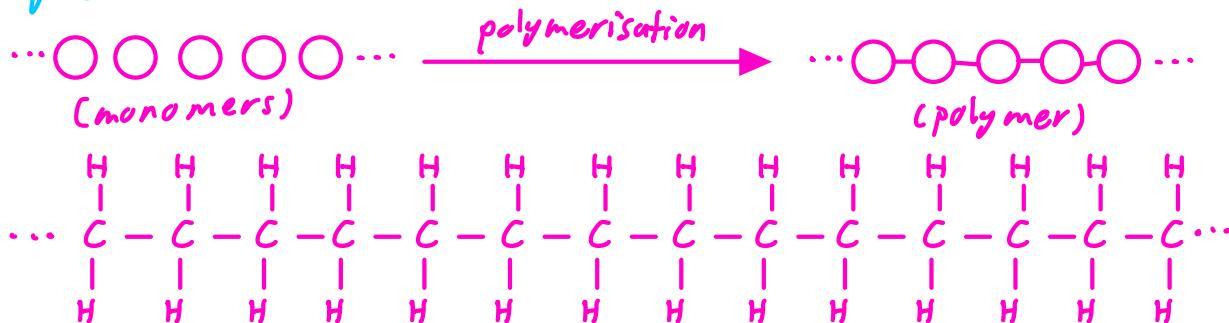
- substance with many repeating units

homopolymer: 1 type of repeating unit

copolymer: 2 types of repeating units

terpolymer: 3 types of repeating units

Polymerisation



Inorganic chemistry

Solubility:

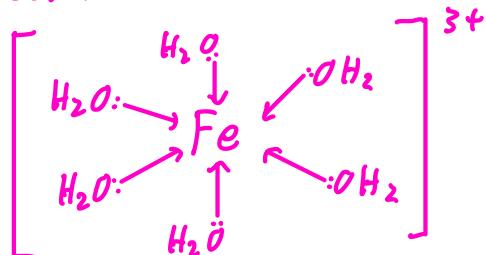
Precipitate formation

- 2 aqueous solutions mixed
- precipitates formed only if mixture contain cations and anions forming insoluble compounds
- can be used to predict cation and anion in solution
(let X denote halogen)

ions	soluble	insoluble
$\text{NH}_4^+, \text{Na}^+, \text{K}^+, \text{NO}_3^-$	all	none
X^-	all else	AgX, PbX_2
SO_4^{2-}	all else	$\text{PbSO}_4, \text{BaSO}_4$
CO_3^{2-}	$\text{NH}_4^+, \text{Na}^+, \text{K}^+$	all else
OH^-	$\text{Na}^+, \text{K}^+, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$	all else

Complex formation

- molecules/ions donating 1 lone e^- pair to central molecule/ion
- dative bond formed
- most metal ions form complex with H_2O
- H_2O molecules donate lone e^- pair
- 6 H_2O bonded to each metal ion
- written in the form $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ (replace atom, number of bonded H_2O , and charge)



OH^- complex

- form complex with hydroxides that can act as both acid and base (amphoteric)
- $\text{Al(OH)}_3, \text{Pb(OH)}_2, \text{Zn(OH)}_2, \text{Cr(OH)}_2$
- $\text{Al(OH)}_4^-, \text{Pb(OH)}_4^{2-}, \text{Zn(OH)}_4^{2-}, \text{Cr(OH)}_4^{3-}$
- group 2 hydroxides not amphoteric
- insoluble in OH^-

NH_3 complexes

- form soluble ammonia complexes
- $\text{Cu}(\text{NH}_3)_4^{2+}, \text{Zn}(\text{NH}_3)_4^{2+}, \text{Ag}(\text{NH}_3)_2^+$

Thermal decomposition:

reaction process

- breaking up of compound by heating
- anions containing oxygen break up when heated
- products depend on reactivity of cation
- more reactive cation, less decomposition

cation	nitrate	carbonate	hydroxide
potassium sodium	nitrate → nitrite + O ₂	no decomposition	no decomposition
calcium magnesium aluminium zinc iron lead copper	nitrate → oxide + NO ₂ + O ₂	carbonate → oxide + CO ₂	hydroxide → oxide + H ₂ O
silver gold	nitrate → metal + NO ₂ + O ₂	carbonate → metal + CO ₂ + O ₂	hydroxide → metal + H ₂ O + O ₂

Redox reactions:

- involve loss and gain of e⁻ and change in oxidation states
oxidising agent

- cause other substances to be oxidised

- reduced during experiment

- KMnO₄ (purple) or K₂Cr₂O₇ (orange)



reducing agents

- cause other substances to be reduced

- oxidised during experiment

- KI





oxidising and reducing agent

- can act as both oxidising and reducing agent in different experiments
- contain element in intermediate oxidation state
- can be oxidised or reduced
- H_2O_2 and Fe^{2+}

Electrochemistry

Redox reactions:

redox equations

- split into reduction and oxidation
- reduction gain e⁻, decrease oxidation state
- oxidation lose e⁻, increase oxidation state
- e⁻ lost overall = e⁻ gained overall
- balanced redox equation has no e⁻ term

balancing redox equations

(if acidic)

1. balance element
2. balance oxygen by adding H₂O
3. balance hydrogen by adding H⁺
4. balance charges by adding e⁻

(if alkaline)

1. add OH⁻ to both sides to neutralise H⁺
2. combine H⁺ and OH⁻ to form H₂O

electrochemical series

- cannot directly measure
- relative measure
- hydrogen fixed at zero
- measures tendency for oxidation and reduction

	Half Reaction	Standard Potential (V)
	F ₂ + 2e ⁻ ⇌ 2F ⁻	+2.87
	Pb ⁴⁺ + 2e ⁻ ⇌ Pb ²⁺	+1.67
	Cl ₂ + 2e ⁻ ⇌ 2Cl ⁻	+1.36
	O ₂ + 4H ⁺ + 4e ⁻ ⇌ 2H ₂ O	+1.23
	Ag ⁺ + 1e ⁻ ⇌ Ag	+0.80
	Fe ³⁺ + 1e ⁻ ⇌ Fe ²⁺	+0.77
	Cu ²⁺ + 2e ⁻ ⇌ Cu	+0.34
	2H ⁺ + 2e ⁻ ⇌ H ₂	0.00
	Pb ²⁺ + 2e ⁻ ⇌ Pb	-0.13
	Fe ²⁺ + 2e ⁻ ⇌ Fe	-0.44
	Zn ²⁺ + 2e ⁻ ⇌ Zn	-0.76
	Al ³⁺ + 3e ⁻ ⇌ Al	-1.66
	Mg ²⁺ + 2e ⁻ ⇌ Mg	-2.36
	Li ⁺ + 1e ⁻ ⇌ Li	-3.05

Electrolysis:

anodes and cathodes

- 1 anode and 1 cathode form a cell

- anode for oxidation

- cathode for reduction

voltage cell: anode negative, cathode positive

electrolysis cell: anode positive, cathode negative

electrode potential of cell

electrode potential > 0 : reaction feasible

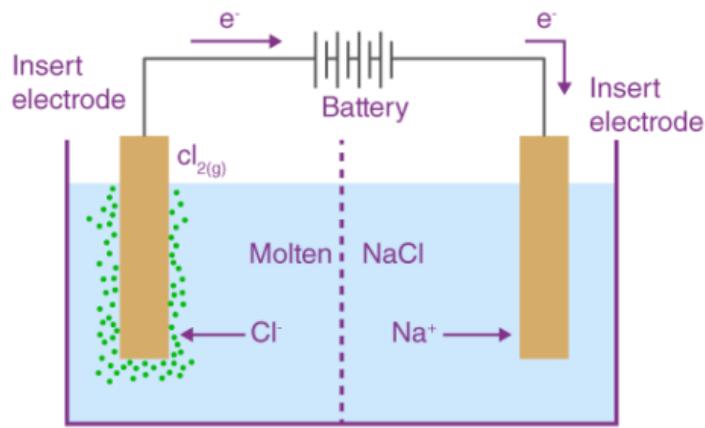
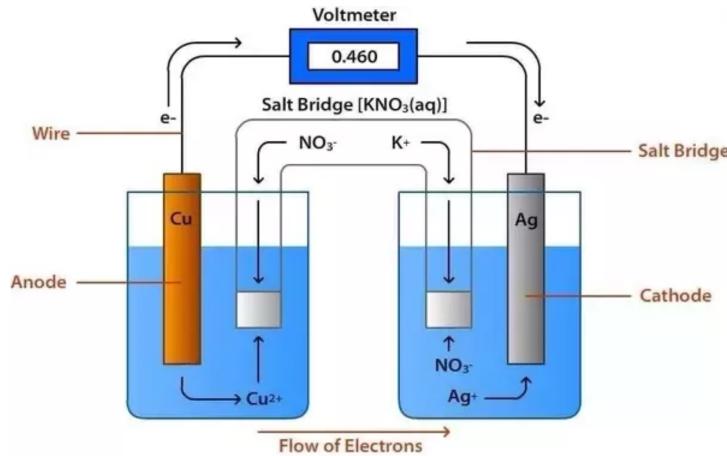
electrode potential < 0 : reaction not feasible

electrode potential of cell = electrode potential of reduction - electrode potential of oxidation

Voltaic cell

chemical potential energy \rightarrow electrical energy

- energetically favourable



electrolysis cell

electrical energy \rightarrow chemical potential energy

- energy provided for reaction

- separate a compound by charge

Purification (Copper)

- impure copper dissolved at anode

- pure copper in solution deposited on cathode

Electroplating

- metal at anode oxidised and dissolved

- metal ions reduced and form layer on cathode

charge equations

$$\text{charge} = q = If = \text{current} \cdot \text{time}$$

$$\text{energy produced} = X = -qE = -\text{charge} \cdot \text{electrode potential of cell}$$