CHEMISTRY

Higher 2 (2017)

(Syllabus 9729)

I. Mole concept and Stoichiometry

Relative atomic mass = $\frac{mass\ of\ 1\ atom}{1/12\ of\ the\ mass\ of\ 1\ Carbon{-}12\ atom}$

Proton = 1u, Neutron = 1u, Electron = $\frac{1}{1840}$ u

Mole = amt of substance which contains as many elementary entities as in 12 grams of carbon-12

→ 6.02 x 10^{23} particles

Empirical formula: simplest whole number ratio of the atoms in one formula unit of the compound.

Molecular formula: actual number of atoms present in one formula unit of the compound.

Percentage yield = $\frac{actual\ yield}{theoretical\ yield}$ x 100%

Avogadro's hypothesis: Equal volume of gases under the same conditions of temp & pressure contain same number of molecules. (except when molecules dimerise [see chapter III. Chem Bonding])

molar volume of gas	V_m = 22.7 $dm^3\ mol^{-1}$ at s.t.p. V_m = 24 $dm^3\ mol^{-1}$ at r.t.p. (where s.t.p. is expressed as 10^5 Pa [1 bar] and 273 K [0 °C], r.t.p. is expressed as 101325 Pa [1 atm] and 293 K [20 °C])

(^molar vol. can be found in data booklet!)

Complete combustion of any hydrocarbon

CxHy (g) + (x + $\frac{y}{4}$) O_2 (g) → xC O_2 (g) + $\frac{y}{2}$ H_2O (l)

Strong acid/base = one that undergoes complete dissociation/ ionisation in aq. Soln

Weak acid/ base = one that undergoes partial dissociation/ ionisation in aq. Soln

→ pH = -lg[H^+]

Type	△ pH	Indicator
Strong acid - Strong base	4-10	(screened) Methyl Orange, Methyl Orange, Phenolphthalein, Thymol Blue, Thymolphthalein
Strong acid - Weak base	3.5-6.5	(screened) Methyl Orange, Methyl Orange
Weak acid - Strong base	7.5-10.5	Phenolphthalein, Thymol Blue, Thymolphthalein
Weak acid- Weak base	No marked △	-

Redox = Simultaneous reduction & oxidation

→ Loss/ gain of O_2

→ Loss/ gain of H

→ Loss/ gain of e^-

→ ↑ / ↓ in oxidation no.

OIL Oxidation = Loss of e^-

RIG Reduction = Gain in e^-

Total N_{e^-} gained by reducing agent = Total N_{e^-} gained by oxidising agent	Total ↑in ox. no. of one species = Total ↓in ox. no. of another species

Oxidation number assignment rules :

1. Ox. no. of atom in elemental state = 0
2. Ox. no. of H in all compounds = +1 (except in metal hydrides [e.g NaH])
3. Ox. no. of fluorine in all compounds = -1
4. Ox. no. of oxygen = -2 (except peroxides = -1) (except superoxides = - $\frac{1}{2}$)
   (except OF_2 = +2)

5. More electronegative atom = -ve ox. no.
   Less electronegative atom = +ve ox. no.
6. Monatomic ions: ox. no. = charge
7. Polyatomic ions: $\sum individual\ ox.no.$ = charge
8. Uncharged compound: $\sum individual\ ox.no.$ = 0

Note: In a covalent bond, ox. no. arises because the more electronegative atom gains both e^-, but by a different extent depending on $\triangle electronegativity$

Disproportionation rxn: a species is simultaneously reduced & oxidized in the same rxn to form 2 different pdts.

<u>Balancing redox eqns in acidic medium</u>

1. Construct the ox. & red. half eqns.
2. Balance the element oxidised/ reduced
3. Balance oxygen atoms (by adding H_2O molecules)
4. Balance hydrogen atoms (by adding H^+ ions)
5. Balance overall charge by adding e^-

<u>In basic medium</u>

Repeat steps 1-5 as in acidic medium..

6. Neutralise H^+ ions by adding required OH^- ions to both sides
7. Combine H^+ ions and OH^- ions to form H_2O

Precipitation rxn: 2 soln rxt to form a ppt of an insoluble salt.

II. Atomic Structure

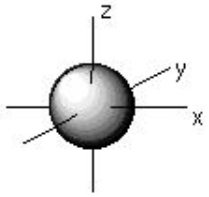
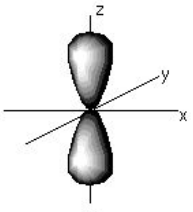
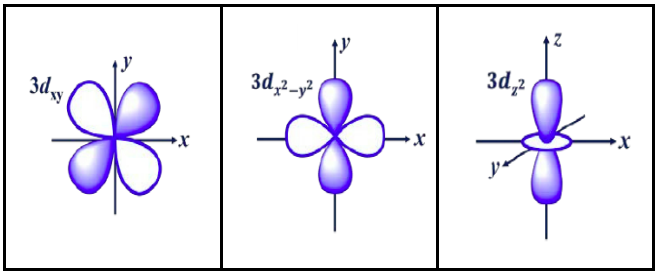
θ of deflection $\sim \left|\frac{charge}{mass}\right|$

Orbital → can accommodate 2 e^-

→ has a distinctive geometrical shape

→ energy of orbital = energy of e^-

Geometry:

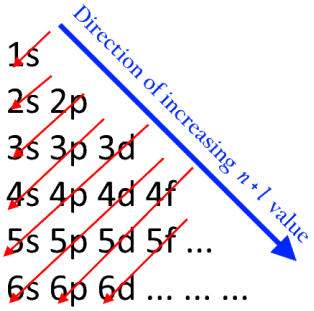
s orbital: spherical, non-directional	p orbital: dumbbell, directional (along x, y, or z axis)	d orbital: 4- lobed shape
	 p_x, p_y, p_z	 d_{xz}, d_{xy}, d_{yz} $d_{x^2-y^2}$ d_{z^2}

Note: In the n^{th} shell,

→ $N_{subshells} = n$

→ $N_{orbitals} = n^2$

Aufbau principle: e^- fill atomic orbitals of the lowest available energy levels before occupying higher levels



Pauli exclusion principle: each orbital can hold maximum of 2 e^-, with opposite spins

E.g 

Hund's rule: orbitals of a subshell must be occupied singly by e^- of parallel spins before pairing to minimise inter electronic repulsion

(except Cr and Cu, see chapter XXII. Transition Metals)

Ground state: when orbitals of lowest available energy levels are occupied

Excited state: e^- absorbs energy, promoted to higher energy level. Such atoms are unstable, can emit energy to return to the ground state.

- Formation of anions: e^- added to the next lowest available orbital. (e^- occupy 4s orbital first because $4s < 3d$ energy level [when both are still vacant])
- Formation of cations: e^- removed from orbital with highest energy. (occupied 3d orbital repels 4s orbital to higher energy level, e^- taken from 4s first before 3d) ($3d < 4s$ energy level)

Isoelectronic species = same N_{e^-}

Strength of electrostatic attraction:

- $N_{electronic\ shells}$ ($\uparrow N_{shells} \rightarrow$ greater distance btwn valence e^- and nucleus $\rightarrow \downarrow$forces of attraction)
- Size of nuclear charge ($\uparrow N_{protons} \rightarrow \uparrow$nuclear charge $\rightarrow \uparrow$forces of attraction)
- Shielding effect ($\uparrow N_{shells} \rightarrow \uparrow$shielding effect $\rightarrow \downarrow$forces of attraction)

Atomic radius: $\frac{1}{2}$ of shortest inter nuclear distance

- Atomic radius $\downarrow$across period ($\uparrow$nuclear charge$\rightarrow \uparrow$attraction $\rightarrow \downarrow size\ of\ e^-\ cloud$)
- Atomic radius $\uparrow$down group ($\uparrow N_{shells} \rightarrow \downarrow$attraction $\rightarrow \uparrow size\ of\ e^-\ cloud$)

Ionisation energy: energy req to remove e^- from atom [for more accurate definition see chapter V. Energetics]

- Endothermic
- I.E $\uparrow$across period ($\uparrow$nuclear charge$\rightarrow \uparrow$attraction$\rightarrow$ I.E $\uparrow$)
- I.E $\downarrow$down group ($\uparrow N_{shells} \rightarrow \downarrow$attraction $\rightarrow$ I.E $\downarrow$)

Irregularity - Grp 2 &13	Irregularity - Grp 15 & 16
1st I.E of $B < Be$, $Al < Mg$ (3p e^- higher energy than 3s e^-)	1st I.E of $O < N$, $S < P$ (3p e^- are paired, thus interelectronic repulsion $\rightarrow$ higher energy level $\rightarrow$ I.E $\downarrow$

- Successive I.E $\uparrow$ (removal of e^- from an increasingly positively charged ion $\rightarrow$ more energy req)

Ionic radius: radius of spherical ion.

- $Cation < Parent\ atom$ ($\downarrow N_{shells} \rightarrow$ $\uparrow$attraction$\rightarrow$ $\downarrow$ radius)
- $Anion < Parent\ atom$ ($\uparrow N_{e^-} \rightarrow$ $\uparrow$inter electronic repulsion$\rightarrow$ $\downarrow$attraction$\rightarrow \uparrow$ radius)
- Ionic radius of isoelectronic ions $\downarrow$ across period. ($\uparrow N_{protons} \rightarrow \uparrow Eff_{nuclear\ charge} \rightarrow \uparrow$ attraction$\rightarrow$ $\downarrow$ radius)

Electronegativity: ability to attract bonding e^-, $\sim \frac{charge}{volume}$

- $\downarrow$ down grp ($\uparrow N_{shells} \rightarrow \downarrow$attraction)
- $\uparrow$across period ($\uparrow$nuclear charge$\rightarrow \uparrow$attraction)

$\Delta EN < 0.5$	Non polar covalent
$0.5 < \Delta EN < 1.6$	Polar covalent
$2.0 < \Delta EN$	Ionic

III. Chem Bonding I

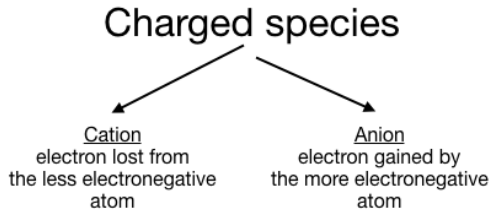
Chemical bonds: forces of attraction between particles.
Octet rule: atoms lose, gain, or share e^- until configuration of 8 valence e^- is obtained
Exceptions:

e^- deficient molecules ($< 8\ valence\ e^-$)
Radicals (unpaired $valence\ e^-$)
$Period\ 3\ elements$ and beyond (existence of low lying vacant 3d orbitals → can accommodate $> 8\ valence\ e^-$ and expand beyond octet) (energy req for promotion of e^- from 3s/3p to 3d is not large)

Ionic bonds: electrostatic forces of attraction between 2 oppositely charged ions
Covalent bonds: sharing of e^- localised between 2 nuclei
→ electrostatic forces of attraction between shared e^- pair and +ve nuclei
Dative bond: shared pair of e^- provided by 1 bonding atom
→ must have a lone pair of e^-, acceptor atom must have vacant low-lying orbital

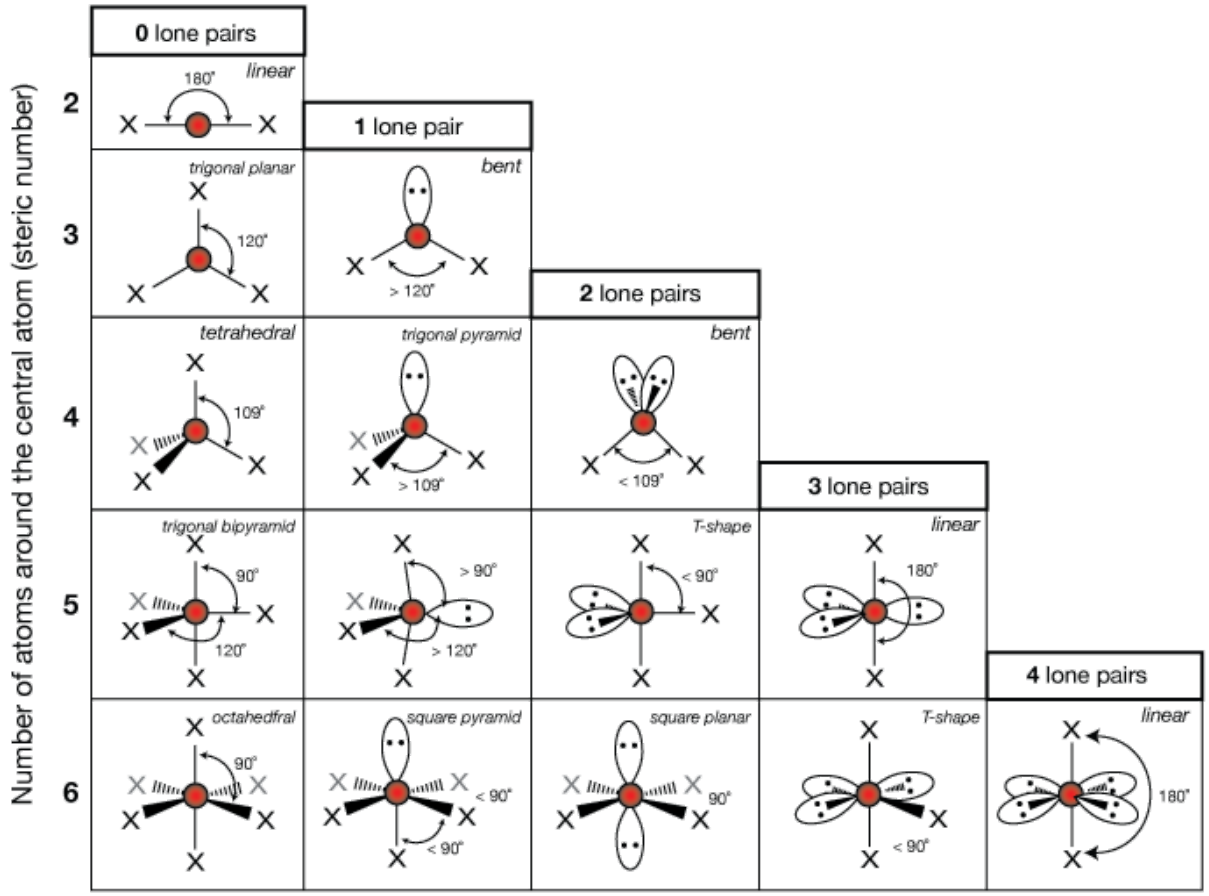
Dot-and-Cross:

1. Identify central & side atoms (Central atom is the most electronegative one)
2. $N_{valence\ e^-}$ of each atom
3. N_{bonds} to form to achieve octet (particularly side atoms)
4. Show lone pairs



VSEPR: molecular geometry of a species
→ e^- pairs are arranged as far as possible to minimise inter electronic repulsion

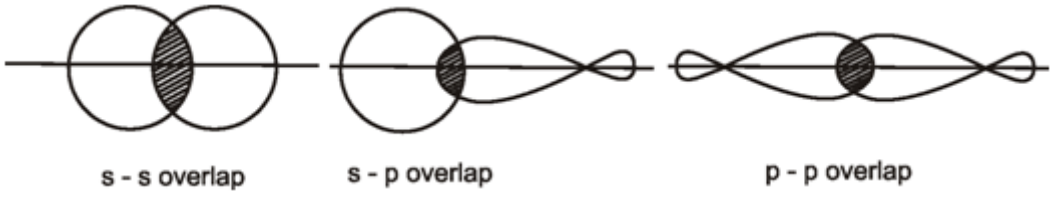
- $l.p - l.p\ repulsion > l.p - b.p\ repulsion > b.p - b.p\ repulsion$
- As electronegativity ↑, ↑ b.p-b.p repulsion, (nearer to nucleus)



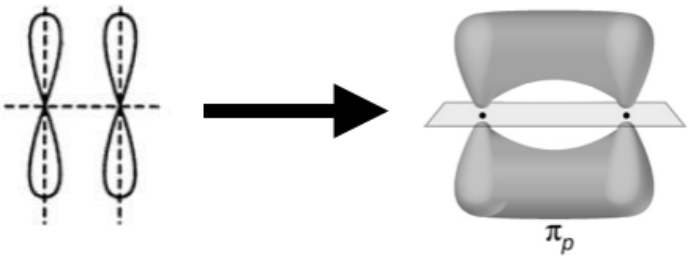
Note: $l.p\ repulsion > b.p\ repulsion$ because the l.p is attracted by only the central positive nucleus, but b.p is attracted by both the central nucleus and the bonding species (therefore b.p e^- lie further away from central nucleus)

σ & π bonds:

σ bond = head-to-head overlap, e^- density concentrated between the nuclei, along the nuclear axis



π bond = side-to-side overlap, e^- cloud above and below the nuclear axis



σ *bond strength* > π *bond strength* (↑degree of overlap)

Single bond → one σ bond

Double bond → one σ bond + one π bond

Triple bond → one σ bond + two π bonds

Bond length: distance between bonding nuclei

→ ↑bond length = ↓bond strength

Bond strength is equivalent to B.E [for more accurate definition of bond energy, see chapter V. Energetics]

Is dependent on:

- N_{bonds} (↑N_{bonds} → ↑$N_{shared\ e^-}$ → ↑ attraction→ ↑bond strength)
- Degree of $Eff_{overlap}$ (when size of orbital ↑→ orbitals become more diffuse→ $Eff_{overlap}$ ↓ → ↓bond strength
- ΔEN (as ΔEN ↑→ ↑polar→ resultant net dipoles cause additional electrostatic forces of attraction→ ↑bond strength)

Ionic with covalent character: electronegative cation polarises the anion→ ↑ degree of covalency

Covalent with ionic character: large ΔEN btwn bonding atoms → large dipole moment → ↑ degree of ionic character

Polar molecules = molecules with net dipole moment (e.g H_2O)

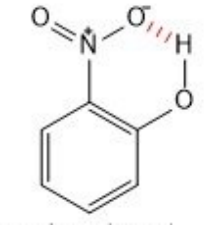
Intermolecular forces of attraction:

Instantaneous dipole-induced dipole	Permanent dipole-permanent dipole	H-bonding
(caused by momentary movements of e^- charge, and is present in all particles)	(polar molecules; forces of attraction between δ^+ and δ^-)	(a form of pd-pd, strong forces of attraction between electron deficient H^+ and lone pair on $F/O/N$ molecules)
• ↑e^-cloud → ↑I.M.F strength • ↑surface area→ ↑ I.M.F strength (e.g branched hydrocarbons)	• ↑δ moments→ ↑ I.M.F strength	• ↑$N_{H-bonds}$ formed with other molecules per molecule→ ↑ I.M.F strength

Ice is less dense than water:
→ In ice, O atom is tetrahedrally bonded to 4 H atoms → rigid, open, 3-d networks occupy larger volume

Mass of some carboxylic acids are more than calculated molar mass
→ Carboxylic acids exist as dimers in {vapor phase and in non-polar solvents} (2 carboxylic acids bonded to each other by H-bonds.)
→ However in {aq. phase} (carboxylic acid forms H-bonds with water instead of with each other → no dimerisation)

2-Nitrophenol has lower boiling point than 4-Nitrophenol



→ intramolecular H-bonding in 2-Nitrophenol→ ↓sites for H-bonding with other molecules → ↓I.M.F strength

Solubility: Solute is said to be soluble if the energy released from forming intermolecular bonds with the solvent molecules is sufficient to compensate for the energy required to overcome the existing solvent-solvent and solute-solute intermolecular bonds.

- Simple molecules with same type of I.M.F mix well
- Ionic solids tend to dissolve well in polar solvents (formation of strong ion-dipole interactions release a lot of energy)

Crystalline solid: a highly-ordered, well defined arrangement of constituents
Ionic lattice:

- Ions held in fixed position, orderly arrangement
- Coordination no. = $N_{nearest\ neighbours}$
- Non-directional

$L.E \sim \left| \frac{q^+ \times q^-}{r_+ + r_-} \right|$ [see chapter V. Energetics]

- Very strong (high m.p & b.p)
- Conducts electricity in molten/ aq. state (presence of mobile charge carriers which are the ions)
- Brittle (displacement along cleavage pt→ brings ions of like charge opp one another → repulsion)

Giant molecular lattice: atoms held tgt in extensive network covalently

- e.g Diamond (C bonded to 4 other C tetrahedrally)
  → Strong
  → Insulator (lack of delocalised e^-)
  → Insoluble
  → High m.p, b.p

  Giant Si structure has weaker covalent bonds than C (orbitals are larger and more diffused→ $\downarrow Eff_{overlap}$ → weaker bonds)
- e.g Graphite (planes of interconnected hexagonal rings) (C bonded to 3C in a trigonal planar geometry)
  → Strong
  → High m.p, b.p
  → Conductor (Single e^- that is not involved in bonding→ $\pi\, e^- cloud$ below & above the planes → delocalised charge carriers that are the e^- which can conduct electricity

parallel to these planes
→ Soft (Van der Waals forces btwn layers)

Simple molecular lattice: molecules attracted to each other by I.M.F

Giant metallic lattice: Lattice of +ve ions surrounded by a sea of delocalised e^-

- Strong, depends on:
  → $N_{valence\ e^-}$ ($\uparrow N_{valence\ e^-} \rightarrow \uparrow$bond strength)
  → Cationic size ($\downarrow$cationic size $\rightarrow \uparrow$bond strength)
- Conductors
  : of electricity (presence of delocalised $e^- \rightarrow$ mobile charge carriers)
  : of heat (e^- able to take in thermal energy)
- Soft (cations can glide over one another without breaking metallic bonds)
- Dense
- High m.p, b.p

IV. The Gaseous State

Ideal gas eqn: $pV = nRT$, R= molar gas constant, $8.31\ JK^{-1}mol^{-1}$

Assumptions for ideal gas eqn:

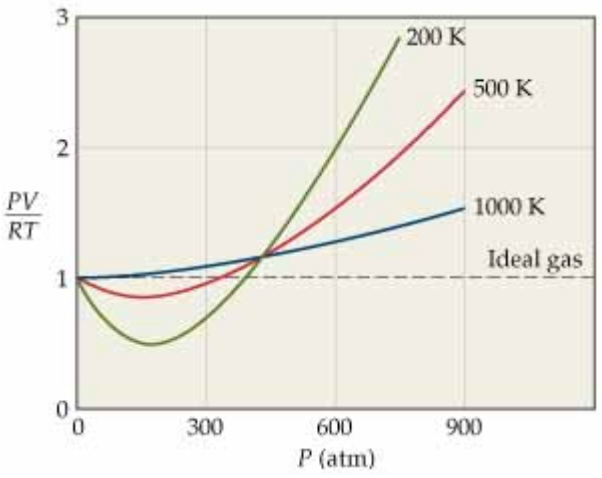
- Particles have negligible vol.
- Negligible forces of attraction between particles
- Constant random motion
- Elastic collisions
- K.E (kinetic energy) $\sim T$

However a real gas:

- Has finite vol. and size
- Experiences intermolecular attractions

A real gas approaches ideality, however, when

1. Low p $\rightarrow$ gas particles have negligible vol.
   $\rightarrow$ attractions negligible
2. High $T \rightarrow$ high K.E to overcome attractions



@ moderately high pressures: $\frac{pV}{RT} < ideal$

((I.M.F significant) thus recorded p is lower)

@ very high pressures: $\frac{pV}{RT} > ideal$

(($V_{free} = V_{container} - V_{gas\ molecules}$) as $V_{gas\ molecules}$ become significant, $V_{container}$ measured becomes artificially high)

Dalton's Law: total pressure of non-rxting gases = $\sum p_{partial}\ of\ individual\ gases$

Where $p_a = \frac{n_a}{n_{total}}\ x\ p_{total}$

Saturated vapor pressure: $N_{particles\ leaving} = N_{particles\ rejoining}$

$\rightarrow$ b.p is when $p_{saturated\ vapor\ pressure} = p_{ext}$

V. Energetics

Enthalpy change: $\Delta H = \Delta energy\ content\ of\ a\ process\ in\ a\ system\ at\ constant\ p$

$\rightarrow\ \Delta H_f = \sum H_{pdts} - \sum H_{rxts}$

$\Theta = standard\ conditions,\ 298K,\ 1bar,\ 1\ mol\ dm^{-3}$

$\Delta H_{rxn}{}^{\Theta}$ = energy absorbed/ released in a rxn, in molar quantities (at Θ).

$\Delta H_f{}^{\Theta}$ = energy change when 1 mole of substance is formed from its constituent elements (at Θ). $\Delta H_f{}^{\Theta} of\ elements$ = 0

$\Delta H_c{}^{\Theta}$ = energy released when 1 mole of substance is completely burnt in excess O_2 (g) (at Θ).

- always exothermic

$\Delta H_{neut}{}^{\Theta}$ = energy change when acid rxts with base → 1 mole of H_2O (at Θ).

$\Delta H_{atomisation}{}^{\Theta} for\ elements$ = energy absorbed to form 1 mole of gaseous atoms from element (at Θ)

$\Delta H_{atomisation}{}^{\Theta} for\ cmpds$ = energy absorbed to form gaseous atoms from 1 mole of the cmpd (at Θ)

- always endothermic

Bond Dissociation Energy, B.D.E = energy req to break 1 mole of particular bond in particular cmpd in gaseous state.

B.E = average energy req to break 1 mole of bonds in the gaseous state

- $B.E\ (X_2) = 2\Delta H_{atom}{}^{\Theta}(X_2)$

1st I.E = energy req to remove 1 mole of e^- from 1 mole of gaseous atoms to form 1 mole of singly charged +ve gaseous ions

2nd I.E = energy req to remove 1 mole of e^- from 1 mole of singly charged +ve gaseous ions to form 1 mole of doubly charged +ve gaseous ions

Note: I.E and B.E values can be found in the data booklet

1st e^- affinity, E.A = energy released when 1 mole of gaseous atoms acquires 1 mole of e^- to form 1 mole of singly -ve charged gaseous ions.

- Exothermic ($energy\ released > energy\ taken\ to\ overcome\ inter\ e^-repulsion$)

2nd E.A = energy absorbed when 1 mole of singly charged -ve gaseous ions acquire 1 mole of e^- to form 1 mole of doubly charged -ve gaseous ions.

- Endothermic (e^- is added to -ve ion, thus energy is required to overcome repulsion between 2 -ve charged species)

L.E = energy released, when 1 mole of solid ionic cmpd is formed from constituent gaseous ions (at Θ)

$\Delta H_{hydration}{}^{\Theta}$ = energy released when 1 mole of gaseous ions are hydrated (at Θ)

$\Delta H_{soln}{}^{\Theta}$ = change in energy when 1 mole of solute dissolves completely in a solvent to give an infinitely dilute solution.

Calorimetry: process of measuring the amount of heat released or absorbed during a chemical reaction.

$$q = mC\Delta T$$

$$\Delta H = -\frac{q}{n_{lim\ rgt}}\ kJ\ mol^{-1}$$

Hess Law: ΔH determined by initial and final states of the system, independent of pathways taken.

- $\sum clockwise\ \Delta H = \sum anticlockwise\ \Delta H$
- $\Delta H_{rxn}{}^{\Theta} = \sum n\Delta H_c{}^{\Theta}(rxts) - \sum m\Delta H_c{}^{\Theta}(pdts)$
- $\Delta H_{rxn}{}^{\Theta} = \sum n\Delta H_f{}^{\Theta}(pdts) - \sum m\Delta H_f{}^{\Theta}(rxts)$
- $\Delta H_{rxn}{}^{\Theta} = \sum B.E_{bonds\ broken\ in\ rxts} - \sum B.E_{bonds\ formed\ in\ pdts}$
- $\Delta H_{soln}{}^{\Theta} = [\sum \Delta H_{hyd}{}^{\Theta}(M^{+}) - \sum \Delta H_{hyd}{}^{\Theta}(X^{-})] - L.E(MX)$

Entropy = measure of disorder within a system, or number of ways a system can arrange itself differently.

- $\Delta S = S_{final} - S_{initial}$
- $\uparrow N_{gas\ molecules} \rightarrow \uparrow S$
- Mixing of particles $\rightarrow \uparrow S$
- $\uparrow T \rightarrow \uparrow S$

Standard Gibbs free energy change : $\Delta G^{\Theta} = \Delta H^{\Theta} - T\Delta S^{\Theta}$, $\Delta G^{\Theta} = \Delta G_{pdt}{}^{\Theta} - \Delta G_{rxt}{}^{\Theta}$

Spontaneous rxn: a rxn that occurs without need for external assistance, irreversible. Said to be thermodynamically feasible.

- Less stable rxts → more stable pdts
- $\Delta G^{\Theta} < 0$, forward rxn spontaneous (exergonic)
- $\Delta G^{\Theta} > 0$, forward rxn not spontaneous (endergonic)

Limitations:
→ Thermodynamic feasibility = spontaneity, whether it can occur
→ kinetic feasibility = whether the rate of rxn is observable (depends on $E_{activation}$)

VI. Reaction Kinetics

$Rate_{rxn} = -\frac{d[rxts]}{dt}$ or $\frac{d[pdts]}{dt}$

Instantaneous rate = rate at a particular time

Average rate = final $\frac{\Delta conc}{\Delta t}$

Initial rate = instantaneous rate @ t=0

$aA + bB \rightarrow cC + dD$, $\frac{d[D]}{dt} = \frac{d}{c}\frac{d[C]}{dt}$

$rate = k[A]^m[B]^n$, where k= rate constant, m & n are orders of rxn wrt to [A] and [B] respectively

Rate law: eqn that shows dependence of rate on [rxts]

Rate constant: constant of proportionality

$\rightarrow \uparrow T/catalyst \rightarrow \uparrow k \rightarrow \uparrow$ rate

Half-life: time taken, t, for [rxt] to decrease to half of its initial concentration

→ for 1st order rxns, $t_{1/2} = \frac{ln2}{k}$

First order rxn: $rate = k[A]$, $t_{1/2}$ *constant*

Second order rxn: $rate = k[A][B]$ *or* $k[A]^2$, $t_{1/2}$ *not constant*

Zero order rxn: rate independent of [A], rate=k

Pseudo order rxn: concentration of particular rxt remains effectively constant throughout the rxn

- Presence of large excess of rxt (e.g solvent is a rxt)
- Presence of catalyst ([catalyst] is constant, takes part in the rxt but is regenerated)

As such, $rate = k'[A]$, $where\ k' = k[B]$

Overall rxn order	Unit for rate constant
0	$mol\ dm^{-3} s^{-1}$
1	s^{-1}
2	$mol^{-1} dm^3 s^{-1}$

Initial rates method: measuring $\Delta[rxts/pdts]$ in the first small Δt

Clock method: measuring t taken for ppt to form (observing visual changes)

Used for:

- Rxting a fixed [pdt]
- Forming a fixed [pdt]

$$rate \sim \frac{1}{t_{taken\ for\ visual\ change\ to\ occur}}$$

Rxn mechanism: collection of elementary steps in the proper sequence

Elementary Step: distinct step, describes a single molecular event (cannot be broken down into simpler steps)
Molecularity of elementary step = $N_{rxting\ particles}$
Intermediate: species formed in one step & consumed in the other
Single step rxn: made of 1 elementary step

- Rxn mechanism identical to stoichiometric eqn
- Rate eqn can be deduced directly

Multi step rxn: ≥ 2 steps, different rates

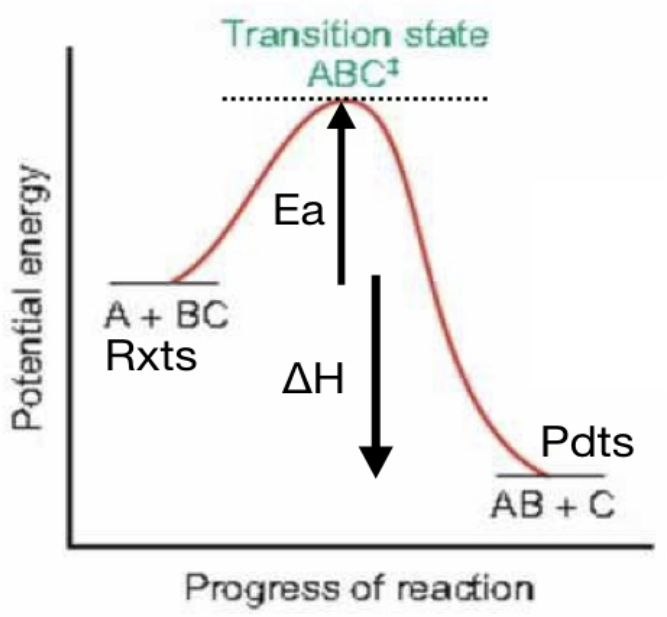
- Rate depends on rate-determining step (slow step)

Rate-determining step: step with highest E_a
Rxn mechanism rules

1. Must agree with stoichiometric eqn (i.e must sum to give overall eqn, as such intermediates do not appear)
2. Must be consistent with observed kinetics

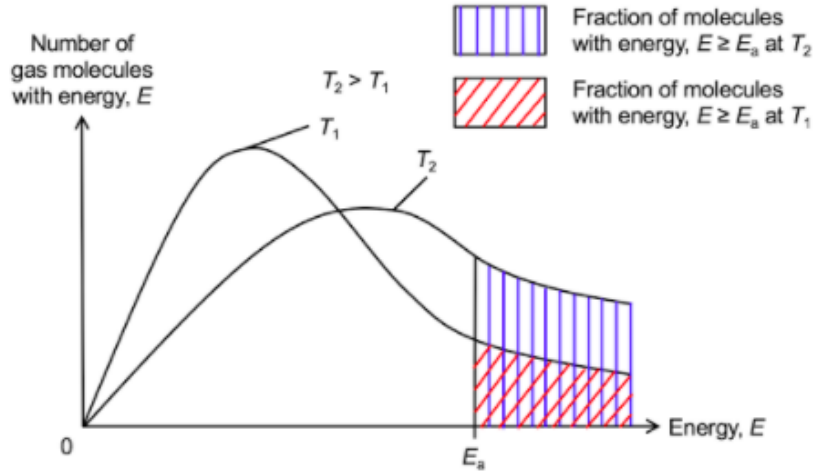
Collision theory: Rxting particles must collide in favorable orientation and with sufficient energy above E_a to rxt.
Transition state theory: what happens during collision
Transition state:

1. Cannot be isolated
2. Can form pdts or back to rxts



Kinetic stability vs Thermodynamic stability

Maxwell-Boltzmann Distribution:



- When $T \uparrow$, peak moves to higher energies, distribution broadens out
- Area under curve remains constant
- When $T \uparrow$, $N_{molecules} with\ energy \geq E_a$ increases

Conc vs Temp vs Catalyst

1. Conc$\uparrow \rightarrow$ probability of collision with correct collision geometry and sufficient energy increases$\rightarrow \uparrow$rxn rate (given that order of rxn w.r.t said rxt $\neq 0$)
2. $T \uparrow \rightarrow K.E_{ave} \uparrow \rightarrow (N_{molecules}\ energy \geq E_a) \uparrow \rightarrow$ rate of rxn $\uparrow$

   Furthermore rate constant, $k = Ae^{-\frac{E_a}{RT}}$, as $T \uparrow$ size of 'k' $\uparrow$
3. Catalyst: $\uparrow$rate of rxn w/o undergoing permanent chemical change, provides an alt. pathway for rxn, $\downarrow E_a \rightarrow (N_{molecules}\ energy \geq E_a) \uparrow \rightarrow$ rate of rxn $\uparrow$

   Furthermore rate constant, $k = Ae^{-\frac{E_a}{RT}}$, as $E_a \downarrow$ size of 'k' $\uparrow$

Catalysis

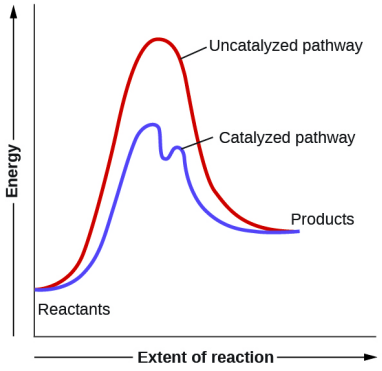
Inhibitor: $\downarrow$rate of rxn

Promoter: $\uparrow$Effectiveness of catalyst

Catalyst poison: inhibitor of eff of catalyst

Homogenous catalyst: catalyst & rxts same phase

→ takes part, is converted to intermediates, and is regenerated



Larger E_a is replaced by 2 smaller E_a

Heterogenous catalyst: catalyst & rxts different phase

→ rxt molecules adsorbed onto catalyst surface. (adsorption onto catalyst→ weakening of covalent bonds within rxting particles) → $\downarrow E_a$

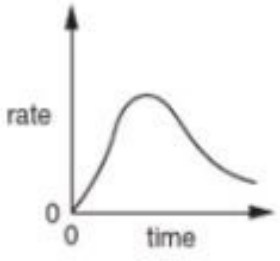
→ $\uparrow [rxting\ particles]$ @ catalyst surface

As such, rate of rxn ↑

Diffusion→ Adsorption→ Rxn→ Desorption → Diffusion

Active sites are freed up again for cycle to repeat until all rxts have rxted

Autocatalysis: pdt acts as catalyst



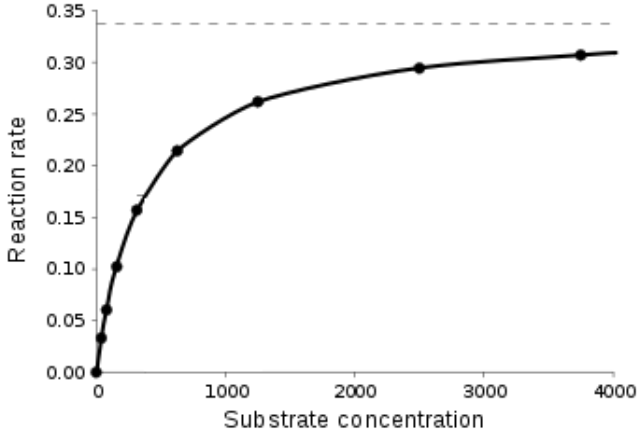
Initially: no catalysis

Finally: $\downarrow [rxts] \rightarrow \downarrow$rate

Enzymes: proteins which act as biological catalysts

- Globular proteins with active sites
- Effective
- Specific
- Effective at body temperatures (denatured at high T, inactive at low T)
- Work over a narrow pH range

(substrate + enzyme → enzyme-substrate complex → enzyme + pdts)



At low [substrate], rate of rxn is 1st order wrt to substrate.

At high [substrate], rate of rxn is 0 order wrt to substrate. (active sites become saturated)

Note: such phenomenon is similar to heterogeneous catalysis

Experimental techniques:

1. Sampling → quenching → titrating
   Withdraw fixed vol of sample at steady intervals, and quench by (adding large vol of cold water, or excess of quenching agent that rxts immediately with all rxts or catalyst) then titrate to determine instantaneous concentration present
2. Measuring color intensity ($concentration \sim color\ intensity$)
   Measure color intensity (absorbance) at steady intervals, and conc of colored species is determined by comparing to calibration curve (color intensity of solns of known concentrations)
3. Measuring gas vol.
4. Measuring electrical conductivity ($N_{ions} \sim conductivity$)
5. Measuring pressure ($V_{gas} \sim N_{gas}$)
   Measure change in $p_{partial}$ of rxt or pdt to determine rate

VII. Dynamic Eqm

Dynamic eqm: state in a reversible rxn in which $rate_{forward} = rate_{backward}$

- No net change in macroscopic properties observable
- Closed system
- Can be attained from either direction
- Same eqm state can be attained from any amt of rxts & pdts (given T constant)

Reaction quotient, $Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

Eqm constant, $K_c = \frac{[C]^c_{eqm}[D]^d_{eqm}}{[A]^a_{eqm}[B]^b_{eqm}}$

Eqm constant for gases, $K_p = \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b}$

$K_{forward} = \frac{1}{K_{backward}}$, $K_{overall} = K_1 \times K_2 \times ....$

$K_{overall} = K^n$, (when eqn is multiplied by a factor of n)

K_c dependent only on ΔT

Catalyst doesn't change K_c (changes $K_{forward}$ but also $K_{backward}$)

Heterogenous eqm: some rxts and products are not in the same phase (do not include such reactants in the K_c expression) (e.g pure solids/ liquids, or excess liquid H_2O when it is a solvent)

Degree of dissociation, $\alpha = \frac{amt\ dissociated}{total\ initial\ amt}$

$\Delta G^{\Theta} = -RT\ln K_c$, R= molar gas constant

Le Chatelier's principle: when a system in eqm is subjected to change, the system will react to counteract the change to re-establish eqm.

Haber process: a reversible industrial synthesis of NH_3

$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$ ΔH^{Θ} = -92 $kJ\ mol^{-1}$

Conditions:

- 450 $^{\circ}C$
- 200 atm
- Iron catalyst
- Removal of NH_3 gas

The pressure chosen for the Haber process is a compromise. A high pressure increases the percentage yield of ammonia but very high pressures are expensive.

The temperature chosen is also a compromise. A high temperature gives a fast reaction but decreases the percentage yield of ammonia. 450°C gives a reasonably fast reaction with a sufficiently high percentage yield of ammonia

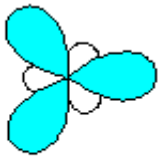
VIII. Chem Bonding II

Hybridisation: mixing of atomic orbitals to generate a set of equivalent orbitals

sp = s + p (linear)

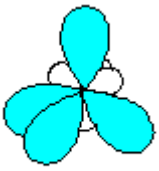
sp orbitals

sp^2 = s + 2p (trigonal planar)



sp^2 orbitals

sp^3 = s + 3p (tetrahedral)



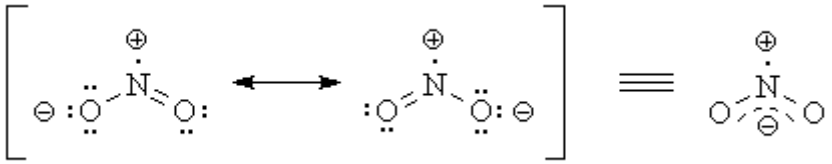
sp^3 orbitals

Greater s-character of sp^x orbital → ↑B.E

Bond lengths:

sp^3–sp^3	154 pm
sp^3–sp^2	150 pm
sp^3–sp	146 pm
sp^2–sp^2	147 pm
sp^2–sp	143 pm
sp–sp	137 pm

Resonance: same arrangement of nuclei, diff arrangement of e^-, delocalisation of e^-. The resonance hybrid is the average of two canonical forms (resonance structures)



Note: drawing of resonant structures is not in syllabus

- Equivalent bond strengths
- Equivalent bond lengths

IX. Intro to Organic Chem

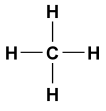
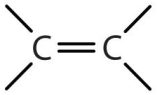
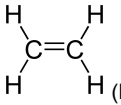
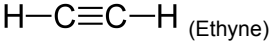
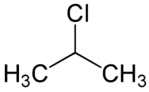
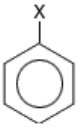
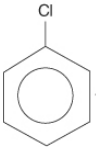
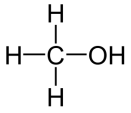
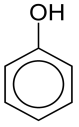
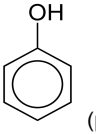
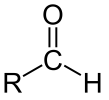
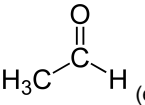
Hydrocarbons

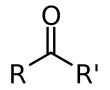
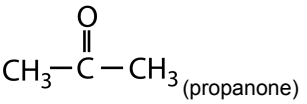
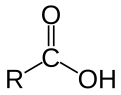
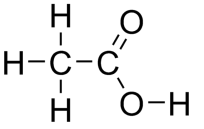
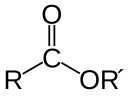
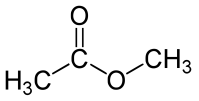
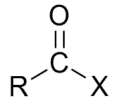
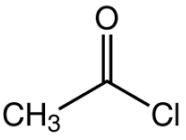
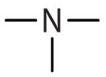
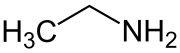
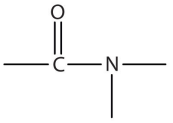
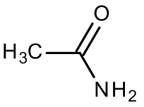
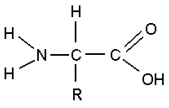
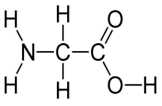
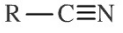
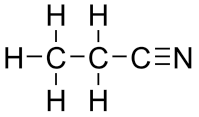
- Aliphatic (open chains)
- Alicyclic (closed ring)
- Aromatic (benzene ring)

Functional group: made up of atom/ grp of atoms that are responsible for the molecule's chemical characteristics

Homologous series: family of cmpds with same functional grps

Number of C	1	2	3	4	5	6	7	8	9	10
Name	meth	eth	prop	but	pent	hex	hept	oct	non	dec

Class	Homologous series	Func grp	Formula	Eg
Hydrocarbons	alkane	$CH_3 - CH_3$	C_nH_{2n+2}	 (methane)
	alkene		C_nH_{2n}	 (Ethene)
	alkyne		C_nH_{2n-2}	 (Ethyne)
Halogen Derivatives	halogenoalkane	R-X, X = (Cl, Br, I)	RX	 (2-chloropropane)
	halogenoarene	 X = (Cl, Br, I)	-	 (chlorobenzene)
Hydroxyl cmpds	alcohol	R-OH	ROH	 (methanol)
	phenol		-	 (phenol)
Carbonyl cmpds	aldehyde		$RCHO$	 (ethanal)

	ketone		$RCOR'$	 (propanone)
Carboxylic acid & derivatives	carboxylic acid		$RCOOH$	 (ethanoic acid)
	ester		$RCOOR'$	 (methyl ethanoate)
	acyl halide	 X = (Cl, Br, I)	$RCOX$	 (ethanoyl chloride)
Nitrogen cmpds	amine		$RN(R')_n$	 (ethyl amine)
	amide		$RCON(R')_n$	 (ethanamide)
	amino acid		$NH_2CH(R)COOH$	 (Aminoethanoic acid)
	nitrile		RCN	 (propanenitrile)

Homolytic fission: breaking of covalent bond, 1 e^- goes to each of the atoms, forming free radicals

Heterolytic fission: breaking of covalent bond, both e^- goes to same atom, forming +ve and -ve ions

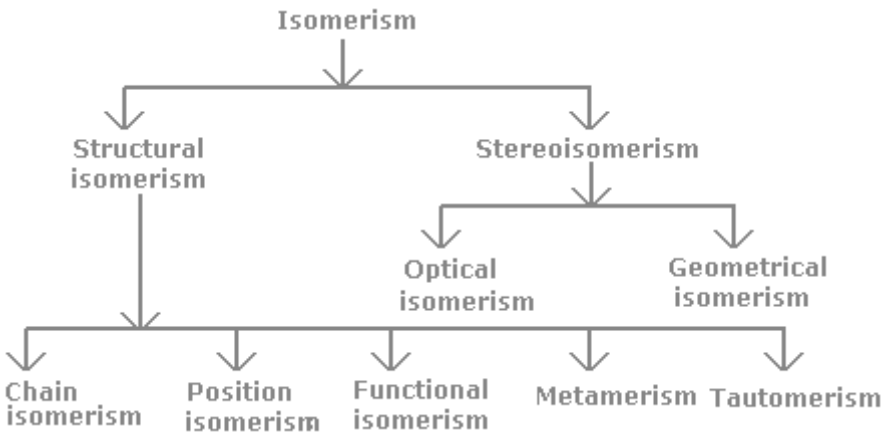
Degree of subst: $N_{alkyl/aryl}\ grps$ bonded to the $alpha\ carbon\ (C_\alpha)$

Suffix priority:
$Carboxylic\ acid > ester > acid\ halide > amide > nitrile > aldehyde > ketone > alcohol > amine$

Substitution reaction: 1 atom/ grp of atoms replaced by another atom/ grp of atoms. 2 rxts react to give 2 pdts (e.g: Free radical subst [see chapter X. Alkanes] Electrophilic Subst of arenes [see chapter XII. Arenes] Nucleophilic Subst of RX [see chapter XV. RX])
Elimination reaction: removal of atoms/ grp of atoms from adjacent carbon atoms to form multiple bonds (e.g: Elimination of alkene [see chapter XI. Alkenes])
Hydrolysis: rxn where H_2O breaks a bond (e.g: acid hydrolysis of ester [see chapter XVIII. Carboxylic & Derivatives]
Condensation: 2 molecules rxt, form bigger molecule, elimination of small molecules (like H_2O/HCl) (e.g: condensation of ROH and RCOOH [see chapter XVI. Hydroxy Cmpds]
Redox rxn
Rearrangement rxn: migration of atom/ grp of atoms from one site to another within same molecule

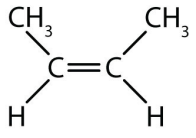
Steric hindrance: when presence of a substituent hinders the approach of an attacking rxt and prevents rxn/ ↓rxty of a particular site

Isomerism: same molecular formula, diff arrangement of atoms

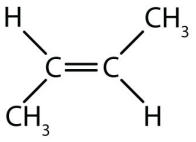


Note: Metamerism and Tautomerism are not in syllabus

Cis-trans isomerism: form of geometric isomerism, arises due to restricted rotation (ring/ double bond)



cis-2-butene



trans-2-butene

For alkenes, each C attached to the double bond must have 2 diff grps attached

Cis-isomer: 2 identical grps on the same side of the double bond (for alkenes)

Trans-isomer: 2 identical groups on opp side of double bond (for alkenes)

- If $N_{C=C}$ is x, N_{max} of cis-trans isomers is 2^x

For cyclic cmpds: ≥ 2 carbon atoms have 2 diff grps attached

Enantiomerism: optical isomerism, same molecular formula, same structural formula, diff spatial arrangement

- Molecule with n chiral centres have max 2^n stereoisomers
- Non-superimposable mirror image
- No plane of symmetry
- ≥ 1 chiral centre (sp^3 hybridised) usually

Physical properties	Identical, but rotate plane-polarised light in opp directions
Chemical properties	Similar, except when interacting with another chiral molecule
Biological properties	Different biological properties

Racemic mixture: equimolar ratio of both enantiomers

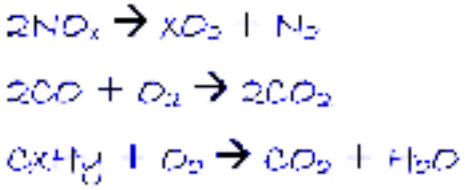
Diastereoisomers: stereoisomers that are not mirror images

Meso cmpd: molecules superimposable on mirror image, with chiral centres (this is due to a plane of symmetry)

Molecules with x chiral centres, y double bonds that cause cistrans isomerism,

$max\ N_{stereoisomers} = 2^{(x+y)}$

Catalytic converter: pollution-reducing unit which turns the harmful chemicals in vehicle exhausts into harmless gases



X. Alkanes

$CH_3 - CH_3$

Saturated vs Unsaturated: single vs double/triple bond

"Degrees of Unsaturation" (or "Index of Hydrogen Deficiency")

- In a hydrocarbon with no double bonds or rings, the number of hydrogens and carbons is related as follows:

  #Hydrogens = (2 × #Carbons) + 2

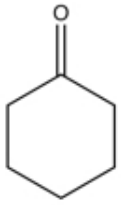
- Each multiple bond *or* ring reduces the hydrogen count by 2, which we refer to as a "degree of unsaturation"
- The degrees of unsaturation in a molecule can be calculated from its molecular formula using the following calculation:

$$\text{Degrees of Unsaturation} = \frac{2C + 2 + N - H - X}{2}$$

C = #carbons H = #hydrogens N = #nitrogens X = #halogens

1 ring = 1 DoU
1 double bond = 1 DoU
1 triple bond= 2 DoU

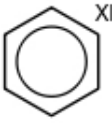
eg. 1:



# rings = 1
# double bonds = 1
# triple bonds = 0
x = 1 + 1 + 2(0) = 2

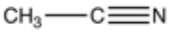
eg. 2:

[a benzene ring is a resonant structure with 3 single bonds and 3 double bonds. See Chapter XII. Arenes]



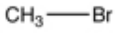
# rings = 1
# double bonds = 3
# triple bonds = 0
x = 1 + 3 + 2(0) = 4

eg. 3:



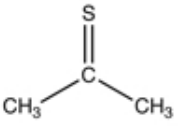
# rings = 0
# double bonds = 0
# triple bonds = 1
x = 0 + 0 + 2(1) = 2

eg. 4:



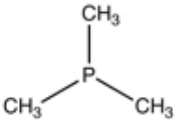
# rings = 0
# double bonds = 0
# triple bonds = 0
x = 0 + 0 + 2(0) = 0

eg. 5:



# rings = 0
# double bonds = 1
# triple bonds = 0
x = 0 + 1 + 2(0) = 1

eg. 6:



# rings = 0
# double bonds = 0
# triple bonds = 0
x = 0 + 0 + 2(0) = 0

Note: not in syllabus, but an extremely useful tool to have in hand (in later topics you will appreciate it more)

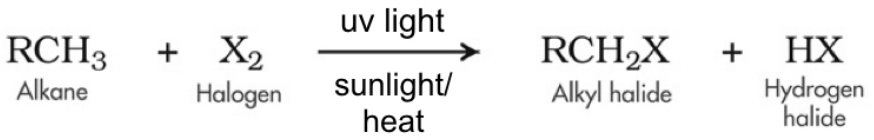
Alkanes are

- non-polar (ΔEN very low)
- I.M.F predominantly id-id

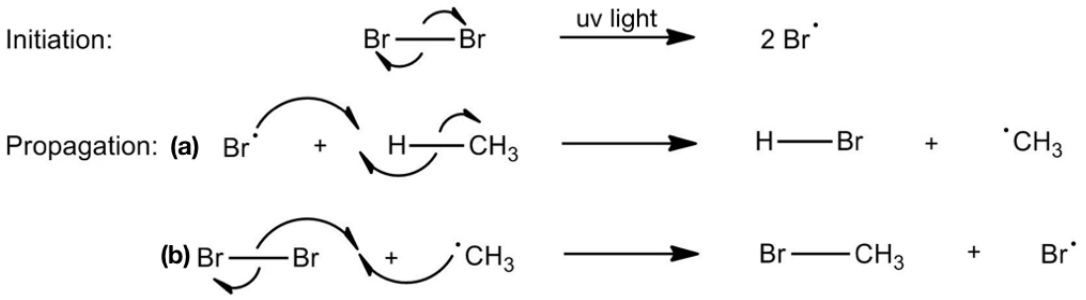
- As branching↑, b.p↓ (as the *surface area:volume* ratio ↓, strength of id-id I.M.F ↓)
  → however m.p indeterminate, depends on the effect of packing in a solid
- Insoluble in water
- Less dense than water (density $\approx 0.8\, g\ cm^{-1}$)
- Unreactive (unaffected by polar reagents)
  → relatively strong C-H & C-C bonds
  → saturated (no areas of high e^- density)

Rxns of alkanes:

- Combustion [see Chapter I. Mole Concept]
- Halogenation

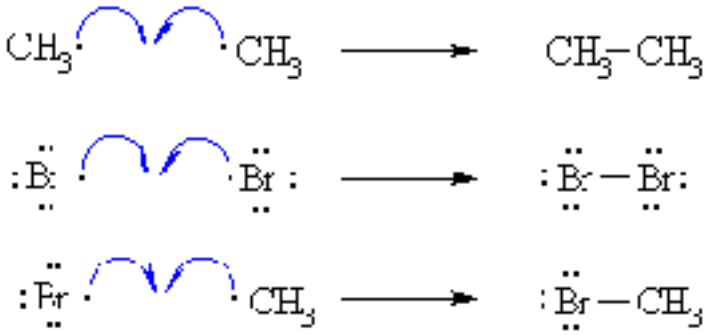


This is the Free Radical Substitution mechanism



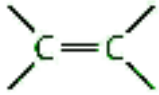
Then (a),(b),(a),(b),.....

Termination:



Note: only trace amts of uv light req because after initiation the rxn propagates itself (a),(b),(a)...

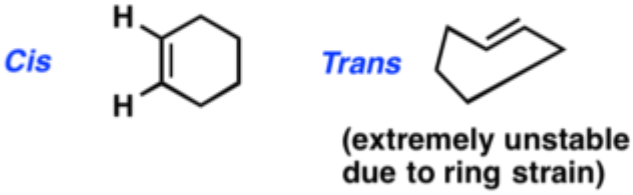
XI. Alkenes



Cis trans isomerism exceptions:

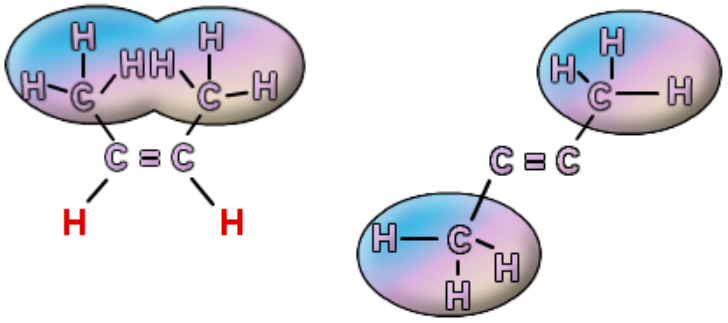
Double bonds in cycloalkenes of 7 or fewer carbons are exclusively *cis*.

The *trans* isomers are too strained to stable under ordinary conditions



Relative stability of cis-trans isomers

→ $cis < trans$



(steric crowding in cis → repulsive forces between the electron clouds of the groups→ ↓stability)

Relative m.p/ b.p of cis-trans isomers

→ cis has higher b.p than trans (slightly polar molecule→ increased dipole-dipole interactions)

→ trans has higher m.p than trans (trans packs better in a lattice structure)

Preparation of alkenes

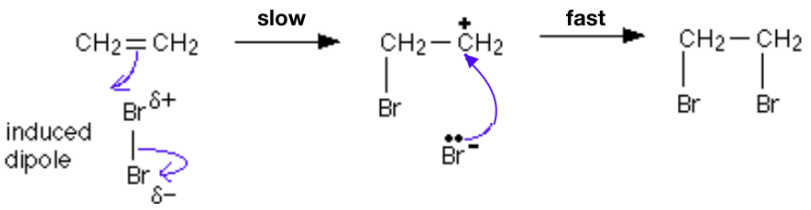
- $RX \rightarrow Alkene + HX$ [see Chapter XV. Halogen Derivatives]
- $ROH \rightarrow Alkene + H_2O$ [see Chapter XVI. Hydroxy Cmpds]

Zaitsev's rule: If more than 1 alkene can be formed by elimination reaction, the more stable alkene is the major pdt. ($\uparrow N_{alkyl\ substituents} = \uparrow stability$)

Reactions of alkenes:

- Electrophilic Addition

Mechanism:

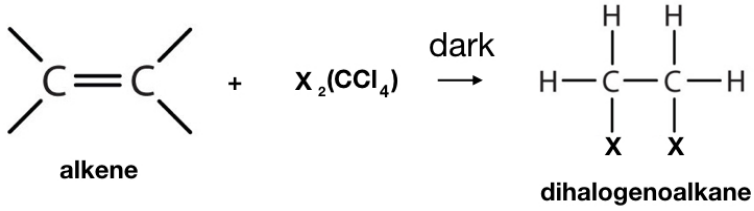


Where the electrophile (in this case Br_2) attacks in the first step

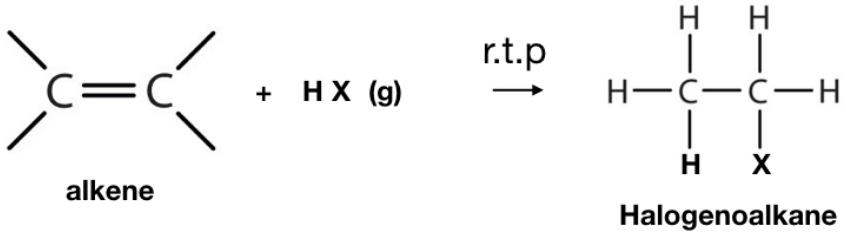
The next most abundant nucleophilic species attacks in the second step

- Stereochemistry: +ve carbon in the second step is sp^2 hybridised, planar, therefore chance of attack from either side is equal. If new chiral centre is generated, a racemic mixture of enantiomers is expected.
- Markovnikov's rule: when assymetrical alkenes goes through electrophilic addn, the more stable carbocation intermediate is formed. The more stable a carbocation, the faster it is formed.
  → alkyl groups are e^- donating, thus they help to disperse the +ve charge on the +ve carbon, thus they are stabilising groups.
  $\uparrow N_{alkyl\ substituents} = \uparrow stability$

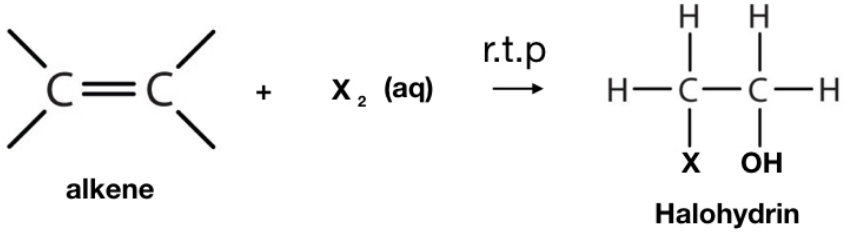
1. "Halogenation"



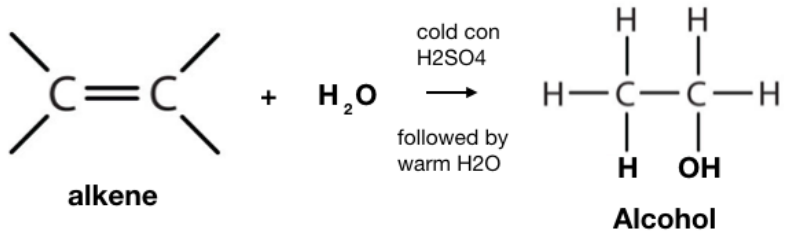
2. "Halogenation"



3. "Halogenation"

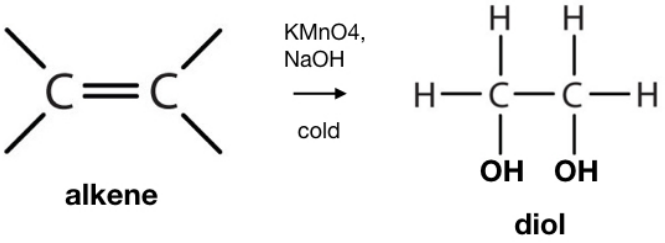


4. “Hydration”



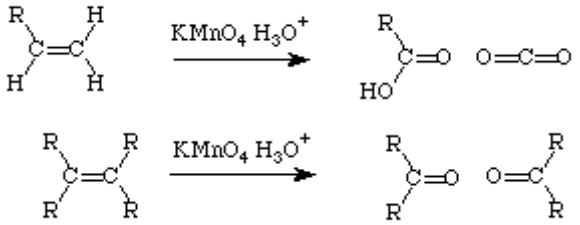
- Oxidation

  1. Mild oxidation

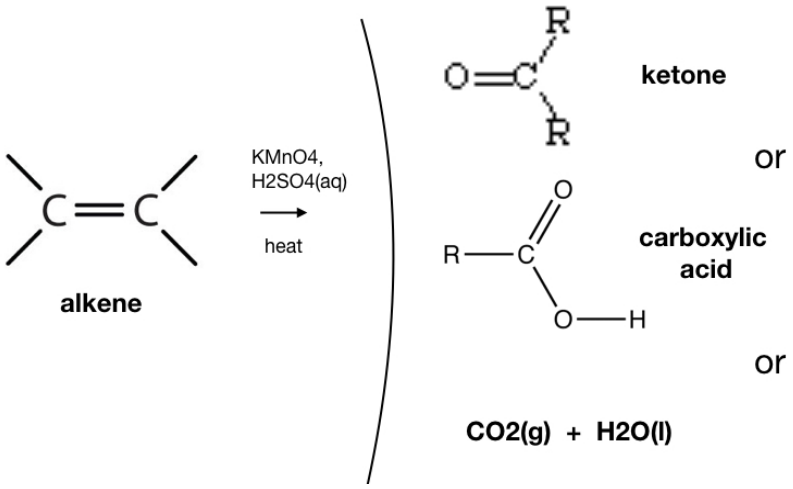


  2. Strong oxidation

Cleave the double bond, and add O atom to both ends.
e.g:

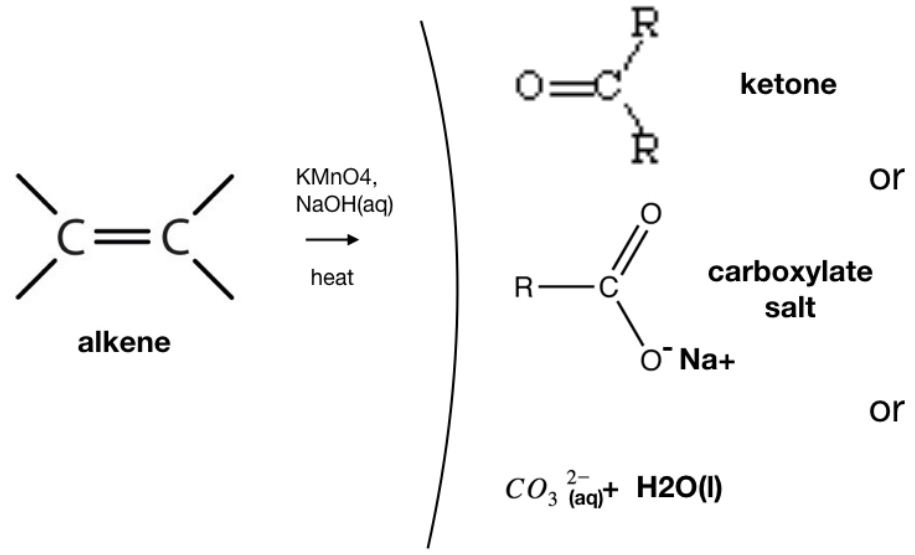


In acidic medium:



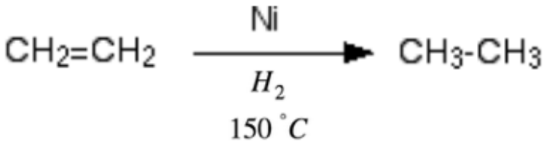
Note: H_2SO_4 is used instead of HCl for acidification because Cl^- wld be oxidised by $KMnO_a$

In alkaline medium:

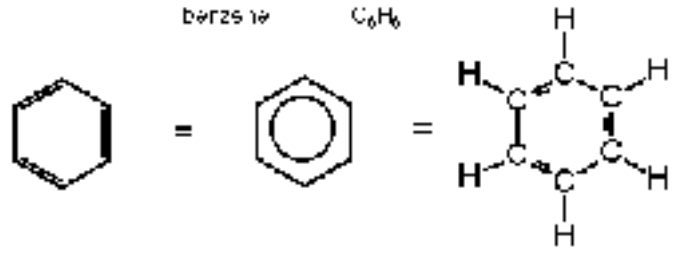


Note: oxidation and reduction mechanisms are not in syllabus. Just need to know the reagents and conditions

- Reduction



XII. Arenes



Note: in this chapter I may use the Kekule structure for benzene sometimes, but note that you should always draw the resonant structure only

Resonance: all C atoms are sp^2 hybridised, thus unhybridized p-orbitals can overlap sideways, continuously. This results in a cloud of delocalised e^-

→ equal bond strength

→ equal bond length

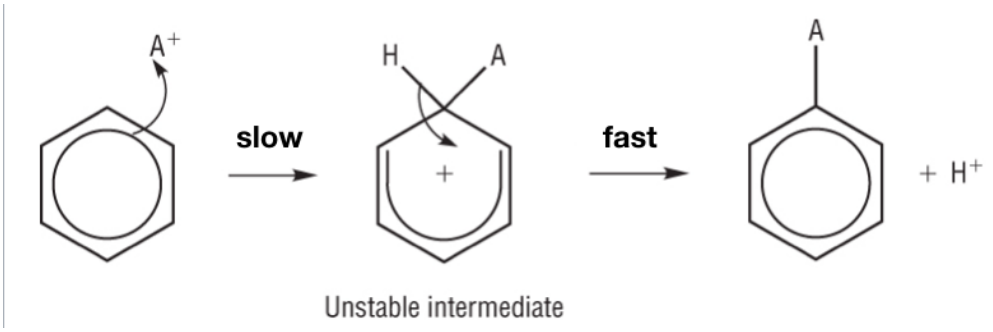
Resonance provides stability therefore addition rxns which involve destruction of the double bond and thus the resonance structure, are not favored

→ as such subst rxns that maintain delocalisation of e^- preferred

Rxns of arenes:

- Electrophilic subst

Mechanism:

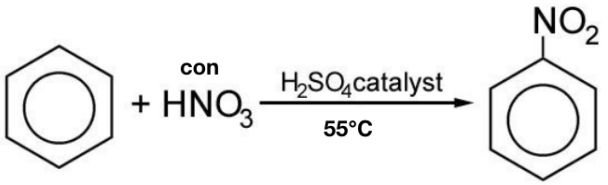


Where A^+ represents an electrophile

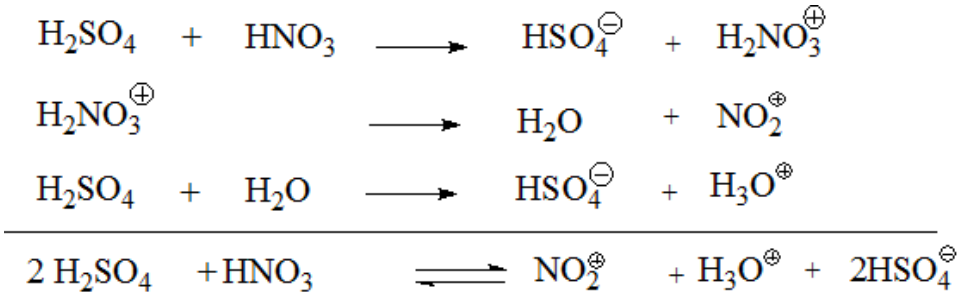
1. Generation of Electrophile, A^+ (this step isn't shown above)
2. Electrophilic attack of A^+ (step 1, slow step)
3. Regeneration of catalyst (step 2, fast step)

Note: this is an overly simplified illustration, refer to below for more detailed mechanisms

1. Nitration



1. Generation of Electrophile, NO_2^+



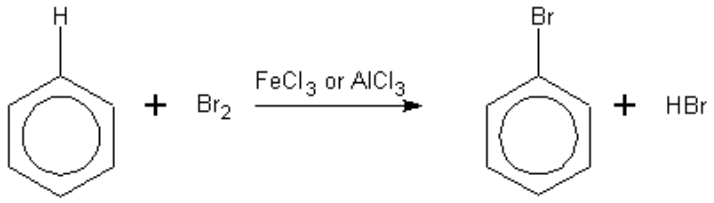
In the first step:

Bronsted Lowry acid = proton donor……(H_2SO_4)

Bronsted Lowry base = proton acceptor……(HNO_3)

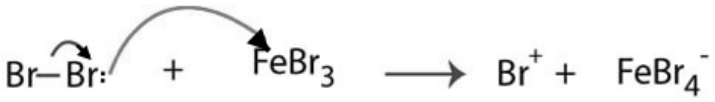
2. Electrophilic attack

2. Halogenation



Mechanism: (electrophilic attack similar to the above displayed in nitration, but generation of electrophile is different)

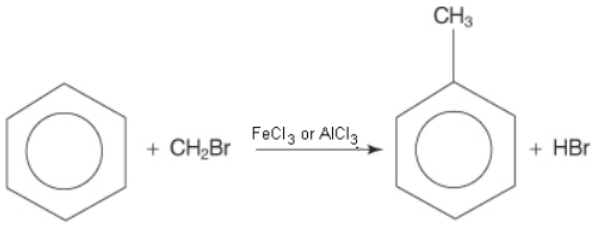
1. Generation of Electrophile, Br^+



Lewis Acid = e^- pair acceptor……(FeX_3)

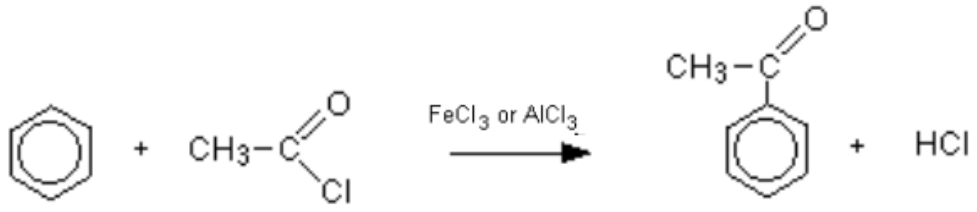
Lewis Base = e^- pair donor……(X_2)

3. Alkylation



Almost exactly similar to halogenation, except that electrophile is CH_2^+

4. Acylation

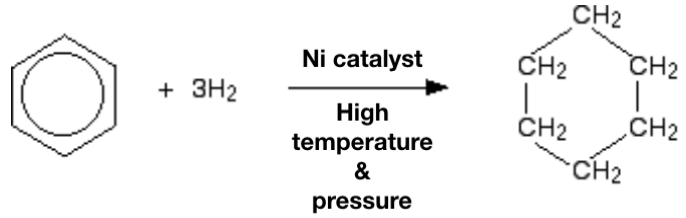


Almost exactly similar to halogenation, except that electrophile is CH_3CO^+

- Combustion

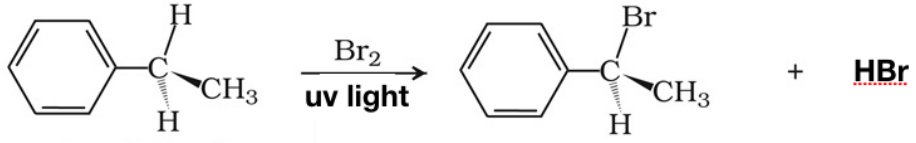
$$C_6H_6(l) + 7.5\ O_2(g) \rightarrow 6\ CO_2(g) + 3\ H_2O(\ell)$$

- Reduction (catalytic hydrogenation)

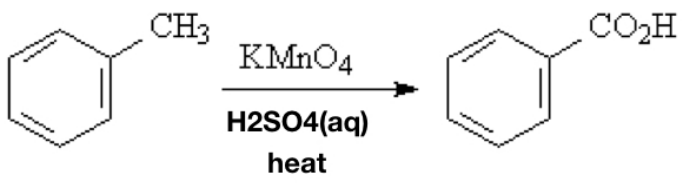


Rxn of Alkylbenzenes:

- Free radical subst (similar to alkanes [see Chapter X. Alkanes])



- Side chain oxidation (only possible if C atom attached to benzene ring is not 3° substituted)

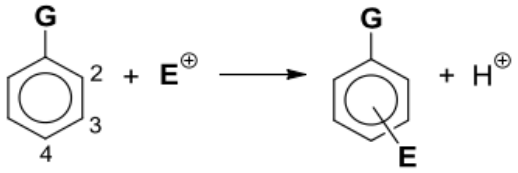


Activating grps	Deactivating grps
Substituents that ↑rxty of the compound compared to the original benzene ring, by ↑ e^- density on the ring.	Substituents that ↓rxty of the compound compared to the original benzene ring, by ↓ e^- density on the ring.

Such groups work via inductive/ resonance effect

8 The orientating effect of groups in aromatic substitution reactions

The position of the incoming group, **E**, is determined by the nature of the group, **G**, already bonded to the ring, and not by the nature of the incoming group **E**.



G	–alkyl –OH or –OR $–NH_2$, –NHR or $–NR_2$ –NHCOR	–Cl, –Br, –I	–CHO, –COR $–CO_2H$, $–CO_2R$ $–NH_3^+$ $–NO_2$, –CN
Reactivity of ring (compared to benzene)	Activated	Deactivated	Deactivated
Position of E (relative to position of G)	2- and/or 4-	2- and/or 4-	3-

Note: the activating and deactivating groups can be found in the data booklet

2,4 directing groups: directs attacking substituents to the 2,4 C relative to its position

3 directing groups: directs attacking substituents to the 3 C relative to its position

Inductive effect: donation/ withdrawal of e^- through σ bond due to ΔEN

Resonance effect: donation/ withdrawal of e^- through π overlap of subst & benzene ring
→ e^- -donating when subst has a *lone pair* of e^- that can delocalise into the benzene ring. (e.g -OH, -Cl)
→ e^- -withdrawing when subst is directly attached by an atom doubly/ triply bonded to a more electronegative atom. (e.g -CO, -NO_2)

XIII. Periodicity I

Across the period
atomic radii ↓
First I.E ↑except Grp 2&13 or Grp 15&16
EN ↑
[see Chapter II. Atomic Structure]

Na-Al strong metallic bonding, Si strong giant covalent, $P_4 - Cl_2$ id-id I.M.F
Electrical conductivity ↑from Na-Al, nil for $P_4 - Cl_2$, slight conductivity for Si

Element	Na	Mg	Al	Si	P	S
Max ox no	+1	+2	+3	+4	+5	+6

Rxns of Period 3 elements:
Combustion:

- $4Na + O_2 \rightarrow 2Na_2O$ (orange flame)
- $2Mg + O_2 \rightarrow 2MgO$ (white flame)
- $4Al + 3O_2 \rightarrow 2Al_2O_3$ (vigorous then slow, due to inhibitive oxide layer)
- $Si + O_2 \rightarrow SiO_2$ (slow)
- $P_4 + 3O_2 \rightarrow P_4O_6$
  $P_4 + 5O_2 \rightarrow P_4O_{10}$ (yellow flame)
- $S + O_2 \rightarrow SO_2$
  $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ (blue flame)
- $2Na + Cl_2 \rightarrow 2NaCl$ (orange flame)
- $Mg + Cl_2 \rightarrow MgCl_2$ (white flame)
- $2Al + 3Cl_2 \rightarrow 2AlCl_3$
- $Si + 2Cl_2 \rightarrow SiCl_4$
- $P_4 + 6Cl_2 \rightarrow 4PCl_3$
  $P_4 + 10Cl_2 \rightarrow 4PCl_5$
- $2S + Cl_2 \rightarrow S_2Cl_2$

Hydration:

- $2Na + 2H_2O \rightarrow 2NaOH + H_2$ (vigorous)
- $Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$ (slow)
- $2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$ (req hot H_2O)

- $Cl_2 + H_2O \rightleftharpoons HCl + HOCl$

Period 3 oxides:

Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3
solid					liq
Conductor of electricity			poor	nil	
Ionic			Giant covalent	Simple covalent	
Soluble		Insoluble		Soluble	
Basic		Amphoteric	Slightly acidic	Soluble to form acid	

Rxns of period 3 oxides

Hydration rxns:

- $Na_2O + H_2O \longrightarrow 2NaOH$
- $MgO + H_2O \longrightarrow Mg(OH)_2$
- $P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$

  $P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$
- $SO_3 + H_2O \longrightarrow H_2SO_4$

Acid-base rxns:

- $Na_2O + 2HCl \longrightarrow 2NaCl + H_2O$
- $MgO + 2HCl \longrightarrow MgCl_2 + H_2O$
- $Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$

  $Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2NaAl(OH)_4$
- $SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$
- $\mathbf{P_4O_6 + 12\ NaOH \longrightarrow 4\ Na_3PO_3 + 6\ H_2O}$
- $12NaOH + P_4O_{10} \longrightarrow 4Na_3PO_4 + 6H_2O$
- $SO_2 + 2NaOH \longrightarrow Na_2SO_3 + H_2O$

  $\mathbf{2NaOH + SO_3 \rightarrow Na_2SO_4 + H_2O}$

$NaCl$	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_5
solid			liq	solid
Electrical conductor		poor	nil	
Ionic		Simple molecular		
Electrostatic forces		id-id		

Rxns of Period 3 Chlorides

Hydration rxns:

- $NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq)$ .....(pH 7)
- $MgCl_{2(s)} + 6H_2O_{(l)} \longrightarrow [Mg(H_2O)_6]^{2+}_{(aq)} + 2Cl^-_{(aq)}$

  $[Mg(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Mg(H_2O)_5(OH)]^+ + H_3O^+$ (pH 6.5)
- $AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$ (lim amt of H_2O)

  $AlCl_{3(s)} + 6H_2O_{(l)} \longrightarrow [Al(H_2O)_6]^{3+}_{(aq)} + 3Cl^-_{(aq)}$

  $[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H_3O^+$ ...(pH 3)
- $SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$ .....(pH 2)
- $PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$ (lim amt of H_2O)

  $POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$ (adding more H_2O)

  $PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$ (when H_2O in excess).....(pH 2)

XIV. Acid-base eqm

Acid

Strength: extent of dissociation in aq

Conc: amt/ vol

Basicity: $N_{H\ atoms}$ ionisable per molecule

Base

Strength: extent of ionisation in aq

$pH = -lg[H^+]$

$pOH = -lg[OH^-]$

$pH + pOH = 14$

Ionic pdt of water,

$K_w = [H^+][OH^-]\ or\ [H_3O^+][OH^-]$

$K_w = 1.0 \times 10^{-14}\ mol^2 dm^{-6}$

$pK_w = -lgK_w$

$= pH + pOH$

$= 14$

For neut. soln,

$pH = pOH = 7$

the constant values above only apply at $25\ ^\circ C$

$K_w \uparrow as\ T \uparrow$, because $H_2O + H_2O \Leftrightarrow H_3O^+ + OH^-$ is endothermic

Weak acids:

$HA \Leftrightarrow H^+ + A^-$

$$K_a = \frac{[H^+][A^-]}{[HA]}\ or\ \frac{[H_3O^+][A^-]}{[HA]}$$

$pK_a = -lgK_a$

For weak polyprotic acids:

$K_{a_1} > K_{a_2} > K_{a_3}$ because successive dissociations involve acidic species that are increasingly more -ve, thus donation of H^+ more difficult

For weak acid, HA at $C_o mol\ dm^{-3}$,

$HA \Leftrightarrow H^+ + A^-$

Conc	HA	H^+	A^-
Initial	C_o	-	-
Change	-x	+x	+x
Eqm	$(C_o - x)$	x	x

As such $K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{(C_o - x)} = \frac{x^2}{C_o}$

Thus $[H^+] = \sqrt{K_a C_o}$, $pH = -lg\sqrt{K_a C_o}$

Assumptions:

1. $[H^+]$ from self-ionisation of H_2O negligible
2. $x << C_o$

When dilute strong acids are involved, self ionisation of H_2O is non-negligible

(When such happens, assume $[H^+]_{water} = 1.0 \times 10^{-7} mol\ dm^{-3}$ (at $25\ ^\circ C$).
$[H^+]_{total} = [H^+]_{nitric\ acid} + [H^+]_{water}$

Weak bases:
$B + H_2O \Leftrightarrow BH^+ + OH^-$
$K_b = \frac{[BH^+][OH^-]}{[B]}$
$pK_b = -\lg K_b$
For weak base, B at $C_o mol\ dm^{-3}$,
$B + H_2O \Leftrightarrow BH^+ + OH^-$

Conc	B	BH^+	OH^-
Initial	C_o	-	-
Change	-y	+y	+y
Eqm	$(C_o - y)$	y	y

As such
$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{y^2}{(C_o - y)} = \frac{y^2}{C_o}$
Thus $[OH^-] = \sqrt{K_b C_o}$, $pOH = -\lg\sqrt{K_b C_o}$
Assumptions:
1. $x << C_o$

Conjugate acid-base pairs:
$K_a\ of\ acid \times K_b\ of\ conjugate\ base = K_w$
$K_b\ of\ base \times K_a\ of\ conjugate\ acid = K_w$
$pK_w = pK_a + pK_b$

Degree of ionisation, $\alpha = \frac{N_{ionised\ molecules}}{N_{initial\ molecules}}$ (at eqm)

Conc	$[HA] \Leftrightarrow [H^+] + [A^-]$		
Initial	C_o	-	-
Change	$-\alpha C_o$	$+\alpha C_o$	$+\alpha C_o$
Eqm	$C_o(1-\alpha)$	αC_o	αC_o

$K_a = \frac{\alpha^2 C_o}{1-\alpha}$
For weak acid, $\alpha \approx 0$, thus
$\alpha = \sqrt{\frac{K_a}{C_o}}$

Salt hydrolysis

Salt: an ionic cmpd formed from acid-base rxns ($[Base]^{+}[Acid]^{-}$)

Hydrolysis occurs if

- Anion from weak acid is a strong conjugate base (e.g CH_3COO^{-})
- Cation from weak base is a strong conjugate acid (e.g NH_4^{+})

Buffer solns: one which resists ΔpH upon addn of a small amt of acid/ base

Mixture of a weak acid + one of its salt (e.g $CH_3COOH \ \& \ CH_3COO^{-}Na^{+}$)	Mixture of a weak base + one of its salt (e.g $NH_3 \ \& \ NH_4Cl$)
$CH_3COOH \Leftrightarrow CH_3COO^{-} + H^{+}$ $CH_3COO^{-}Na^{+} \rightarrow CH_3COO^{-} + Na^{+}$	$NH_3 + H_2O \Leftrightarrow NH_4^{+} + OH^{-}$ $NH_4Cl \rightarrow NH_4^{+} + Cl^{-}$
CH_3COO^{-} from complete ionisation of $CH_3COO^{-}Na^{+}$ oppresses forward rxn of $CH_3COOH \Leftrightarrow CH_3COO^{-} + H^{+}$	NH_4^{+} from complete ionisation of NH_4Cl oppresses forward rxn of $NH_3 + H_2O \Leftrightarrow NH_4^{+} + OH^{-}$
Addn of small $[H^{+}]$: $CH_3COO^{-} + H^{+} \rightarrow CH_3COOH$ Since $[CH_3COO^{-}]$ large, all $[H^{+}]$ removed, $pH \approx constant$ Addn of small $[OH^{-}]$: $CH_3COOH + OH^{-} \rightarrow CH_3COO^{-} + H_2O$ Since $[CH_3COOH]$ large, all $[OH^{-}]$ removed, $pH \approx constant$	Addn of small $[H^{+}]$: $NH_3 + H^{+} \rightarrow NH_4^{+}$ Since $[NH_3]$ large, all $[H^{+}]$ removed, $pH \approx constant$ Addn of small $[OH^{-}]$: $NH_4^{+} + OH^{-} \rightarrow NH_3 + H_2O$ Since $[NH_4^{+}]$ large, all $[OH^{-}]$ removed, $pH \approx constant$

$pH = pK_a + lg(\frac{[A^{-}]}{[HA]})$ (buffer solns involving weak acids)

$pOH = PK_b + lg(\frac{[BH^{+}]}{[B]})$ (buffer solns involving weak bases)

Buffer capacity: ability to resist ΔpH

- Absolute capacity: depends on absolute concentration of conjugate acid/ base present
- Relative capacity: max buffer capacity when $(\frac{[salt]}{[acid/\ base]}) = 1$

  $pH = pK_a \ or \ pK_b$

Effective buffer range: $0.1 \leq \frac{[salt]}{[acid/\ base]} \leq 10$

XIV. Solubility eqm

NO_3^- are all soluble
Na^+, K^+, Li^+, NH_4^+ are all soluble
CO_3^{2-}, PO_4^{3-} usually insol. except abovementioned
O^-/OH^- usually insol. except abovementioned or with large grp 2
CrO_4^{2-} usually insol. except abovementioned or with small grp 2
Halides, X^- usually sol. except with Ag^+/Cu^+
SO_4^{2-} usually sol. except with Ba^{2+}/Ca^{2+}

$$K_{sp} \text{ of } M_aX_b(s) = [M^{b+}(aq)]^a[X^{a-}(aq)]^b$$

Ksp measures conc of ions in a saturated soln

Solubility: max amt of solute which can dissolve in given amt of solvent at a particular temp

$Ionic\ pdt > K_{sp}$, precipitation
$Ionic\ pdt < K_{sp}$, no precipitation

Common ion effect: when a salt in a soln alr contains an ion common to the salt, increases ionic pdt above K_{sp}, reducing solubility

Complex ion effect: formation of a complex ion that reduces the conc of metal ions, thus reducing ionic pdt below K_{sp}, improving solubility.

XV. Halogen Derivatives

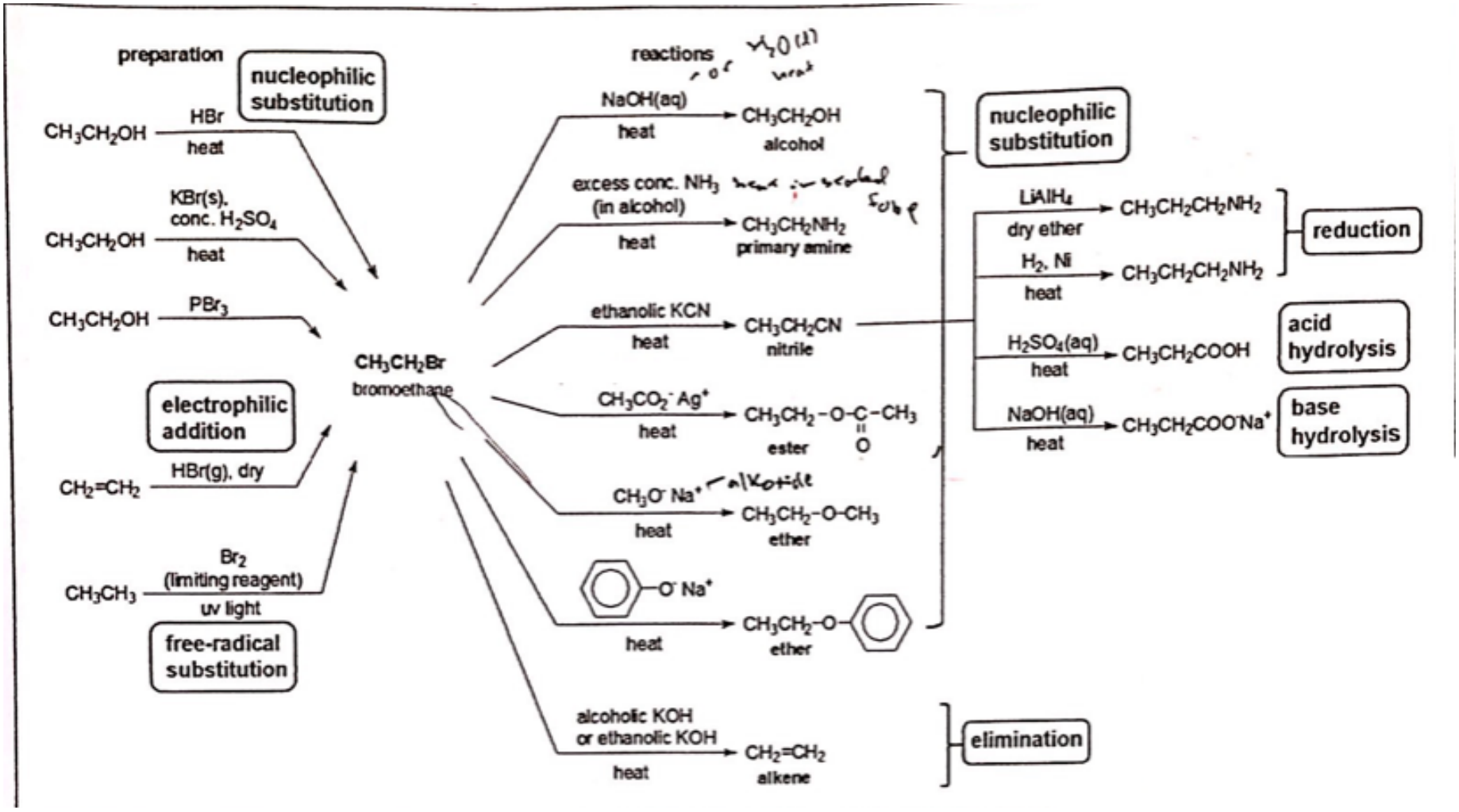
$R - X$

Halogen containing organic cmpds, $X : (Cl, Br, I)$

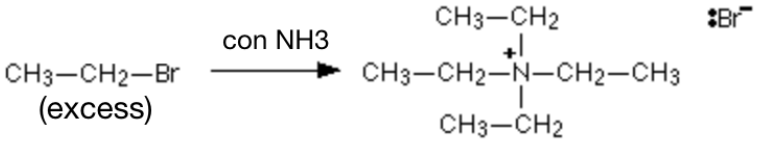
Physical properties of RX:

- Polar
- B.p higher than corresponding alkane
- $\uparrow size\ of\ R_{grp} \rightarrow \uparrow id - id\ I.M.F$
- $\uparrow size\ of\ X \rightarrow \uparrow id - id\ I.M.F$
- Solubility $\downarrow$ as $N_{C\ atoms} \uparrow$

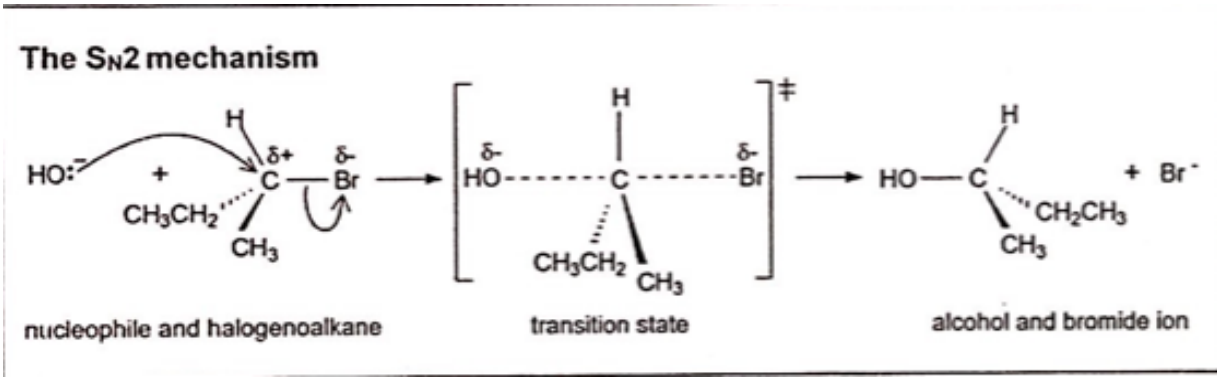
Rxns & preparations of RX:


preparation
nucleophilic substitution
CH3CH2OH
HBr
heat
KBr(s), conc. H2SO4
PBr3
electrophilic addition
CH2=CH2
HBr(g), dry
CH3CH3
Br2 (limiting reagent)
uv light
free-radical substitution
CH3CH2Br
bromoethane
reactions
NaOH(aq)
CH3CH2OH
alcohol
excess conc. NH3 (in alcohol)
CH3CH2NH2
primary amine
ethanolic KCN
CH3CH2CN
nitrile
CH3CO2- Ag+
CH3CH2-O-C-CH3
O
ester
CH3O- Na+
CH3CH2-O-CH3
ether
O- Na+
CH3CH2-O
ether
alcoholic KOH or ethanolic KOH
CH2=CH2
alkene
elimination
nucleophilic substitution
LiAlH4
dry ether
CH3CH2CH2NH2
H2, Ni
reduction
H2SO4(aq)
CH3CH2COOH
acid hydrolysis
NaOH(aq)
CH3CH2COO-Na+
base hydrolysis

(Special case for NH_3 : If NH_3 is not in excess, polyalkylation takes place

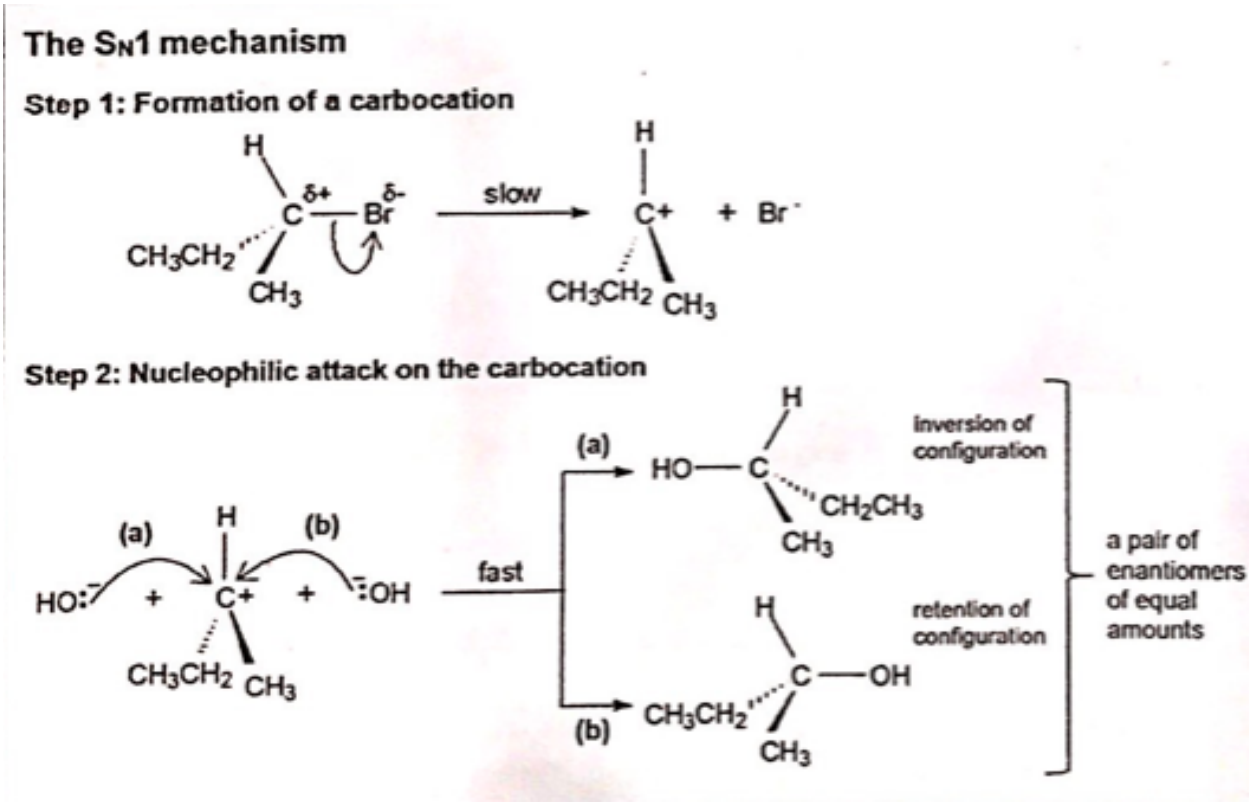


Mechanism for RX:

- 

  (Rate determining step is bimolecular. Rate is dependent on both [Nphile] & [RX])
  Factors affecting rxty : strength of C-X bond (faster if weaker) & degree of steric hindrance.

  Degree of $e^-deficiency$, δ^+ on the C atom doesnt affect rxty as much as B.E(C-X).

- 

  (Rate determining step is unimolecular. Rate is dependent on only [RX])
  Factors affecting rxty : strength of C-X bond (faster if weaker) & carbocation stability

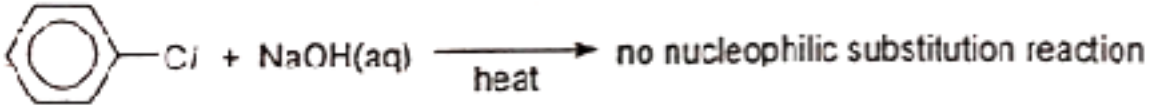
Choice of $S_N1\ vs\ S_N2$ mechanism

1° RX	S_N2 mechanism
2° RX	S_N2 mechanism and S_N1 mechanism
3° RX	S_N1 mechanism

(for more subst C atom, alkyl substituents provide steric hindrance to backside attack of

nucleophile, → S_N1 preferred)
(for more subst C atom, alkyl substituents disperse +ve charge on +ve C atom, thus stabilising the carbocation, → S_N1 preferred)

Halogenoarenes:



- **Reasons: (1) C–Cl bond is strengthened due to partial double bond character.**
  (2) Steric hindrance and electronic repulsion due to the benzene ring.

Electrophilic subst of halogenoarene occurs instead [see Chapter XII. Arenes]

Distinguishing tests:

Test for RX

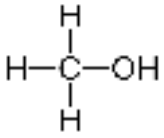
1. Add NaOH(aq) to the sample and heat.
2. Cool the mixture.
3. Acidify with dilute nitric acid.
4. Then add $AgNO_3$(aq).

Observation: AgX(s) precipitate

chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))

Note: color of halide ppts can be found in data booklet

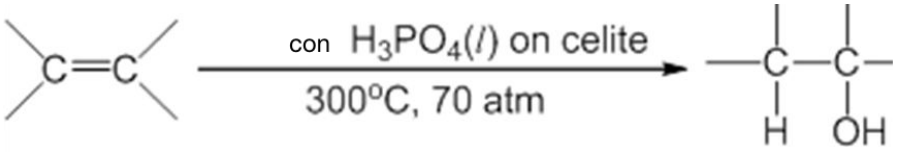
XVI. Hydroxy Cmpds



Alcohols: org cmpds with -OH grp

Preparation of alcohols:

- Hydration of alkene [see Chapter XI. Alkenes]
  Industrial method:



- Reduction of Carboxylic Acid & Carbonyl Cmpds [see Chapter XVII. Carbonyl cmpds and see Chapter XVIII. Carboxylic Acids & Derivatives]
- Nucleophilic subst of RX [see Chapter XV. Halogen Derivatives]

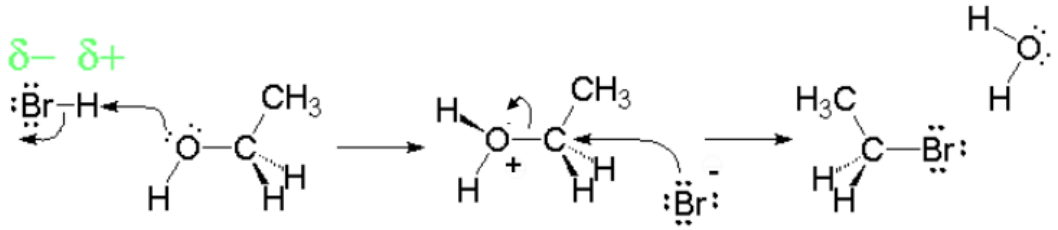
Rxns of alcohols:

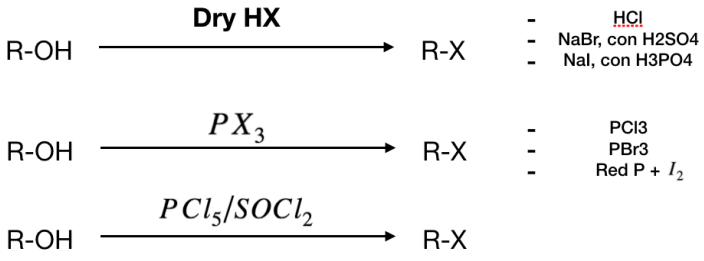
- Combustion

  $C_2H_5OH + 3O_2 \rightarrow 3H_2O + 2CO_2$

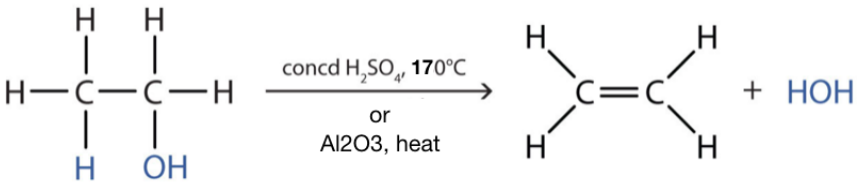
- C-O bond fission (Nucleophilic Subst)

Mechanism:

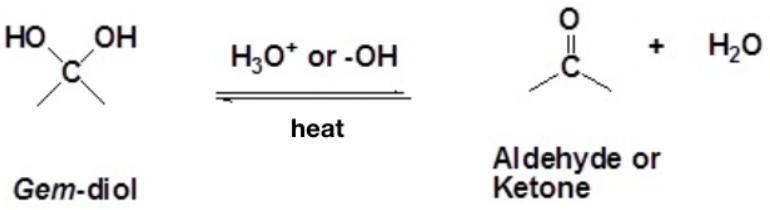




- Elimination (dehydration)

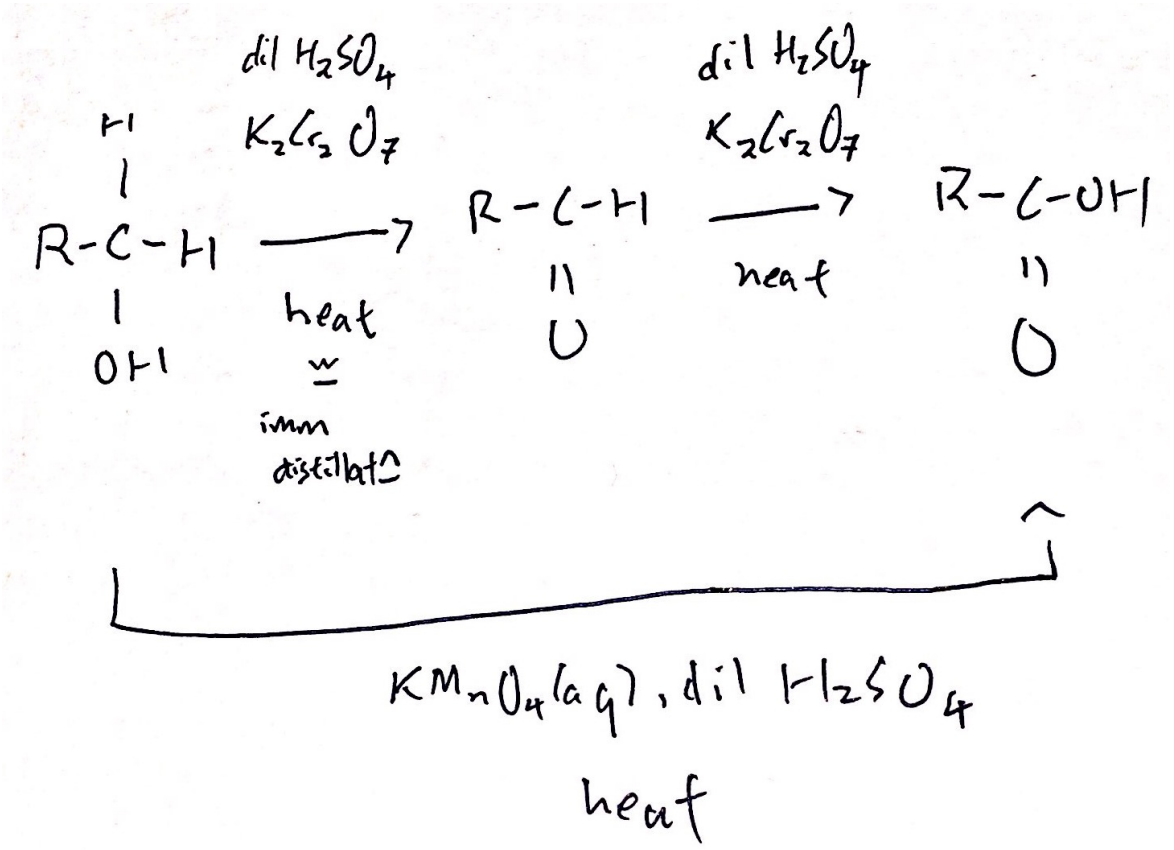


Special case for “gemdiols”: two -OH grps bound to the same C atom
Elimination to form ketones

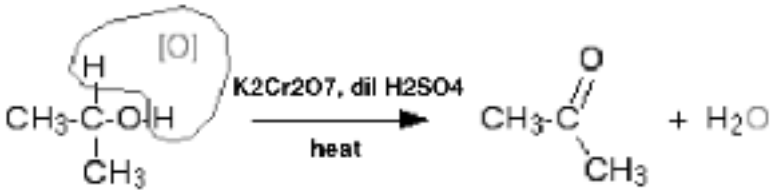


- Oxidation

1. Primary alcohols



2. Secondary alcohols

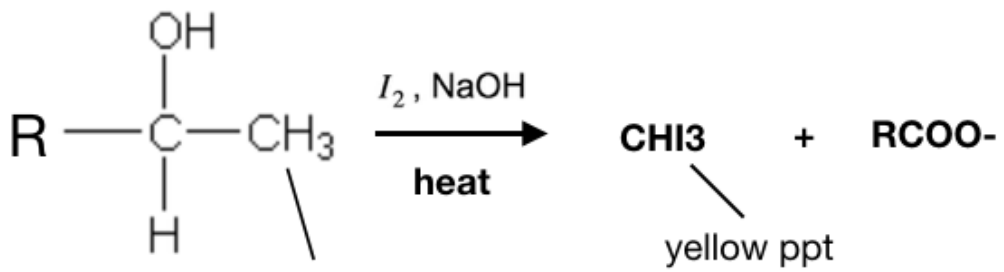


3. Tertiary alcohols can’t be oxidised

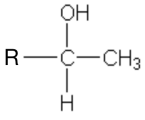
4.

Special case of oxidation: iodoform test

R can be H or alkyl



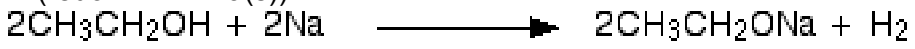
can be CI_3, CHI_2, CH_2I



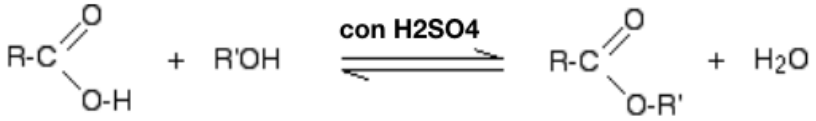
$$+ 4I_2 + 6OH^- \rightarrow CHI_3 + RCOO^- + 5I^- + 5H_2O$$

- O-H bond fission

  1. (redox rxn w Na(s))

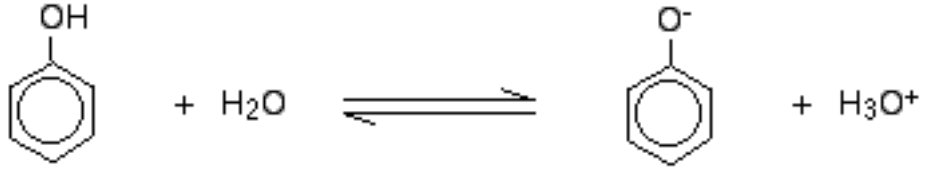


  2. (condensation rxn w RCOOH)



  3. (condensation rxn w RCOX)

Phenol: -OH group directly attached to a benzene ring

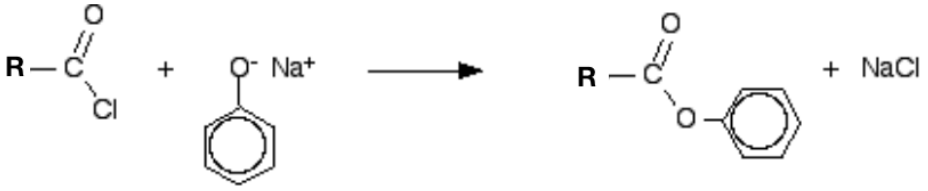


a **phenoxide** ion

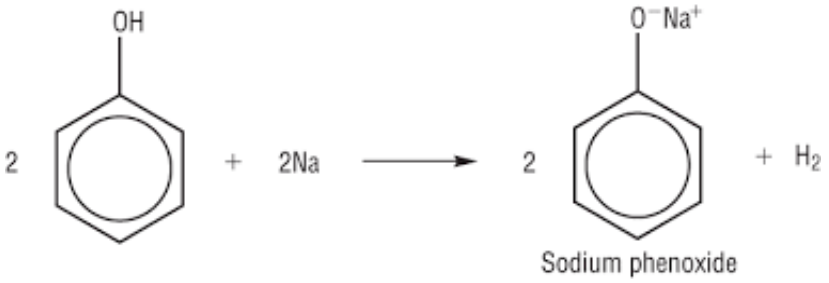
(Phenols are acidic, because the negative charge on the O atom in the conjugate base can delocalise into the benzene ring. This disperses the -ve charge on the O atom and thus stabilises the conjugate anionic base, and thus phenols are acidic)

Rxns of phenols

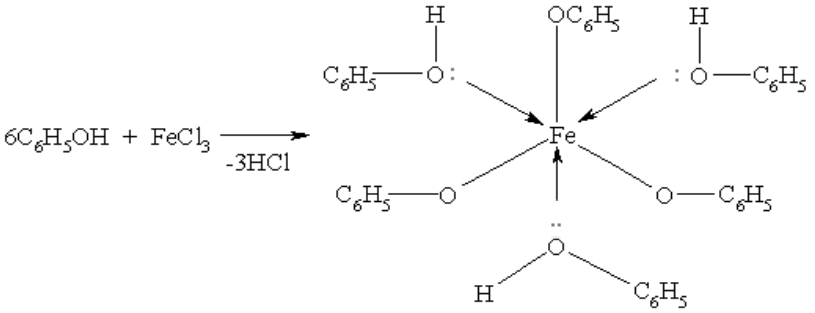
- Condensation rxn w Acyl Halides (acylation)



- Acid base rxn (Amongst Phenol and Alcohols, only RCOOH acidic enough to react with Na_2CO_3)
- Combustion
- Redox rxn with Na(s)



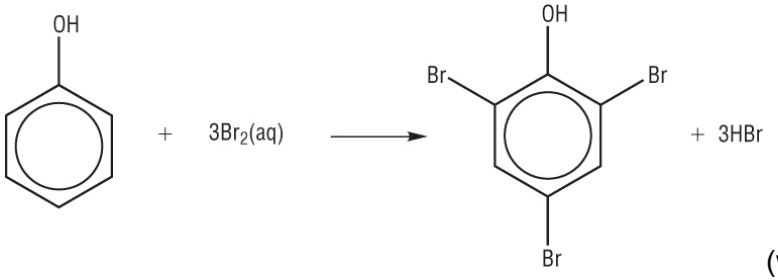
- Complexation with $FeCl_3(aq)$ to give violet coloration



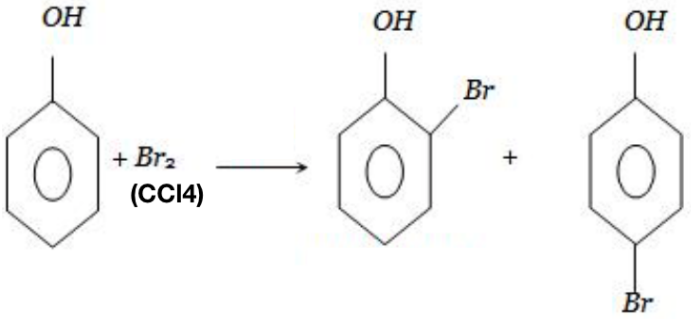
Not necessary to know how to draw the complex, just need to know of the violet coloration

- Electrophilic substitution (Recall -OH is an activating grp. → Esub occurs without harsh cond)

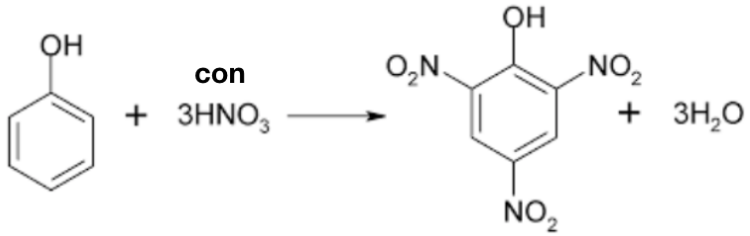
1. (Halogenation of the benzene ring)

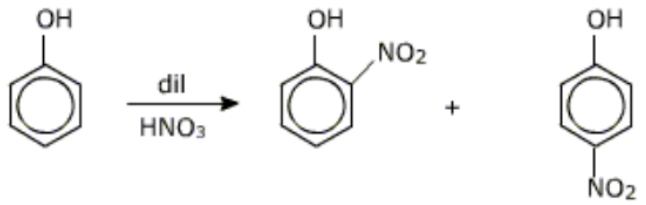


(white ppt observed)

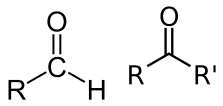


2. (Nitration of the benzene ring)




OH
dil
HNO3
OH
NO2
+
OH
NO2

XVII. Carbonyl Cmpds



(C=O) group

Physical properties:

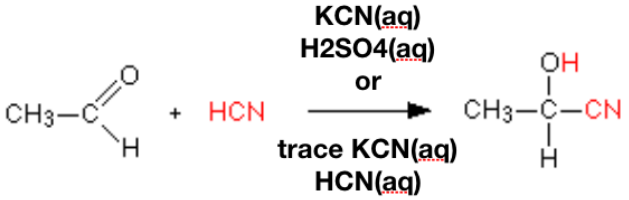
Soluble if < 5 C atoms

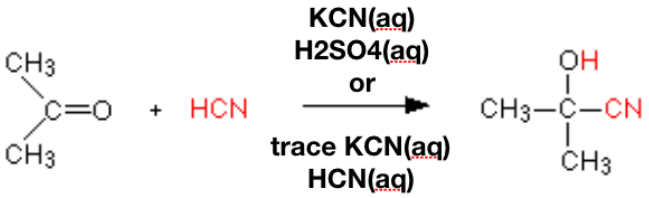
Preparation:

- Oxidation from ROH [see Chapter XVI. Hydroxy cmpds]
- Oxidation from Alkenes [see Chapter XVI. Alkenes]
- Electrophilic sub of benzene [see Chapter XVII: Arenes]

Rxns:

- Nucleophilic Addn



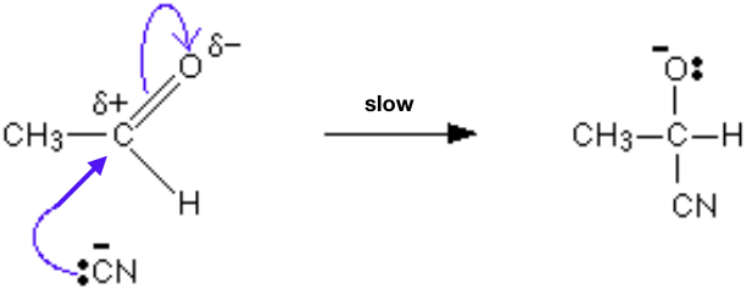


Mechanism:

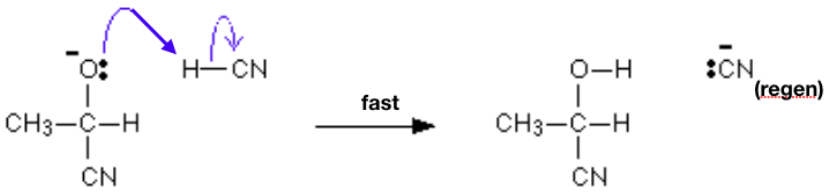
Step1 : Generation of nucleophile

$KCN(aq) \rightarrow K^{+}(aq) + CN^{-}(aq)$

Step 2: Nucleophilic attack



Step 3:

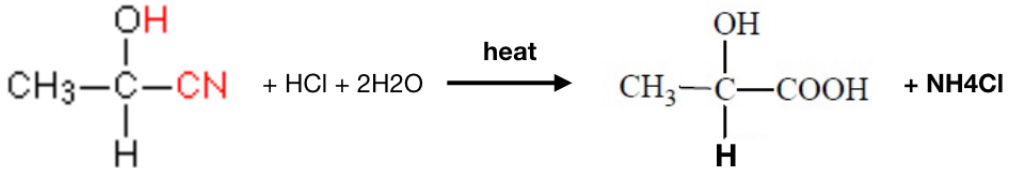


Thus $rate = k[Carbonyl\ cmpd][CN^-]$

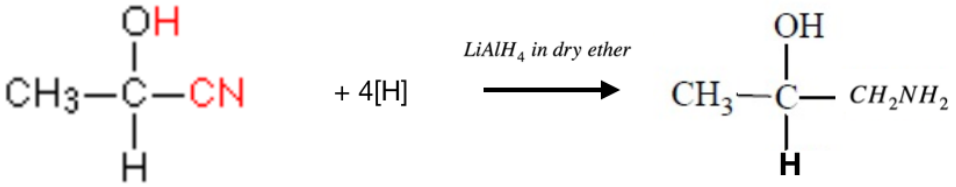
The cyanohydrin is a racemic mixture of enantiomers. (equal chance of attack from both sides of the sp^2 hybridised C atom in step 2)

Further rxn of cyanohydrins:

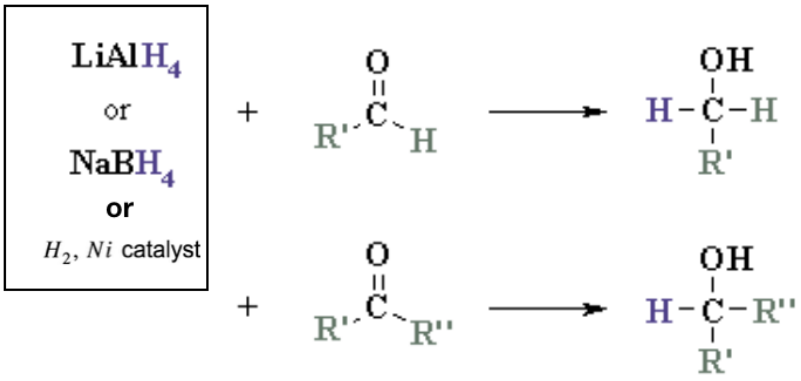
A. hydrolysis



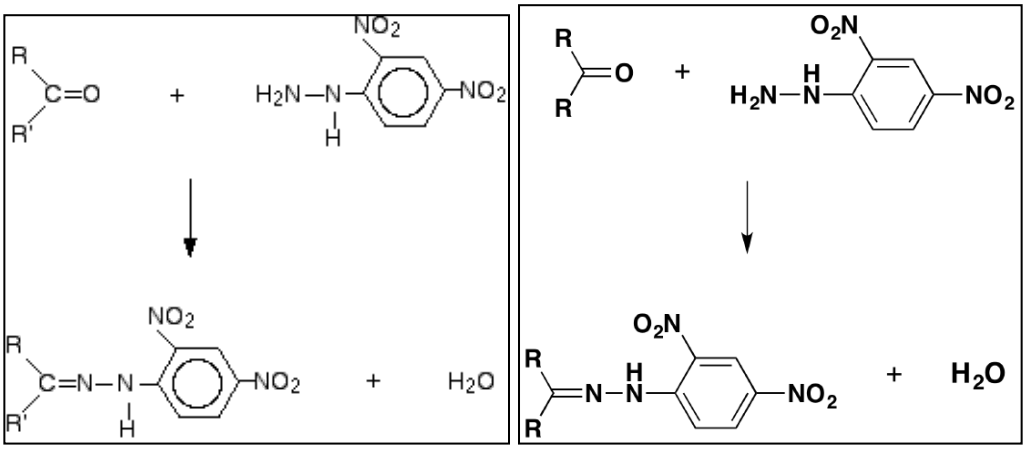
B. reduction



- Reduction



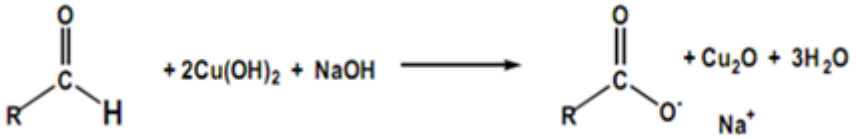
- Condensation (addn elimination rxn with 2,4DNPH)



(orange ppt observed)

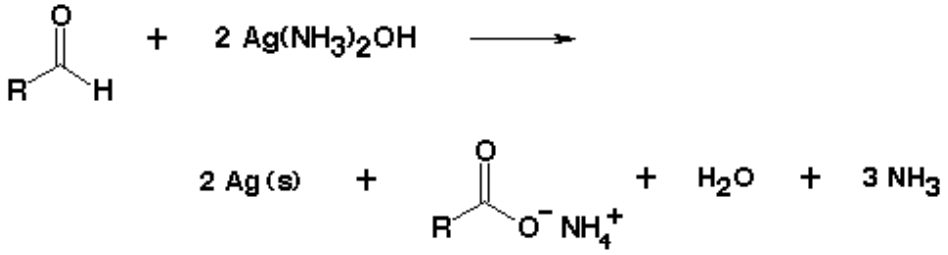
- Oxidation (only for aldehydes)

  1. Fehling's test



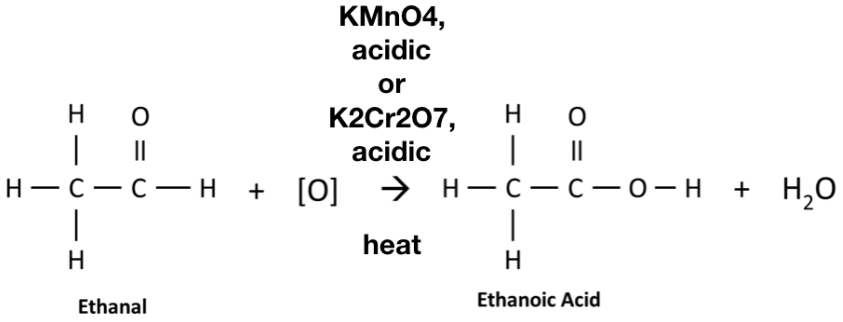
(red brown Cu_2O (s) ppt observed) (works only for aliphatic aldehydes)

2. Tollen's test



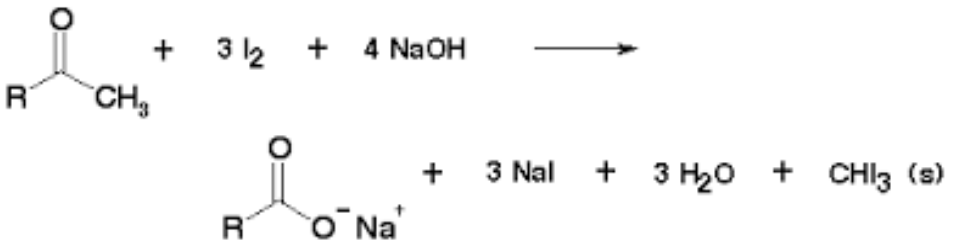
(silver mirror observed)

3. Ox by KMNO4/ K2Cr2O7



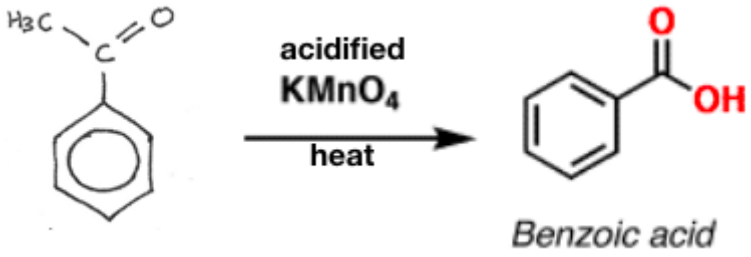
(Decolorization of purple KMnO4 observed) (K2Cr2O7 orange→ green)

Special case of Oxidation of Methyl Ketones: Iodoform test



(yellow ppt CHI3 observed)

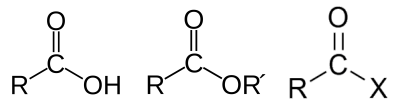
Another special case of Oxidation of Ketones can be seen in aromatic ketones



Benzoic acid

Aromatic carbonyl cmpds:
↓rxty towards rxns, since carbonyl C is less e^- deficient (e^- on benzene ring delocalise onto C=O structure)

XVIII. Carboxylic Acid & Derivatives



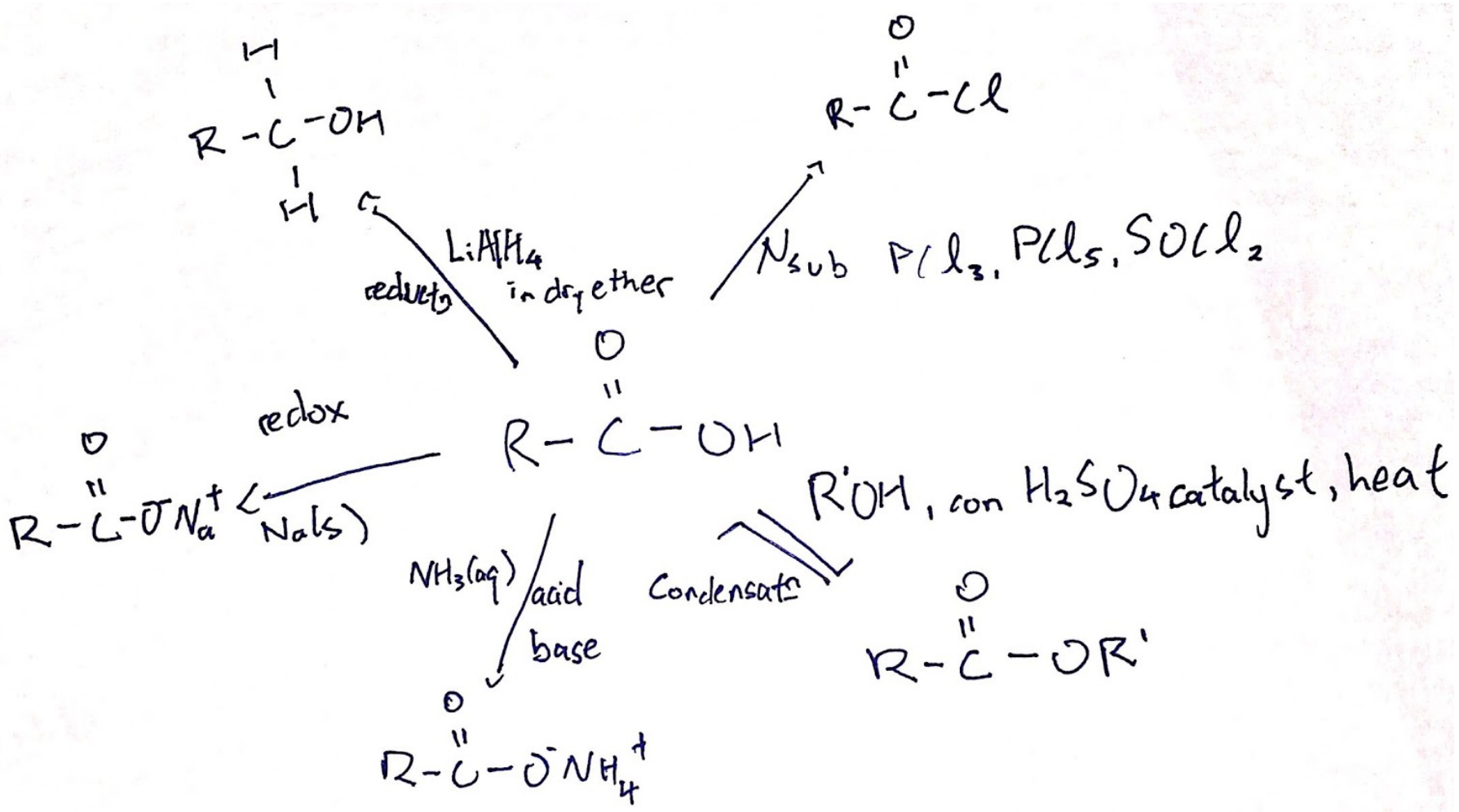
Physical properties of RCOOH:

- Not very volatile, I.M.F stronger due to H-bonding
- Soluble if $N_{C\ atoms} \leq 4$
- Benzoic acid soluble in hot water, forms white crystalline solid when cooled

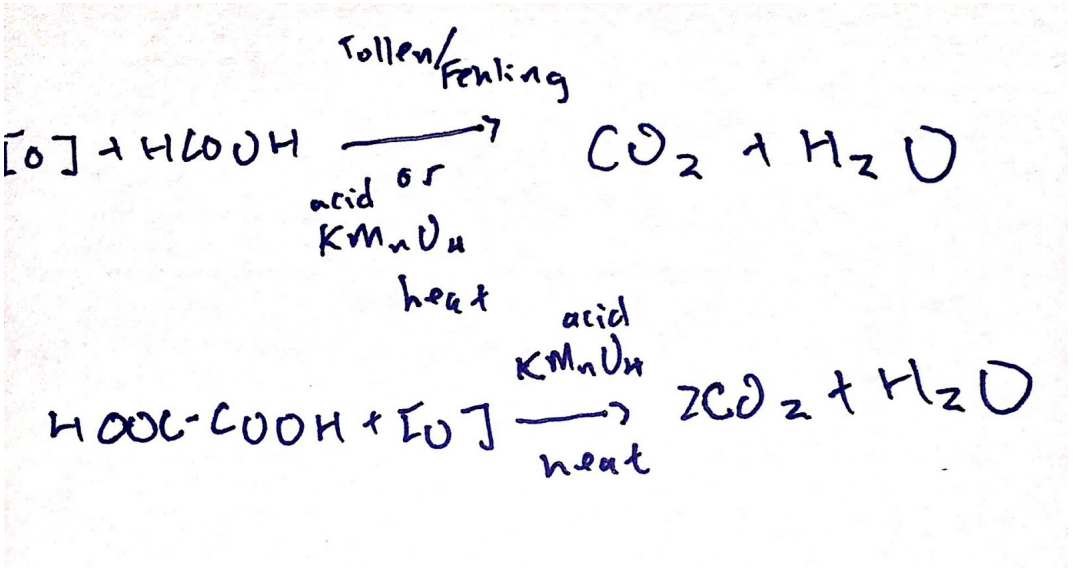
Preparation of RCOOH:

- Oxidation of alkene [see Chapter XI. Alkenes]
  Ox of carbonyl cmpds [see Chapter XVII. Carbonyl cmpds]
- Hydrolysis of RCN [see Chapter XV. RX]
  Hydrolysis of Acyl halides [see Chapter XVIII. Carboxylic Acid & Derivatives]

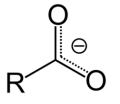
Rxns of RCOOH:


LiAlH4
in dry ether
reduction
Nsub PCl3, PCl5, SOCl2
redox
Na(s)
NH3(aq)
acid
base
Condensation
R'OH, con H2SO4 catalyst, heat

RCOOH is generally immune to oxidation, except



Why is RCOOH acidic?

The conjugate base, $RCOO^-$ has resonant structure 

, and thus the -ve charge is delocalised over two highly electronegative O atoms, thus is stabilised and RCOOH is acidic.

Affected by

→ Nature of subst attached to -COOH grp. (e^- withdrawing/ e^- donating)

→ N_{subst} *attached*

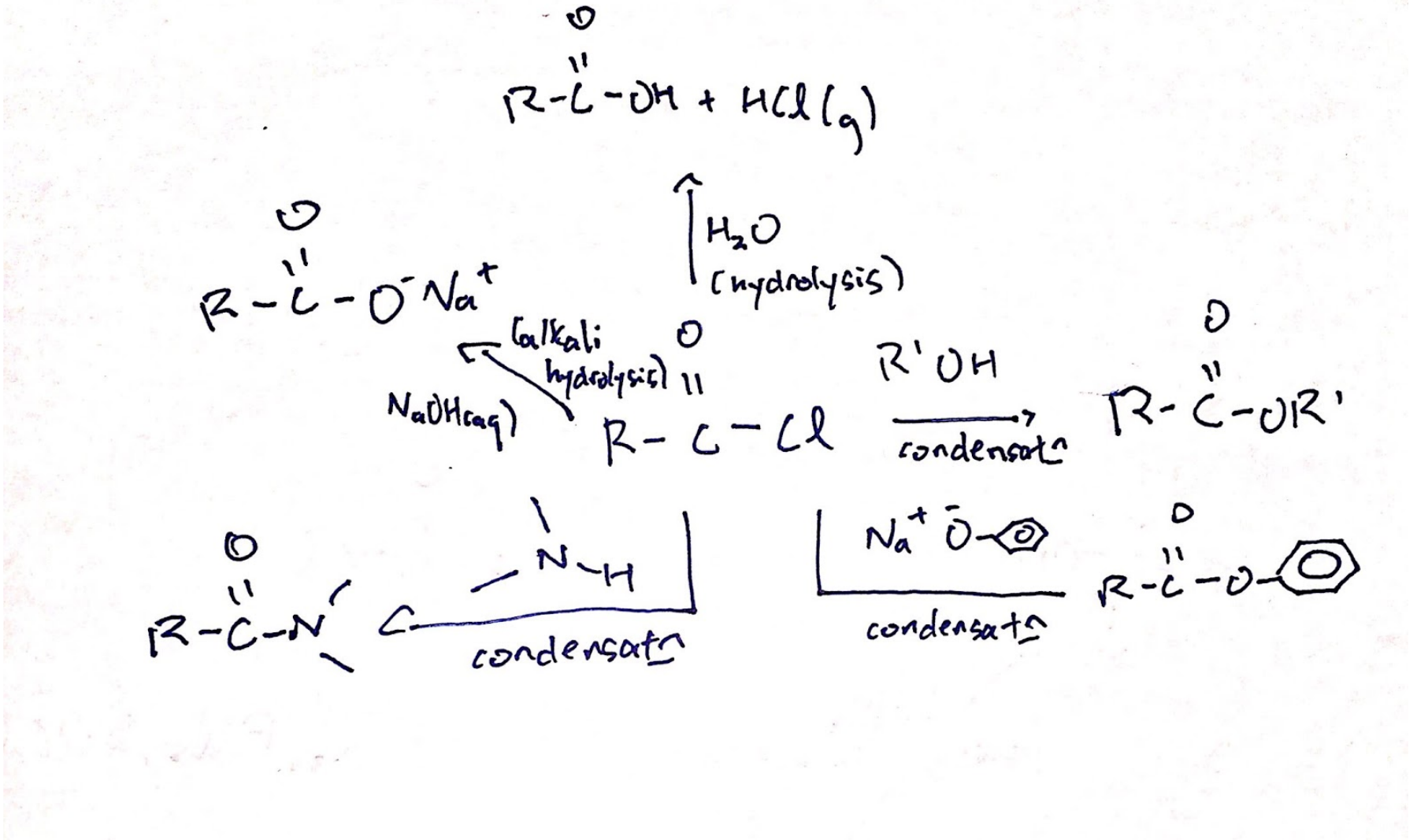
→ Position of subst attached to -COOH (proximity to -COOH func grp)

Carboxylic derivatives

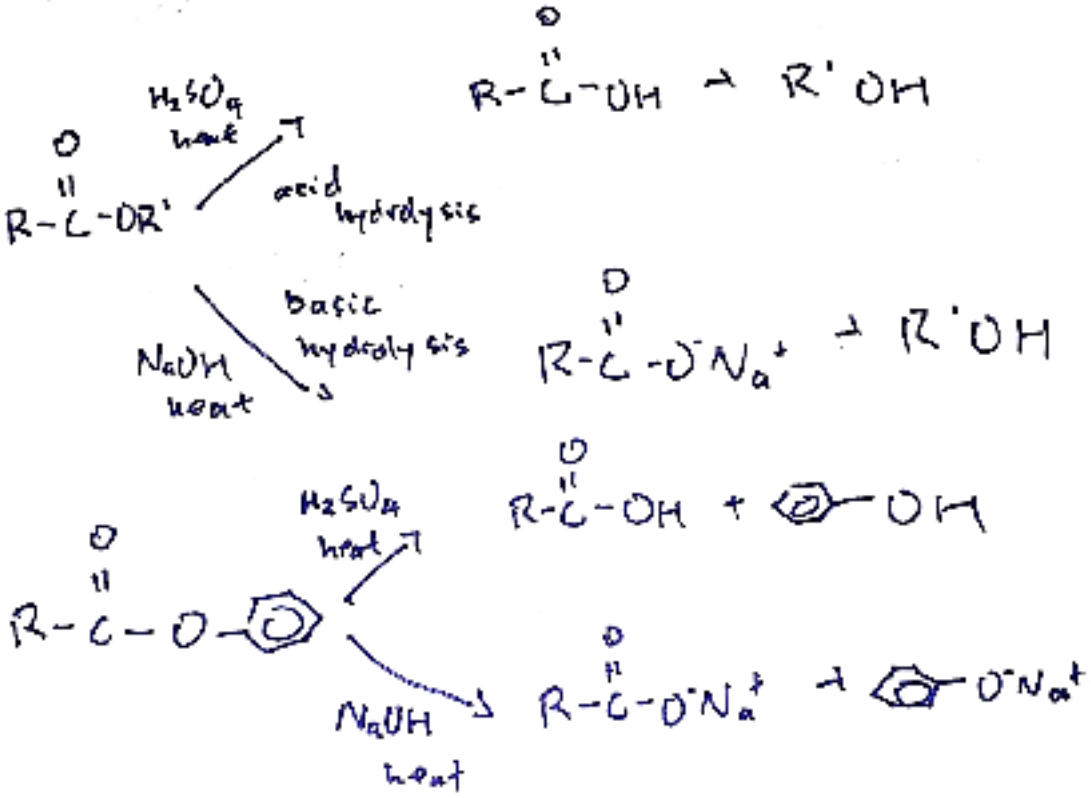
Physical properties

- Esters smell nice
- Acyl Chlorides hydrolyse rapidly in water

Rxns of Acyl Halides

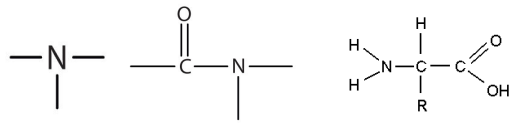

R-C-OH + HCl(g)
H2O
(hydrolysis)
R-C-O⁻Na⁺
(alkali
hydrolysis)
NaOH(aq)
R-C-Cl
R'OH
condensation
R-C-OR'
N-H
condensation
Na⁺ O⁻
condensation
R-C-O-

Rxns of Esters

- 

Note: esters are considered inert in our syllabus, apart from being able to be hydrolysed

XIX. Nitrogen Derivatives



Derivatives of ammonia

N is $sp^3 hybridised$

Physical properties of amine:

- Small amine molecules are soluble in water (presence of H-bonds)
  Aromatic amines dissolve in org cmpds

Why are amines basic?

available l.p on N atom for coordination with a proton

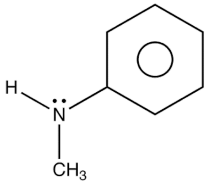
<u>Factors that affect basicity</u>

- The availability of that lp for coordination w a proton
- Ease in which protonated amine can undergo solvation with water and so become stabilised

Rank in terms of basicity:

$$3^\circ \text{ amine} > 2^\circ \text{ amine} > 1^\circ \text{ amine} > NH_3$$

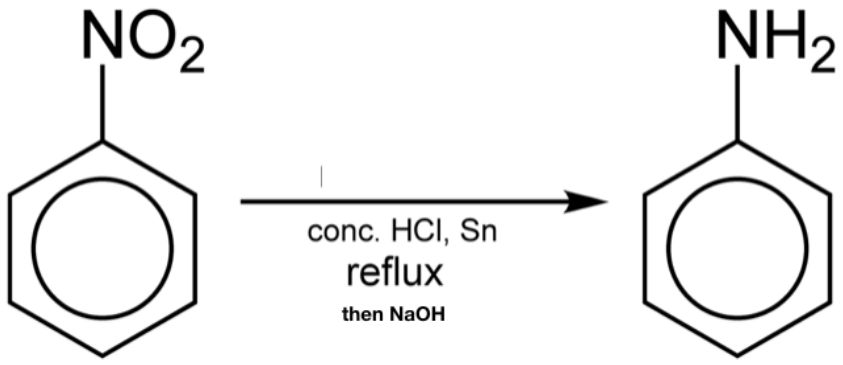
Presence of e^- donating alkyl grps increase availability of lp for donation



For aromatic amines, the lp delocalises into the benzene ring, and is unavailable for donation

Preparation of amines:

- Reduction of amides [see Chapter XIX. Nitrogen Derivatives]
- Hydrolysis of amides [see Chapter XIX. Nitrogen Derivatives]
- Reduction of nitrobenzene

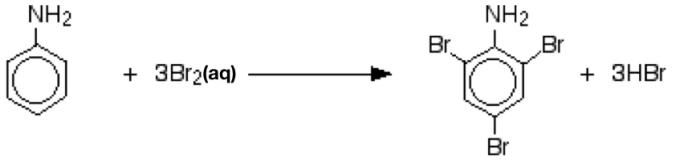


Rxns of amines:

- Acid-base rxn

Amine:	*Amine salts:*
Larger amines insol.	Very Soluble
Organic soluble	Organic Insoluble
Volatile	Non Volatile

- Nucleophilic subst with RX [see Chapter XV. RX]
- Condensation rxn with acyl halides [see Chapter XVIII. Carboxylic Derivatives]
- Electrophilic subst of phenyl amine

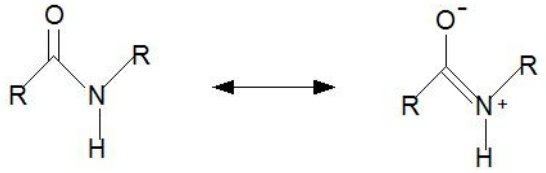


(white ppt observed)

Amides

Physical properties of amides:

- Less volatile due to presences of H-bonds
- Soluble due to H-bonds

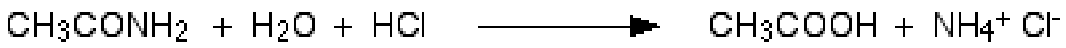


Amides lack basicity, because the lp on N atom delocalises over the entire amide structure → lp no longer located on a single atom as an intensely -ve region of space→ unavailable for coordination w a proton

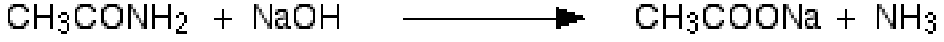
Rxns of amides:

- Hydrolysis

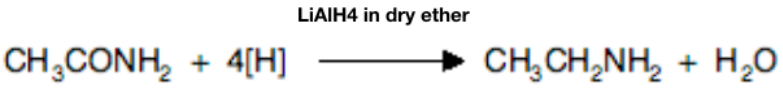
  1. Acidic medium, heat



  2. Basic medium, heat

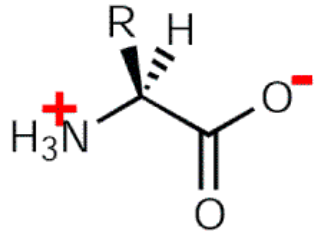


- Reduction



Amino Acids

In solid state, zwitterionic structure exists



Very strong ionic bonds among zwitterions

Soluble in water, insoluble in non-polar solvents

Amphoteric (acidic part is NH_4^+, basic part is COO^-)

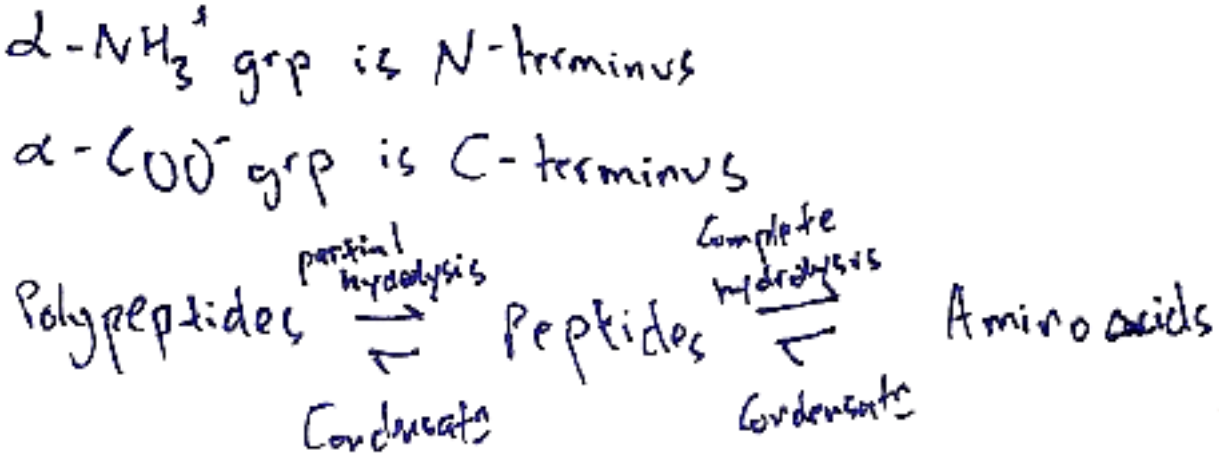
Isoelectric pt: pH at which [zwitterion] is maximum, amino acid does not migrate under the effect of an electric field

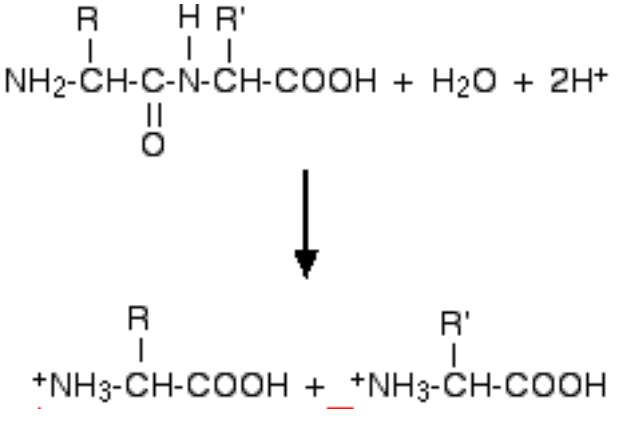
Rxns of amino acids:

- Participates in reactions identical to amines and carboxylic acids [see Chapter XVII. Carboxylic Acids]

Rxns of proteins:

- Undergo acidic/ basic hydrolysis





(acidic hydrolysis)

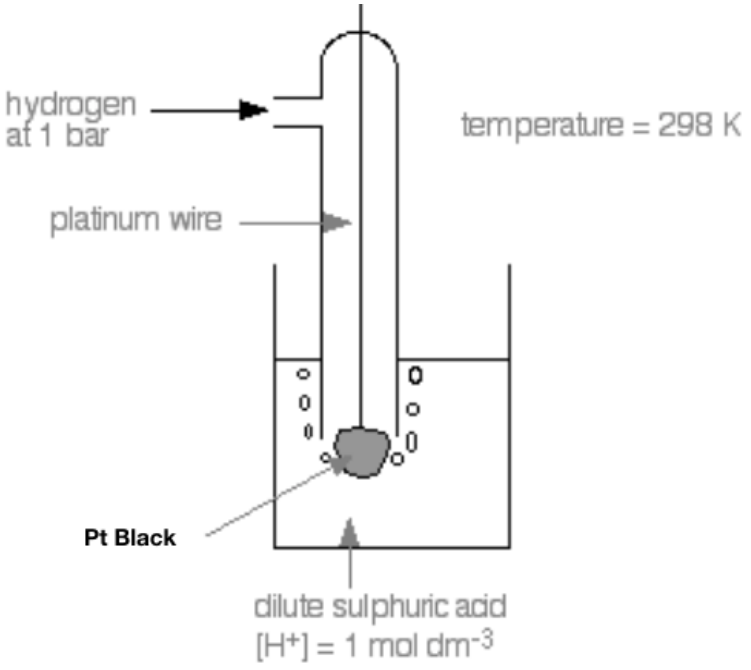
XX. Electrochem

AN OX Anode- attracts anions, oxidation
RED CAT Cathode- attracts cations, reduction

Electrolyte: conductor of electricity via flow of charge carried by its ions
Electrode potential : p.d across a cell consisting of electrode and the standard hydrogen electrode. Dependent on temperature, [ions], partial pressure

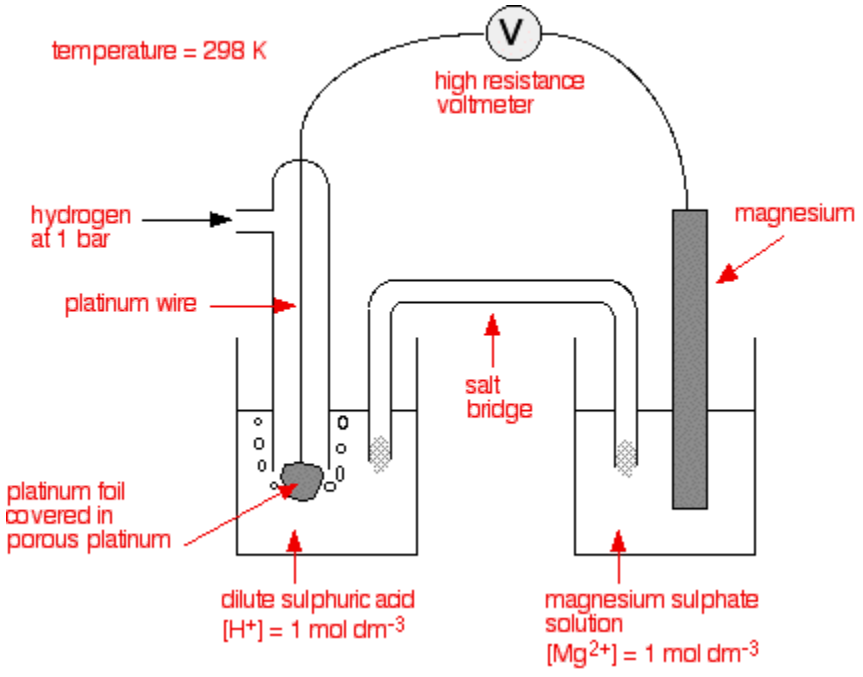
As such, standard conditions, as said in Chapter V. Energetics, are used for electrochem.

Standard Hydrogen Electrode: reference electrode



	E^{Θ}/V
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00

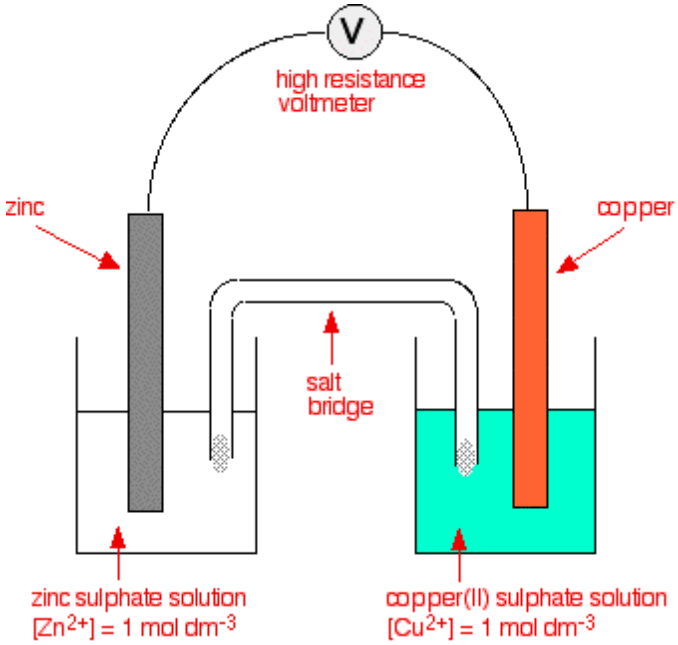
(arbitrarily assigned 0V)



	E^{Θ}/V
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	–2.38

Magnitude of E^{Θ}: measure of tendency of forward rxn

Voltaic cells = electrochemical cells



$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$ $E^{\circ} = +0.34$ V (cathode, redn)

$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$ $E^{\circ} = -0.76$ V (anode, ox)

1. Zn(s) loses $2e^-$, entes soln as $Zn^{2+}(aq)$
2. $Cu^{2+}(aq)$ gains $2e^-$, reduced to Cu(s)
3. $2e^-$ travels via wire from Zn to Cu

Salt bridge:

- Contains an electrolytic soln whose ions dont rxt with other ions in the cell/ w the electrodes
- The ions in the salt bridge migrate to neutralise charge buildups due to redox rxns at both electrodes
- Used to complete the circuit and maintain charge neutrality

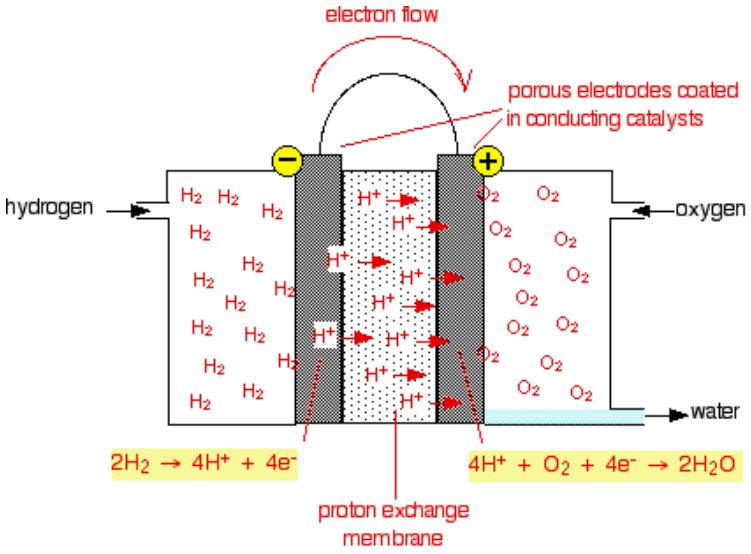
Standard cell potential, $E^{\Theta}_{cell} = E^{\Theta}_{cathode} - E^{\Theta}_{anode}$

E^{Θ}_{cell} +ve: spontaneous, thermodynamically feasible

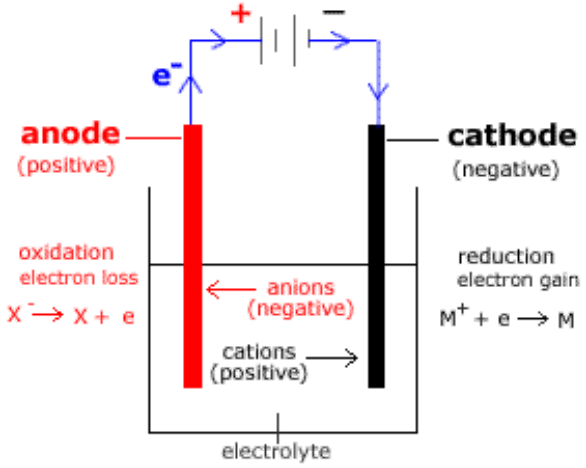
E^{Θ}_{cell} -ve: not spontaneous

$\Delta G^{\Theta} = -nFE^{\Theta}$, n= $N_{moles\ of\ e^{-}\ transferred}$, F= 96500 $C\ mol^{-1}$ (value of F can be found in Data Booklet)

Hydrogen fuel cell:



Electrolysis: supplying e^{-} to make a non spontaneous rxn occur



Selective discharge: if more than one species can be discharged, we need to compare the electrode potential of the competing species.

Using LCP, weigh external factors that are not as in standard conditions, and determine if $E_{cathode/anode}$ value should be higher or lower than given E^{Θ}

(if reduction favored more, $E_{cathode/anode}$ becomes less -ve/ more +ve)

(if oxidation favored more, $E_{cathode/anode}$ becomes less/ more -ve)

Faraday's first law: the mass of substance and or volume of gas liberated during electrolysis is dependent on charge passed through the cell.

$Q = It,\ I = current,\ t = time$

$Q = n_e F,\ n_e = amt\ of\ e^- in\ mol$

Faraday's second law: amt of charge req to discharge 1 mol of an element depends on the charge on the ion.

XXI. Periodicity II

Group 2 trend down the group:

Atomic radius	↑
EN	↓
m.p	-
First I.E	↓
Metallic Character	↑
E^{Θ}	More -ve

Thermal decomposition:

$MCO_3(s) \rightarrow MO(s) + CO_2(g)$

Why does thermal stability ↑down the grp?

- ↓charge density→ ability to distort e^- cloud and polarise $C-O$ bond ↓
- Therefore more heat req to break covalent C-O bond, causing ↑decomp temp

Group 17 trend down the group:

Bond-length	↑
EN	↓
M.p, b.p	↑
First I.E	↓
E^{Θ}	Less +ve

Thermal stability of HX:

↓stability down the group

Bond	Energy/kJ mol^{-1}
H—F	562
H—Cl	431
H—Br	366
H—I	299

Find B.E from data booklet

Thermal stability is dependent on H-X bond strength. B.E(HX) down the group becomes less endothermic.

As the size of halogens ↑→ valence orbital more diffuse→ $\downarrow Eff_{overlap}$

Furthermore $\Delta EN \downarrow \rightarrow$ polarity ↓

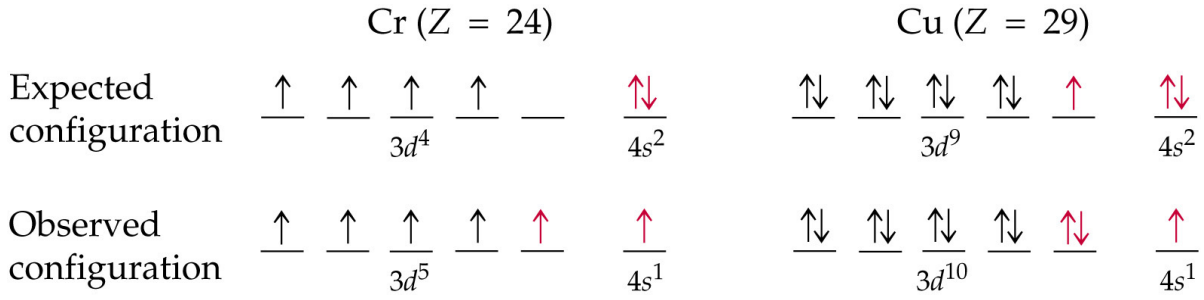
XXII. Transition Metals

Transition element: d-block element which can form ≥1 stable ion w ≥1 partially filled d orbital

4	5	6	7	8	9	10	11
22	23	24	25	26	27	28	29
Ti	V	Cr	Mn	Fe	Co	Ni	Cu
titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper
47.9	50.9	52.0	54.9	55.8	58.9	58.7	63.5

Physical properties

- Hard, high densities
- High m.p & b.p
  (Valence 3d & 4s e^- are close in energy, both available for delocalisation into the sea of e^- → strong metallic bonding)
  (Dips at Mn & Zn because stable $3d^5$ & $3d^{10}$ configuration respectively less available for delocalisation
- Good conductors (sea of mobile e^-)
- Atomic radii relatively constant. (While nuclear charge ↑, 3d-4s repulsion ↑also)
- I.E relatively constant. (While nuclear charge ↑, 3d-4s repulsion ↑also)



Chemical properties

d-block	s-block
Variable ox states	Fixed ox states
colored	white
Catalytic action	No catalytic action
Stable complexes	Less able to form complexes

Why variable ox states? :
Valence 3d & 4s e^- are close in energy, both available for bond formation → can form different no. of ionic/covalent bonds, ox state varies.

$Highest\ possible\ ox\ state = N_{unpaired\ d\ e^-} + 4s\ e^-$

Catalysis:

- Heterogenic
  - availability of 3d e^- for bond formation w the rxt molecules or the availability of low lying vacant orbitals which can accept e^- pairs from rxt molecules
  -availability of partially filled 3d sub-shell which allows for ready transfer of e^- to and from rxt molecules, facilitating formatn of weak bonds w rxt molecules
- Homogenic
  -ability to exist in variable ox states
  -ease in which it can be converted from one ox state to the other
  -facilitates formatn & decomp of intermediate cmpds btwn transition metal ions and rxts

Complex: a central metal ion/ atom linked to 1 or more surrounding ions/ molecules by dative covalent bonds.

N_{bonds} exceeds ox state of the metal ion

Ligand: ion/ molecule w lp to donate unto low-lying orbital of central metal ion/ atom
Dative covalent bond: bond formatn btwn filled orbitals overlapping w vacant orbitals
Coordination no. = $N_{coordinate\ bonds}$ formed with ligands

Monodentate ligand: Can form 1 coordinate bond
Bidentate ligand: Can form 2 coordinate bonds
Hexadentate ligand: Can form 6 coordinate bonds (e.g $[Cu(edta)]^{2-}$)

Why transition metals form complexes?

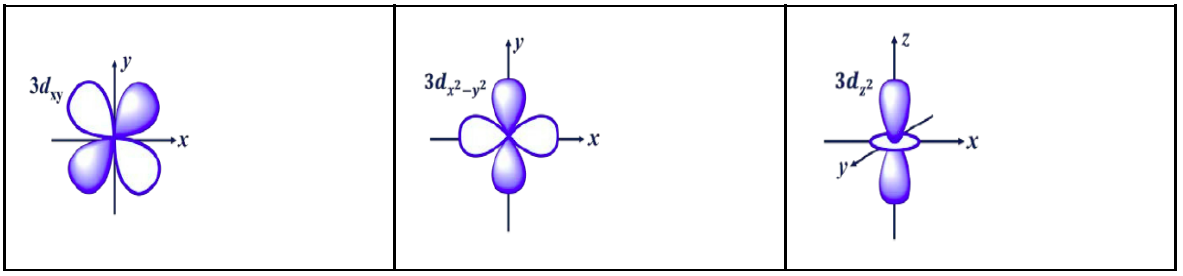
- Low lying vacant orbitals to accomodate l.p from ligands to form coordinate bonds
- Relatively small & highly charged → high charge density → able to attract lp from ligands

Coord no.	Shape	e.g
2	linear	$[Ag(NH_3)_2]^+$
		$[Ag(CN)_2]^-$
		$[CuCl_2]^-$
4	tetrahedral	$[Ni(CO)_4$
		$[Zn(NH_3)_4]^{2+}$
		$[CoCl_4]^{2-}$
		$[Cu(CN)_4]^{3-}$
4	Square planar	$[Ni(CN)_4]^{2-}$
		$[Cu(NH_3)_4]^{2+}$

		$[CuCl_4]^{2-}$
6	octahedral	$[Fe(CN)_6]^{3-}$
		$[Fe(CN)_6]^{4-}$
		$[Ni(NH_3)_6]^{2+}$

Why are transition metals colored?

Originally, all 5 d-orbitals are degenerate (same energy level)
In complexes, they split and have 2 different energy levels

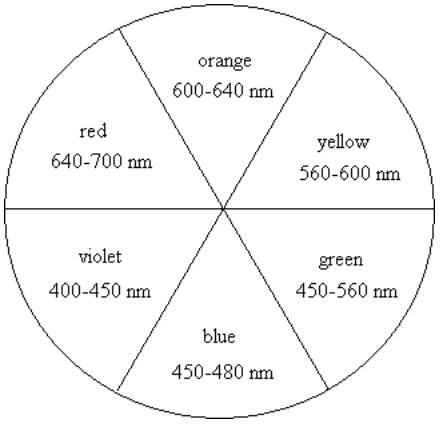


d_{xz} , d_{xy} , d_{yz} $d_{x^2-y^2}$ d_{z^2}

Tetrahedral complexes:
Ligands approach btwn the x,y,z axes, and thus repel the $3d_{z^2}$ & $3d_{x^2-y^2}$ orbitals that have electron density situated along the axes, to lower energy levels, compared to the $3d_{xz}$, $3d_{xy}$, $3d_{yz}$ orbitals situated between the axes

Octahedral complexes:
Ligands approach along the x,y,z axes, and thus repel the $3d_{z^2}$ & $3d_{x^2-y^2}$ orbitals that have electron density situated along the axes, to higher energy levels, compared to the $3d_{xz}$, $3d_{xy}$, $3d_{yz}$ orbitals situated between the axes

Electrons from the lower energy levels can absorb light energy and be promoted (d-d transition) to the higher energy level vacant 3d orbitals



The energy of the light absorbs corresponds to a certain wavelength and thus color. The color observed is the complement of the color absorbed (opp each other on the color wheel)

Factors affecting color of transition metal complexes:

- Identity of the metal & its ox state
- Nature of the Ligands attached

Rxns of transition metals:

- Precipitation rxns [see Chapter XIV. Solubility eqm]
- Redox rxns (refer to the Data booklet for half eqns)
- Ligand exchange: ligands forming the complex of higher K_{stab} replacing those forming the complex of lower K_{stab}

  K_{stab} : stability constant, measure of how stable Complex A is vs Complex B.

$$[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$$

$$K_{stab} = \frac{[\,[CoCl_4]^{2-}\,] \times [H_2O]^6}{[\,[Co(H_2O)_6]^{2+}\,] \times [Cl^-]^4}$$

(e.g)

Ligand strength:
$H_2O < NH_3 < S_2O_3{}^{2-} < CN^- < edta^{4-}$

Qualitative Analysis

9(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(Tests for gases can be found in the Data Booklet)

Thermal decomposition:

1. Ammonium salts
   $NH_4Cl \Leftrightarrow NH_3 + HCl$
   Pungent NH_3 (g) evolved, white solid on upper end of base
2. Nitrates
   a. $2KNO_3 \rightarrow 2KNO_2 + O_2$
   O_2 (g) evolved relights glowing splint
   b. $2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2$
   Blue solid turned black. O_2 (g) evolved. Pungent NO_2 (g) turned $FeSO_4(aq)$ brown
   c. $Zn(NO_3)_2 \rightarrow ZnO + 2NO_2 + \frac{1}{2}O_2$
   ZnO (s) yellow residue remained, turned white upon cooling. Pungent $2NO_2$ evolved.
   O_2 evolved.
3. Carbonates
   a. $CuCO_3 \rightarrow CuO + CO_2$
   Green solid turned black. CO_2 (g) evolved
   b. $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$
   CO_2 (g) evolved.

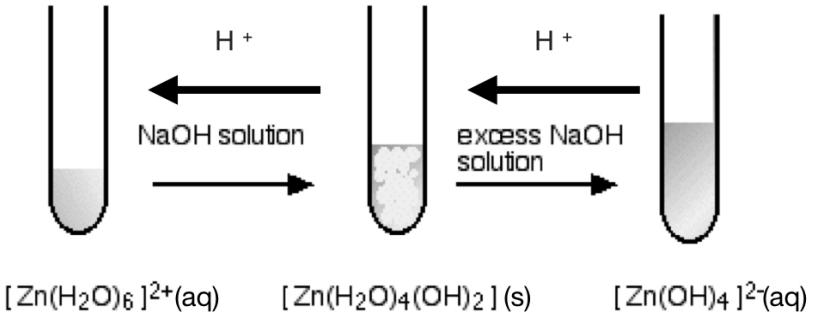
Triply charged cations:

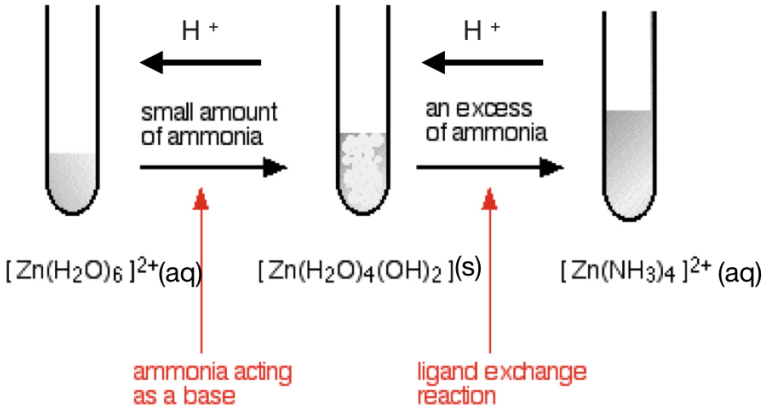
E.g $[Fe(H_2O)_6]^{3+} + 3H_2O \Leftrightarrow [Fe(OH)_3(H_2O)_3](s) + 3H_3O^+(aq)$

Acidic enough to rxt with Na_2CO_3, a weak base

Amphoteric Hydroxides: Al, Zn, Cr

Junction Test:





Summary of Reactions of Cations

Cation \ Reagent	NaOH (aq)	NH_3 (aq)	Na_2CO_3 (aq)	HCl (aq)	H_2SO_4 (aq)	KI (aq)	K_2CrO_4 (aq)	Other Reagents/ Remarks
NH_4^+ (aq) colourless	NH_3 evolved on warming the solution	–	NH_3(g) evolved on warming the solution (CO_3^{2-} is a weak base)	no ppt.	no ppt.	- KI did not turn brown - no ppt.	no ppt. no colour change	—
Mg^{2+} (aq) colourless	white ppt. insoluble in excess NaOH(aq) $Mg(OH)_2$ (s)	white ppt. - insoluble in excess NH_3(aq) - dissolved on adding NH_4Cl(s)	white ppt. $MgCO_3$(s)	no ppt.	no ppt.	- KI did not turn brown - no ppt.	no ppt.	—
Ca^{2+} (aq) colourless	white ppt. (if solutions are concentrated) $Ca(OH)_2$ (s)	No ppt.	white ppt. $CaCO_3$(s)	no ppt.	no ppt.	- KI did not turn brown - no ppt.	no ppt.	—
Ba^{2+} (aq) colourless	white ppt. (if solutions are concentrated) $Ba(OH)_2$ (s)	No ppt.	white ppt. $BaCO_3$(s)	no ppt.	white ppt. $BaSO_4$(s)	- KI did not turn brown - no ppt.	yellow ppt. insoluble in NaOH(aq) $BaCrO_4$(s)	—
Pb^{2+} (aq) colourless	white ppt. soluble in excess NaOH(aq) $Pb(OH)_2(s) \rightarrow [Pb(OH)_4]^{2-}$(aq)	white ppt. insoluble in excess NH_3(aq) $Pb(OH)_2$(s)	White ppt. $PbCO_3$(s)	White ppt. soluble in hot H_2O $PbCl_2$(s)	White ppt. insoluble in hot H_2O $PbSO_4$(s)	yellow ppt. soluble in hot water PbI_2(s)	yellow ppt. soluble in NaOH(aq) $PbCrO_4$(s) $\rightarrow [Pb(OH)_4]^{2-}$(aq)	conc. HCl: white ppt. soluble in excess conc. HCl $PbCl_2(s) \rightarrow [PbCl_4]^{2-}$(aq)
Al^{3+} (aq) colourless acidic	white ppt. soluble in excess NaOH(aq) $Al(OH)_3(s) \rightarrow [Al(OH)_4]^-$(aq)	white ppt. insoluble in excess NH_3(aq) $Al(OH)_3$(s)	Effervescence of CO_2(g) and white ppt. $Al(OH)_3$(s)	no ppt	no ppt	- KI did not turn brown - no ppt.	no ppt.	—
Zn^{2+} (aq) colourless	white ppt. soluble in excess NaOH(aq) $Zn(OH)_2(s) \rightarrow [Zn(OH)_4]^{2-}$(aq)	white ppt. soluble in excess NH_3(aq) $Zn(OH)_2(s) \rightarrow [Zn(NH_3)_4]^{2+}$(aq)	White ppt. $ZnCO_3$(s)	no ppt.	no ppt.	- KI did not turn brown - no ppt.	no ppt.	—
Mn^{2+} (aq) pale pink	off-white ppt. - insoluble in excess NaOH(aq) - turned brown on standing $Mn(OH)_2(s) \rightarrow Mn(OH)_3(s)$ - dark brown ppt. with H_2O_2 $Mn(OH)_2(s) \rightarrow MnO_2(s)$	off-white ppt. - insoluble in excess NH_3(aq) - dissolved on adding NH_4Cl (s) - turned brown on standing $Mn(OH)_2(s) \rightarrow Mn(OH)_3(s)$ - dark brown ppt. with H_2O_2 $Mn(OH)_2(s) \rightarrow MnO_2(s)$	off-white ppt, turning brown on heating. $MnCO_3$(s) formed and oxidized to higher O.S. on heating.	no ppt.	no ppt.	- KI did not turn brown - no ppt.	no ppt.	$NaBiO_3$ + dilute HNO_3 pink/purple colouration $K_2S_2O_8$ + dilute H_2SO_4 + $AgNO_3$(aq) pink/purple colouration $Mn^{2+}(aq) \rightarrow MnO_4^-(aq)$
Cu^{2+} (aq) blue	blue ppt. insoluble in excess NaOH(aq) $Cu(OH)_2$(s) black ppt. formed on heating CuO(s)	blue ppt. soluble in excess NH_3(aq) to form a deep blue solution $Cu(OH)_2(s) \rightarrow [Cu(NH_3)_4]^{2+}$(aq)	Blue-green ppt. turned black on heating $CuCO_3(s) \rightarrow CuO(s)$	no ppt.	no ppt.	cream ppt (CuI) in brown solution (I_2) - on adding $Na_2S_2O_3$(aq), brown solution decolourised - with excess $Na_2S_2O_3$(aq), cream ppt. dissolved.	brown ppt. $CuCrO_4$(s)	conc. HCl - green solution blue $[Cu(H_2O)_6]^{2+}$(aq) + yellow $[CuCl_4]^{2-}$(aq) - yellow solution formed with more conc. HCl yellow $[CuCl_4]^{2-}$(aq)
Cr^{3+} (aq) green acidic	grey-green ppt. soluble in excess NaOH(aq) to form a green solution $Cr(OH)_3(s) \rightarrow [Cr(OH)_6]^{3-}$(aq)	grey-green ppt. insoluble in excess NH_3(aq) $Cr(OH)_3$(s)	Effervescence of CO_2(g) and grey-green ppt. $Cr(OH)_3$(s)	no ppt.	no ppt.	- KI did not turn brown - no ppt.	no ppt.	Excess NaOH(aq) + H_2O_2(aq) + heat yellow solution $Cr^{3+}(aq) \rightarrow CrO_4^{2-}$(aq)
Fe^{2+} (aq) pale green	dirty green ppt. - insoluble in excess NaOH(aq) - turned brown on standing $Fe(OH)_2(s) \rightarrow Fe(OH)_3(s)$	dirty green ppt. - insoluble in excess NH_3(aq) - turned brown on standing $Fe(OH)_2(s) \rightarrow Fe(OH)_3(s)$	Green ppt turning brown on standing. $FeCO_3(s) \rightarrow FeCO_3.Fe(OH)_2$	no ppt.	no ppt.	- KI did not turn brown - no ppt.	no ppt.	H_2O_2 (aq) : yellow solution ($Fe^{2+} \rightarrow Fe^{3+}$(aq)) $KMnO_4/H_2SO_4$ purple colour discharged + yellow solution $K_3[Fe(CN)_6]$(aq) dark blue ppt. : $Fe_4[Fe(CN)_6]_3$(s)
Fe^{3+} (aq) yellow/brown acidic	reddish-brown ppt. insoluble in excess NaOH(aq) $Fe(OH)_3$(s)	reddish-brown ppt. insoluble in excess NH_3(aq) $Fe(OH)_3$(s)	Effervescence of CO_2(g) and brown ppt. $Fe(OH)_3$(s)	no ppt.	no ppt.	Brown solution (and perhaps black ppt.) I_2(aq) (and perhaps also I_2(s))	orange-brown ppt. $Fe_2(CrO_4)_3$ (s)	NH_4SCN (aq) or KSCN(aq) blood red colouration: $[Fe(SCN)(H_2O)_5]^{2+}$(aq) $K_4[Fe(CN)_6]$(aq) dark blue ppt. : $Fe_4[Fe(CN)_6]_3$(s)

With the exception of sulfate anions, most of the common anions of the salts prescribed in the syllabus can be detected by either dilute acid (e.g. dilute HCl or H_2SO_4) or concentrated sulfuric acid.
Other reagents can also be used to identify specific cations (e.g. aqueous $AgNO_3$ to test for halides, Devarda's Alloy to test for NO_2^-).

Summary of Reactions of Anions

Anion \ Reagent	dilute HCl or dilute H_2SO_4	conc. H_2SO_4	$AgNO_3$(aq)	$BaCl_2$(aq)/ $Ba(NO_3)_2$(aq)	$Pb(NO_3)_2$ (aq)/ $(CH_3COO)_2Pb$ (aq)	$KMnO_4$(aq)/ H_2SO_4(aq)	KI (aq)	Other Reagents/ Remarks
Cl^- (aq) colourless	no gas evolved	(with solid Cl^-) HCl (g) evolved – formed dense white fumes with conc. NH_3(aq)	white ppt, AgCl (s), insoluble in dilute HNO_3 but soluble in aq NH_3 $AgCl(s) \rightarrow [Ag(NH_3)_2]^+(aq)$	no ppt.	white ppt, $PbCl_2$(s), soluble in hot water – upon cooling, white crystals formed	– decolouration of purple $KMnO_4$ – Cl_2 evolved	no ppt. no colour change	conc. H_2SO_4 + MnO_2 + heat: Cl_2(g) evolved
Br^- (aq) colourless	no gas evolved	(with solid Br^-) HBr(g) evolved & Br_2(g) evolved	cream ppt, AgBr(s), insoluble in dilute HNO_3 but partially soluble in aq. NH_3 $AgBr(s) \rightarrow [Ag(NH_3)_2]^+(aq)$	no ppt.	white ppt, $PbBr_2$(s), soluble in hot water – upon cooling, white crystals formed	– decolouration of purple $KMnO_4$ – yellow/brown solution – when shaken with hexane, orange-brown organic layer formed $Br_2(aq) \Leftrightarrow Br_2(org)$	no ppt. no colour change	NaOCl (or other oxidising agent) + acid yellow or brown solution of Br_2(aq) then + hexane + shake reddish-brown/orange-brown organic layer containing Br_2
I^- (aq) colourless	no gas evolved	(with solid I^-) purple I_2(g) evolved. H_2S(g) and SO_2(g) may also be evolved.	yellow ppt, AgI (s), insoluble in dilute HNO_3 and insoluble in aq. NH_3	no ppt.	yellow ppt, PbI$_2$(s), soluble in hot water – upon cooling, yellow crystals formed	– decolouration of purple $KMnO_4$ – yellow/brown solution – when shaken with hexane, violet organic layer formed $I_2(aq) \Leftrightarrow I_2(org)$	no ppt. no colour change	NaOCl (or other oxidising agent) + acid then + hexane + shake see $KMnO_4$ + dilute H_2SO_4 $CuSO_4$(aq) cream ppt. in brown solution then + $Na_2S_2O_3$(aq) Brown colour discharged. Cream ppt. dissolved in excess $Na_2S_2O_3$
NO_3^- (aq) colourless	no gas evolved	brown fumes of NO_2 evolved if warmed with Cu	no ppt.	no ppt.	no ppt.	no decolouration of purple $KMnO_4$	no ppt. no colour change	Devarda's alloy/Al + NaOH + heat NH_3(g) evolved Gp II solid nitrates give NO_2 and O_2 on heating. Gp I nitrates give O_2 but no NO_2.
NO_2^- (aq) colourless	NO_2 (g) evolved – brown gas which turned $FeSO_4$(aq) brown	vigorous reaction. NO_2 evolved – brown gas which turned $FeSO_4$(aq) brown	white ppt, $AgNO_2$(s), only with conc. solutions – soluble in dilute HNO_3 and aq. NH_3	no ppt.	no ppt.	– decolouration of purple $KMnO_4$ $NO_2^-(aq) \rightarrow NO_3^-(aq)$ NO_2^-(aq) is reducing	brown solution $I^-(aq) \rightarrow I_2(aq)$ NO_2^-(aq) is oxidising	Devarda's alloy/Al + NaOH + heat: NH_3(g) evolved $FeSO_4$(aq) + dilute H_2SO_4 brown colouration
CO_3^{2-} (aq) colourless	CO_2(g) evolved – effervescence – gave white ppt. when bubbled into $Ca(OH)_2$(aq)	vigorous reaction CO_2(g) evolved – effervescence – gave white ppt. when bubbled into $Ca(OH)_2$(aq)	white ppt, Ag_2CO_3(s), – soluble in dilute HNO_3 with evolution of CO_2(g) – soluble in aq. NH_3 – turned yellow or brown with excess reagent	white ppt, $BaCO_3$(s) – soluble in dilute HCl with evolution of CO_2 – soluble in dilute HNO_3 with evolution of CO_2	white ppt, $PbCO_3$(s) – soluble in dilute HCl with evolution of CO_2 – soluble in dilute HNO_3 with evolution of CO_2	no decolouration of purple $KMnO_4$	no ppt. no colour change	—
SO_3^{2-} (aq) colourless	SO_2(g) evolved – decolouration of purple acidified $KMnO_4$ Note: warming may be needed as SO_2 is quite soluble in H_2O	vigorous reaction, SO_2(g) evolved – ~~decolouration of purple acidified $KMnO_4$~~	white ppt, Ag_2SO_3(s), – soluble in dilute HNO_3 with evolution of SO_2(g)	white ppt, $BaSO_3$(s) – soluble in dilute HCl with evolution of SO_2 – soluble in dilute HNO_3 with evolution of SO_2 Note: $BaSO_3$ is readily oxidised to $BaSO_4$ which is insoluble in acids	white ppt, $PbSO_3$(s) – soluble in dilute HCl with evolution of SO_2 – soluble in dilute HNO_3 with evolution of SO_2 Note: $PbSO_3$ is readily oxidised to $PbSO_4$ which is insoluble in acids	– decolouration of purple $KMnO_4$ $SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq)$ SO_3^{2-}(aq) is reducing	no ppt. no colour change	I_2 (aq) brown colour discharged; SO_3^{2-} acts as a reducing agent.
SO_4^{2-} (aq) colourless	no gas evolved	no gas evolved	no ppt. – white ppt of Ag_2SO_4 only with conc. solutions	white ppt, $BaSO_4$(s), insoluble in dilute HNO_3	white ppt, $PbSO_4$(s) – insoluble in dilute HNO_3 – insoluble in hot water	no decolouration of purple $KMnO_4$	no ppt. no colour change	—