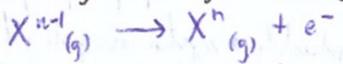


## ATOMIC STRUCTURE

$I_n$  - energy required to remove an  $e^-$  from each of 1 mol of gaseous  $[n-1] + \text{ions/atoms}$



R.A.M ( $\text{g.mol}^{-1}$ ) - weighted mean mass of an element/compound as compared to  $\frac{1}{12}$  th the mass of a carbon-12 atom

Electronic Config.:  $\text{Fe}^{2+}$  ion:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$   $\text{Mn}^{+}$  ion:  $[\text{Ar}] 4s^1 3p^5$

## Time of Flight Mass Spectrometry

- Electron Impact (EI) - low  $M_r$ , fragments  
high energy  $e^-$  freed from electron gun at vapourised sample
- dissolved sample in [polar] volatile solvent (e.g.  $\text{H}_2\text{O}$ ), injected through fine hypodermic needle
  - knock 1  $e^-$  off each atom, forms  $1^+$  ion

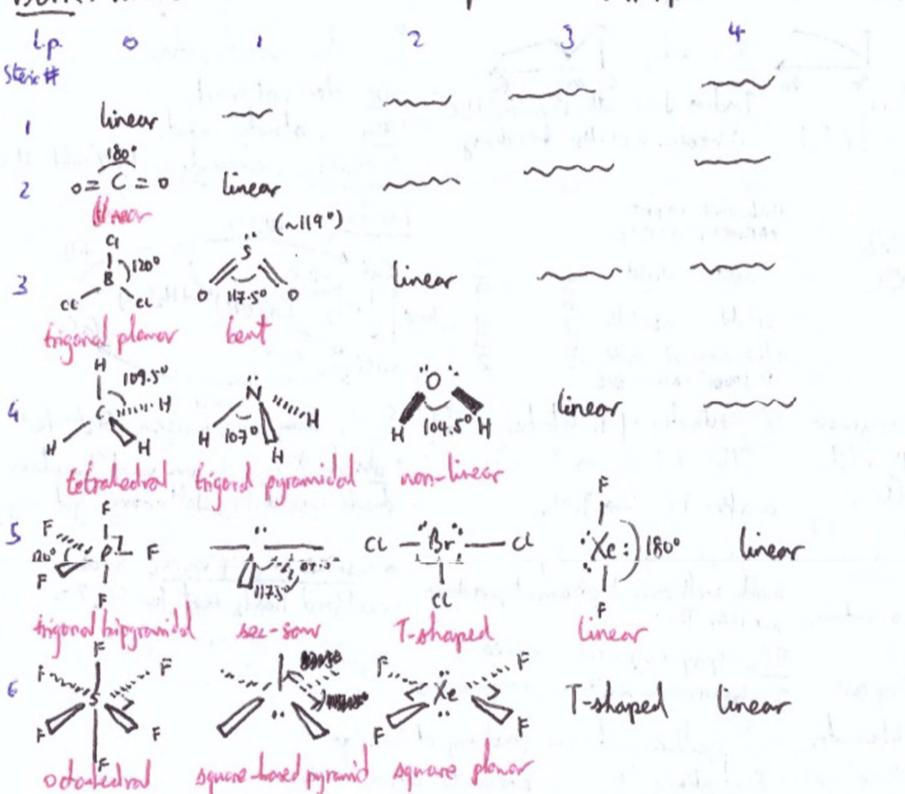


- accelerated by the electric field to some KE ( $\sim 1\text{m}$ )
- drifts down flight tube of known length
- the ions discharged on metal plate as  $e^-$  move generating current.

$$t = d \sqrt{\frac{m}{2KE}}$$

## STRUCTURE & BONDING

VSEPR: Valence Shell Electron Pair Repulsion



## Intermolecular Forces

Permanent Dip-Dip:  $\text{CCl}_4$  → differing E-N → polar bonds  
→ shift in  $e^-$  density → dipoles  
→  $\delta^+$  and  $\delta^-$  uneven → polar molecule  
→  $\delta^+$  in one attracts  $\delta^-$  in another  
∴ attraction between polar molecules  
→ e- orbit randomly, inst. dipoles  
→ distort neighbours, induces more dipoles  
→ new dipoles in way overall attractive  
∴ more  $e^-$   $\propto$  greater induced dipoles  $\Rightarrow$  stronger

Induced Dip-Dip:  $\text{H}_2\text{O}$  →  $\text{H}_2\text{O}$  "S" "S" "S" "S"

Hydrogen Bonding:  $\text{H}^+$  "O" "O" "O" "O"  
→ H bonded to sufficiently more E.N atom (only F, O, N)  
→  $-OH$ ,  $-NH$  or hydrogen fluoride  
✓ Lip. of  $e^-$  ✓  $\delta^+/\delta^-$  connection → bonded to L.p. of  $e^-$  on F, O, N

## Types of Bonding

### Ionic

- high m+b.p.
- water soluble (ex.  $\text{Al}_2\text{O}_3$ )
- conducts when molten

### Predicting Strength

- charge density (size/charge)
- high  $=$  stronger = higher m+b.p. ( $\text{CaCl}_2$ )

### Examples

Water → high surface tension  
→ fluid; reforming H bonds  
→ higher b.p. - H bonds (+vdW/dip-dip)  
→ i.e. H bonds in more open tetrahedral layout w/ large spaces  $\therefore$  floats

### Metallic

- strength of d.l.e- and atomic radius
- transfer heat by conduction when collide close enough

### Monatomic

- vander Waals of  $e^-$
- low m+b.p.

Covalent  $\text{H}-\text{N}:$   $+ \text{H}^+ \rightarrow \left[ \begin{array}{c} \text{H} \\ | \\ \text{H}-\text{N} \end{array} \right]^+$   
→ dative/co-ordinate - both  $e^-$  from same atom

Simple Molecules:  $\text{P}_4$  (white),  $\text{S}_8$

→ Giant Molecules:  $\text{SiO}_2$ ,  $\text{Si}, \text{Ge}$

(red)  $\text{P}$

SE6 promotes

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## COLLISION THEORY

- conc.: more particles of reactant present, increased # of successful collisions
- pressure: particles forced closer together, increased # "
- temp: particles gain more KE, move faster, increased # of collisions w/ sufficient E.
- S.A.: increased exposed surface of reactants; more collisions can occur, increased # in period
- catalyst: alternative reaction pathway, lower  $t_a$ , increased # of collisions w/ sufficient E.

$E_a^{(5)}$  - min E reacting particles need for a successful collision

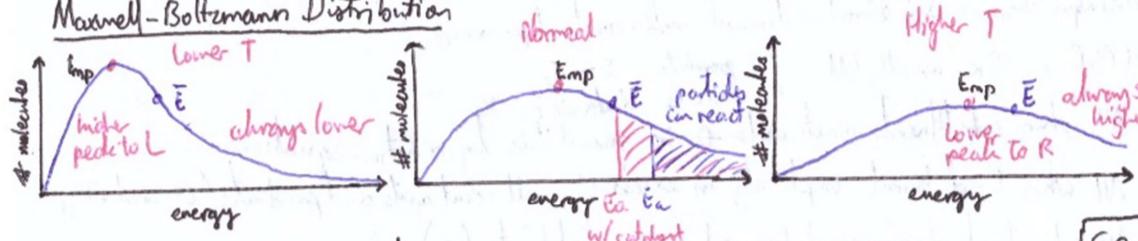
rate of reaction = rate of change in concentration

Most collisions unsuccessful: only small prop. of particles have  $t_a$  required to be successful

Catalyst - substance increases rate w/o changing amount or chemical composition

- doesn't affect position of equilibrium as both forwards/reverse reactions equally sped up
- ⇒ multistep: catalyst used, then reformed; only affects rate equilibrium attained

## Maxwell-Boltzmann Distribution

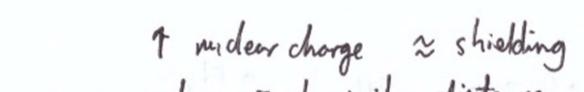
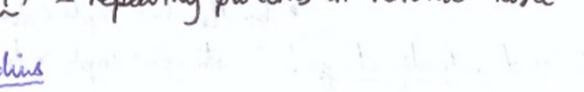
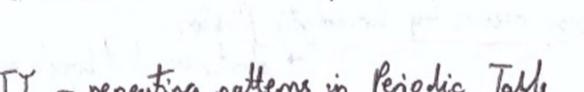
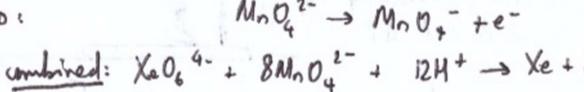
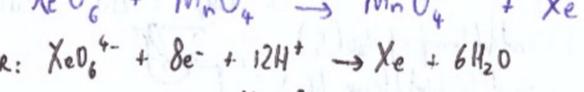
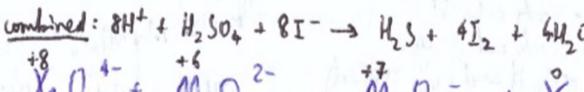
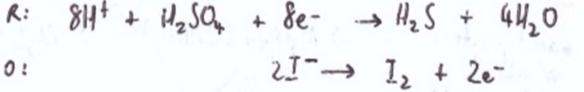
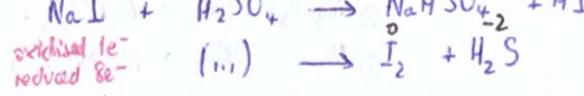
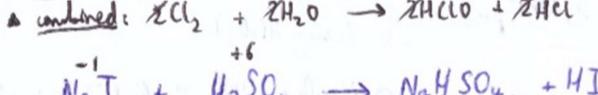
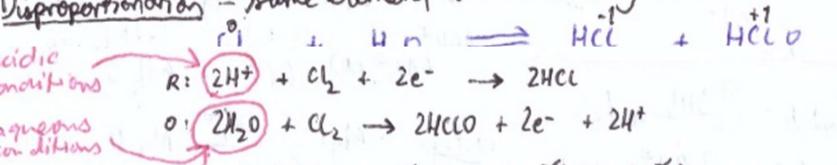


OXIDATION STATES redox: transfer of e<sup>-</sup> min state = -8; max = +group no.

OILRIG = oxidation is loss of e<sup>-</sup> oxidizing agents are e<sup>-</sup> acceptors  
reduction is gain of e<sup>-</sup> reducing agents are e<sup>-</sup> donors

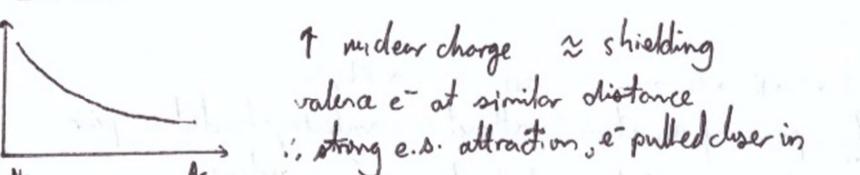
- Compounds → Group I / II always +1 and +2 respectively.
- O has 2- unless bonded to F or in peroxides (state = -1)
- H has +1 unless bonded to metals (hydride: state = -1)
- F always -1. Halogen has -1 unless bonded to more reactive halogen/oxygen.
- binary compounds - more E.N. elements have -ve oxidation states.
- d-block/p-block - have varying oxidation states.

Disproportionation - same element simultaneously oxidized and reduced



PERIODICITY - repeating patterns in Periodic Table (Period III)

## Atomic Radius



## First Ionisation Energy (I<sub>1</sub>)

- across period ↑ nuclear charge ↑ general trend
- across subshell slight ↑ distance shielding ↓ Mg → Al
- halfway 3p e<sup>-</sup> repulsion in orbital ( $3p^3/3p^4$ ) ↓ P → S

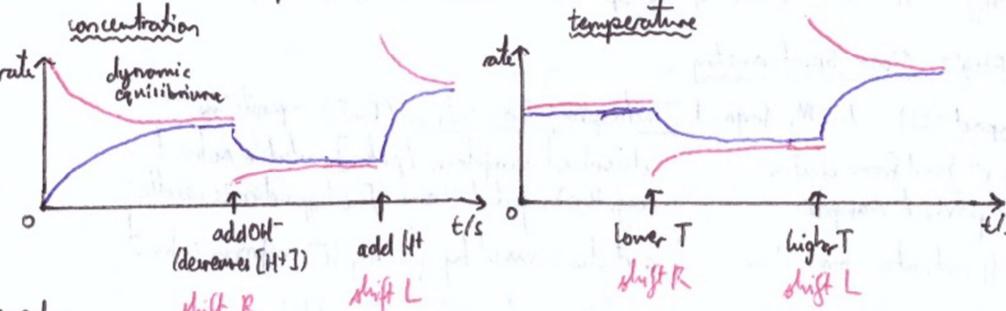
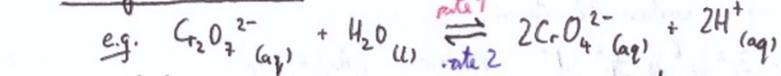
## Melting + Boiling Points

- Na → Al (metallic) -↑ ionic charge ↓ radius ∴ higher m+b/p
- Si (giant covalent) - many strong covalent bonds in macromolecule
- P → Cl (simple covalent) - size of London forces  $\propto$  the- (P, S<sub>8</sub>/Cl<sub>2</sub>)
- Ar (monatomic) - weakest van der Waals (only 18e<sup>-</sup>)

## EQUILIBRIA, LE CHÂTALIER RICE [ ]

- Dynamic Equilibrium: forwards and reverse rates = proportion of reactants/products static over time
- Le Châtelier: if a constraint is applied to a system in equil., it will shift to counter constraint effect

• Homogeneous Reaction: all reactants & products in same physical state



## Haber Process

- $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$
- high T (~450°C): lower T increases yield, but slow rate
  - high p (~200 atm): high p = more NH<sub>3</sub>, but facilitates ↓ rate/yield
  - passed over iron catalyst - affects rate, not yield

$K_c \rightarrow$  only constant at constant temperature. Unaffected by pressure/concentration

$$K_c = \frac{\text{prod}}{\text{react}}$$

- values:  
0: all the way to L  
1: "about halfway"  
2: all the way to R

units:  
(mol.dm<sup>-3</sup>)  
identification  
when  $c_{\text{tot}} = a_{\text{tot}}$ , NO UNITS!

## GROUP II ALKALINE-EARTHT METALS

- Trends: ↑ atomic radius ↑ m+b/p ↑ water reactivity  
↓ shielding ↓ distance ↓ ionic radius (↓ I<sub>1</sub>) ↓ weaker metallic bonding

### Solubility

	(OH) <sub>2</sub>	SO <sub>4</sub> <sup>2-</sup>	Cl <sub>2</sub>	CO <sub>3</sub> <sup>2-</sup>
Mg <sup>2+</sup>	white ppt	svanheits solvate		
Xe <sup>2+</sup> + 2OH <sup>-</sup> → K(OH) <sub>2</sub>	slight	slight	w	
Xe <sup>2+</sup> + SO <sub>4</sub> <sup>2-</sup> → XSO <sub>4</sub>	soluble	insoluble	w	
Ba <sup>2+</sup> + SO <sub>4</sub> <sup>2-</sup> → BaSO <sub>4</sub>	white	white	soluble	

### Uses:

Mg(OH)<sub>2</sub> antacid, milk of magnesia

sparsely soluble: Mg(OH)<sub>2</sub> ↓ H<sub>2</sub>O form suspension w/ low [OH<sup>-</sup>]

no alkaline burns (pH ~10.5)

Mg(OH)<sub>2</sub> → Mg<sup>2+</sup> + 2OH<sup>-</sup>

reacts w/ stomach acid to neutralise mother Ti.

H<sup>+</sup> + OH<sup>-</sup> → H<sub>2</sub>O

equilibrium shifts, removing OH<sup>-</sup>.

Ca(OH)<sub>2</sub> slaked lime, soil/alkaline.

CaO combining with water to form calcium hydroxide

From limestone, cheap. More pH ~12

Neutralises SO<sub>2</sub> ↓ prevents acid rain

alkaline than Mg(OH)<sub>2</sub> but not too high

Ca(OH)<sub>2</sub> gear pellet - absorbs O<sub>2</sub> in rebreathers

↑ water reactivity

Be does not react

Mg v. slowly reacts

Ca/Sr/Ba increasingly react w/ cold H<sub>2</sub>O

Reactions:  $\text{H}_2\text{O} (\text{g}) \rightleftharpoons \text{H}_2\text{O} (\text{l})$

heat ↑ + CO<sub>2</sub> → Ca(OH)<sub>2</sub> + H<sub>2</sub>O (l) + CO<sub>2</sub> → CaCO<sub>3</sub> + H<sub>2</sub>O (l)

+ HCl → BaSO<sub>4</sub> X-ray tracer, imagery, SO<sub>4</sub><sup>2-</sup> test

+ absorbs X-rays, barium meal, hemless due to insolubility Ba<sup>2+</sup> v. toxic, gut imagery

→ insolubility of BaSO<sub>4</sub> makes acidified BaCl<sub>2</sub> test for SO<sub>4</sub><sup>2-</sup>.

Ba<sup>2+</sup> + SO<sub>4</sub><sup>2-</sup> → BaSO<sub>4</sub> (s)

## GROUP VII

- Trends: ↑ m+b/p (X<sub>2</sub>) ↓ oxidising agent ↓ reducing agent ↑ water reactivity  
more e<sup>-</sup>; stronger ionic forces ease at which e<sup>-</sup> is gained ease at which e<sup>-</sup> is lost  
↓ electronegativity (in valence shell) ↓ further ↓ lower e.s. ↓ easier to lose  
shielding/distance increases ↓ stronger power when dose ↓ easier to lose

Testing: Ag<sup>+</sup> (aq) + X<sup>-</sup> (aq) → AgX (s)

ADD ACIDIFIED AgNO<sub>3</sub> WITH NH<sub>3</sub>

Cl<sub>2</sub> white ppt.

AgNO<sub>3</sub> + NaCl → NaNO<sub>3</sub> + AgCl (s)

AgCl (s) + 2NH<sub>3</sub> (aq) → [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (aq) + Cl<sup>-</sup> (aq)

Br<sub>2</sub> cream ppt (i.e. AgBr (s))

redissolves in concentrated NH<sub>3</sub>

I<sub>2</sub> yellow ppt. (i.e. AgI (s))

AgI (s) does not react w/ NH<sub>3</sub>.

with CONC. H<sub>2</sub>SO<sub>4</sub> (reducing ability)

① Br<sub>2</sub> is red/orange vapor

② I<sub>2</sub> is purple vapor

③ SO<sub>2</sub> turns orange K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> paper green

④ H<sub>2</sub>S turns white lead(ethoate) paper black (rotten eggs!)

Properties: F<sub>2</sub> (g) yellow

Cl<sub>2</sub> (g) green

Br<sub>2</sub> (l) orange

I<sub>2</sub> (s) grey

At<sub>2</sub> (g) black

## Halide Ions (Halates)

ClO<sup>-</sup> hypochlorite chlorate (I)

ClO<sub>2</sub><sup>-</sup> chlorite chlorate (II)

ClO<sub>3</sub><sup>-</sup> chlorate chlorate (V)

ClO<sub>4</sub><sup>-</sup> perchlorate chlorate (VII)

redissolves in dilute NH<sub>3</sub> (waterless)

AgCl (s) + NH<sub>3</sub> (aq) → [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (aq) + Cl<sup>-</sup> (aq)

redissolves in concentrated NH<sub>3</sub>

I<sub>2</sub> (s) does not react w/ NH<sub>3</sub>.

with CONC. H<sub>2</sub>SO<sub>4</sub> (reducing ability)

① Br<sub>2</sub> is red/orange vapor

② I<sub>2</sub> is purple vapor

③ SO<sub>2</sub> turns orange K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> paper green

④ H<sub>2</sub>S turns white lead(ethoate) paper black (rotten eggs!)

chlorate transparent

Ditropoxidation of Cl

(CHLORINE W/ COLD DILUTE NaOH)

NaCl + NaClO + H<sub>2</sub>O

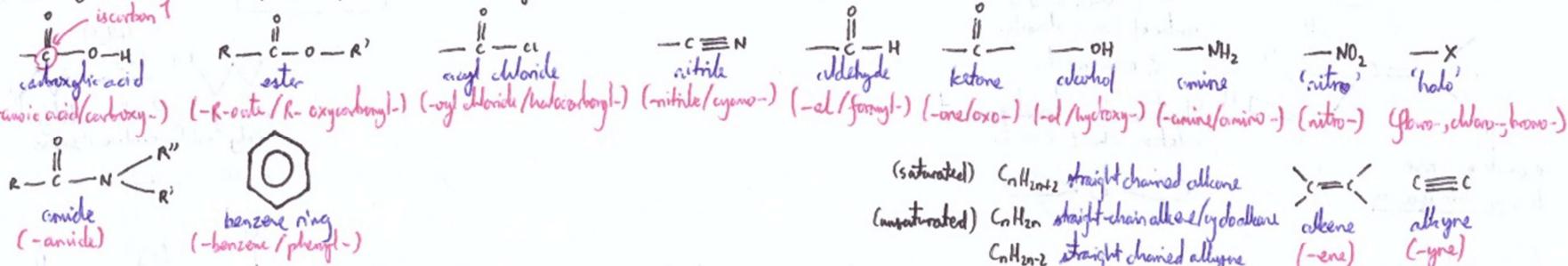
water treatment

Cl<sub>2</sub> (g) + H<sub>2</sub>O (

## IUPAC

1 meth	1 mono	6 hex	11 undec
2 eth	2 di	7 sept	12 dodec
3 prop	3 tri	8 oct	13 tridec
4 but	4 tetra	9 non	14 tetradec
5 pent	5 penta	10 dec	

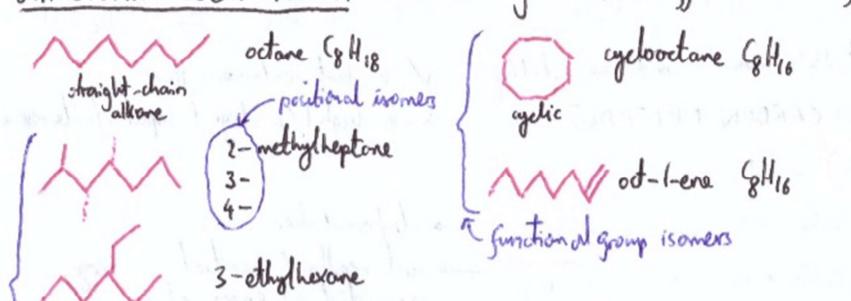
Homologous Series - family of compounds w/ same general formula and functional groups). Successive members differ by  $\text{CH}_2$ .



## Rules

- # of carbons, longest chain, find prefix
- describe C-C bonding (-ane/-ene/-yne)
- add 'cyclo' if cyclic pattern
- note side-chains (ethyl)/substituent groups + locants (which C)
- alphabetical, lowest numbers

STRUCTURAL ISOMERISM - same molecular formula, but different structural formula



- Aliphatic - hydrocarbon molecules with single, double, triple bonds. Can be branched, straight, cyclic. Denoted as group 'R'.

- Aromatic - organic molecule with del. ring of e<sup>-</sup> e.g. 

(saturated)  $\text{C}_{n+2}$  straight-chain alkane

(unsaturated)  $\text{C}_{n+1}$  straight-chain alkene/alkyne

$\text{C}_{n+2}$  straight-chain alkyne

$\text{C}\equiv\text{C}$

alkene

(-ene)

(-yne)

More branched = weaker van der Waals  
↓ lower b.p. (∴ weaker i.m. forces)

Ozone Depletion  $\text{O}_3 \xrightarrow{\text{UV}} \text{O}_2 + \text{O}$  bond matches 2 of UV 200-300 nm

Ozone enhances absorption of harmful UV light preventing it reaching Earth  
acts as heat conductor; surface habitable

CFCs (chlorofluorocarbons) diffuse into stratosphere, produce chlorine free-radicals  
 $\text{F}-\overset{\text{F}}{\underset{\text{F}}{\text{C}}}-\text{Cl} \xrightarrow{\text{UV}} \text{F}-\overset{\text{F}}{\underset{\text{F}}{\text{C}}}^{\cdot\text{I}} + \text{Cl}^{\cdot}$  homolysis of C-Cl  
 $\text{F}-\overset{\text{F}}{\underset{\text{F}}{\text{C}}}-\text{Cl} \xrightarrow{\text{UV}} \text{F}_2\text{C}\text{H}_2 + \text{Cl}^{\cdot}$  especially weak

Each Cl<sup>·</sup> molecule can last decades and decompose ~100,000 O<sub>3</sub> molecules  
UV → can cause skin cancer by destroying DNA  
→ cataracts in eyes → reduce plankton in oceans

CF<sub>3</sub> → used in fridges → non-flammable, non-toxic  
→ absorb E. when vaporised by latent heat

Cl<sup>·</sup> + O<sub>3</sub> → ClO<sup>·</sup> + O<sub>2</sub> ClO<sup>·</sup> + O<sub>3</sub> → 2O<sub>2</sub> + Cl<sup>·</sup> overall: 2O<sub>3</sub> → 3O<sub>2</sub>  
NO + O<sub>3</sub> → NO<sub>2</sub> + O<sub>2</sub> NO<sub>2</sub> + O<sub>3</sub> → 2O<sub>2</sub> + NO overall: 2O<sub>3</sub> → 3O<sub>2</sub>

## Internal Combustion Engines

Unreactive N<sub>2</sub> reacts w/ O<sub>2</sub> at high T and p. N<sub>2</sub> + O<sub>2</sub> → 2NO(g) or N<sub>2</sub> + 2O<sub>2</sub> → 2NO<sub>2</sub>(g)

Sulfur impurities, S + O<sub>2</sub> → SO<sub>2</sub>(g) e.g. C<sub>4</sub>H<sub>10</sub>S<sub>2</sub> + 1/2O<sub>2</sub> → 4CO<sub>2</sub> + 5H<sub>2</sub>O + 2SO<sub>2</sub>

## Pollution Problems

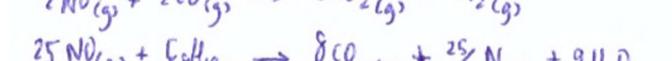
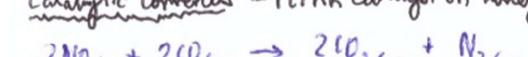
→ SO<sub>2</sub> causes acid rain: SO<sub>2</sub> + H<sub>2</sub>O + 1/2O<sub>2</sub> → H<sub>2</sub>SO<sub>4</sub>(aq)

→ CO<sub>2</sub>, CH<sub>4</sub> cause global warming by greenhouse effect.

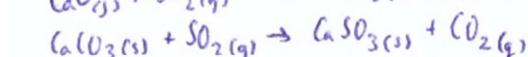
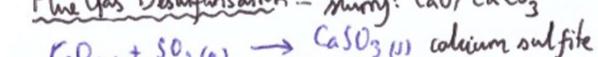
→ CO, soot, NO<sub>x</sub> cause photochemical smog → breathing problems.

## Removing Air Pollutants

Catalytic Converters - Pt/Rh catalyst on honeycomb



Fine Gas Desulfurisation - slurry: CaO/CaCO<sub>3</sub>



oxidized CaSO<sub>3</sub> + [O] → CaSO<sub>4</sub> calcium sulfate used in construction

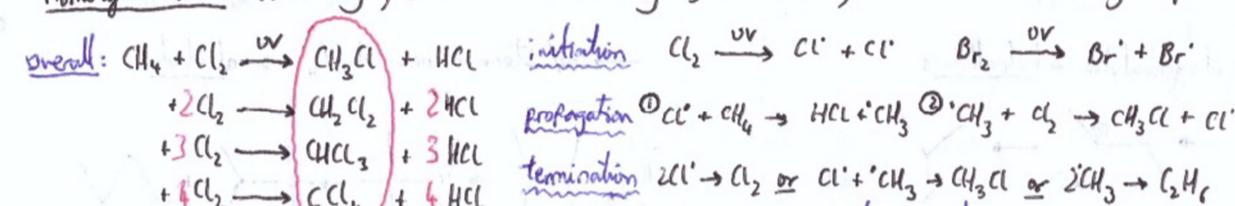
ALKANES saturated hydrocarbons, used mainly as fuels

## Free-Radical Substitution

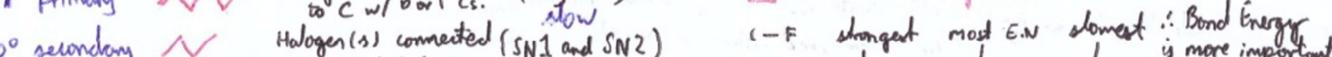
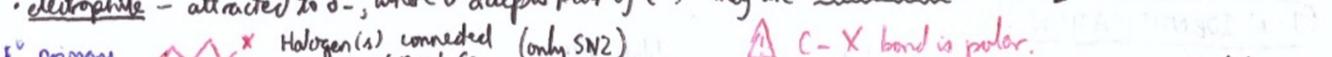
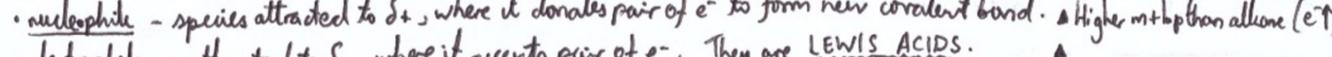
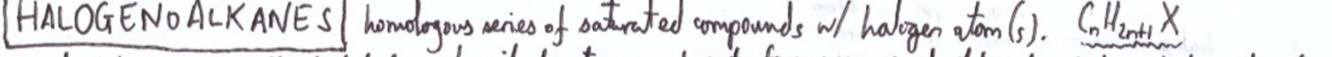
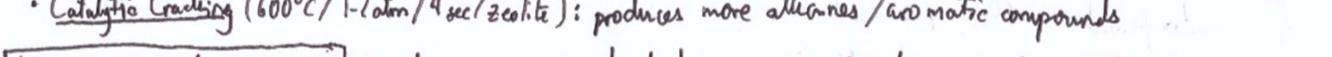
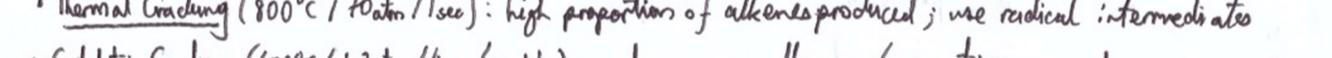
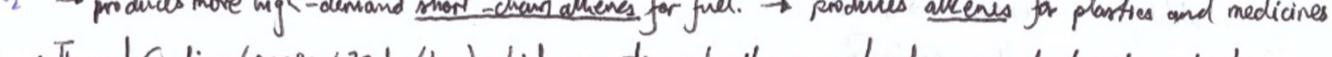
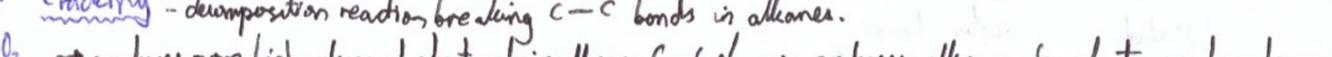
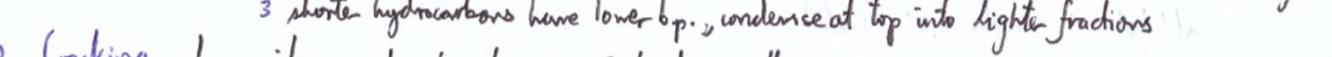
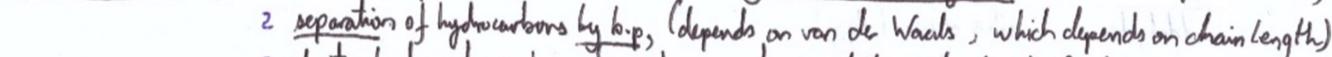
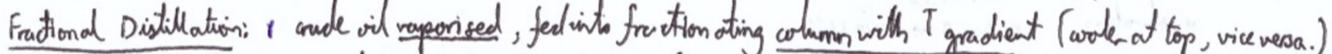
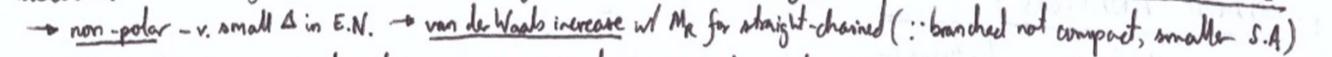
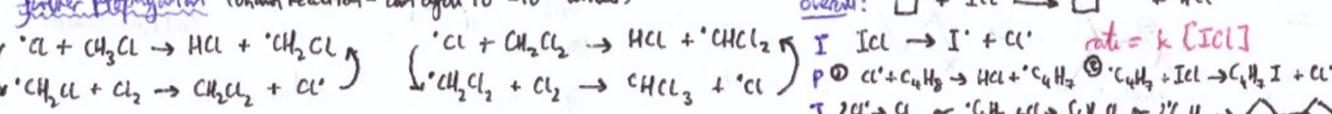
Free-Radical - atom/group w/ unpaired e<sup>-</sup> Substitution - replacing atom/group in a reaction

Mechanism - detailed step-by-step sequence; illustration of how overall chemical reaction happens

Homolytic Fission - breaking of covalent atom leaving 2 free-radicals; each leaves with 1e<sup>-</sup> from pair

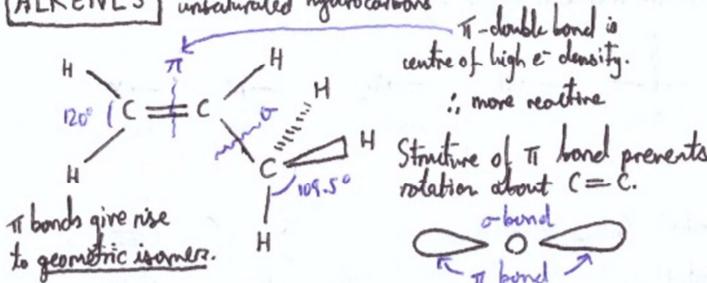


further propagation (chain reaction - can cycle 10<sup>5</sup>-10<sup>7</sup> times)



## ALKENES

unsaturated hydrocarbons



$\pi$ -double bond is centre of high e- density.

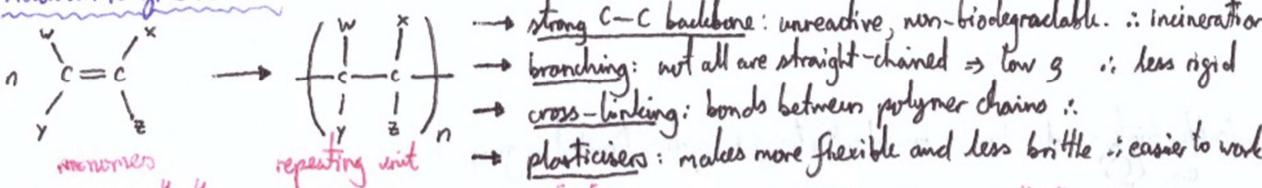
$\therefore$  more reactive

Structure of  $\pi$  bond prevents rotation about  $(=C)$ .

$\alpha$ -bond

$\pi$  bond

## Addition Polymerisations



monomers

Poly(ethene)  $\text{f}(\text{c}-\text{c})\text{n}$

HDPE

longer chains

: more rigid

higher melt temp

rigidity

carrier bags

LDPE

branching

: less rigid

lower melt temp

flexibility

carrier bags

Poly(tetrafluoroethene)  $\text{f}(\text{c}-\text{c})\text{n}$

a.k.a. PTFE / Teflon

Hard-wearing plastic

" rigid.

: Sometimes hard to work with.

Poly(propene)  $\text{f}(\text{c}-\text{c})\text{n}$

uses: ropes, carpets

Poly(phenylethene)  $\text{f}(\text{c}-\text{c})\text{n}$

a.k.a. polystyrene

Polychloroethene  $\text{f}(\text{c}-\text{c})\text{n}$

a.k.a. polyvinyl chloride / PVC

Hard-wearing plastic

" rigid.

: Sometimes hard to work with.

Poly(ethylene)

a.k.a. polyethylene

Hard-wearing plastic

" rigid.

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Poly(phenylethene)

a.k.a. polystyrene

Hard-wearing plastic

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Poly(chloroethene)

a.k.a. polyvinyl chloride / PVC

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Enthalpy Definitions  $\ominus$ : under standard conditions/states ( $\Theta_{st}$ )

$\Delta H$  - change in  $H$  stored in chemicals, constant  $p$

$\Delta H^\circ_f$  formation -  $\Delta H$  when 1 mol compound formed from elements, all reactants and products  $\ominus \Theta_{st}$

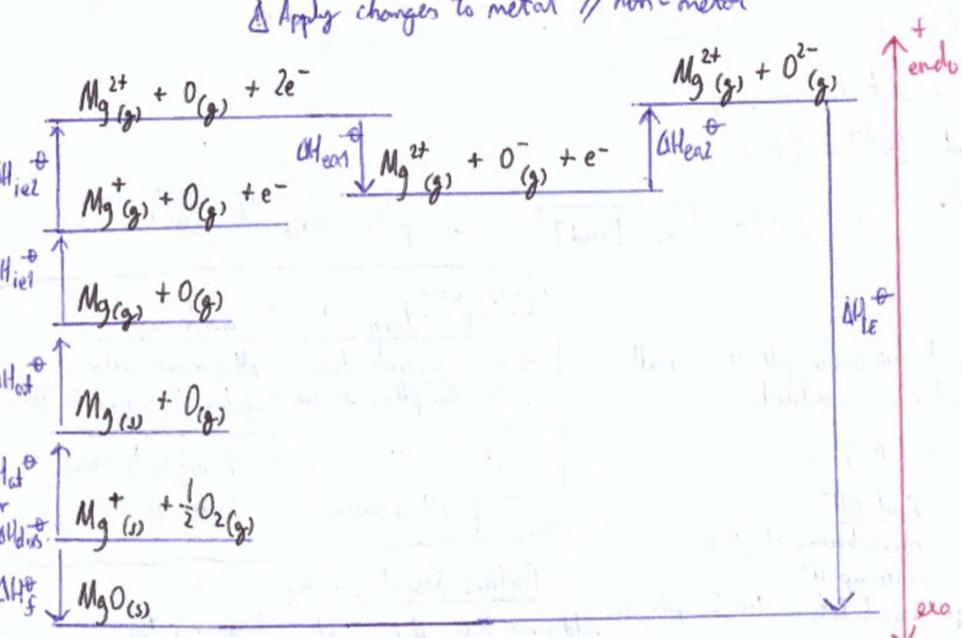
$\Delta H_{\text{ion}}$   $\oplus$  first e<sup>-</sup> -  $\Delta H$  when 1 mol gaseous 1<sup>-</sup> ions formed  $O(g) + e^- \rightarrow O^-(g)$   
affinity from 1 mol gaseous atoms  $\Delta H$  - ve (EXO) : attr. between e<sup>-</sup> and neutral atom

$\Delta H_{\text{ion}2}$   $\oplus$  second e<sup>-</sup> -  $\Delta H$  when 1 mol gaseous 2<sup>-</sup> ions formed  $O(g) + e^- \rightarrow O^{2-}(g)$   
affinity from 1 mol gaseous 1<sup>-</sup> ions  $\Delta H$  the (ENDO) : repulsion between e<sup>-</sup> and -ve ion

$\Delta H_{\text{lattice}}$  (formation) -  $E$  released when 1 mol solid ionic lattice : energy released changing forms from its gaseous ions  $\ominus \Delta H$  - ve for apart gases  $\rightarrow$  solids

$\Delta H$   $\ominus$  bond dissociation -  $\Delta H$  when all bonds of same type in 1 mol of gaseous molecules is broken  $(Cl_2) \rightarrow 2Cl(g)$

Born-Haber Cycle - used as L.E. cannot be directly measured, induced route by Hess' Law  
 $\Delta$  Apply changes to metal // non-metal



Free-Energy Change ( $\Delta G$ ) - measure to predict reaction feasibility

$$\Delta G = \Delta H - TAS$$

Gibbs Free Energy, Enthalpy Change, Entropy

$$T = \frac{\Delta H}{\Delta S}$$

$\uparrow$  divide  $J \cdot mol^{-1} \cdot K^{-1}$  by 1000

note that -ve  $\Delta G$  doesn't guarantee reaction will happen. G.F.E. tells nothing about rate /  $E_a$ .

Ensure  $\Delta G_p$  feasibility range account for states of matter (e.g. requires water vapor)

$\Delta$  Equilibrium when reaction starts off spontaneous, but  $\Delta G$  flip sign as product made.

Entropy - measure of disorder, "universe moves to processes more likely to happen"

$$\Delta S = S_{\text{products}} - S_{\text{reactants}}$$

$K_c$  equilibrium constant ( $c$ ) some power  
 $K_a$  acidic dissociation const.  $mol \cdot dm^{-3}$   $K_a = [H^+] \times \frac{[A^-]}{[HA]}$   
 $K_b$  base dissociation const.  
 $K_p$  equilibrium const. of pressure ( $p$ ) some power

### MEASURING RATES OF REACTION

Progress of reaction • How long for [set change] to occur

$\rightarrow$  change in pH: electronic pH probe, indicator

$\rightarrow$  change in mass: collect gas in syringe, volume gas = mass lost

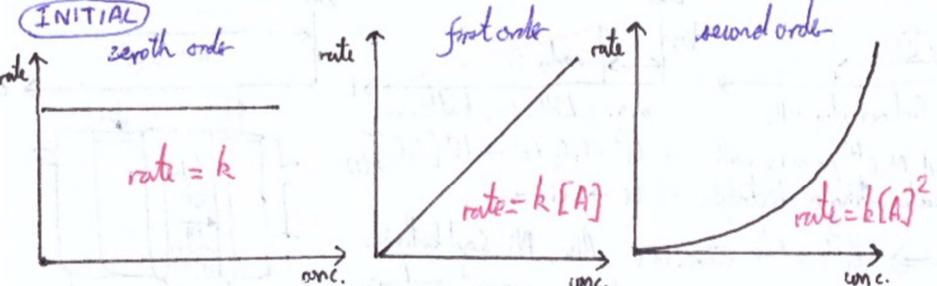
$\rightarrow$  turbidity/color change: transparency, rate  $\propto \frac{1}{t}$

$\rightarrow$  dilatometry: change in volume of solution

$\rightarrow$  change in electrical conductivity: reactant consumes ions in solution

$\rightarrow$  change in electrical conductivity: reactant consumes ions in solution

### INITIAL



Rate-Determining Step (r.d.s) - the slowest step in a multi-step mechanism

$\rightarrow$  only reactants used up to / including r.d.s affect the rate

$\Delta$   $\rightarrow$  cannot be single-step if catalyst involved

Half-life ( $t_{1/2}$ ) - time for half a reactant to react

ARRHENIUS EQUATION  $x = \frac{1}{T}, y = \ln k$

$$k = Ae^{-E_a/RT}$$

$$lnk = \ln A - \frac{E_a}{RT}$$

$$y = \ln A - \frac{E_a}{R}x$$

$$\Rightarrow A = e^y \text{ - intercept}$$

$$\Rightarrow E_a = -R \cdot \text{gradient}$$

REACTANT L overall more

PRODUCT R overall more

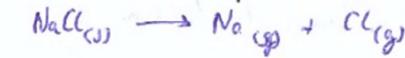
CATALYST L first, then regenerated or R

INTERMEDIATE R first, then L

$\Delta H_{\text{ad}}$   $\oplus$  atomisation of a(n) element -

$\Delta H$  when 1 mol aqueous atoms formed from elements  $\ominus \Theta_{st}$   
 $\frac{1}{2} I_2(s) \rightarrow I(g)$   $\Delta$  not same as bond dissociation enthalpy

$\Delta H$  when 1 mol compound converted to gaseous atoms



$\Delta H_{\text{hyd}}$  hydration -  $\Delta E$  when 1 mol aqueous ions is  $Na^+(g) + (aq) \rightarrow Na^+(aq)$

formed from gaseous ions  $\Delta H$  - ve (EXO)

$\Delta H_{\text{sol}}$   $\oplus$  solution -  $\Delta H$  when 1 mol ionic compound completely dissolved in excess  $H_2O$



Perfect Ionic Model - bonds all ionic, perfect spheres w/ no covalent character

$\triangleright$  THEORETICAL vs. EXPERIMENTAL (more/less endo/exothermic)

$\rightarrow$  deviation from perfect ionic model, which the theoretical value relies on

$\rightarrow$  assumes perfect spheres instead of polarised ones with no degree of covalency

$\therefore$  some covalent character

$\triangleright$  FACTORS AFFECTING LATICE ENTHALPY

- 1 Compare atomic size / size of charge  $\Rightarrow \{$  higher/lower  $\}$  charge density
- 2 More  $\{$  strong/weak  $\}$  attraction than other ion

$\triangleright$  FACTORS AFFECTING HYDRATION ENTHALPY

- 1 Compare charge density
- 2 Attracts the (S on O/S+ on H) in  $H_2O$  molecules  $\{$  more/less  $\}$  strongly

GROUP II SOLUBILITY

enthalpy cycle: solid/ionic lattice  $\xrightarrow{\Delta H_{\text{sol}}}$  aqueous ions

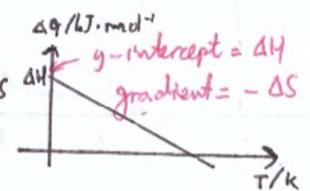
$\Delta H_{\text{ad}}$   $\ominus$   $\Delta H_{\text{hyd}}$  (neut) +  $\Delta H_{\text{hyd}}$  (-ve)

Change only spontaneous if  $\Delta G$  is -ve. High  $\Delta G$  = more likely.

$$\text{FREE-ENERGY GRAPHS}$$

$$\Delta G = \Delta H - TAS$$

$$y = c - mx$$



$\triangleright$  FACTORS AFFECTING ENTROPY

$\rightarrow$  Atom Arrangement: S amorphous solids  $>$  S perfect crystals

$\rightarrow$  Physical State: S<sub>gas</sub>  $>$  S<sub>liquid</sub>  $>$  S<sub>solid</sub>  $\rightarrow$  Complexity: bigger molecules = greater degree of freedom

$\rightarrow$  Mixing: greater # ways to arrange. Dissolving  $\uparrow S$ .  $\rightarrow$  Moles: greater # particles

$\triangleright$  WHAT MAKES A GOOD CHANGE TO MEASURE?

$\rightarrow$  ease of measurement

$\rightarrow$  change corresponds to same overall change in conc. every time

$\rightarrow$  change corresponds to small proportion of total reaction ( $at \rightarrow 0$ )

$\triangleright$  Following Reaction Over Time - measure quantity  $\propto [A]$  over time

(Continuous Monitoring)

$\rightarrow$  volume of gas produced over time intervals

$\rightarrow$  mass lost for gas-producing reaction

$\rightarrow$  absorption/transmission - assuming coloured reactant at particular  $\lambda$   $\Rightarrow$  use colorimeter

(CONTINUOUS MONITORING)

$$y = -kx + c$$

$$k = -m$$

decreasing  $t_{1/2}$

$$y = \frac{1}{kx + c}$$

$$k = \frac{\ln 2}{t_{1/2}}$$

constant  $t_{1/2}$

$$y = e^{-kx}$$

draw tangent at  $[A]$

Work out  $k$  from

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

increasing  $t_{1/2}$

UNITS:

$$\text{rate: mol} \cdot dm^{-3} \cdot s^{-1}$$

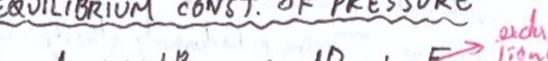
$$\text{rate} = k[A]^m[B]^n$$

overall order =  $m+n$

$$k = \frac{c}{t_{1/2}}$$

Calculating k's unit:

EQUILIBRIUM CONST. OF PRESSURE



exch. liquid

$K_p$  equilibrium const. of pressure

$$\frac{[P(D)]^d}{[P_A]^a[P_B]^b}$$

units =  $(Pa)^{d-a-b}$

$X_n$  mole fraction  $\frac{\text{moles of } n}{\text{total moles}}$

$P_n$  partial pressure  $X_n \cdot \text{total pressure} = \frac{P_n \cdot \Sigma P}{\Sigma n}$

Acids, Bases and pH  $\begin{cases} \text{Strong: completely dissociates in solution} \\ \text{Weak: partially} \end{cases}$

- Arenius - acids release  $H^+$  in (aq), bases release  $OH^-$
- Bronsted-Lowry - acids donate  $H^+$  (donors), bases accept  $H^+$  (acceptors)
- Lewis - acids accept (p), bases donate (p).

### pH and WATER

water slightly dissociates (1 in 10 million)

$$K_w = \frac{[H^+][OH^-]}{[H_2O]} \xrightarrow{\text{assume constant}} [H^+] = [OH^-]$$

$$K_w = 1 \times 10^{-14} \text{ mol}^2 \cdot \text{dm}^{-6}$$

$$\Rightarrow K_w = K_w \cdot [H_2O] = [H^+][OH^-]$$

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

$$\Rightarrow K_w = [H^+]^2 \text{ so } [H^+] = \sqrt{K_w}$$

$$\therefore pH = -\log_{10}(\sqrt{1 \times 10^{-14}}) = 7.00$$

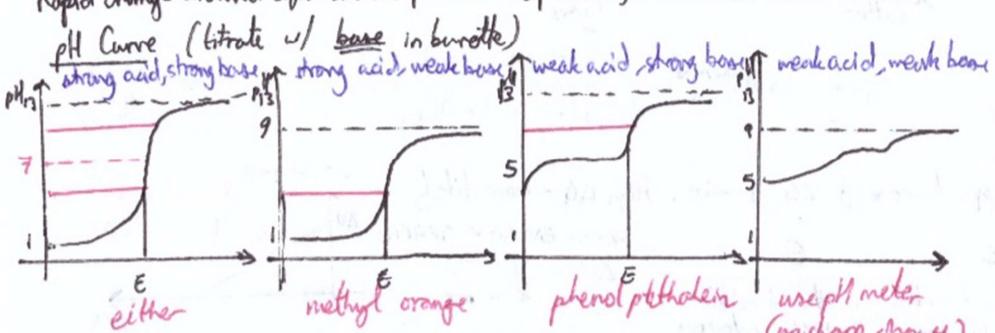
Indicators  $\begin{cases} \text{main species} \\ \text{at low pH} \end{cases}$   $\begin{cases} \text{main species} \\ \text{at high pH} \end{cases}$   
weak acids where  $HA \rightleftharpoons H^+ + A^-$  ( $HA$  and  $A^-$  different colours)

UNIVERSAL INDICATOR mixture of indicators to show many colours at different pHs

strong acid	methyl orange	red	yellow	pH range
strong base	phenolphthalein	colorless	pink	8.2 - 10.0

Equivalence Points -  $n$  acid added =  $n$  acid present  $\begin{cases} n, B, \text{not always} \\ \text{at pH = 7} \end{cases}$

Rapid change around equivalence point. Endpoint of indicator should coincide.



Diprotic Acids have 2 equivalence points.

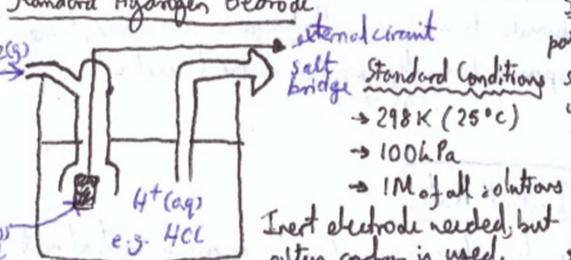
Electrode Potentials  $E^\circ$  (Electrochemical Cells) (a.k.a. using batteries to measure redox reactions)

ELECTROCHEMICAL CELLS: two different metals dipped in salt solutions of their own ions connected by a wire and salt bridge. This takes place as a redox reaction.

Electrode Potential ( $E^\circ$ ): measures how easily each metal loses  $e^-$  (is oxidised)

$$E^\circ_{\text{cell}} = E^\circ_{\text{R.H.S.}} - E^\circ_{\text{L.H.S.}} = E^\circ_{\text{red}} - E^\circ_{\text{oxi}}$$

Standard Hydrogen Electrode



Standard Electrode Potential ( $E^\circ$ ):

potential of a half-cell measured under standard conditions when the half-cell is connected to a standard hydrogen electrode.

Electrochemical Series - long list of  $E^\circ$ , written as reductions

half-equations

$E^\circ / V$   $\begin{cases} \checkmark \text{ changes in T, P, J} \text{ (Le Chatelier)} \\ \text{equilibrium} \times \text{max current/length of cell-life} \\ \text{lies LEFT} \times \text{S.A. of electrode} \\ \times \text{size of salt bridge} \end{cases}$

### Reactivity

The more reactive a metal is, the more it wants to lose  $e^-$  to form a  $+ve$  ion. Thus, they'll have more  $-ve E^\circ$  (strongest reducing agent).

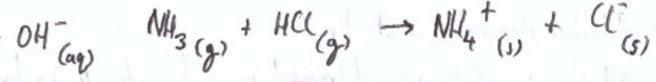
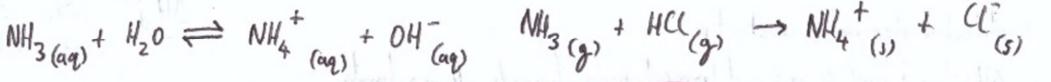
### Predicting Direction of Reactions

- Write 2 redox half-equations as reduction reactions.  $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$   $E^\circ = -0.76V$
- Work out which  $\frac{1}{2}$  equation is more  $-ve E^\circ$ .  $2MnO_4^{2-}(aq) + 2H_2O(l) + 2e^- \rightarrow MnO_4^{2-}(aq)$
- Write out  $\frac{1}{2}$  equation with:
  - more  $-ve E^\circ$  going in backwards direction (oxidation).
  - more  $+ve E^\circ$  going in forwards direction (reduction).
- Combine 2  $\frac{1}{2}$  equations, writing out full redox reaction.

This is the feasible direction, and will give a  $+ve E^\circ$ .

e.g.  $NH_3$  is Amphoteric base in  $H_2O$ ,

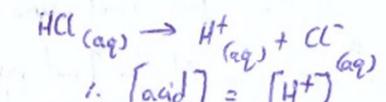
but only Bronsted-Lowry in  $HCl$



Calculating pH  $pH = -\log_{10}[H^+]$

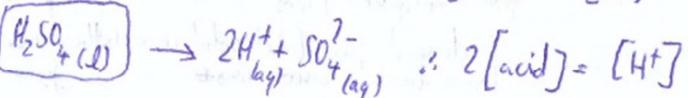
$\triangleright$  Strong Acids  $pH = -\log_{10}[H^+]$

Monoprotic - 1 molecule of acid releases 1 proton when dissociating



$$\therefore [acid] = [H^+]$$

Diprotic - 1 molecule releases 2 protons

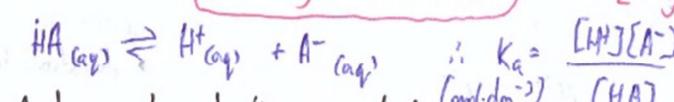


$$\therefore 2[acid] = [H^+]$$

$\triangleright$  Strong Bases  $pH = -\log_{10}\left(\frac{K_w}{[OH^-]}\right)$

Check if mono/di- protic, then use  $K_w$ .

$\triangleright$  Weak Acids  $pH = -\log\sqrt{K_a \cdot [acid]}$



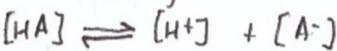
Acid is weak; only tiny amount dissociates.

$\therefore [HA] \approx [acid]$  and  $[H^+] \approx [A^-]$  all  $H^+$  comes from acid

$$K_a = \frac{[H^+][A^-]}{[HA]} \approx \frac{[H^+]^2}{[acid]} \Rightarrow [H^+] \approx \sqrt{K_a \cdot [acid]}$$

Buffer Action shampoos, biological washing powders

buffer - solutions that resist changes in pH when small amounts of acid / bases added.



$\begin{array}{l} \text{Add } H^+ \\ \text{equilibrium shifts L} \end{array}$

$\begin{array}{l} \text{Add } OH^- \\ \text{equilibrium shifts R} \end{array}$

$\begin{array}{l} \text{makes more } HA, \text{ uses } A^- \\ \text{uses up } H^+ \end{array}$

$\therefore$  good buffer needs lots of  $A^-$  to replenish

Acid is weak  $\therefore [HA] \approx \text{acid}$ ;  $[A^-] \approx \text{base}$

$$K_a = [H^+] \cdot \frac{[base]}{[acid]} \Rightarrow [H^+] = k_a \cdot \frac{n_{acid}}{n_{base}}$$

(conjugate pairs)



Given  $K_a$  values, smaller  $pK_a$  = stronger acid

Changes:  $n_{acid}$  added

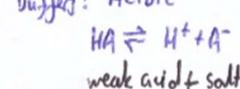
$\therefore \log_{10}(k_a \cdot \frac{n_{acid} + n_{base}}{n_{base}})$

MIXTURES	
strong acid	neutralisation, pH of excess
weak acid	weak base excess = buffer sol.

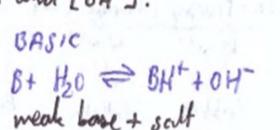
### Buffers Resist Dilution

Add more  $H_2O$ ,  $H_2O$  slightly dissociates. Pushed equally by  $[H^+]$  and  $[OH^-]$ .

Buffers: Acidic



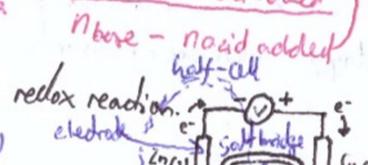
weak acid + salt



weak base + salt

Changes:  $n_{acid}$  added

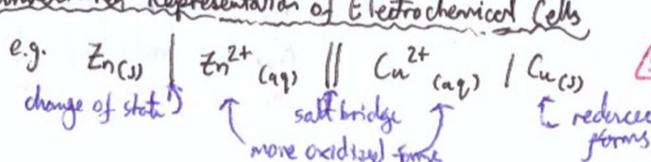
$\therefore \log_{10}(k_a \cdot \frac{n_{acid} + n_{base}}{n_{base}})$



After paper soaked in  $KNO_3(aq)$  v. soluble, high  $[KNO_3]$ , inert (muddy)

$\Delta$  always show state symbols

### Conventional Representation of Electrochemical Cells



change of state  $\uparrow$  salt bridge  $\downarrow$  reduced forms

STANDARD  $E^\circ$ : e.g.  $Pt(s) | H_2(g) | H^+(aq), || Sn^{2+}(aq) | Sn(s)$

always on left

e.g.  $Pt(s) | Cl^-(aq), OH^-(aq), ClO_4^-(aq), || NO_3^-(aq), H^+(aq) | NO(g) | Pt(s)$

Batteries - used as commercial source of electrical energy

NON-RECHARGEABLE (irreversible) for low-power gadgets, used for a short period of time

RECHARGEABLE (reversible) used in most modern electronics (e.g. phones)

FUEL CELLS alkaline, hydrogen-oxygen fuel cell used to power electrical vehicles

$E^\circ$  works  $\uparrow$   $V_{min}$  works  $\downarrow$   $t$

e.g. Zinc-Carbon dry cells  $V_{min}$  works  $\downarrow$   $t$

$Zn(s)$  and  $MnO_2(s)$  mix with  $H_2O$   $\rightarrow Li^+ | Li_2O_2 | e^-$

$\Delta Li \rightarrow Li^+ + e^-$

Also, Ni-Cd batteries. Reverse current for charge.

$\Delta O_2 + 2H_2O(l) + 4e^- \rightarrow 4OH^-$

$\Delta H_2O(l) + 2OH^- \rightarrow H_2O(l) + 2e^-$

overall:  $2H_2 + O_2 \rightarrow 2H_2O(l)$

Fuel Cells?

+ only waste product is  $H_2O$

+ don't need to be recharged as long as  $H_2/O_2$  supplied

=  $H_2$  production, not (neutral)

Transition Metals (ex. Sc/Zn) : d-block metals, that form ions/compounds w/ a partially-filled d-subshell.

Metals	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
oxidation state	+3	+2	+2	(+1)	+2	+2	+2	+2	+1	+2
		+3	+3	+2	(+3)	+3	+3	(+4)	+2	(+3)
		+4	+4	+3	+4	(+4)	+4	(+5)		
		+5	+6	+5	+6	(+5)	(+6)	(+6)		
						+7				

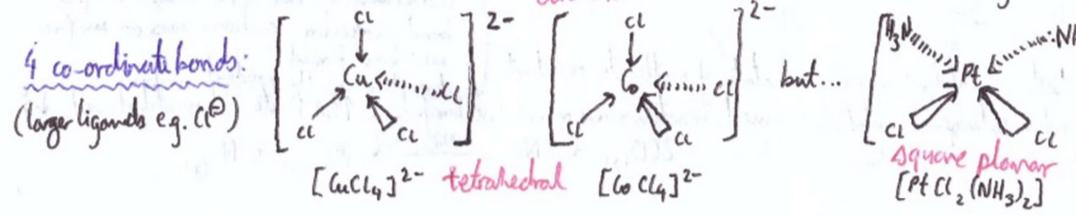
### Properties:

- high density / m + bp
- can form complexes
- can form colored compounds/ions
- good catalysts : exist in variable oxidation states

COMPLEX IONS: a central transition metal ion/atom surrounded by co-ordinately bonded ligands

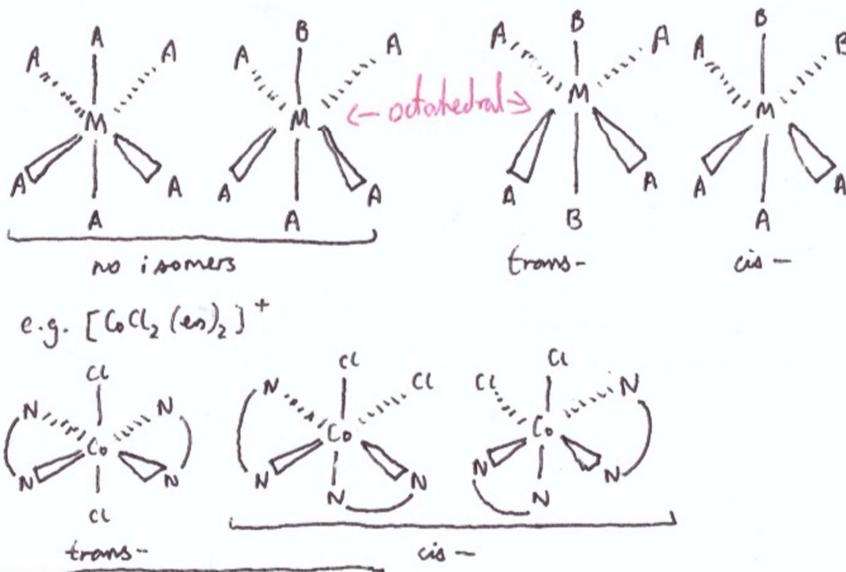
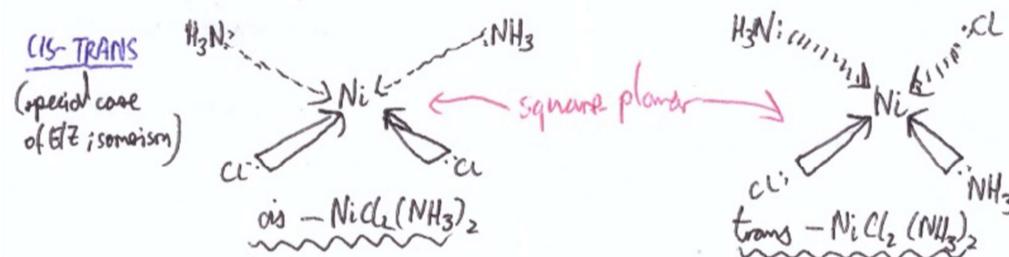
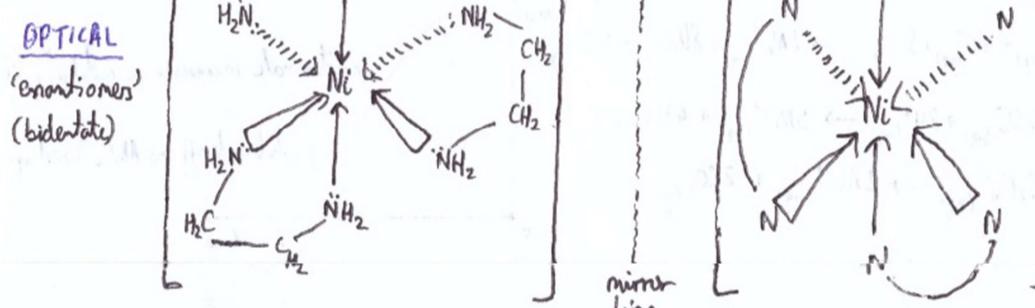
$$\text{Oxidation State of Metal Ion} = \frac{\text{Total Charge of Complex}}{\text{Sum of the Charges of the Ligands}}$$

2 co-ordinate bonds:  $[H_3N : \rightarrow Ag \leftarrow :NH_3]^{\oplus}$  linear



6 co-ordinate bonds: (smaller ligands e.g.  $H_2O$ ,  $NH_3$ )  $[Cu(H_2O)_6]^{2+}$  octahedral

ISOMERISM - specifically stereoisomers



### SOLUTIONS & PRECIPITATES

	initial (aq)	initial NaOH(aq)	excess NaOH(aq)	initial NH3(aq)	excess NH3(aq)	conc. HCl
Cr <sup>3+</sup> green	green gel ppt.	green gel ppt.	dark green sol.	green sol. ppt.	dark green sol.	
Mn <sup>2+</sup> v. pale pink	v. pale pink	white ppt.	white ppt.	Mn(OH) <sub>2</sub>	Mn(OH) <sub>2</sub>	
Fe <sup>2+</sup> pale-green	pale-green	dark green ppt.	brown or Eo	dark green ppt.	no further reaction	
Fe <sup>3+</sup> yellow-brown	yellow-brown	brown gel ppt.	Fe(OH) <sub>3</sub>	brown gel ppt.	no further reaction	
Co <sup>2+</sup> pink	pink	blue gel ppt.	blue gel ppt.	Co(OH) <sub>2</sub>	dark brown sol. blue/brown	
Ni <sup>2+</sup> green	green	green gel ppt.	Ni(OH) <sub>2</sub>	green gel ppt.	dark pink/blue sol.	
Cu <sup>2+</sup> blue	blue	blue gel ppt.	Cu(OH) <sub>2</sub>	blue gel ppt.	deep blue sol. yellow-green	
Zn <sup>2+</sup> colourless	colourless	white gel ppt.	Zn(OH) <sub>2</sub>	white gel ppt.	clear colourless sol.	
Al <sup>3+</sup> colourless	colourless	white gel ppt.	Al(OH) <sub>3</sub>	Al(OH) <sub>3</sub>	white gel ppt.	

Co-ordination Number: # of dative bonds w/ transition metal ions

### Transition Metals Electron Configuration

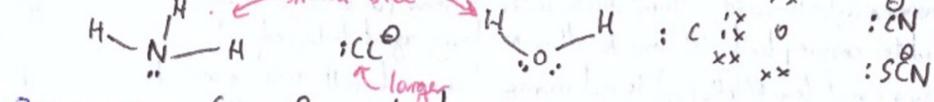
- fill up lowest energy subshell first (ex. half subshell stability of Cr/Cu)
- fill orbitals singly, before sharing

- for ions, remove e<sup>-</sup> from t<sub>2g</sub> orbital first
- then remove from 3d based on ion charge

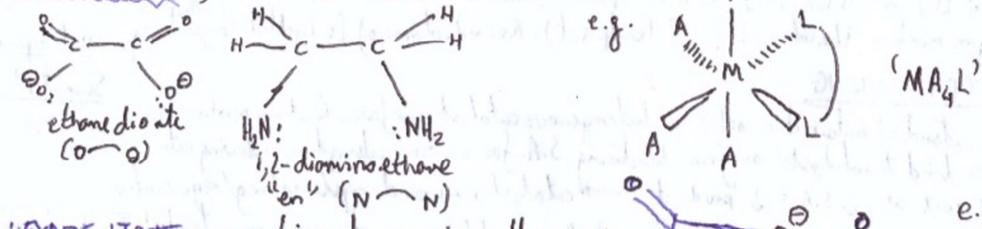
LIGAND: a molecule/ion that forms a co-ordinate bond with a transition metal by donating a pair of electrons

### TYPES OF LIGANDS

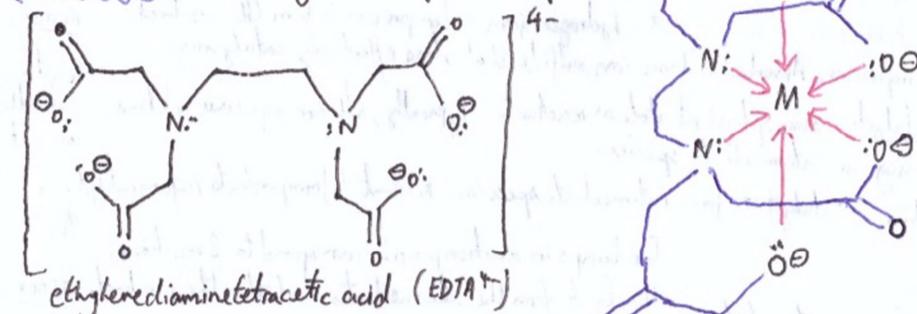
exchange of  $NH_3/H_2O$  ligands retains co-ordination # exchange of  $H_2O$  by Cl can cause change



BIDENTATE: forms 2 co-ordinate bonds

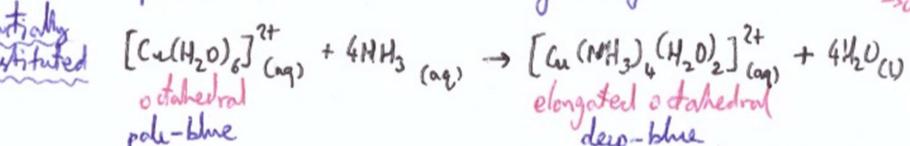
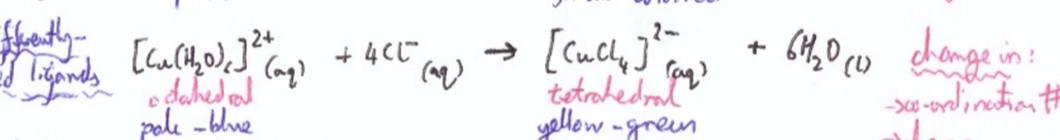
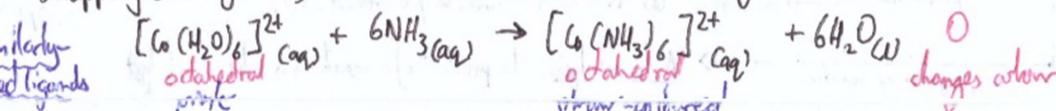


HEXADENTATE: one ligand occupies all spaces

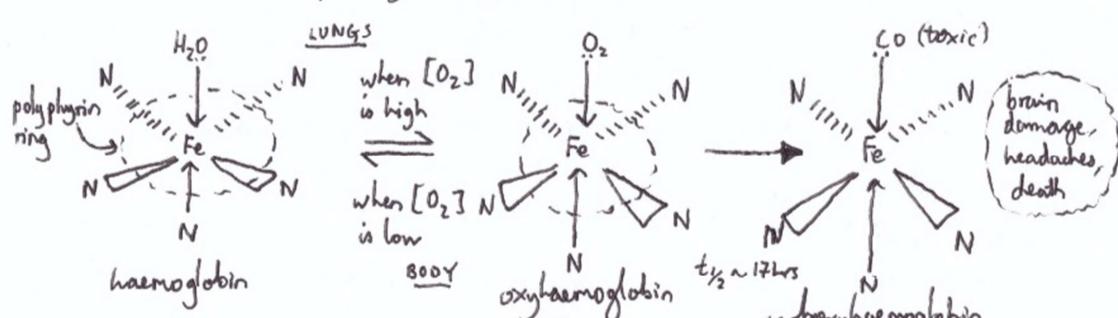


### LIGAND SUBSTITUTION

Swapping one ligand for another. Results in a colour change.

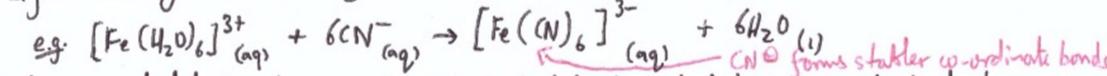


HAEMOGLOBIN: protein found in blood that transports O<sub>2</sub> around body. Contains Fe<sup>2+</sup> ions. It's an iron (II) complex w/ a multidentate ligand (porphyrin). These are the 4 N atoms that donate e<sup>-</sup> to form a circle around the Fe<sup>2+</sup>.

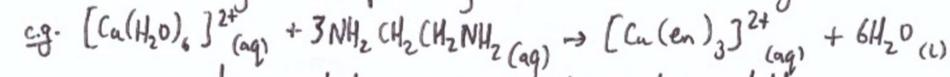


### CHELATE EFFECT

Ligand exchange reactions easily reversible, unless new complex is much stabler.

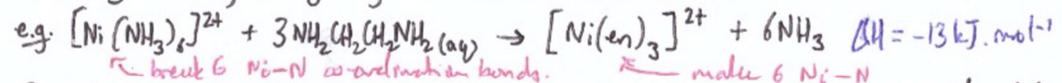


When monodentate ligands are replaced by bidentate/hexameric ligands, it's harder to reverse.



ΔS increases as ratio of particles is 4:7, so latter complex is stabler.

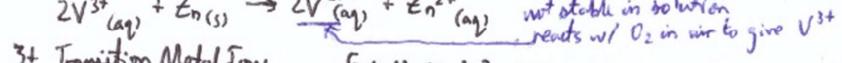
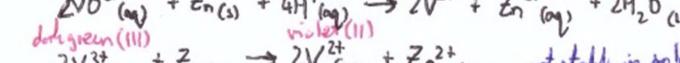
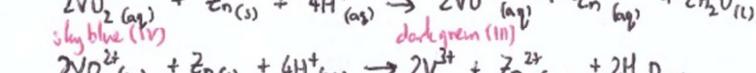
ΔH usually v. small; strength of bonds broken > bonds made.



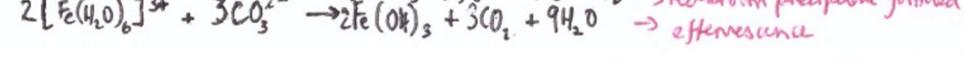
break 6 N≡N co-ordination bonds.

make 6 Ni-N co-ordination bonds.

Sequential Reduction of Vanadium - reduction of vanadate (V) vary by zinc in acidic solution



### 3+ Transition Metal Ions



⚠️ Incomplete d-subshell leads to coloured compounds.

## Redox Potentials - how easily atom/ion is reduced to a lower oxidation state

More the redox potential = more unstable ion = more likely to be reduced

redox potential ≠ electrode potential (varies based on environment i.e. in)

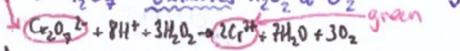
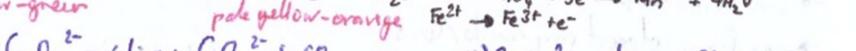
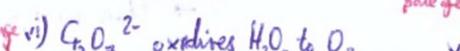
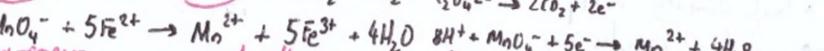
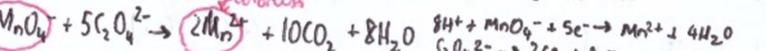
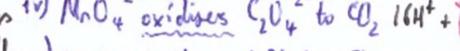
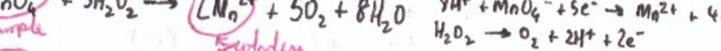
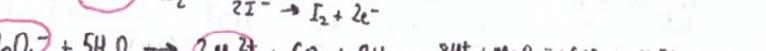
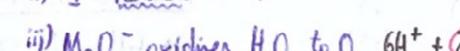
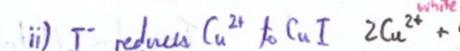
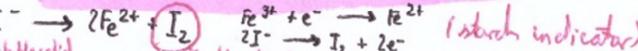
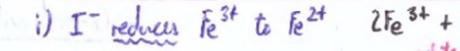
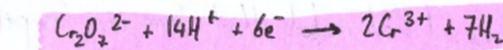
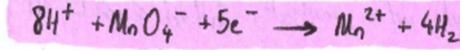
Affected by: o ligands: E° measured is (aq) anion surrounded by water ligands.

Different ligands make redox potential ↑ or ↓ based on how well they bind to metal in oxidation state.

o pH: some ions need H<sup>+</sup> ions present to be reduced (e.g. 2VO<sup>3+</sup>). Others

release OH<sup>-</sup> ions when reduced (e.g. CrO<sub>4</sub><sup>2-</sup>). Redox potential (generally) increases with increasing pH.

## REDOX IN TRANSITION METALS



## Titration - how much [O] is needed to react w/ [H].

→ If you know [O/H], you can work out [H/O].

→ Variable oxidation states; often present in either oxidising/reducing agent.

→ Colour changes: easy to spot endpoints. e.g. [MnO<sub>4</sub>]<sup>-</sup> must be excess to avoid error in titration.

1 Measure quantity of reducing agent (e.g. Cr<sup>2+</sup>) using pipette. Put into conical flask.

2 Using measuring cylinder, add ~20cm<sup>3</sup> dilute H<sub>2</sub>SO<sub>4</sub> to flask (in excess: not exact).

Acid added to ensure plenty H<sup>+</sup> ions to allow oxidising agent to be reduced.

3 Add oxidising agent (e.g. KMnO<sub>4</sub>) to reducing agent using a burette, swirling conical.

4 Added [O] reacts w/ [H]. Reaction continues until all [H] used up. Next drop will give mixture the color of [O] (endpoint). Record volume of [O] added. (concrecency).

## CATALYST POISONING → stuck to surface

Reactants adsorbed onto active sites on heterogeneous catalyst surface. Reaction mixture's impurities bind to catalyst's surface blocking S.A. for reaction adsorption: slowing rate.

→ ↑ cost as ↓ S.A. = ↓ product → catalyst may need replenishing/regenerating

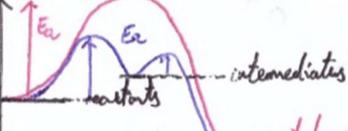
o Pb poisons catalytic converter's catalyst - vehicles w/ catalytic converters must use unleaded

o S poisons Haber process iron catalyst - hydrogen from Haber process is from CH<sub>4</sub> → natural gas w/ S impurities. Absorbed S forms iron sulfide that stops effectively catalysing.

Homogeneous Catalysts - same physical state as reactants. Typically, all are aqueous solutions.

Works by forming an intermediate species.

1 Reactants combine w/ catalyst to form intermediate species. 2 Reactant to form products / reform catalyst.



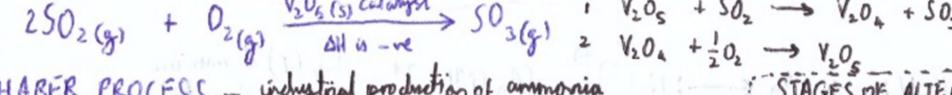
Two bumps in reaction profile correspond to 2 reactions: the Ea to form the intermediates, and then the product.

Catalyst always reformed so can carry on catalysing the reaction (unless poisoned ☹).

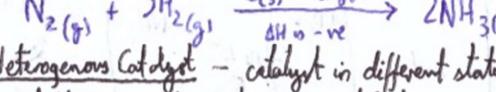
Auto-catalysis: the product of a reaction is also a catalyst

CATALYSTS - transition metals (and compounds) make good catalyst because they can gain/lose e<sup>-</sup> within their d-orbitals, with multiple stable oxidation states. ∴ transfer e<sup>-</sup> to speed up reactions.

CONTACT PROCESS - industrial production of H<sub>2</sub>SO<sub>4</sub>. V<sub>2</sub>O<sub>5</sub> catalyses the reaction in 2 steps.



HABER PROCESS - industrial production of ammonia



STAGES OF ALTERNATIVE ROUTE

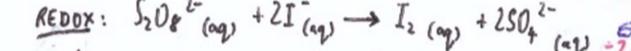
- 1 reactants adsorbed onto metal catalyst surface
- 2 bond weakening, reaction occurs on surface
- 3 new bond formed

Heterogenous Catalyst - catalyst in different state of matter to reactants

Support Medium - when heterogenous catalysts are used, reaction occurs on catalyst surface. ∴ PS.A ↑ rate = less catalyst need = ↓ \$

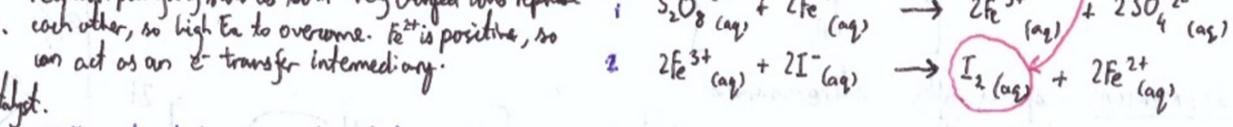
e.g. Catalytic Converters use a thin layer of rhodium. 2CO<sub>(g)</sub> + 2NO<sub>(g)</sub>  $\xrightarrow{\text{Rh catalyst}}$  2CO<sub>2(g)</sub> + N<sub>2(g)</sub>

Fe<sup>2+</sup> catalysing reaction between S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and I<sup>-</sup>  $\xrightleftharpoons{-2O^{2-}}$  test by adding starch solution (blue-black)

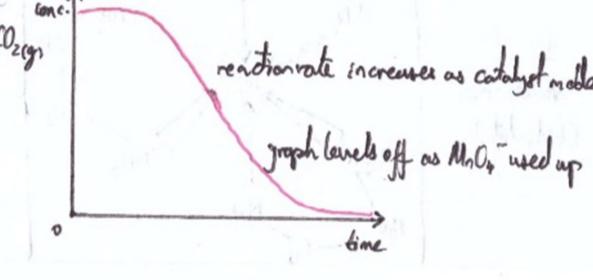
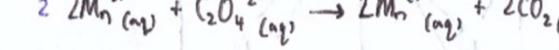
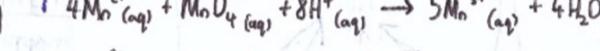
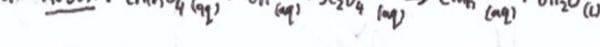


Reaction painfully slow as both -vely charged ions repel each other, so high Ea to overcome. Fe<sup>2+</sup> is positive, so

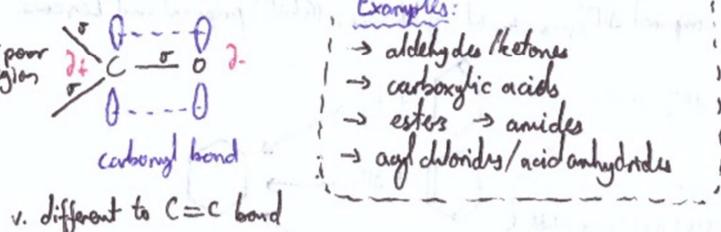
can act as an e<sup>-</sup> transfer intermediary.



Mn<sup>2+</sup> autocatalysing reaction between MnO<sub>4</sub><sup>-</sup> and CrO<sub>4</sub><sup>2-</sup>

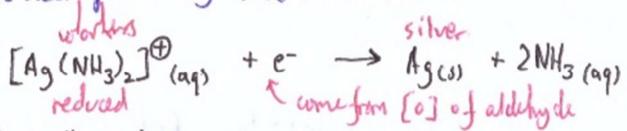


## Carbonyl Compounds



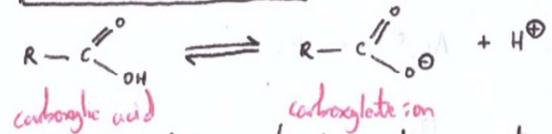
## TESTING ALDEHYDES & KETONES

Tollens' Reagent: colorless solution of  $\text{AgNO}_3$  dissolved in  $\text{NH}_3(\text{aq})$ . When heating a t.e. w/ an aldehyde, a silver mirror forms. As aldehyde is oxidised, the diamine/silver ions in Tollens' reagent are reduced producing silver and ammonia.



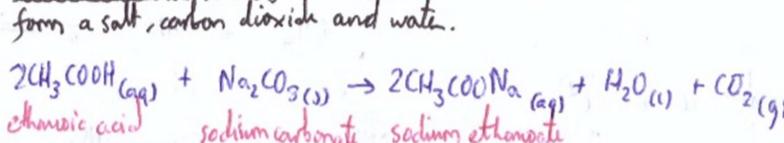
Ketone's don't react.

## CARBOXYLIC ACIDS

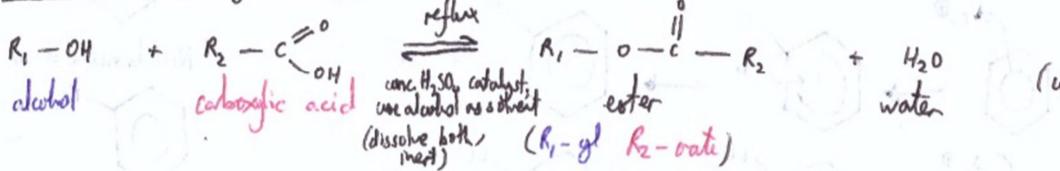


Equilibrium lies left as carboxylic acids are weak.

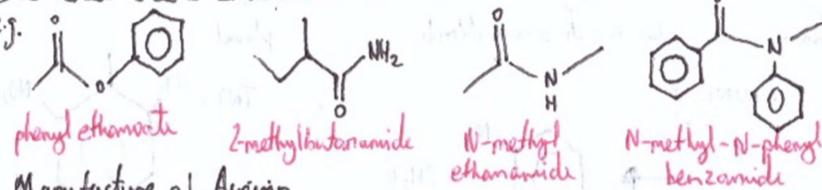
## Reaction w/ Carbonates



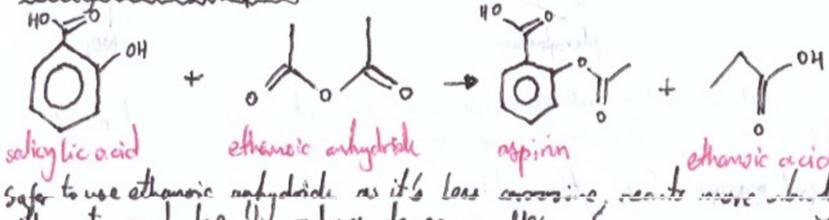
## Reaction w/ Carboxylic Acids



## REACTANTS



## Manufacture of Aspirin



REFUX - boiling in hottest possible

DYING AGENT - anhydrous salt (e.g.  $\text{CaH}_2/\text{MgSO}_4$ ) that is inert. Binds to water to be hydrated w/ter mixture to remove solid drying agent.

WASHING - remove unwanted side-product/reagent. (e.g.  $\text{NaHCO}_3(\text{aq})$  removes acid, forms insoluble salt).

RECRYSTALLISATION - purifies solid organic product. Add v. hot solvent to impure solid until just dissolved. This gives saturated solution of impure product.

Leave crystals to cool slowly. Impurities stay in solution in much smaller amounts so take much longer to crystallise out. Remove crystals by

filtration, wash w/ ice-cold solvent, then dry.

TESTING PURITY - put small sample in glass capillary tube in m.-point apparatus. Pure will have  $\pm 2^\circ\text{C}$  range, similar to known sample.

FILTER UNDER REDUCED PRESSURE - use Büchner funnel

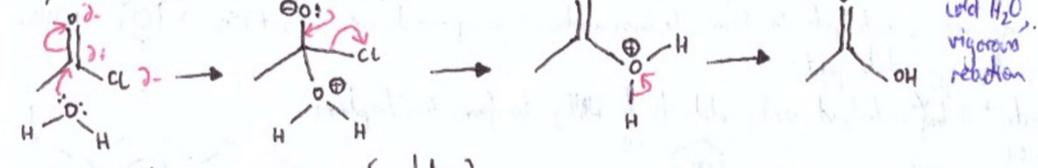
## ACYL CHLORIDES

e.g. benzoyl chloride

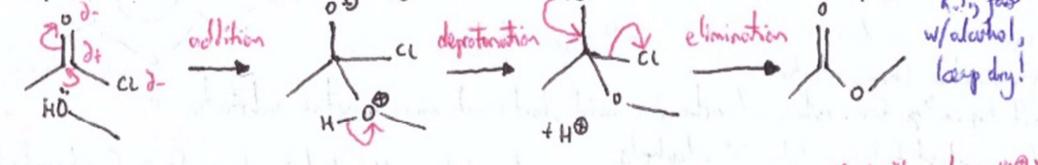
- Very, very reactive! ∵ not good selectivity
- At room temperature and fast.
- Don't want  $\text{HCl}$ , o/w strong acid protonates amide produced ∵ keep dry!
- Rubbish atom economy

## Nucleophilic Addition - Elimination

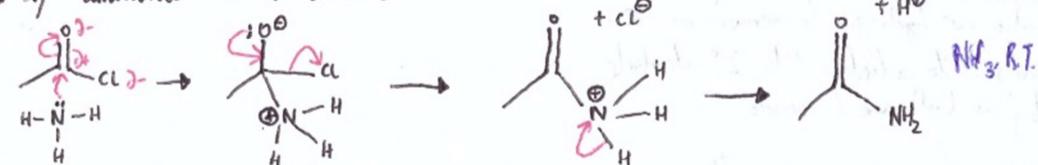
→ w/ cold  $\text{H}_2\text{O}$  → carboxylic acids



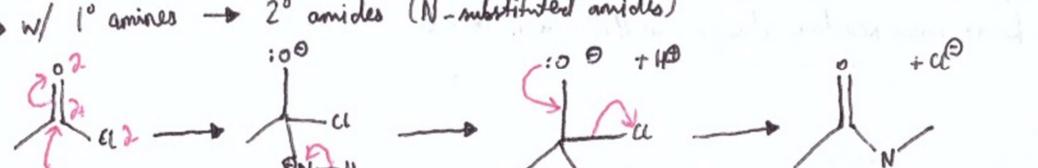
→ w/ alcohols → esters (acylation)



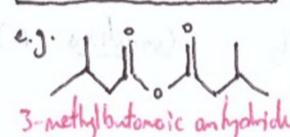
→ w/ ammonia → 1° amides



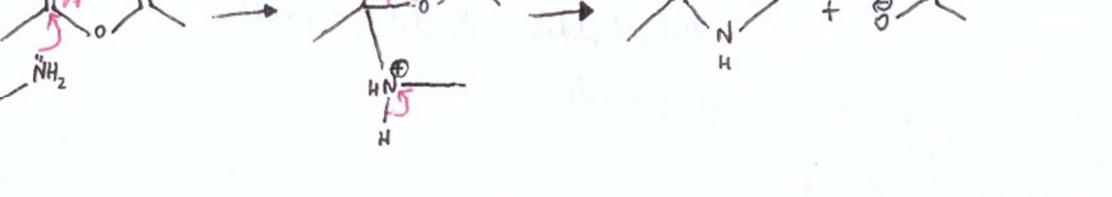
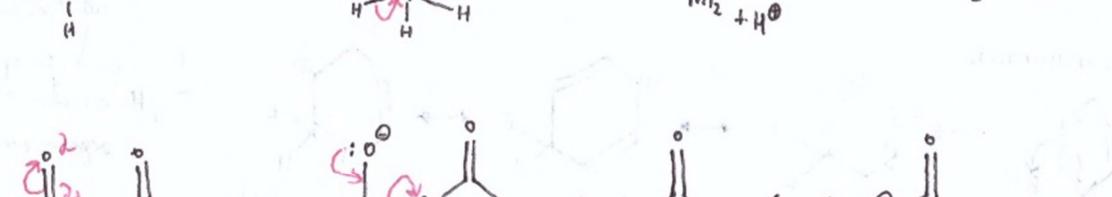
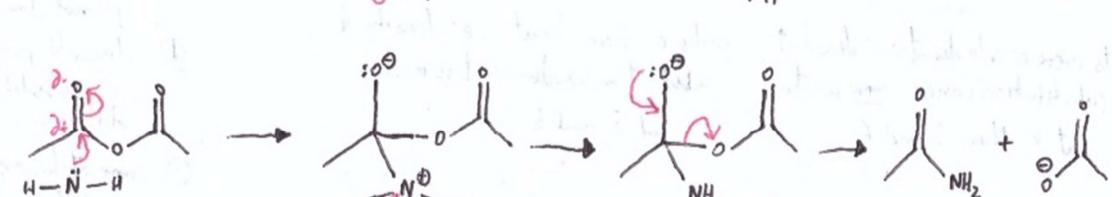
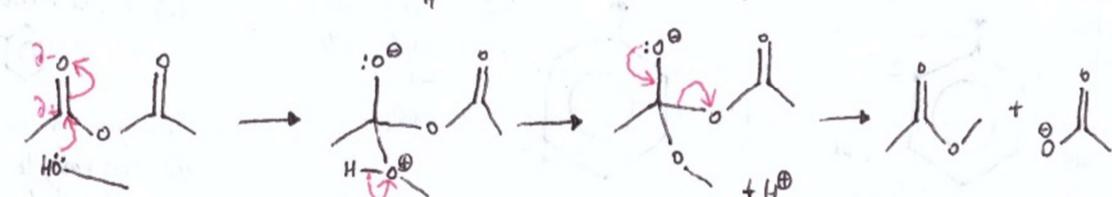
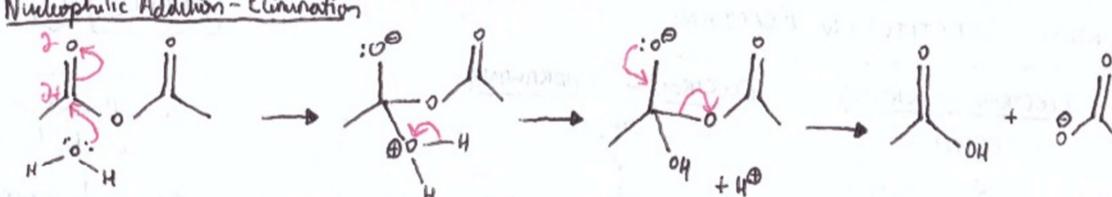
→ w/ 1° amines → 2° amides (N-substituted amides)



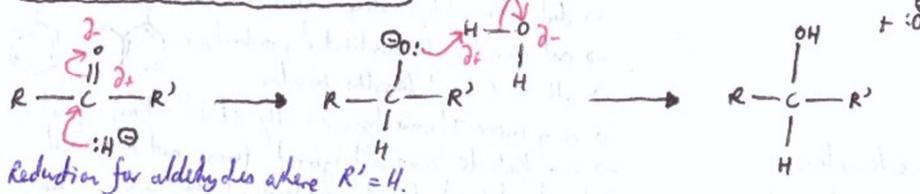
## ACID ANHYDRIDES



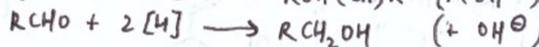
## Nucleophilic Addition - Elimination



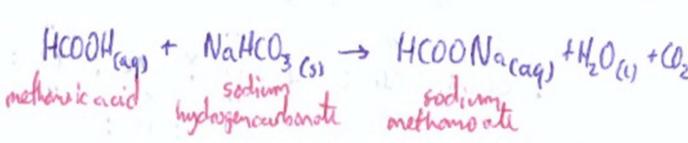
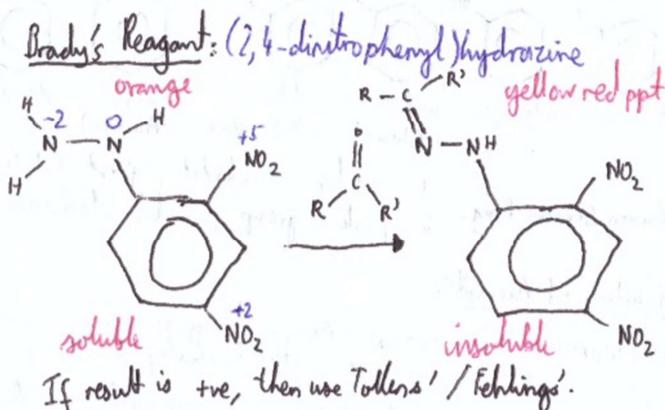
## REDUCING ALDEHYDES/KETONES



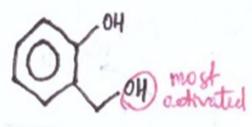
Reduction for aldehydes where  $\text{R}' = \text{H}$ .



- $\text{NaBH}_4$  (sodium borohydride) dissolved in water w/ methanol
- $\text{LiAlH}_4$  (lithal) in non-aqueous solvent



(condensation)



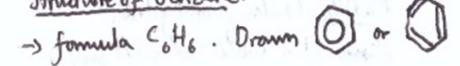
→ Much milder; more reactive than  $\text{-COCl}$ , but less than acyl chloride

→ Some selectivity (chooses most activated  $-\text{OH}$ )

→ Close to 100% atom economy - side product is weak acid ( $\text{-COOH}$ ) that can be recycled to make more anhydride

## Aromatic Chemistry

### Structure of Benzene:

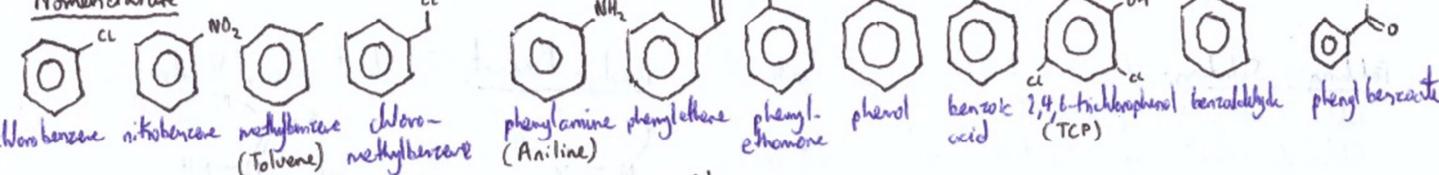


→ planar cyclic structure w/ delocalized ring of  $e^-$

: final unpaired  $p\pi$ -orbitals above and below plane

→ same bond length (140 pm) between  $C-C$  (147 pm) and  $C=C$  (135 pm)

### Nomenclature



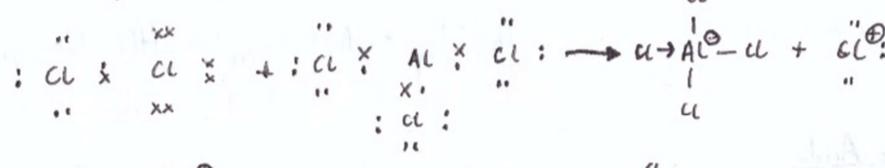
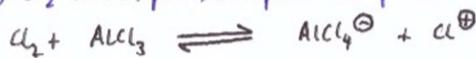
1. number C skeleton first (1 to 6)

2. pick a group, number clockwise or anticlockwise, whichever sums to give smallest number

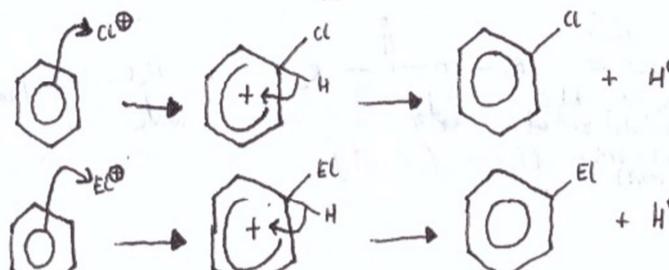
### Reaction of Aromatics

ELECTROPHILIC SUBSTITUTION: Benzene ring is area of high  $e^-$  density. Conditions much tougher than w/ alkenes as so attracts electrophiles ( $e^-$ -pair acceptors). delocalized system makes benzene more stable, less reactive.

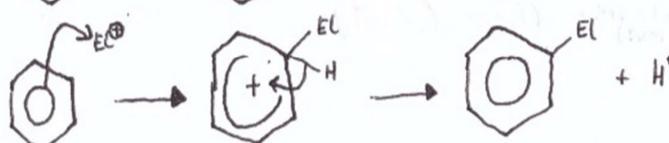
1 (halogenation only)  $Cl_2$  is non-polar, so a poor electrophile. Anhydrous  $AlCl_3$  acts as catalyst.



2 (halogenation)



(general)



3 (halogenation only)  $H^\oplus$  ion removed from benzene ring reacts w/  $AlCl_4^\ominus$ , regenerating  $AlCl_3$

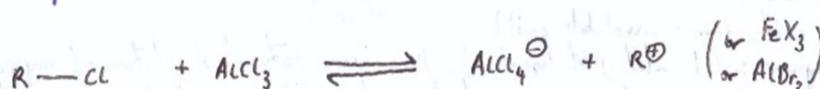


### FRIEDEL-CRAFTS REACTIONS

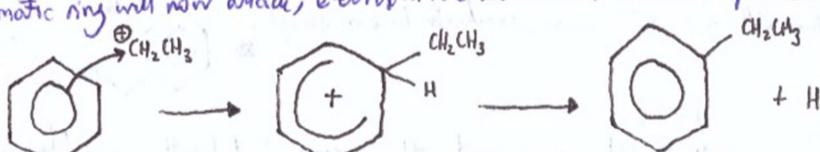
#### (フリーデルクラフツ)

ALKYLATION - substitution of alkyl groups (e.g.  $CH_3$ ,  $C_2H_5$ ,  $C_3H_7$ , etc.)

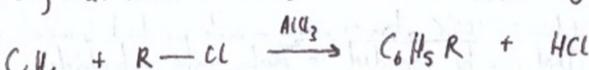
anhydrous  $AlCl_3$  acts as a Lewis acid catalyst, except...  
b.p. to make up its octet.  $Cl^\oplus$  is attracted by  $AlCl_3$  making  $C-Cl$  more polar,



Aromatic ring will now attack; electrophilic substitution will take place.



Conditions:  $R_2Ti$ , dry inert solvent (ether), haloalkane ( $R-X$ ), anhydrous  $AlCl_3$

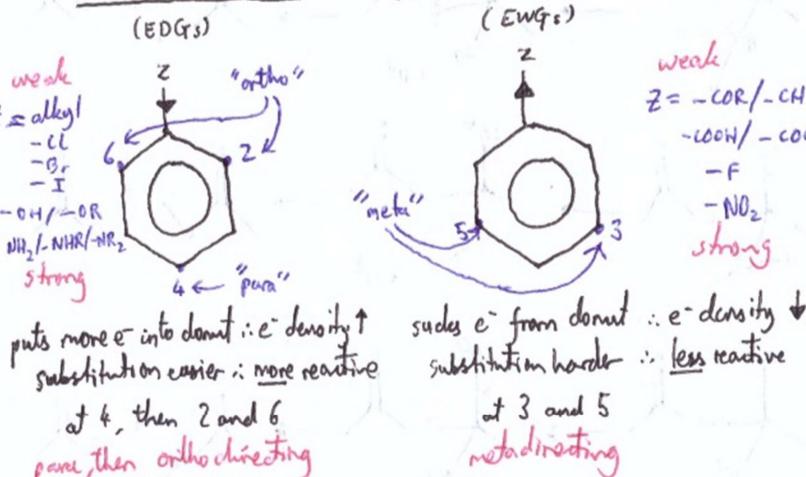


### FURTHER SUBSTITUTION REACTIONS

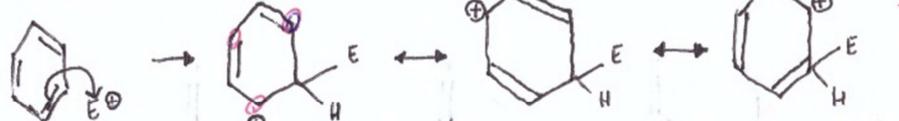
#### (さらなる代替)

##### ELECTRON-DONATING (EDGs)

##### ELECTRON-WITHDRAWING (EWGs)



### EXPLANATION

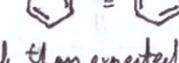
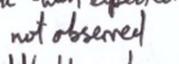


EDGs stabilize 2,4,6 intermediates. EWGs destabilize 2,4,6; but 3,5 is stable.

The functional group already on the ring affects:

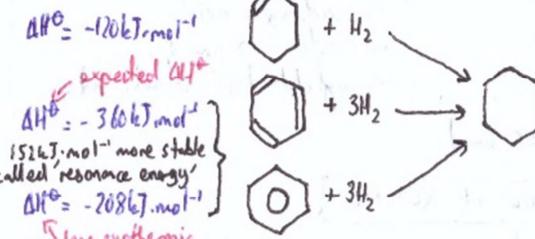
- ease of substitution
- position of next substituent

### Kekulé's (Bad) Model:

- did not readily undergo electrophilic addition (not true  $C=C$ )
- only one 1,2-disubstituted product i.e.  = 
- all  $C-C$  bond lengths similar
- ring more thermodynamically stable than expected
- two Kekulé resonant hybrid forms not observed
- sharply-defined, fixed bond lengths (would be blurry when X-ray diffracted)

### Stability of Benzene:

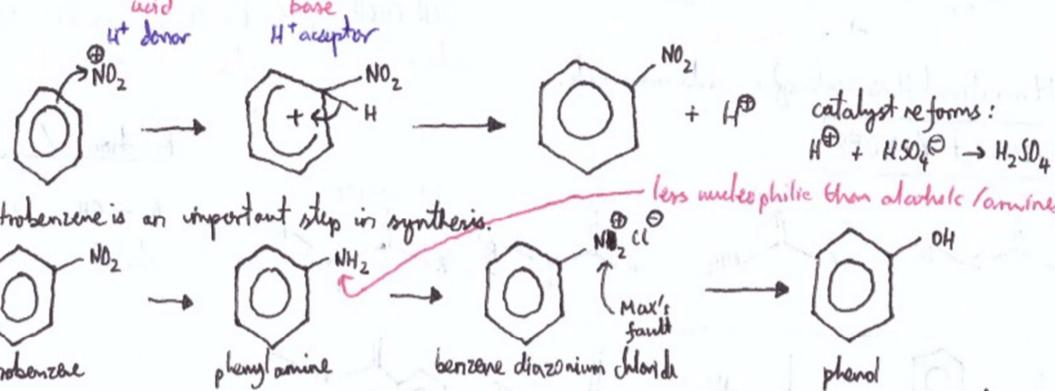
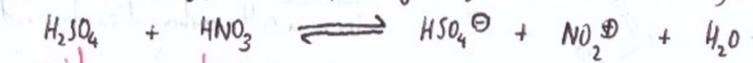
Benzene far more stable than Kekulé's cyclohexa-1,3,5-triene  
Compared  $\Delta H^\circ$  hydrogenation of cyclohexene, Kekulé's proposal and benzene



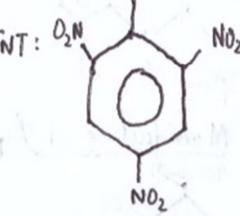
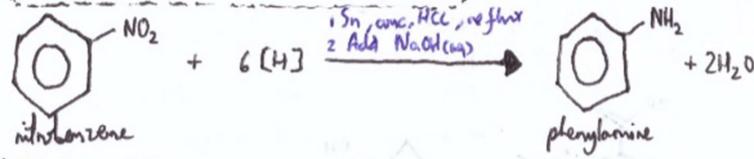
Breaking bonds is endothermic; making bonds is exothermic.  
∴ more E to break bonds in  than  ∴ benzene is stable  
In delocalized ring,  $e^-$  density shared over more atoms ∴ E of molecule lowered

NITRATION: special electrophilic substitution - first step in historically important chain of reactions to make dyes/explosives

Conditions: conc.  $HNO_3$ , conc.  $H_2SO_4$  catalyst, reflux at  $55^\circ\text{C}$  ( $< 55^\circ\text{C}$  for mononitration)

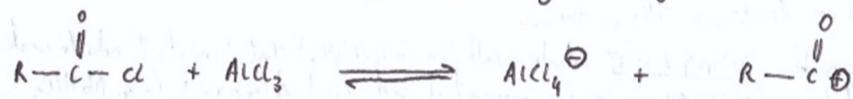


### FORMATION OF AROMATIC AMINES:

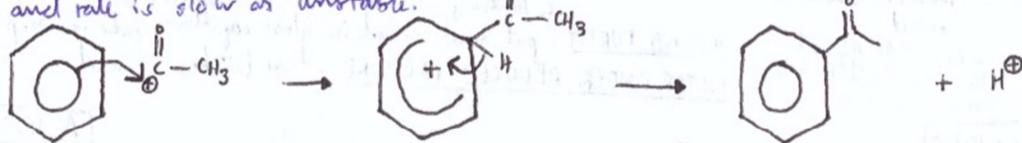


Electrophilic substitution of benzene rings. Catalyst needed as attacking species isn't strong enough electrophile. It doesn't have enough character to react w/ benzene. Haloalkanes/acyl chlorides are polar but C isn't b+ enough.

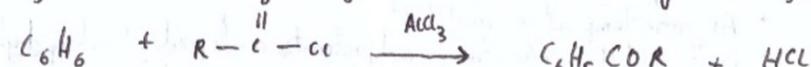
ACYLATION - substitution of acyl groups (e.g. ethylbenzene)



The acyl carbocation is stabilised so this reaction is more reliable than alkylation. Ketones can be easily converted to other functional groups. Alkylation cannot rearrange its carbocation so sublim. yield, and rate is slow & unstable.



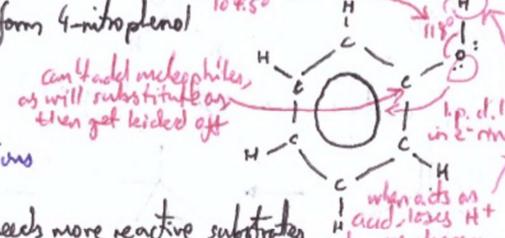
Conditions: R.T., dry inert solvent (ether), acyl chloride ( $R-C(=O)-Cl$ ), anhydrous  $AlCl_3$ , reflux  $50^\circ\text{C}$



### PHENOL

The lone pair on oxygen can delocalise into the benzene ring (which is v. activated). This has several effects:

1. Benzene ring  $\pi$  system now has way more  $e^-$  so is attracted to electrophiles  
① will react w/  $Br_2$  w/o a catalyst to form tribromophenol compound, i.e.  $\begin{array}{c} OH \\ || \\ \text{benzene ring} \\ || \\ Br \end{array} + 3Br_2 \rightarrow \begin{array}{c} OH \\ || \\ \text{benzene ring} \\ || \\ Br \\ | \\ Br \end{array} + 3HBr$   
② decolorises  $Br_2$  (aq), white ppt.
- ③ can be mononitrated by catalyst, only cold, dilute  $HNO_3$  to form 4-nitrophenol  
④  $\begin{array}{c} OH \\ || \\ \text{benzene ring} \end{array} + HNO_3 \rightarrow \begin{array}{c} OH \\ || \\ \text{benzene ring} \\ || \\ NO_2 \end{array}$



2. Lone pair on oxygen is now less available to other reactions

- ① less easy to form esters than alcohols  
phenol doesn't typically form esters w/ carboxylic acids, but needs more reactive substrates
- ② doesn't perform substitutions like 3° alcohols  
no substitution at the OH w/ nucleophiles - no nucleophiles attracted to it as it's on C absorbed by delocalized ring; also no hydrogen to remove on C.
- ③ cannot be oxidised to a ketone like 2° alcohols  
no H nearby as both are C bonds

3. Lone pair is spread out among many atoms

- ④ pH in water ~4.5, more acidic than most alcohols. Turns blue litmus red, but doesn't react w/  $Na_2CO_3$ .  
∴ oxygen can house more negative charge, so H is easier to lose.