# IMPORTANT!!!

leggo

FACTORS affecting strength of diff kinds of BONDS

Date No.

## A. Covalent Bond strength

1. no. of bonds between atoms

↑ no. of bonds → ↑ no. of shared electrons → ↑ electrostatic attraction between bond pairs and two nuclei → ↑ bond strength

2. size of atom

↑ size of bonding atom → ↑ orbital size → valence orbital more diffuse → overlap of orbitals less effective → ↓ bond strength

3. difference in electronegativity

↑ difference in electronegativity of bonded atoms → ↑ electrostatic attraction between bonding electrons and nuclei → ↑ bond strength

4. Hybridisation, 's' character of hybrid orbital

↑ 's' character (ie. $sp^3 \rightarrow sp^2 \rightarrow sp$) → 's' orbital spherical, electrons closer to nucleus → overlap of orbitals more effective → ↑ bond strength

## * B. Ionic bonds with COVALENT CHARACTER

* can use interchangeably

1. charge density of cation i.e. $|\frac{q}{r}|$

↑ charge, ↓ size → ↑ polarising power on anion → ↑ distortion → ↑ covalent character

2. size of anion

↑ charge, ↑ size → ↑ polarisability → ↑ distortion of electron cloud → ↑ covalent character

ionic — $AlF_3$ — $Al_2O_3$ — $AlCl_3$ — $AlBr_3$ — covalent

## * C. Covalent bonds with IONIC CHARACTER (polar covalent bond)

↑ difference in electronegativity of bonding atoms → ↑ bond dipole moment → more polar if net dipole moment is not zero / dipole moments do not cancel each other out

## D. Id-id interactions (instantaneous — induced)

1. no. of electrons / electron cloud size

↑ no. of electrons / electron cloud size → ↑ polarisability / distortion → ↑ strength of id-id interactions

2. surface area for molecular interaction

↑ surface area → ↑ id-id interactions (straight chained vs branched)

*boiling/melting points involve breaking of IMF and NOT covalent bonds

E. **pd-pd interactions**

polar molecules have both pd-pd and id-id interactions, stronger IMF than just id-id in non-polar compounds. However, ↑no. of electrons → ↑id-id will still be predominant factor

F. **Hydrogen bonding**

proximity of electron deficient H and F/O/N atom with lone pair

- if near enough → intra-molecular bonding → less sites available for intermolecular bonding → less extensive intermolecular H-bonding *

G. **Ionic Bond strength** => lattice energy

1. lattice energy $\propto \left|\frac{q^+ \cdot q^-}{r^+ + r^-}\right|$

i) higher charge → greater electrostatic attraction between ions

ii) smaller radius → shorter distance between ions → ↑ attraction

H. **Metallic Bond Strength** => charge density

1. no. of valence electrons available for bonding

↑no. of valence $e^-$ → ↑ no. of delocalised $e^-$ → ↑ electrostatic FOA between positive ions and $e^-$

2. size of cation

↓ size → ↑ charge density → ↑ attraction for delocalised $e^-$

↓ bond strength
↓ energy of overlap of less valence orbitals
↑ valence orbitals more diffuse

covalent – no. of bonds, → no. of shared electrons ↑ attraction btw bond pairs, ↑ diff in electro, ↑ size, ↑ orbital

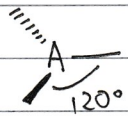
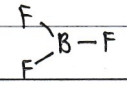
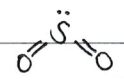
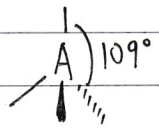
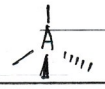
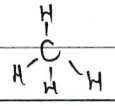
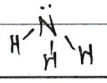
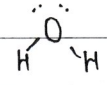
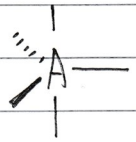
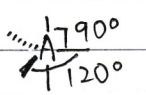
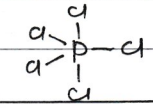
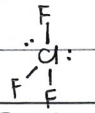
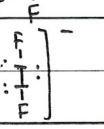
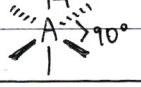
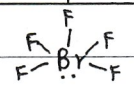
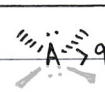
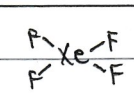
* 2) lone pair of $e^-$ : $e^-$ deficient H ratio => $H_2O$ > $NH_3$ or HF

$H_2O$: 2 l.p., 2H ; $NH_3$: 1 l.p., 3H ; HF: 3 l.p., 1H

3) Electronegativity : F > O > N

# VSEPR THEORY

Date. No.

| no. of regions of e⁻ density | electron-pair geometry | no. of lone pairs | molecular geometry | examples | bond angle |
|---|---|---|---|---|---|
| 2 | linear   | 0 | linear   | $BeCl_2$ Cl-Be-Cl<br>$CO_2$ O=C=O | 180° |
| 3 | trigonal planar   | 0 | trigonal planar   | $BF_3$   | 120° |
| | | 1 | bent   | $SO_2$   | <120° |
| 4 | tetrahedral   | 0 | tetrahedral   | $CH_4$   | 109° |
| | | 1 | trigonal pyramidal   | $NH_3$   | 107° |
| | | 2 | bent   | $H_2O$   | 105° |
| 5 | trigonal bipyramidal   | 0 | trigonal bipyramidal   | $PCl_5$   | 90° or 120° |
| | | 1 | seesaw   | $SF_4$   | N.A. |
| | | 2 | T-shape   | $ClF_3$   | 90° |
| | | 3 | linear   | $IF_2^-$   | 180° |
| 6 | octahedral   | 0 | octahedral   | $SF_6$   | 90° |
| | | 1 | square pyramidal   | $BrF_5$   | N.A. |
| | | 2 | square planar   | $XeF_4$   | 90° |

σ is normal bond, π is the special bond

tetrahedral – $sp^3$

trigonal planar – $sp^2$

linear – $sp$

* $\dot{C}H_3$ is $sp^2$ hybridised, but $\dot{C}F_3$ is $sp^3$ hybridised.

# EXPERIMENTAL TECHNIQUES TO MONITOR CONCENTRATION

Date. No.

A) Sampling (quenching + titration)

1. The reactants are mixed and the stopwatch is started simultaneously.
2. Aliquots of the reactant mixture are withdrawn and quenched at regular time intervals (eg. 2 mins) using excess $(KI(aq))$. $(I^-)$ reacts with $(MnO_4^-)$ instantaneously and quantitatively to form $(I_2)$.
3. The amount of $(I_2)$ found in each aliquot is found by titrating against standard $(Na_2S_2O_3(aq))$.
4. Plot a graph of volume of $(Na_2S_2O_3(aq))$ → titrant against time, which is similar to a graph of $([MnO_4^-])$ against time. (volume $Na_2S_2O_3(aq)$ ∝ amount of $I_2$ formed ∝ amount of unreacted $MnO_4^-$ ∝ $[MnO_4^-]$ remaining)
5. Instantaneous rate is found by drawing a tangent to the curve and finding its gradient $g_1$, where rate = $-g_1$.

*with $H_2O_2$, use large volume of cold water, titrate with standard acidified $KMnO_4$.

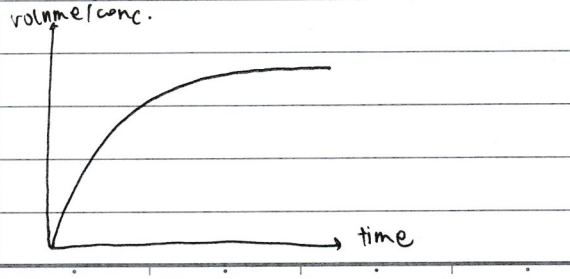
* cold water is added to halt the reaction so that the composition of the mixture in the aliquot does not change anymore

*with ester, use cold water, titrate with NaOH.

B) Colourimetry

1. $(MnO_4^-)$ is violet. since colour intensity ∝ $([MnO_4^-])$, change in colour intensity of $MnO_4^-$ over time may be used to determine rate of reaction.
2. Colour intensity is measured with a colourimeter at regular time intervals.
3. Samples of $(KMnO_4)_{(aq)}$ of various concentrations e.g. 0.001, 0.005, 0.010 $moldm^{-3}$ are prepared, with their colour intensities measured. A calibration curve is obtained by plotting colour intensity against concentration. The concentration of $(KMnO_4)$ corresponding to each colour intensity obtained in 2. is found using the calibration curve. $[KMnO_4]$ is plotted against time.
4. Instantaneous rate is found by drawing a tangent to the curve and finding its gradient $g_1$. rate = $-g_1$.

Graph for A & B:



Date. No.

C) volume method.

$2H_2O_{2(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$

1. since gas is evolved, can monitor change in volume over time.
2. Collect $(O_{2(g)})$ in a graduated gas syringe and measure the volume at regular time intervals.
3. volume of $(O_2) \propto [O_2]$, so plot a graph of volume of $O_2$ against time.
4. Instantaneous rate is found by drawing a tangent to the curve and finding the gradient $g_1$,

rate = $-g_1$.

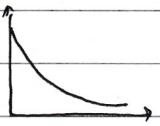
OR

plot a graph of $V_\infty - V_t$ against time, where

$V_t$ = volume of $O_2$ evolved at time t,

$V_\infty$ = " at end of reaction

$V_\infty - V_t$ = " yet to be evolved at time t.



$(V_\infty - V_t) \propto [H_2O_2]$, so graph of $V_\infty - V_t$ against time is similar to $[H_2O_2]$ against time.

* significance of $(V_\infty - V_t)$: It is directly proportional to the $[H_2O_2]$ present in the solution at time t.

Imb: k is affected only by temp. & presence of catalyst.

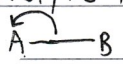
# ORGANIC CHEM

Date. No.

a) Homolytic Fission

A· + B· one e⁻ goes to each atom, form free radicals

b) Heterolytic Fission



$A^-$: + $B^+$ both e⁻ goes to one atom, forming +ve and -ve ions.

Homolytic

i) Electrophile — loves electrons, are e⁻ deficient, attracted to e⁻ rich sites, have empty orbital to accept e⁻

e.g. $BF_3$, $H^+$, $Br^+$, $NO_2^+$, $R^+$, C=C bonds (e⁻ rich π bonds)

ii) Nucleophile — attracted to regions of positive charge, have at least one pair of lone e⁻.

e.g. $OH^-$, $Br^-$, $CN^-$, $NH_3$, $H_2O$, $R\text{-}NH_2$

A) Addition- occurs only to unsaturated reactants, 2 substances give one product, breaking of one π bond to form 2 σ bonds

B) Substitution - an atom/group replaced by another, 2 substances give two products

C) Elimination - removal of atoms/groups from two neighbouring carbons

| Mechanism | Functional Group |
|---|---|
| Nucleophilic substitution | $OH^- + \overset{\delta+}{C}-X^{\delta-}$, where X is any halogen |
| Nucleophilic addition | $-\overset{\delta+}{C}=O$ carbonyl |
| Electrophilic addition | $>C=C<$ alkenes |
| Electrophilic substitution | $\delta-$ benzene ring, arenes |
| Free radical substitution | $-\dot{C}-$ alkanes |

* $\delta^-$ or $\delta^+$ is in relation to carbon atoms!!!

| Functional Group | Name | Suffix | E.g. |
|---|---|---|---|
| $-C(=O)-O-H$ | carboxylic acid | -oic acid | butanoic acid |
| $-C(=O)-O-R$ | ester | alkyl... oate | methyl ethanoate |
| $-C(=O)-X$ | acid halide | -oyl halide | ethanoyl chloride |
| $-C(=O)-NH_2$ | amide | -amide | butanamide |
| $-C\equiv N$ | nitrile | -nitrile | propanenitrile |
| $-C(=O)-H$ | aldehyde | -al | butanal |
| $>C=O$ | ketone | -one | butanone |
| $-OH$ | alcohol | -ol | propanol |
| $-NH_2$ | amine | -amine | ethanamine |
| $-H$ | alkane/alkene/alkyne | -e | propane/propene/propyne |

# ALKANES

Date. No.

i) Reduction of Alkenes to form Alkanes

$C_nH_{2n}$ + $H_2$ $\xrightarrow{Ni + heat\ OR\ Pt\ OR\ Pd}$ $C_nH_{2n+2}$

alkene alkane

conditions: Ni catalyst + heat OR Pt catalyst OR Pd catalyst

ii) Combustion

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$CH_4 + \frac{3}{2}O_2 \rightarrow CO + 2H_2O$

$CH_4 + O_2 \rightarrow C + 2H_2O$, with C as soot.

iii) Free-Radical Substitution: Reaction with Halogens

$C_nH_{2n+2}$ + $X_2$ $\xrightarrow{UV\ light\ OR\ sunlight\ OR\ heat}$ $C_nH_{2n+1}X$ + $HX$

halogen hydrogen halide

conditions: UV light or sunlight or heat – this supplies energy for homolytic fission of halogen-halogen bond (bond breaking) to form free radicals

$Cl_2$ used: - decolourisation of yellow green $Cl_2$

- formation of white HCl fumes that turn damp blue litmus paper red.

$Br_2$ used: - decolourisation of brown $Br_2$

- " white HBr fumes "

Free Radical: A reactive species that has a single unpaired electron

# alkenes

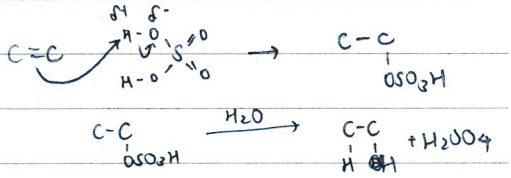
Date No.

$C=C$ —($Br_2$ in $CCl_4$, dark, room temp.)→ $C(Br)-C(Br)$

$C=C$ —(dry $HX(g)$, room temp.)→ $C(H)-C(Br)$ ←(ethanolic NaOH, heat under reflux)

$C=C$ —($Br_2(aq)$, dark, room temp.)→ $C(Br)-C(OH)$

$C=C$ —(cold, conc $H_2SO_4$, $H_2O$, heat)→ $C(H)-C(OH)$




←(excess conc $H_2SO_4$, 170°C, OR $Al_2O_3$, 400°C, or $H_3PO_4$, 250°C)

$C=C$ —($H_2$(Ni, 150°C/Pd, rtp.) (Pd/C, heat))→ $C(H)-C(H)$

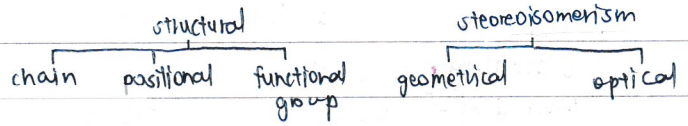
rmb to balance with [O] and $H_2O$

$C=C$ —($KMnO_4$, $H_2SO_4$, heat under reflux)→ $R-C(=O)-OH$ [strong oxidation]
purple $KMnO_4$ decolourised, $CO_2$ forms white ppt. in $Ca(OH)_2$

$C=C$ —(cold $KMnO_4$, NaOH, cold)→ $C(OH)-C(OH)$ [mild oxidation] (only for alkaline)
purple $KMnO_4$ decolourised, black ppt of $MnO_2$

$C=C$ —($KMnO_4$, NaOH, heat under reflux)→ $R-C(=O)-O^-Na^+$ → $R-C(=O)-OH$ [strong oxidation in alkaline medium]

$Br_2$ in $CCl_4$ — reddish brown
$Br_2(aq)$ — orange
$I_2$ in $CCl_4$ — purple
$I_2(aq)$ — yellowish brown



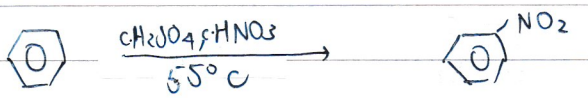

has vacant orbitals and

electrophile: $e^-$ deficient species that accepts lone pairs to form a bond

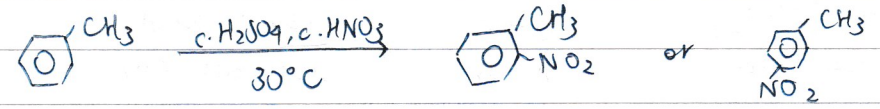
nucleophile: species that is able to donate a lone pair to another species to form a dative covalent bond

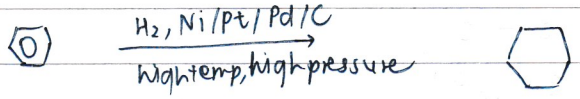
$Cl_2(g)$ — yellow green
$Br_2(g)$ — brown

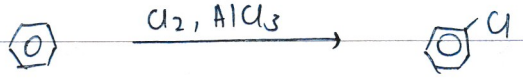
# arenes



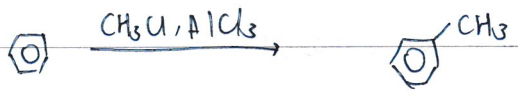

$HNO_3 + 2H_2SO_4 \rightleftharpoons 2HSO_4^- + H_3O^+ + NO_2^+$

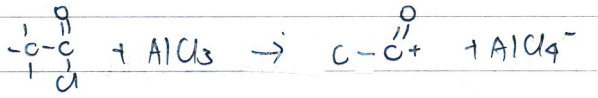


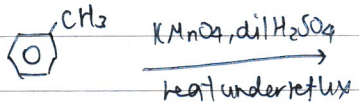



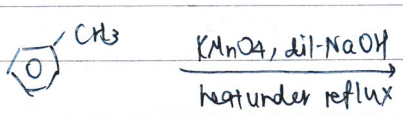

$Cl_2 + AlCl_3 \rightleftharpoons Cl^+ + AlCl_4^-$



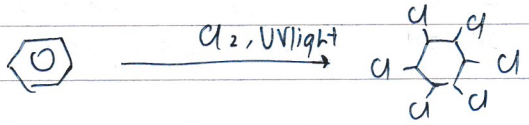



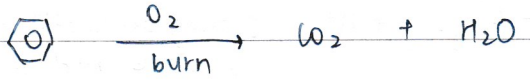

decolourisation of purple $KMnO_4$




decolourisation of purple $KMnO_4$
black ppt of $MnO_2$ → only in alkaline




free radical addition.




→ makes compound more stable

activating, e⁻ donating. lone pair of e⁻ donated to contribute to resonance
- $NH_2$, OH
- $OCH_3$
- $CH_3$

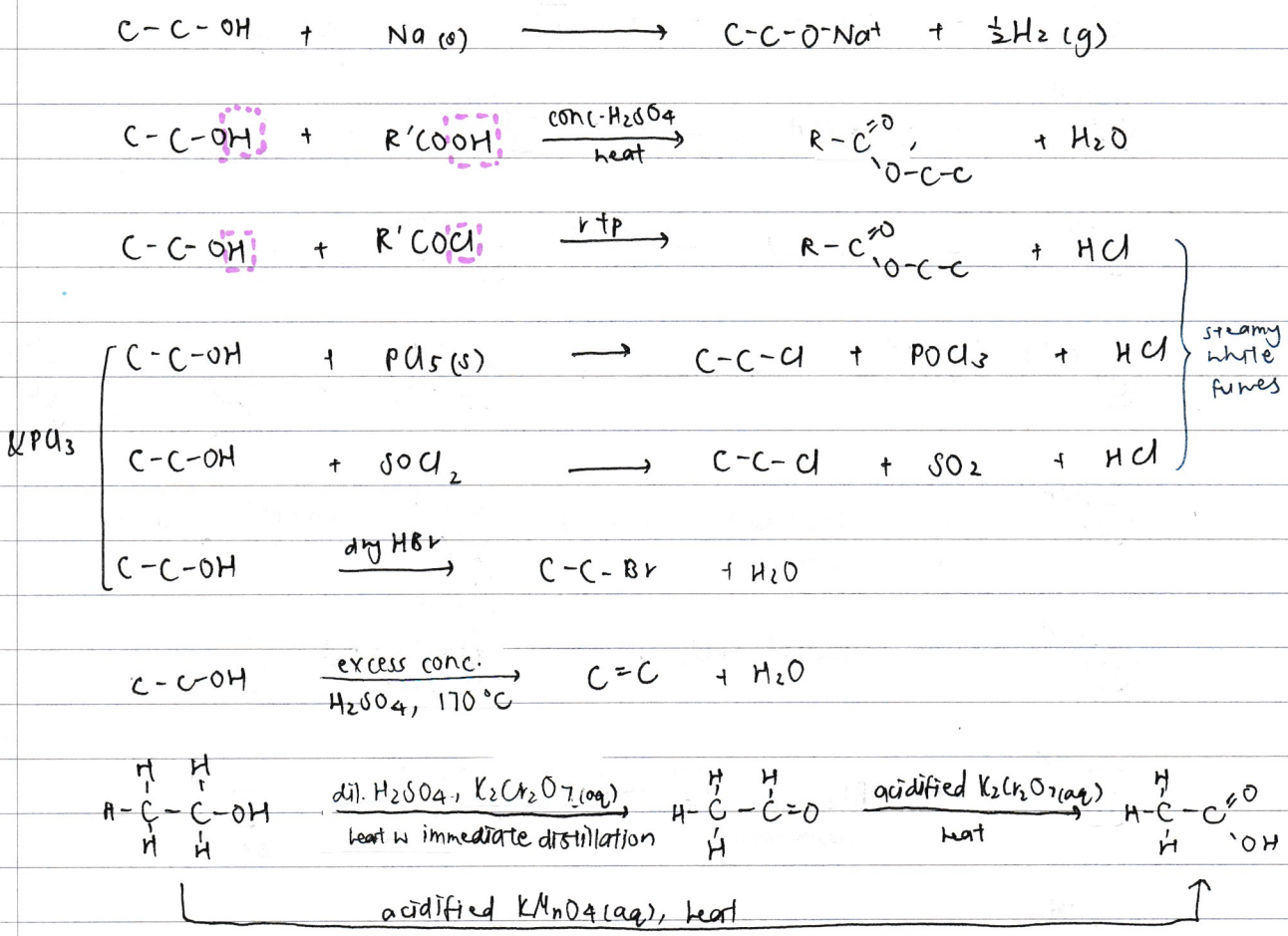
} 2, 4

deactivating, e⁻ withdrawing
- F, Cl, Br, I
- COOH
- $NO_2$

} 3

# alcohols

Date No.




methyl 2° alcohol
or
C-C-OH —4I₂, 6NaOH(aq), warm→ $CHI_3$ + H-C(=O)-O⁻Na⁺ + 5NaI + 5H₂O

yellow crystals

most acidic ... least acidic

phenol > water > alcohol

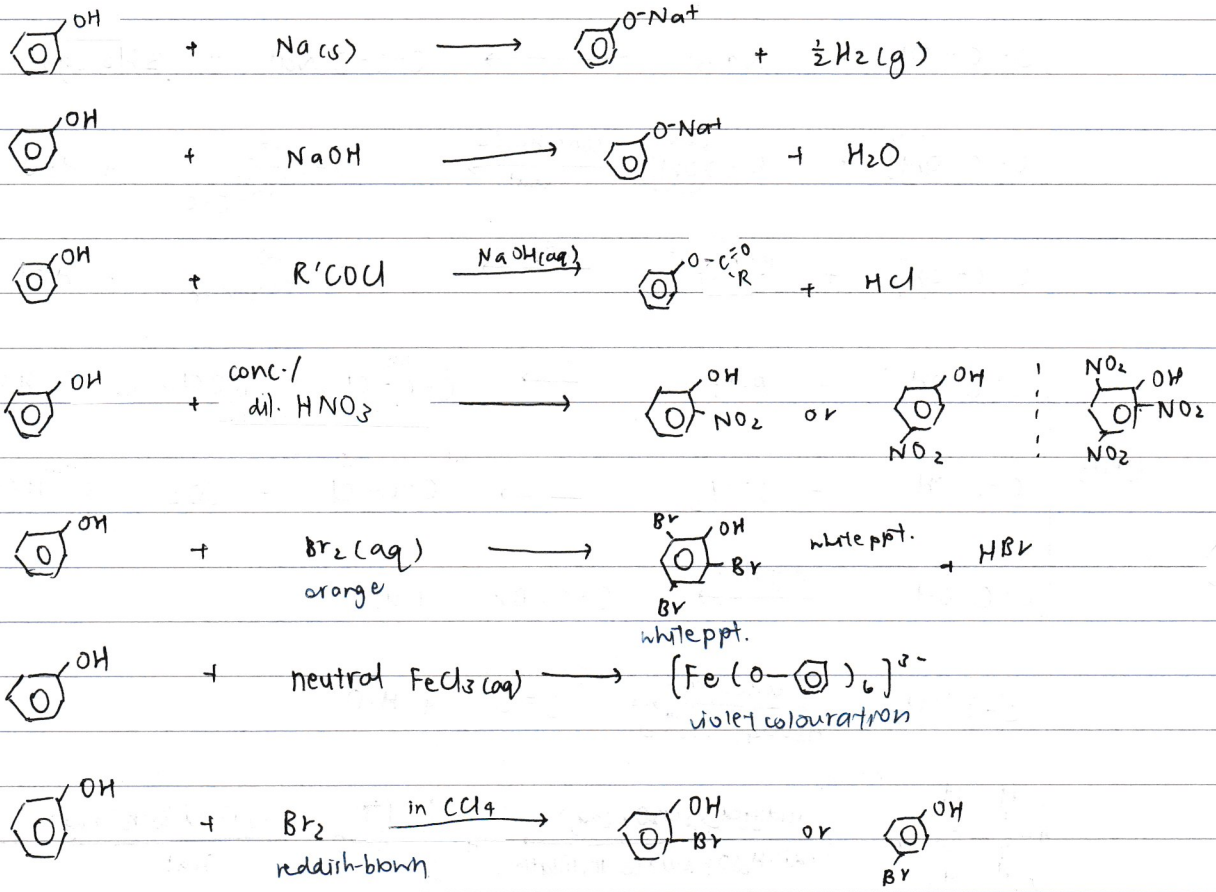
→ alkoxide ion, $RO^-$, is most unstable due to e⁻-donating effect of alkyl group, intensifies electron density on O atom, destabilises anion.

→ phenoxide ion is most stable due to resonance stabilisation
- p-orbital of O⁻ overlaps with π orbitals of benzene ring, negative charge on O delocalises into the ring, negative charge dispersed.

1° alcohol oxidised to aldehyde, 2° alcohol oxidised to ketone.

solubility: ≤5C, soluble.

# phenols


+ Na(s) → + ½H2(g)
+ NaOH → + H2O
+ R'COCl NaOH(aq) + HCl
+ conc./ dil. HNO3 → or
+ Br2(aq) orange → white ppt. + HBr
+ neutral FeCl3(aq) → violet colouration
+ Br2 reddish-brown in CCl4 → or

# Halogenoalkanes

Date No.

## preparation of halogeno alkanes

**$e^-$ addition: alkenes → halogenoalkanes**

$$C{=}C \xrightarrow[\text{heat}]{HX(g),\ dry} C(H)-C(X)$$

$$C{=}C \xrightarrow[\text{dark}]{X_2,\ CCl_4} C(X)-C(X)$$

**nucleophilic substitution: alcohol → halogenoalkanes**

$$C-C(OH) \xrightarrow[\text{heat}]{HX(g),\ dry} C-C(X) + H_2O$$

$$3R\text{-}OH + PX_3 \xrightarrow[\text{dry}]{\text{room temp}} 3R\text{-}X + H_3PO_3$$

$$R\text{-}OH + PCl_5 \xrightarrow[\text{dry}]{\text{room temp}} R\text{-}Cl + POCl_3 + HCl$$

$$R\text{-}OH + SOCl_2 \xrightarrow[\text{dry}]{\text{room temp}} R\text{-}Cl + SO_2 + HCl$$

(steamy white fumes)

## NUCLEOPHILIC SUBSTITUTION OF HALOGENOALKANES

$$C-C(X) + OH^- \xrightarrow[\text{heat}]{NaOH/KOH\ (aq)} C-C(OH) + X^-$$

$$C-C(X) + CN^- \xrightarrow[\text{heat}]{\text{ethanolic KCN}} C-C(CN) + X^-$$

i) $C-C(CN) + 4[H] \xrightarrow[\text{heat}]{LiAlH_4 \text{ in dry ether}} -C-C-C-N-$ (primary amine)

ii) $C-C(CN) + 2H_2 \xrightarrow[\text{heat}]{H_2/Ni \text{ catalyst}} -C-C-C-N-$ (primary amine)

iii) $C-C(CN) + H^+ + 2H_2O \xrightarrow[\text{heat}]{\text{dil } HCl/H_2SO_4} C-C-C(=O)OH + NH_4^+$ (carboxylic acid)

iv) $C-C(CN) + OH^- + H_2O \xrightarrow[\text{heat}]{NaOH/KOH\ (aq)} C-C-C(=O)O^- + NH_3$

carboxylate ion

$$C-C(X) + C-C(O^-) \xrightarrow[\text{heat}]{Na,\ R\text{-}OH} C-C(O-C-C) + X^-$$ (ether)

because $Na + C-C(OH) \longrightarrow C-C(O^-Na^+) + H_2$

$C-\underset{X}{C} + NH_3 \xrightarrow[\text{heat in sealed tube}]{\text{excess, c. } NH_3 \text{ in ethanol}} C-\underset{NH_2}{C} + HX$ (1° amine)

$C-\underset{X}{C} + NH_3 \longrightarrow C-\underset{NH_3^+}{C} + X^- \xrightarrow{OH^-} C-\underset{NH_2}{C} + H_2O + X^-$

in presence of excess halogenoalkane, polyalkylation occurs.

$R-X + NH_3 \longrightarrow \boxed{RNH_2} + HX$ → stronger nucleophile than $NH_3$ due to $e^-$ donating alkyl group

$RNH_2 + R-X \longrightarrow \boxed{R_2NH} + HX$

$R_2NH + R-X \longrightarrow \boxed{R_3N} + HX$ → even stronger nucleophiles because of more alkyl groups

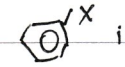
$R_3N + R-X \longrightarrow R_4N^+X^-$

elimination

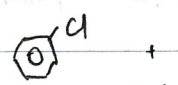
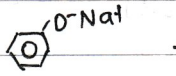
$C-\underset{X}{C} + OH^- \xrightarrow[\text{heat}]{\text{conc. NaOH/KOH}} C=C + X^- + H_2O$

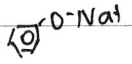
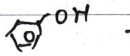
different from + aq NaOH/KOH, that gives $C-\underset{OH}{C}$, an alcohol. (substitution)
However both usually occur at the same time

# halogenoalkanes

 is less reactive as X is $e^-$ withdrawing, rendering it deactivated.

- C-X bond has partial double bond character because p-orbital of X atom overlaps with $\pi$ $e^-$ cloud of benzene ring. lone pair of $e^-$ in p orbital of X can delocalise into benzene ring.
  ∴ C-X bond strong, more energy required to break
- repulsion between $e^-$ rich benzene ring & nucleophile, nucleophilic attack hindered.

 + 2NaOH $\xrightarrow{350°C / 150 atm}$  + NaCl + $H_2O$

 + $H^+$ ⟶  + $Na^+$

[only industrial, not in lab]
(difficult as C-X bond is very strong)

DISTINGUISHING TEST FOR HALOGENOALKANES.

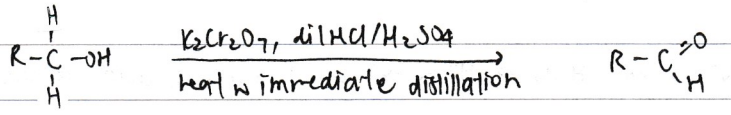
1. Add NaOH(aq), heat, then cool (to prevent decomposition of $AgNO_3$)
2. Add excess $HNO_3$ to neutralise excess NaOH.
3. Add $AgNO_3$ : get AgCl (white), AgBr (cream) or AgI (yellow)

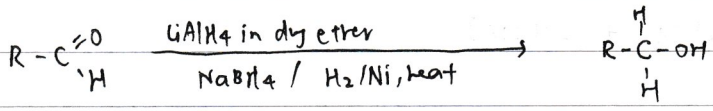
* cannot add $AgNO_3$ directly as C-X bond is hard to break, change to C-OH bond first.

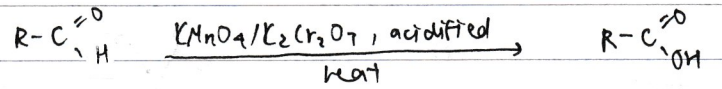
# carbonyl

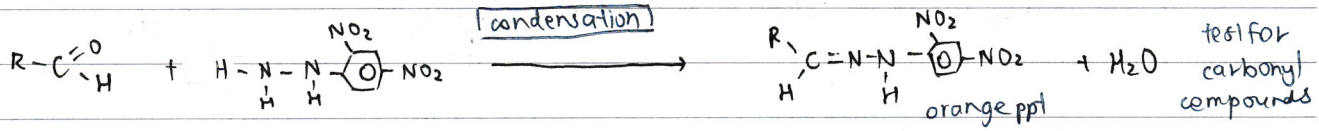
Date No.

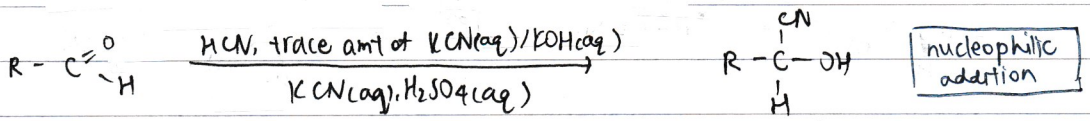
Formation (oxidation)



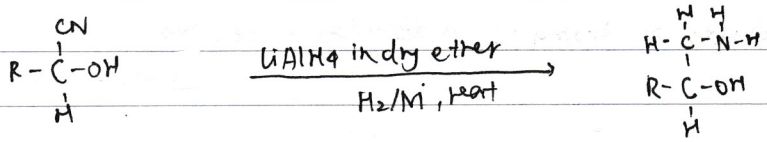



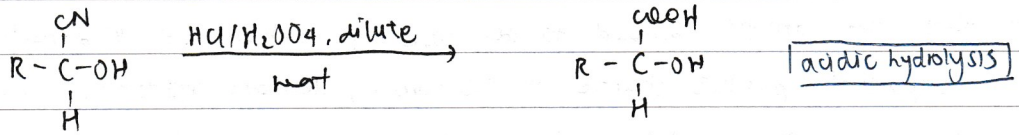



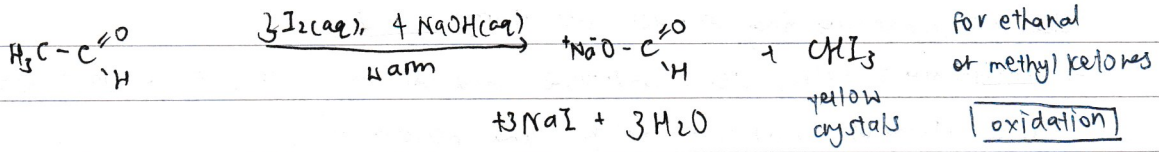



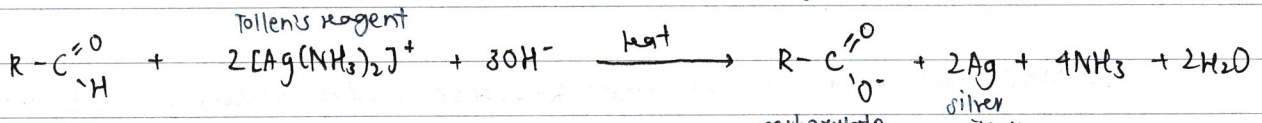

i)




ii)

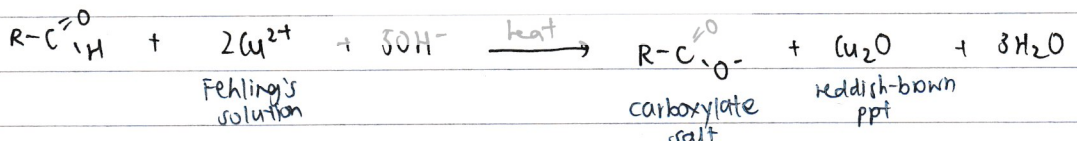



→ positive test for all aldehydes, this is oxidation

oxidation




* positive test for all aliphatic aldehydes

solubility: ≤5C soluble

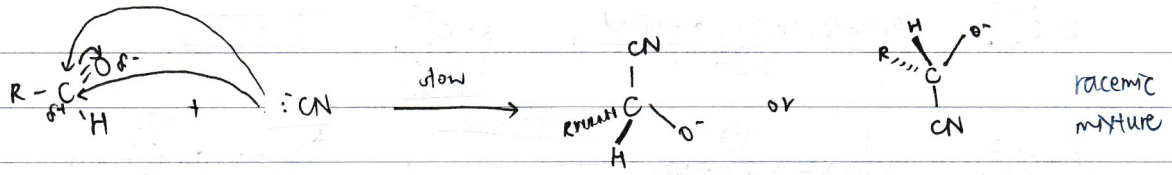
Nucleophilic addition to form cyanohydrins

Step 1: $KCN \rightarrow K^+ + CN^-$ (not $HCN \rightarrow H^+ + CN^-$ as it is a weak acid, dissociates partially)

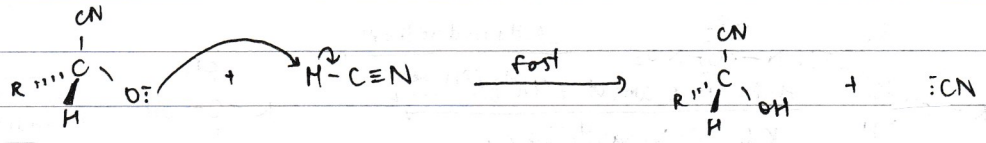
$HCN, KOH \Rightarrow HCN + OH^- \rightarrow H_2O + CN^-$

$(2KCN + H_2SO_4 \rightarrow K_2SO_4 + 2HCN)$

Step 2:




Step 3:




Aliphatic aldehydes > Aromatic aldehydes > ketones

most reactive — least reactive

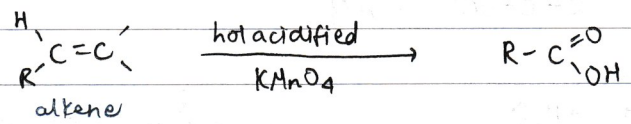
1. Alkyl / aryl groups bonded to the carbonyl carbon are $e^-$ donating and reduce the partial positive charge on the carbon, decrease attraction for nucleophiles
   → alkyl groups through inductive effect, aryl groups through resonance ($e^-$ from $\pi$ $e^-$ cloud delocalise into p orbital of carbonyl C, make it less $\delta^+$)
   → benzene ring is bulky, steric hindrance, and carbonyl C less $e^-$ deficient due to $\pi$ e⁻ cloud of carbonyl group and benzene ring

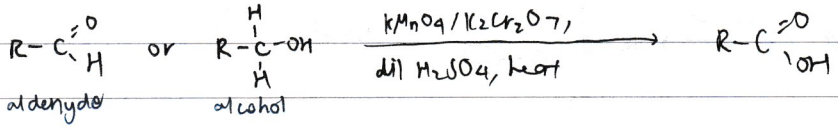
2. Alkyl / Aryl groups increase steric hindrance, hinders nucleophilic attack.

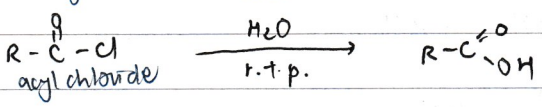
# carboxylic acids

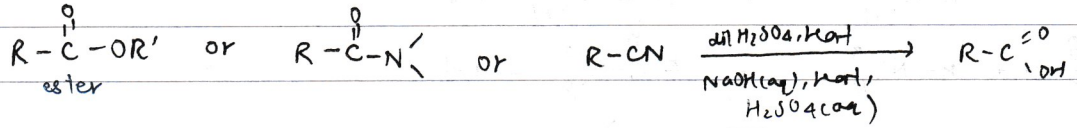
Date No.

## Formation:

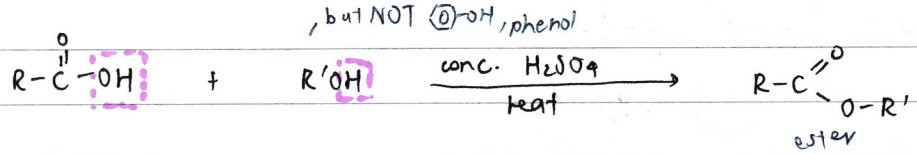


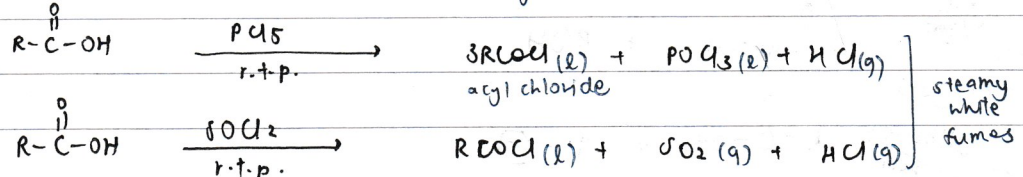



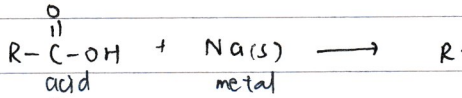



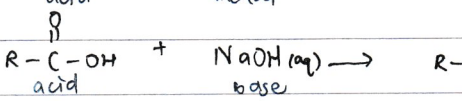

## Reactions:



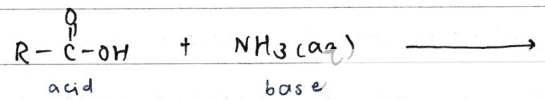


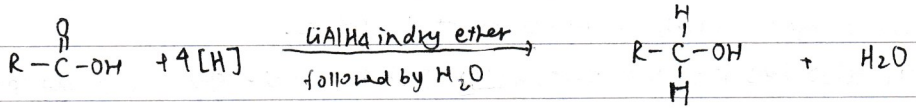


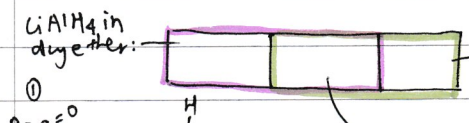





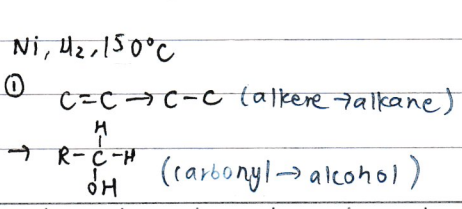


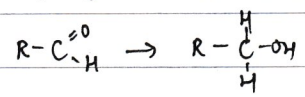

summary of reduction reactions:





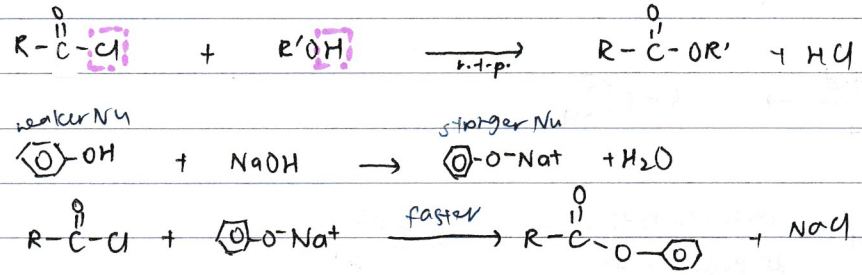

only thing NaBH4 can reduce:



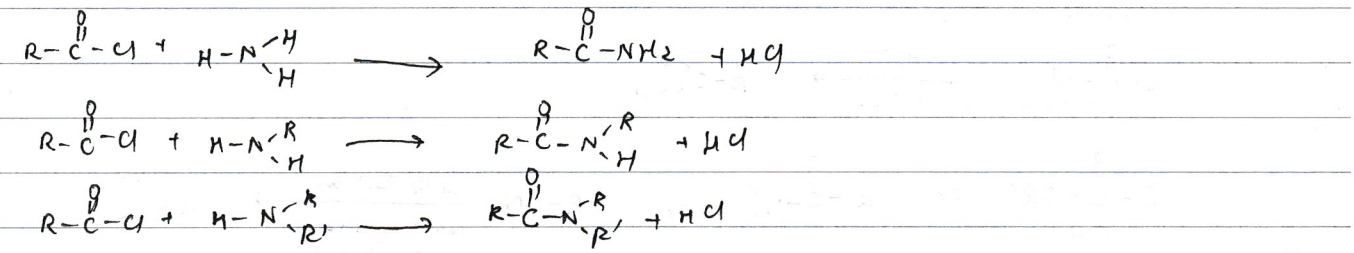

② -CN → -CH2NH2 (nitrile → amine)

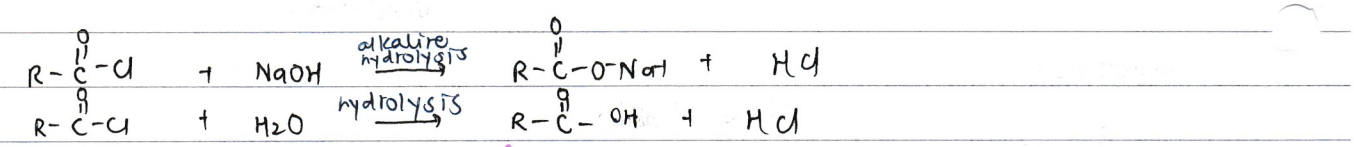
A'ZONE

# acyl chlorides

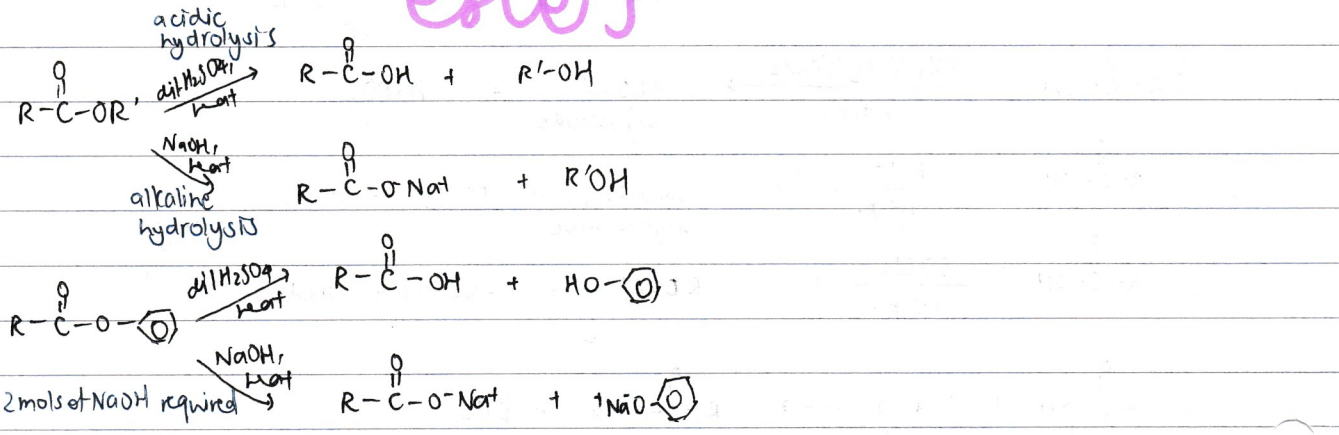








# esters



solubility: ≤4 C soluble.

(least acidic) (most acidic)

alcohols < water < phenols < carboxylic acids.

→ carboxylate ion, $RCOO^-$, forms 2 equivalent resonance structures with the negative charge delocalised over two highly e⁻-ve O atoms. Resonance stabilised.. carboxylate ions most stable, hence most acidic.

→ phenoxide ion also has resonance stabilisation: -ve charge on O disperses into π e⁻ cloud of benzene ring. However, resonance effect not as great.

# amines

Date No.

## Formation:

$CH_3CN \xrightarrow[\text{dry ether}]{LiAlH_4 \text{ in}} CH_3CH_2NH_2$ (reduction) OR $CH_3CONH_2 \xrightarrow[\text{dry ether}]{LiAlH_4 \text{ in}} CH_3CH_2NH_2$

* $CH_3CH_2Cl \xrightarrow[\text{heat in sealed tube}]{\text{excess c. } NH_3} CH_3CH_2NH_2 + NH_4^+Cl^-$

## Reactions

$CH_3CH_2NH_2 + HCl(aq) \longrightarrow CH_3CH_2NH_3^+Cl^-$

weak base — strong acid — salt

$CH_3CH_2NH_2 + CH_3COOH \longrightarrow CH_3CH_2NH_3^+(aq) + CH_3COO^-(aq)$

weak base — weak acid

$CH_3CH_2NH_2 + CH_3COCl \longrightarrow CH_3CH_2-\underset{H}{N}-\underset{O}{C}-CH_3 + HCl$

$CH_3CH_2NH_2 + \text{C}_6\text{H}_5\text{-COCl} \longrightarrow CH_3CH_2-N(H)-C(=O)-\text{C}_6\text{H}_5 + HCl$

nucleophilic sub

excess $CH_3CH_2NH_2$ $\xrightarrow[\text{heat in sealed tube}]{\text{limited } CH_3CH_2Br \text{ in alcohol}}$ $CH_3CH_2-N(H)-CH_2CH_3 + HBr$ OR $CH_3CH_2-N^+(H)(CH_2CH_3)-H\ Br^-$

nucleophilic sub

$CH_3CH_2NH_2 \xrightarrow[\text{heat}]{\text{excess } CH_3CH_2Br} (CH_3CH_2)_4N^+Br^-$

* similar to excess $CH_3CH_2Cl \xrightarrow[\text{in sealed tube}]{\text{c. } NH_3, \text{heat}} (CH_3CH_2)_4N^+Cl^-$

5Cs or less → liquid soluble in NaOH, when heated leaves as pungent gas

$CH_3CH_2NH_2 \xrightarrow[\text{gently}]{NaOH(aq) \text{ warm}}$ pungent gas evolved turns moist red litmus blue

or $CH_3CH_2NH_3^+ \rightarrow RNH_3^+ + OH^- \rightarrow RNH_2 + H_2O$ (leaves as gas)

or amide or ammonium salt:

$R'CONHR + OH^- + H_2O \rightarrow R'COO^- + RNH_2$

$R'COO^-RNH_3^+ + OH^- \rightarrow R'COO^- + RNH_2 + H_2O$

soluble in solution

gas if ≤ 5C, oily layer separates out if ≥ 6 C

# phenylamine

$\text{C}_6\text{H}_5\text{-H} \xrightarrow[55°C]{c.HNO_3, c.H_2SO_4} \text{C}_6\text{H}_5\text{-NO}_2 \xrightarrow[NaOH(aq)]{Sn, \text{conc. } HCl \text{ reflux}} \text{C}_6\text{H}_5\text{-NH}_2$

$\text{C}_6\text{H}_5\text{-NH}_2 \xrightarrow[\text{heat}]{CH_3CH_2Br} \text{C}_6\text{H}_5\text{-N(H)-CH}_2\text{CH}_3$ or $\text{C}_6\text{H}_5\text{-N(CH}_2\text{CH}_3)_2$ or $\text{C}_6\text{H}_5\text{-N}^+\text{(CH}_2\text{CH}_3)_2\ Br^-$

$\text{C}_6\text{H}_5\text{-NH}_2 + RCOCl \longrightarrow \text{C}_6\text{H}_5\text{-N(H)-C(=O)-R}$ ! $\xrightarrow[\text{strong heating}]{NaOH(aq)} \text{C}_6\text{H}_5\text{-NH}_2 + {}^+NaO\text{-C(=O)-R}$

$\text{C}_6\text{H}_5\text{-NH}_2 \xrightarrow[\text{rtp.}]{Br(aq)} \text{Br}_2\text{C}_6\text{H}_2\text{-NH}_2$ (2,4,6-tribromophenylamine)

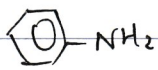
$\text{C}_6\text{H}_5\text{-NH}_2 \underset{NaOH(aq)}{\overset{HCl(aq)}{\rightleftharpoons}} \text{C}_6\text{H}_5\text{-NH}_3^+Cl^-$

solubility: ≤5C soluble

# amides

$CH_3CONH_2 \xrightarrow[\text{strong heating}]{NaOH(aq)} CH_3COO^- + NH_2$

$CH_3CONH_2 \xrightarrow[\text{strong heating}]{HCl(aq)} CH_3COOH + NH_3^+$




$< NH_3 < CH_3CH_2NH_2$

least basic — most basic

larger $K_b$ → smaller $pK_b$ → greater basic strength

- $-CH_2CH_3$ group is $e^-$ donating, increasing $e^-$ density at the N atom, making the lone pair of $e^-$ on N more available for coordination with a proton.
- in phenylamine, lone pair of $e^-$ on N delocalises into $\pi$ $e^-$ cloud of benzene ring, decreasing the $e^-$ density at the N atom, making the lone pair of $e^-$ on N less available for coordination with a proton.
- amides do not have basic properties as the lone pair of $e^-$ on N delocalises into the $\pi$- $e^-$ cloud of the C=O group, making the lone pair of $e^-$ on N unavailable for coordination with a proton

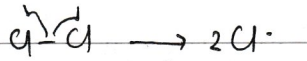
# mechanisms

Break bond: arrow from bond to δ⁻ molecule. Form bond: arrow from lone pair to δ⁺ region.

Date No.

1) F.R.S. Double bond: bond to bond or lone pair to bond

Step 1: Initiation



Step 2: Propagation

a) $CH_3CH_3 + Cl\cdot \longrightarrow CH_3CH_2\cdot + HCl$

b) $CH_3CH_2\cdot + Cl_2 \longrightarrow CH_3CH_2Cl + Cl\cdot$

Then a), b), a), b) ... a chain reaction occurs.

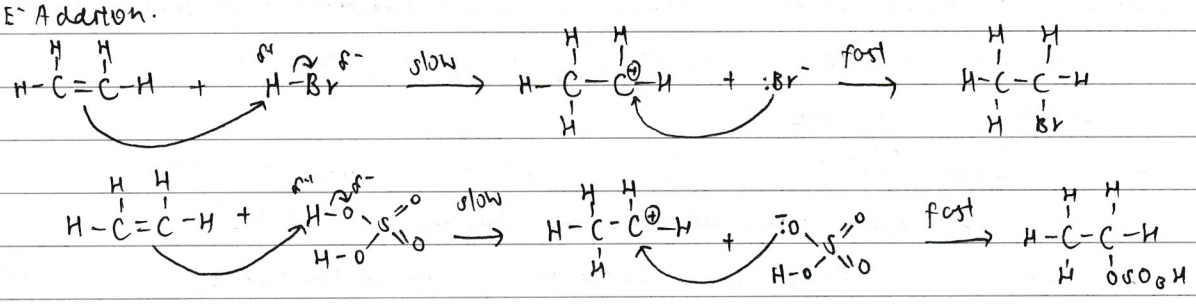
Step 3: Termination.

$Cl\cdot + Cl\cdot \rightarrow Cl_2$

$Cl\cdot + CH_3CH_2\cdot \rightarrow CH_3CH_2Cl$

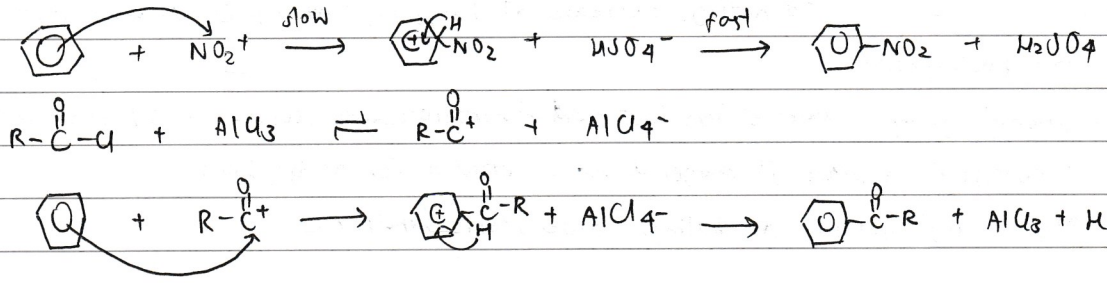
$CH_3CH_2\cdot + CH_3CH_2\cdot \rightarrow CH_3CH_2CH_2CH_3$

2) E⁻ Addition.



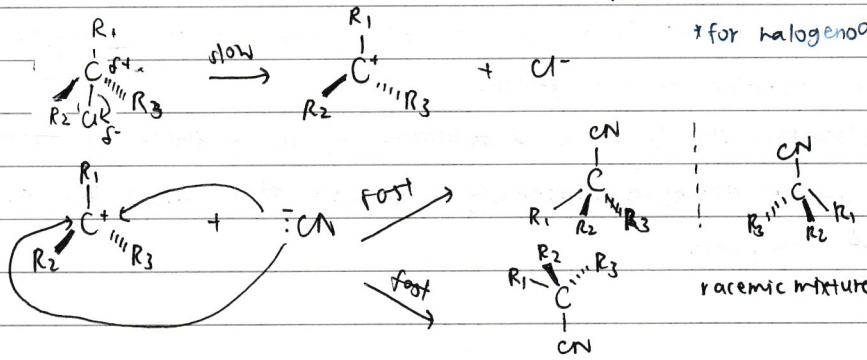
3) E⁻ Substitution

Generation of electrophile: $HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^-$



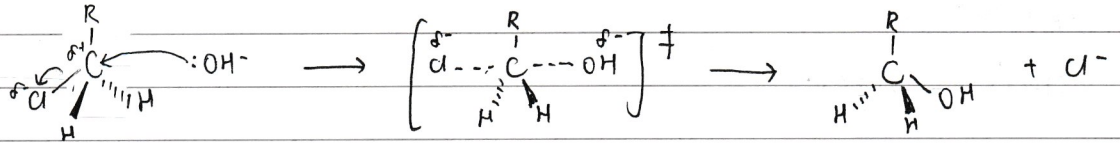
4) $S_N1$ — means unimolecular nucleophilic sub, 2 steps, 1 product (favours tertiary)

* for halogenoalkanes + nucleophile or + amine.

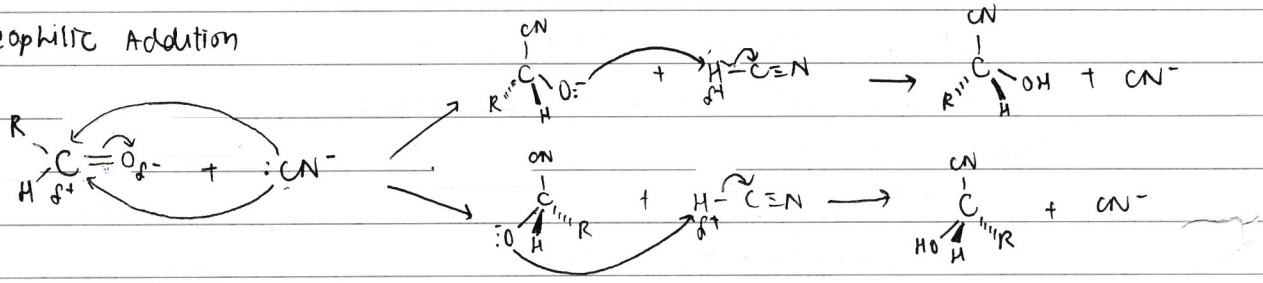


Date No.

$S_N2$ — bimolecular nucleophilic substitution, 1 step, 2 products (favours primary)



5) Nucleophilic Addition



STABILITY of Alcohol / Phenol / Carboxylic Acid: (dispersal of -ve charge on ion)

- Alkoxide ion, $RO^-$, less $e^-$ donating alkyl groups that intensify the -ve charge on O atom, least stable
- phenoxide ion,  , less resonance stabilisation, -ve charge on O delocalises into $\pi$ $e^-$ cloud of benzene ring, disperses -ve charge, more stable
- carboxylate ion, $RCOO^-$, forms 2 equivalent resonance structures, with -ve charge delocalising over two highly $e^-$ -ve O atoms, disperses -ve charge, most stable.

REACTIVITY OF CARBONYL COMPOUNDS: ($\delta+$ charge on carbonyl C)

- alkyl groups are $e^-$ donating, decrease $\delta+$ charge on carbonyl C, decrease attraction for nucleophiles.
- phenyl groups cause $e^-$ from $\pi e^-$ cloud of benzene ring to delocalise into p-orbital of carbonyl C, decrease $\delta+$ charge, decrease attraction for nucleophiles.
- alkyl & aryl groups are bulky, cause steric hindrance

BASICITY OF amides / phenylamine / amine (availability of lone pair)

- lone pair on N delocalises into $\pi$ $e^-$ cloud of C=O group in amides, making the lone pair unavailable for coordination with proton.
- lone pair on N delocalises into $\pi$ $e^-$ cloud of benzene ring, less available for coordination
- alkyl groups are $e^-$ donating, intensify $e^-$ density of N atom, increase availability of lone pair.

# proteins

Date No.

1) PRIMARY STRUCTURE (a polypeptide chain)

definition: refers to the sequence of amino acids in the polypeptide chain.

→ determines overall shape, functions and properties

Hydrolysis

① acid/base-catalysed hydrolysis. → complete hydrolysis

conditions: conc-HCl (6mol $dm^{-3}$), 100-200°C, 10-36 h in a sealed tube

② enzymatic hydrolysis

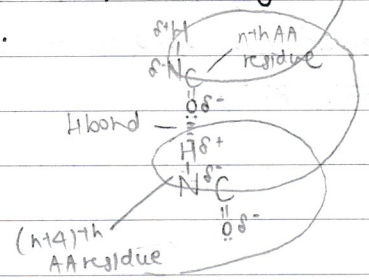
→ selectively hydrolyse specific peptide bonds.

SECONDARY STRUCTURE

definition: the way in which segments of the polypeptide backbone orientate into a regular pattern through H bonding between N-H & C=O groups of the peptide linkages in the polypeptide backbone.

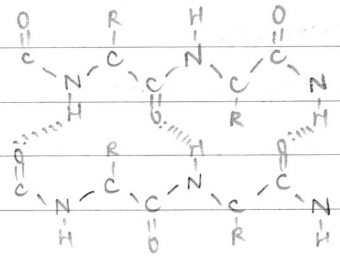
① α-helix

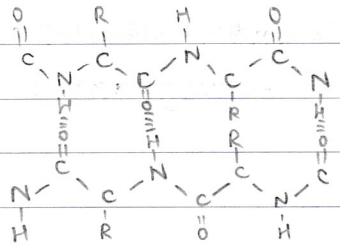
- it has a regular (right-handed) coiled spiral polypeptide chain held together by intra-chain H-bonds between the C=O group of the nth amino acid and the N-H group of the $(n+4)^{th}$ amino acid residue.
- R-groups point outwards of the helix, perpendicularly. They form bonds to stabilise the overall folding of the chain.




② β-pleated sheets (multiple polypeptide chains combined)

- polypeptide chains aligned side-by-side in rows, connected by H-bonding between all peptide linkages.
- intra chain H bonding between C=O group of peptide in one strand and N-H group of another peptide group in adjacent strand.
- R groups project above and below the sheet perpendicularly.
- anti ll more stable as N-H·····O atoms lie in straight line, stabilises H bonds. In ll, N-H···O atoms lie at an angle.



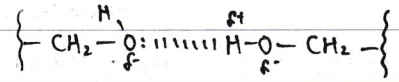


A'ZONE

TERTIARY STRUCTURE (folding of the combined polypeptide chains / 2° structure)

definition: 3D-arrangement of protein due to folding of secondary structures together with spatial disposition of R-groups. Folds are held together due to R-group interactions.

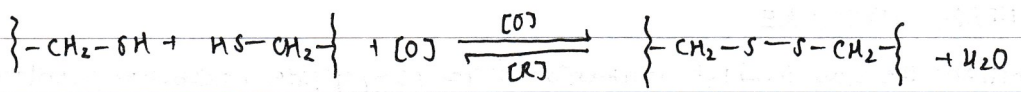
① H-bond between polar R-groups



② ionic interactions between oppositely charged groups ($COO^-$, $NH_3^+$)

③ VDW forces between non-polar groups.

④ disulfide linkages



QUATERNARY STRUCTURE (multiple 3° structures held together by R-group interactions)

definition: spatial arrangement and association of polypeptide subunits. Combination of several protein chains into larger 3D structure, held together by R-group interactions.

Haemoglobin

- a protein made up of 4 polypeptide chains (2 α-subunits, 2 β-subunits).
- considerable R group interactions
- each subunit datively covalently bonded to a haem residue.
- one haemoglobin molecule can bind to 4 $O_2$ molecules.

$$Hb + 4O_2 \rightleftharpoons HbO_8.$$

DENATURATION

① Heavy metal ions
- e.g. $Cu^{2+}$, $Ag^+$, compete with $-NH_3^+$ to form ionic interactions with $COO^-$ groups (in R groups)
- $Hg^{2+}$ reacts w R-groups containing -SH groups, disrupt disulfide linkages.

② Heating - strong molecular vibrations agitate polypeptide chains, and overcome both VDW forces and H-bonding.

③ pH changes alter ionic charges on R groups containing $COO^-$ & $NH_3^+$ groups.
$COO^- + H^+ \rightarrow COOH$, $NH_3^+ + OH^- \rightarrow NH_2 + H_2O$, destroy ionic interactions

④ organic solvents / detergents - contain hydrophobic & hydrophilic groups can disrupt the hydrophobic (VDW) and hydrophilic (H-bond) interactions.

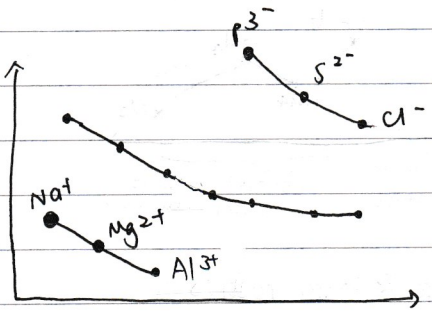
⑤ Oxidising / Reducing agents - form or destroy disulfide linkages.

# periodicity

Date No.

## Chemical Periodicity

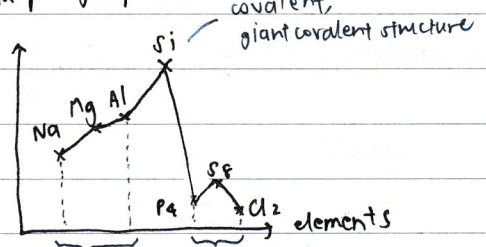
1. mp./bp.
   - giant metallic structure: Na → Al
     - charge density of metal ion ↑
     - no. of valence e⁻ ↑
   - giant covalent structure: Si highest
   - simple molecular: $S_8 > P_4 > Cl_2 > Ar$
2. I.E.
3. electrical conductivity
   - Na < Mg < Al
   - Si metalloid (low e⁻ conductivity)
   - insulators
4. electronegativity
   - ↑ due to ↑ effective nuclear charge
5. atomic & ionic radius
   - $Na^+ > Mg^{2+} > Al^{3+}$ (11, 12, 13)




| | Na | Mg | Al | Si | P | S | Cl |
|---|---|---|---|---|---|---|---|
| oxide | basic (ionic oxides are basic) | | amphoteric ionic & covalent character | | acidic (covalent oxides are acidic) | | |
| water, $H_2O$ | soluble | partially soluble | insoluble | | soluble | | |
| HCl | ✓ | ✓ | ✓ | × | × | × | × |
| NaOH | × | × | ✓ | ✓ | ✓ | ✓ | ✓ |
| chloride | ionic | | | covalent | | | |
| | dissolves | | | hydrolysis | | | |

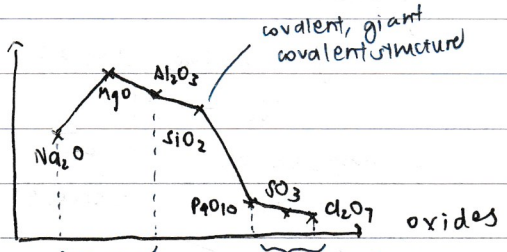
AMPHOTERIC OXIDES: LAZ (lead, aluminium, zinc)

## m.p. graphs

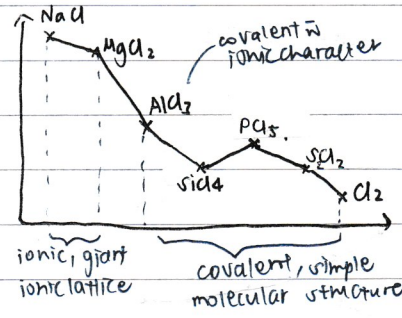



$S_8 > P_4 > Cl_2$,

hence $S_8$ has stronger id-id interactions due to >no. of e⁻, >surface area

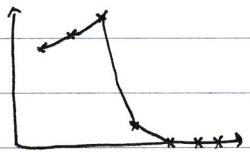



$Al_2O_3$ is ionic ⅄ covalent character due to polarising effect of $Al^{3+}$ which has high charge density, hence lower m.p.




$AlCl_3$ dissociates in water to form $Al^{3+}$ and $Cl^-$ ions, hence can conduct electricity in aq.

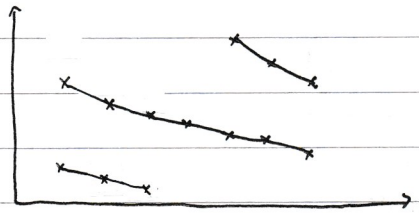
electrical conductivity



increase from Na to Al as they contribute more valence e⁻ to sea of delocalised e⁻.

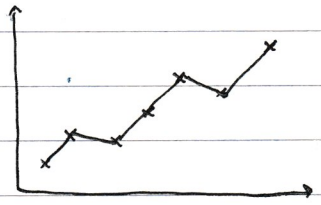
Si is a metalloid, not have absence of charge carriers.

## atomic & ionic radius



1. atomic radius ↓ bc nuclear charge↑, shielding effect constant ∴ E.N.C.↑
2. - cations have one less principal quantum shell, less e⁻ than parent atom
   - ↓shielding effect, ↑attraction between nucleus & valence e⁻
3. - anions have more e⁻ than parent atom, inter-e⁻ repulsion causes e⁻ cloud to expand, ↓ attraction between nucleus & valence e⁻

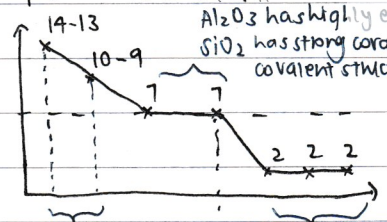
## I.E.



drop b/w Mg & Al: Al involves taking away of e⁻ from 3p subshell, Mg is 3s subshell, e⁻ in 3p further away from nucleus, less energy required to remove.

drop b/w P and S: e⁻ to be removed from S is paired, so inter-e⁻ repulsion, easier to remove.

## pH of oxides in water




$Al_2O_3$ has high lattice energy, insoluble.
$SiO_2$ has strong covalent bonds, giant covalent structure, insoluble

$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$

$H_3PO_4 + 3NaOH \rightarrow Na_3PO_4 + 3H_2O$

dissolve to form alkaline solutions, MgO slightly soluble due to high L.E, highly exothermic, hard to break.

basic, react w acids to form salt & water

$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$

$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4]$

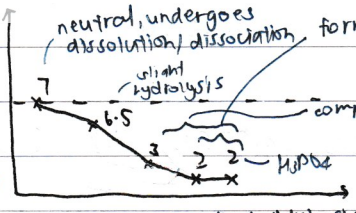
dissolve to form acids, so solution is acidic

acidic, react with bases ↓0 form salt & water

$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$

↳ solid, does not dissolve

## pH of chlorides in water




$MgCl_2$ undergoes slight hydrolysis, $AlCl_3$ undergoes hydrolysis, forms $H_3O^+$. cation has high charge density, draws lone pair of e⁻ on O towards itself

$[Mg(H_2O)_6]^{2+} + H_2O \rightarrow [Mg(H_2O)_5OH]^+ + H_3O^+$

$[Al(H_2O)_6]^{3+} + H_2O \rightarrow [Al(H_2O)_5OH]^{2+} + H_3O^+$

$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

or $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

$2NaO + H_2O \rightarrow 2NaOH$

$NaOH + HCl \rightarrow NaCl + H_2O$

Date No.

| Acidic solution | Alkaline solution |
|---|---|
| SA | SB |
| WA | WB |
| salt of WB / CA | salt of WA / CB |
| WA + CB (salt) | WB + CA (salt) |
| $H^+$ | $OH^-$ |
| use $K_a$ | use $K_b$ |

pH of weak acid = $-\log\sqrt{K_a \cdot C_{of\,WA}}$ => $[H^+] = \sqrt{K_a \cdot C}$

pOH of weak base = $-\log\sqrt{K_b \cdot C_{of\,WB}}$ => $[OH^-] = \sqrt{K_b \cdot C}$

calculating pH of dilute strong acid: ↝ assume pH of water = 7

$pH = -\log[H^+] = -\log([H^+_{of\,SA}] + 1.0\times10^{-7})$

degree of ionisation, $\alpha$, = $\frac{n_{ionised}}{n_{initial}} = \frac{n_{H^+ or\,OH^-}/V}{n_{initial}/V} = \frac{[H^+]\text{ OR }[OH^-]}{C_0}$

when conc. is unknown, of e.g. $[H^+]$ or $[OH^-]$, let it be x & solve.

Buffer solution: WA & its salt, or WB and its salt

↳ $pH = pK_a + \lg\frac{[salt]}{[acid]}$ $pOH = pK_b + \lg\frac{[salt]}{[base]}$

at M.B.C., [salt] = [acid] or [base], pH = pKa, pOH = pKb

↳ half equi point if WA / WB in flask, double equi point if SA/SB in flask.

| indicator | $pK_{In}$ | pH range | colour in acid | colour in base | colour at end point |
|---|---|---|---|---|---|
| methyl orange | | 3.1-4.4 | red | yellow | orange |
| (screened methyl orange | | 3.1-4.4 | violent | green | grey |
| bromothymol blue | | 6.0-7.6 | yellow | blue | green |
| thymol blue | | 8.0-9.6 | yellow | blue | green |
| phenolphthalein | | 8.3-10.0 | colourless | pink | light pink (alkaline titrant) colourless (acidic titrant) |

$[Ag(NH_3)_2]^+$, $[Cu(NH_3)_4]^{2+}$, $[Zn(NH_3)_4]^{2+}$

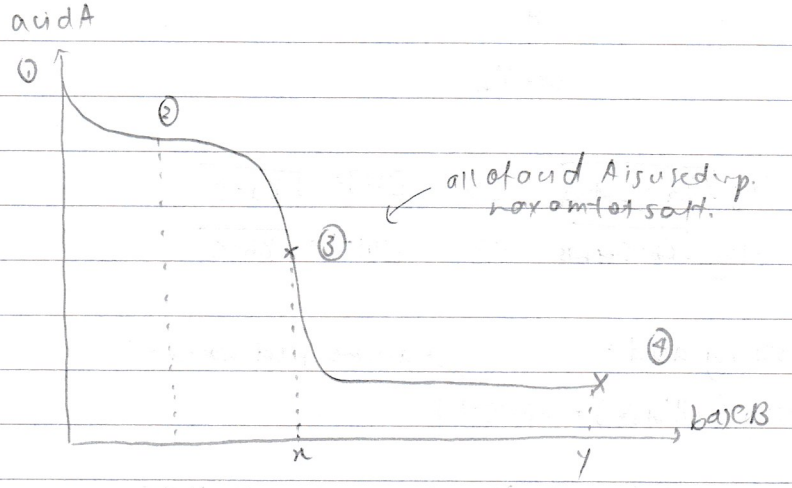
$PbCl_4^{2-}$

$[Zn(OH)_4]^{2-}$, $[Al(OH)_4]^-$, $[Pb(OH)_4]^{2-}$, $[Cr(OH)_6]^{3-}$

phenolphthalein

$pK_{a1}$ is lower / $K_{a1}$ is higher because the positively charged proton is more readily lost from the neutral acid molecule than the negatively charged conjugate base.

$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$




① $pH = -\log\sqrt{K_a \cdot C}$ or $pOH = -\log\sqrt{K_b \cdot C}$

② - @ NBC directly: $pH = pK_a$ or $pOH = pK_b$

- @ buffering range: $pH = pK_a + \lg\frac{[salt]}{[acid]}$ ← if [ ] of acid & base are same, just see how much salt formed, how much acid left

or $pOH = pK_b + \lg\frac{[salt]}{[base]}$

③ $pH = -\log\sqrt{K_a \cdot [salt]}$ ← Imp new volume. use $C_1V_1 = C_2V_2$ to find volume x; if acid & base are equimolar

or $pOH = -\log\sqrt{K_b \cdot [salt]}$

This is where all acid/base is fully used up, max amt of salt.

④ $pH = -\log[H^+]$ ← excess $[H^+]$ (unreacted) which is of volume y-x.

strong/weak acid is a proton donor - that dissociates fully/partially in water.
strong/weak base is a proton acceptor that ionises fully/partially in water.

| | | | |
|---|---|---|---|
| $MnO_4^-$ purple | → $MnO_4^{2-}$ | green solution | strongly alkaline |
| | → $MnO_2$ | black solid | weakly alkaline/acidic/neutral |
| | → $Mn^{2+}$ | light pink/ colourless solution | strongly acidic. |

# electrochem

Date No.

FUEL CELL

$O_2$ is reduced ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$)

Fuel (sometimes $H_2$) is oxidised. ($H_2 \rightarrow 2H^+ + 2e^-$)

- can be replaced with say ($C_2H_6$, then $2C_2H_6 + 7O_2 \rightarrow 2CO_2 + 6H_2O$

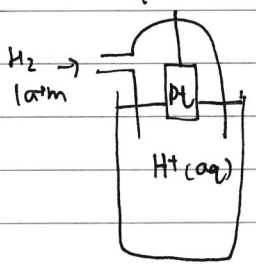
(half eq is $C_2H_6 + 4H_2O \rightarrow 2CO_2 + 14H^+ + 14e^-$

Battery cells are rechargeable as the reaction can be readily reversed and electrons can flow in the opposite direction when current is passed through it.

electrical energy $\underset{\text{discharging}}{\overset{\text{charging}}{\rightleftharpoons}}$ chemical energy

purpose of salt bridge: to maintain electrical neutrality by preventing accumulation of charges in both half-cells through allowing migration of ions

*if aqueous solution, don't write $[H_2O]$, just write $[H^+]$




| Voltaic | Electrolytic |
|---|---|
| - battery | - electrolyte |
| - fuel | → cathode is -ve |
| → cathode is +ve } when discharging | → anode is +ve |
| → anode is -ve } when discharging | |

# chemical energetics

Date No.

$\Delta H_r^\circ$ = $\Delta H_c$ (reactants) − $\Delta H_c$ (products)

$\Delta H^\circ$ = $\Delta H_f$ (products) − $\Delta H_f$ (reactants)

$\Delta H_c$ => when one mole of substance is completely combusted

$\Delta H_{neut}$ => acid and base reacting to form one mole of water

$\Delta H_{atom}$ => standard state to one mole of gas

e.g. $NaCl(s) \rightarrow Na(g)$, $\frac{1}{2} Cl_2(g) \rightarrow Cl(g)$

B.E. => breaking bonds in gaseous state

e.g. $CH_4(g) \rightarrow C(g) + 4H(g)$ 4. B.E. (C-H)

I.E => when one mole of gaseous atoms loses one mole of $e^-$

E.A. => when one mole of gaseous atom gains one mole of $e^-$

L.E. => one mole of solid ionic compound formed from constituent gaseous ions

$\Delta H_{soln}$ => one mole of substance completely dissolved in solvent

e.g. $MgSO_4(s) \rightarrow Mg^{2+}(aq) + SO_4^{2-}(aq)$

$\Delta H_{hyd}$ => one mole of gaseous ions hydrated.

$Mg^{2+}(g) + aq \rightarrow Mg^{2+}(aq)$

L.E = $\Delta H_{hyd} - \Delta H_{soln}$

$q = mc\Delta T$, $H = -\frac{q}{n}$

m ↑ mass of solution; n ↑ of solution

# group II

Date No.

**Metal + $O_2$ :** $M + \frac{1}{2}O_2 \rightarrow MO$

Mg: white flame, Ca: brick red flame, Sr: crimson flame, Ba: pale green flame.

**Metal + water :** $M + 2H_2O \rightarrow M(OH)_2 + H_2$ (bubbles of $H_2$ gas)

Be does not react, Mg reacts slowly with cold water, vigour increases down the group

**Metal + HCl / $H_2SO_4$ :** gives salt and $H_2$.

* solubility of sulfates decrease down the group: $BaSO_4$ is INSOLUBLE.

**MO + water :** $MO + H_2O \rightarrow M(OH)_2$ (fizzes and hisses, heat given out)

BeO does not react, MgO reacts slowly, the rest vigorously.

* BeO is amphoteric, the rest are basic (ionic). MgO has slight covalent character.
  ↳ so it remains a solid

**$M(OH)_2$ + water :** solubility increases down the group, dissolve to give alkaline solutions

$Mg(OH)_2$ is slightly soluble: $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$ pH: 9

$Ca(OH)_2$ is slightly soluble: $Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$ pH: 10

Sr / $Ba(OH)_2$ are more soluble: $M(OH)_2(s) + aq \rightarrow M^{2+}(aq) + 2OH^-(aq)$ pH: 13

$BeO + 2HCl \rightarrow BeCl_2 + H_2O$

$BeO + 2NaOH + H_2O \rightarrow Na_2[Be(OH)_4]$

$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4]$

# transition metals

Date No.

Heterogenous catalysts: T.Ms have partially filled 3d subshell which allows for ready exchange of electrons to and from reactant molecules, facilitating formation of weak bonds with reactant molecules.

e.g. $H_2$, Ni, heat for hydrogenation of alkenes or Fe for $N_2 + 3H_2 \rightarrow 2NH_3$

Homogenous catalysts: T.M have variable oxidation states and have relative ease in converting from one O.S. to another, which facilitates formation of intermediate compounds between T.M ions and reactants.

e.g. $Fe^{3+}$ in E.S. of benzene, $Fe^{2+}$ in $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$

Transition metal: A d-block element that can form one or more stable ions with at least one partially filled 3d orbital / with a partially filled 3d subshell.

Complex: It is a central metal atom/ion linked to one or more surrounding ions/molecules (ligands) by dative covalent bonds. If the species carries an overall charge, it is a complex ion.

Ligand: An ion/molecule which contains at least one donor atom bearing at least one lone pair of electrons which can be donated into a low lying vacant orbital (usually 3d orbitals) of a central metal atom/ion, forming a coordinate/dative covalent bond.

Coordinate/Dative covalent bond: Represents bond formation as occurring between filled orbitals on a ligand overlapping with vacant orbitals on the central metal atom.

coordinate number: Total number of coordinate bonds that central metal atom/ion forms with ligands

3d electrons provide poor shielding effect as they are occupying highly diffused 3d orbitals compared to 3s and 3p

# group VII

Date No.

| | $F_2$ | $Cl_2$ | $Br_2$ | $I_2$ |
|---|---|---|---|---|
| Physical appearance at r.t.p. | pale yellow gas | pale green gas | reddish-brown liquid | black solid |
| Colour in water | colourless | yellowish-green | orange | yellowish-brown |
| Colour in organic solutions | colourless | yellowish-green | reddish-brown | violet |

$X_2$ – covalent bonding, simple molecular structure, non-polar, diatomic

① M.p. / B.p. increases down group

- ↑ electron cloud size → ↑ polarisability of electron cloud → stronger id-id interactions.

② Radii ↑, Electronegativity ↓, I.E. ↓

↑ no. of principal quantum shells → valence $e^-$ further away from nucleus → less attraction

↳ bonding $e^-$ further away from nucleus → ↓ ability of atom to attract bonding $e^-$

③ B.E. decreases down the group.

- ↑ atomic size → valence orbitals more diffuse → less effective overlap between bonding orbitals

* F-F not as strong due to small atomic size, great repulsion between l.p of $e^-$ on each F atom

④ Solubility in water – oxidation of $H_2O$

$F_2$ reacts with cold water readily: $2F_2 + 2H_2O \rightarrow 4HF + O_2$

$Cl_2$ disproportionates partially: $Cl_2 + H_2O \rightleftharpoons HCl + HOCl$

- HOCl is a weak acid, decomposes to form: $2HOCl \rightleftharpoons 2HCl + O_2$

$Br_2$ is moderately soluble, $I_2$ is slightly soluble.

⑤ Oxidising power decreases down the group.

A) Displacement Reaction

- more reactive halogen displaces less reactive halogen from its compound by oxidising it.

e.g. $Cl_2 + Br^- \rightarrow Br_2 + Cl^-$, note the colour Δ (shake with $CCl_4$ after rxn)

B) Reaction with Thiosulfate

- $Cl_2$ & $Br_2$ are strong enough OAs to oxidise $S_2O_3^{2-}$ ($+2$) to $SO_4^{2-}$ ($+6$): $S_2O_3^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 8e^-$

- $I_2$ is a weak OA, only oxidises $S_2O_3^{2-}$ ($+2$) to $S_4O_6^{2-}$ ($+2.5$): $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$

C) Reaction with $OH^-$ (cold & hot)

| | 0°C | 15°C | 75°C |
|---|---|---|---|
| $Cl_2$ | $ClO^-$ | | $ClO_3^-$ |
| $Br_2$ | $BrO^-$ | $BrO_3^-$ | |
| $I_2$ | $IO_3^-$ | | |

cold $OH^-$ @ 15°C: $Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$

hot $OH^-$ @ 75°C: $3ClO^- \rightarrow 2Cl^- + ClO_3^-$

overall in hot $OH^-$: $3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + 3H_2O$

in acidic medium: $X^- + XO_3^- + 6H^+ \rightarrow X_2 + 3H_2O$

D) Reaction with Hydrogen – forming HX

- Less vigorous rxns down the group as ① oxidising power ↓ ② H-X bond strength ↓ → $\Delta H_r$ less exo

$F_2$ – r.t.p, dark. $Cl_2$ – UV light. $Br_2$ – 300°C, Pt catalyst. $H_2 + I_2 \rightleftharpoons 2HI$ – heat strongly using Pt/ed asbestos

fast & explosive | slow

# hydrogen halides

Date No.

$I_2$ is soluble in $I^-$ as: $I_{2(s)} \rightleftharpoons I_{2(aq)}$ } formation of $I_3^-$ complex ↓$[I_{2(aq)}]$, P.O.E of 1st eq. shifts right.

$I_{2(aq)} + I^-_{(aq)} \rightleftharpoons I_3^-{}_{(aq)}$

HX are colourless gases at r.t.p.

① M.p. / B.p. ↑ down group

* HF exception as it forms intermolecular H-bonding, not just rstrd.

② Thermal stability ↓ down group, B.E. ↓

- ↑ halide size → valence orbital more diffuse → less effective overlap between bonding orbitals
- ↓ electronegativity difference → ↓ bond polarity → ↓ electrostatic FOA between bonding e & nuclei
- $F_2$ & $Cl_2$ stable, $Br_2$ slight decomposes, $I_2$ readily

③ Acid strength ↑ — All except HF are strong acids

- for dissociation to occur (all dissociate completely except HF), H-X bond must be broken

A) Reaction with conc. acid

solid halide, NaX, forms HX with c. $H_2SO_4$: $NaX + H_2SO_4 \rightarrow NaHSO_4 + HX$

- HX can be further oxidised to $X_2$ by $H_2SO_4$.
- reducing power of $X^-$ increases down the group, so $H_2SO_4$ gets reduced further.

$Cl^-$: $NaCl + H_2SO_4 \rightarrow HCl_{(g)} + NaHSO_4$.

HCl not oxidised further by c. $H_2SO_4$, steamy white fumes of HCl.

$Br^-$: $NaBr + H_2SO_4 \rightarrow HBr_{(g)} + NaHSO_4$

$2HBr_{(g)} + \overset{+6}{H_2SO_4} \rightarrow Br_{2(l)} + \overset{+4}{SO_2} + 2H_2O$

Reddish-brown liquid / vapour observed. Colourless gas with burning sulfur smell turns moist blue litmus red. Mixture of HBr and $Br_2$.

$I^-$: $2HI + H_2SO_4 \rightarrow I_{2(s)} + \overset{+4}{SO_2} + 2H_2O$

$6HI + H_2SO_4 \rightarrow 3I_{2(s)} + \overset{0}{S} + 4H_2O$

$8HI + H_2SO_4 \rightarrow 4I_{2(s)} + \overset{-2}{H_2S} + 4H_2O$

Black crystals / violet vapour formed. Colourless gas with rotten egg smell turns moist blue litmus red.

* To prepare pure HBr & HI, use c-$H_3PO_4$ as it is not as volatile & oxidising as $H_2SO_4$.

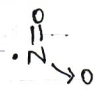
B) Reaction with $AgNO_3$ and then excess/conc. $NH_3$

| | |
|---|---|
| AgCl soluble in excess $NH_3$ | $AgX_{(s)} \rightleftharpoons Ag^+ + X^-$ |
| AgBr soluble in conc. $NH_3$ | $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$ |
| AgI insoluble in conc. $NH_3$ | - formation of complex, $[Ag^+]$↓, P.O.E. of 1st eq shifts right, I.P of AgX decreases till below Ksp, soluble. |

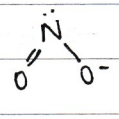
However, Ksp of AgI is very low, I.P. cannot be smaller.

# dot & cross diagrams

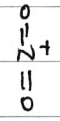
Date No.



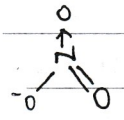
$NO_2$



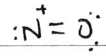
$NO_2^-$



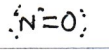
$NO_2^+$



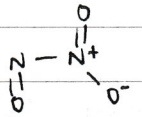
$NO_3^-$ - resonance



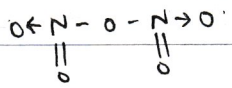
$NO^+$



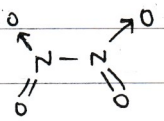
$NO^-$



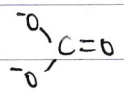
$N_2O_3$



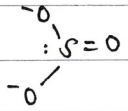
$N_2O_5$



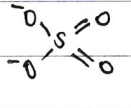
$N_2O_4$



$CO_3^{2-}$



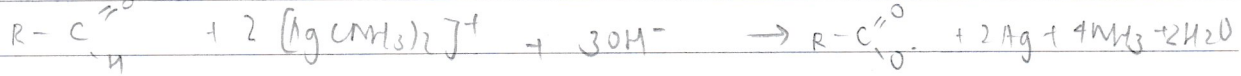
$SO_3^{2-}$



$SO_4^{2-}$

$S_2O_8^{2-} \rightarrow SO_4^{2-}$

$S_2O_3^{2-} \rightarrow S_4O_6^{2-}$



$R-C(=O)-H + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow R-C(=O)-O^- + 2Ag + 4NH_3 + 2H_2O$

$R-C(=O)-H + 2Cu^{2+} + 5OH^- \rightarrow R-C(=O)-O^- + Cu_2O + 3H_2O$

$CH_3-CH_2OH + 4I_2 + 6NaOH \rightarrow H-C(=O)-O^-Na^+ + CHI_3 + 5NaI + 5H_2O$

$CH_3-C(=O)-H + 3I_2 + 4NaOH \rightarrow H-C(=O)-O-Na + CHI_3 + 3NaI + 3H_2O$

$R-C(=O)-H + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow R-C(=O)-O^- + 2Ag + 4NH_3 + 2H_2O$

$R-C(=O)-H + 2Cu^{2+} + 5OH^- \rightarrow R-C(=O)-O^- + Cu_2O + 3H_2O$