#### Atomic structure

State the definition of atomic mass

It is the ratio of the average mass of one atom of an element to 1/12 the mass of one <sup>12</sup>C atom

• State the definition of isotopic mass

It is the ratio of the mass of one atom of an isotope of an element to 1/12 the mass of one <sup>12</sup>C atom

• Given information about the N–O bond in NO<sub>3</sub><sup>-</sup> why is it inaccurate to represent NO<sub>3</sub><sup>-</sup> as having double and single bonds?

N–O is of length that is intermediate between theoretical N–O and N=O bond length, so inaccurate.

- Suggest the mixing and overlap of atomic orbitals which account for the partial double bond character in N-O bond.
- 1. Mixing
- 2. Overlap
- 3. Explain how resonance arises
  - a. Continuous side-way overlap  $\rightarrow$  pi electrons delocalize  $\rightarrow$  gives rise to resonance structure  $\rightarrow$  partial double bond character
- Explain if the molecule NCCN is polar

C-N bond is polar

dipole moments cancel each other because **atoms are arranged linearly** no net dipole moment

• How does id-id and pd-pd arise

Electrons in electron cloud move randomly  $\rightarrow$  uneven distribution of electron cloud  $\rightarrow$  instantaneous dipole  $\rightarrow$  induce dipole in adjacent molecule

- Bond angle in graphene (**planar**) is 120<sup>°</sup>.
- Why is Sr denser than Ca

Increase in mass is *more significant* than increased size of Sr. No need to bring in strength of metallic bonding.

Redox

• Ag2O + H2O2 -> 2Ag + O2 + H2O. Explain why H2O2 acts as RA.

Oxygen appears 2 times on the reactant side (disproportionation), so don't focus on o.s. Of O. Focus on other reactant (Ag).

Physical periodicity

- Explain why successive I.E. increases generally. [2m]
- 1) Number of protons constant, number of electrons decreasing.
- 2) Nuclear attraction increases

# • (Given data) State and explain the group number of element xx. [2m]

- 1) There is a large spike from which I.E. to which I.E.
- The XXth electron is removed from the inner principal quantum shell / There are xx valence electrons

• Calculate energy needed to remove xxx moles of electrons Total energy = ionisation energy \* amt of electrons Cuz ionisation energy is energy for 1 mole of electrons

• Why ionic radii of a random ion and a TM ion are similar

TM ion: higher nuclear charge, greater shielding effect, further away from nucleus. But nuclear attraction is similar cuz 3d electrons provide poor shielding

Chemical Bonding

- Explain the shape of xxx.
- 1) State number of lone pairs and bond pairs.
- 2) By VSEPR theory, electron pairs are placed as far apart as possible to minimise mutual repulsion.
- Suggest a bond angle of xxx.
- 1) State number of lone and bond pairs.
- 2) xx repulsion is larger than xx repulsion (lplp > lpbp > bpbp)
- 3) If qn say use VSEPR theory, state that by VSEPR, electrons are placed as far apart as possible to minimise interelectronic repulsion

VSEPR: includes both 2 and 3

• Why is C-C bond btw sp2-sp3 orbitals stronger than btw sp3-sp3 orbitals

Btw sp2-sp3: Covalent bond has <u>higher % of s character</u> More effective orbital overlap

Content:

- CCl4 and SiCl4 are simple molecules!
- strength of covalent bond:
  - Bond order:
    - i. # of orbitals overlapped
    - ii. electron density between bonding atoms
    - iii. attraction between bonding nuclei and shared electrons
  - Effectiveness of orbital overlap:
    - i. % of s character in hybrid orbital
      - "sp2-sp2 overlap in X is more effective than sp3-sp3 overlap in Y due to higher % of s character in hybrid orbitals."

ii. atomic size

Why can AICI3 form dative bonds to become a dimer

Al atom has empty orbital, can accept lone pair electrons from CI

• Intramolecular H bond

Only possible if the ring has more than 5 atoms. If less, there is ring strain, not possible. Keywords: XXX forms intramolecular H bonding which <u>reduces the number of sites available for</u> <u>intermolecular H bonding.</u>

• Intramolecular H bond → conjugate base of cis isomer is more stable than trans isomer → cis isomer is more acidic

Past mistake: less extensive H bond  $\rightarrow$  less acidic (illogic!)

- At the start, define structure and bonding
  - X, Y and Z have simple covalent molecular structure with weak intermolecular forces of attraction.
- Amino acids: exist as zwitterions, not giant ionic lattice structures.
- H bond:
  - $\circ$  Same extensiveness  $\rightarrow$  See polarity.
    - O–H bond is more polar than N–H bond. More energy...stronger H bond.
- Explain why KCl is not volatile
  - Exactly the same as why it has a high boiling point. (Structure: ionic lattice + Bonding: ionic + large amt of energy needed to overcome during boiling  $\rightarrow$  thus non volatile)
- Explain the difference in solubility of X and Y
  - If they have same bond type, compare bond strength
- VS Explain the difference in solubility of X and Y in solvent
  - More favourable interactions are formed between X and solvent
- VS Explain why X dissolves in solvent
  - Energy released from formation of interactions between solvent and X is sufficient to provide for energy required to overcome FOA between X molecules
- Why can graphene conduct electricity
  - (each sp2 hybridised carbon forms covalent bonds with 3 other carbon atoms)
  - continuous lateral overlap of unhybridized p orbitals
  - o p electrons can delocalise to conduct electricity
- Ionic compounds characteristics:
  - Hard and brittle
  - Conduct electricity in molten state, not in solid state
  - High melting, boiling point
- Id-id
  - Greater Mr/surface area -> greater electron cloud size -> dipoles are more easily induced
- Why trans isomer is more stable than the cis isomer
  - Less steric hindrance

#### Gaseous state

- State the 3 assumptions of the kinetic theory as applied to ideal gases
- 1) Gas particles have negligible volume as compared to the volume of container
- 2) Intermolecular FOA btw particles and btw particles and walls are negligible
- 3) Collisions btw particles are perfectly elastic (not important)
- Explain why experimental value of amount is higher than theoretical value

Break assumption 2: non-negligible FOA cuz there is significant idid (or pdpd, depending on the molecule) interactions between particles  $\rightarrow$  pressure is lower

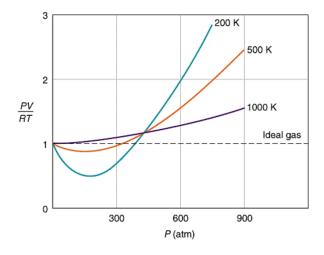
- Explain the conditions needed for real gas to behave more like ideal gas.
- Low pressure

Volume of particles become smaller relative to volume of container Gas particles further apart from one another Experience less intermolecular FOA

- High temp

Greater KE, overcome intermolecular FOA

• If a gas has more deviation at low pressure, it should have more deviation at high pressure too.



- Assumptions: (when qn asks why pressure is different from calculated pressure)
  - Ideal gas
  - There are other gases that contribute to total pressure
    - Qn has 1 vessel with only O2 gas, another vessel with O2 and water. The 2nd vessel is assumed to only have O2, but may have water vapor that contributes to total pressure.
- UNITS OF VOLUME IN PV=NRT MUST BE METER CUBED.

**Kinetics** 

Explain why reaction does not occur in the laboratory but takes place readily in \_\_\_\_\_.

- Why not in lab: High activation energy
- Why can in somewhere else: have catalyst to lower activation energy
- given conc-time graph, prove reaction is zero order wrt reagent
- straight line graph
- rate is indep of [?]
- given 2 conc-time graphs, prove rxn is 1st order
- calculate gradients and show working in answer
- Why is this reaction unlikely to happen?

Activation energy too high OR look at number of reactants  $\rightarrow$  if many reactant species  $\rightarrow$  unlikely for X reactants to collide at same time for successful collision

• Why is rate of reaction between S2O8<sup>2-</sup> and I<sup>-</sup> slow / why is reaction observed to not occur Negatively charged  $\rightarrow$  high activation energy  $\rightarrow$  few particles have high enough energy for reaction to proceed  $\rightarrow$  slow rxn

(exam skill: if previous part alr ask to show that reaction can possibly occur, gibbs free energy, then next part should be regarding rate/kinetics)

Content: rate=k[?]  $\rightarrow$  Sn1 unimolecular rate=k[?][?]  $\rightarrow$  Sn2 bimolecular

• Explain why HCl doesn't react with alkenes via free radical addition unlike HBr. Quote bond energies  $\rightarrow$  H-Cl bond is stronger  $\rightarrow$  *higher activation energy (link)*  $\rightarrow$  rxn does not occur

• Why is large excess of A added

[A] is constant. [A] does not affect rate.

• How did second order reaction become first-order

At first rate=k[A][B]

A is in excess, [A] is constant, reaction becomes pseudo first-order reaction

• Continuing above qn: outline suitable experiment to determine value for k.

Continuous method: add excess A

Sampling: add reactants tgt. at suitable time intervals, extract an aliquot using a pipette. Quenching: add a large volume of ice cold water to the rxn mixture to quench it. Titration: titration with NaOH, plot graph of V NaOH against time, find half life. k=ln2/half life

- How does heterogeneous catalyst work
  - 1. Rxts adsorb onto active sites of catalyst. Weak interactions form between catalyst and rxts
  - 2. On catalyst
    - a. Catalyst brings rxts close together
    - b. Interatomic/intramolecular bonds in rxts are weakened. Rxt molecules are brought closer together.
    - c. Activation energy is lowered

3. Rxts desorb from catalyst, regenerating catalyst

• Given that rate = k[A], explain which step is the rate-determining step.

- 1.  $A \rightarrow B + C$
- 2.  $B + C \rightarrow B + D + E$
- 3.  $A + D \rightarrow B$

Step 1 is the rate determining step. The reaction is 1st order wrt A, so the rate determining step can only have 1 A.

• If the experiment was repeated at the same condition but [reactant] is doubled, how does the value of rate constant change?

Rate constant is only dependent on temperature **and catalyst**, so it is unchanged.

• In an enzyme-catalysed reaction, how does rate vary with [substrate]?

portion of graph	Explain graph	active sites	order of reaction wrt substrate (no need if little marks)
low [substrate]	As [X] increases, rate increases proportionally	not fully occupied.	1st order
increasing [substrate]	no longer proportional to [X]	more are occupied	0th to 1st order
high [substrate]	Constant rate. Increasing [X] has no effect on rate.	all fully occupied	0th order

If only 1m:

Only describe low and high [X]

- Draw product-time graph if concentration of reactant halved.
  - maximum product halves
  - half life is constant
- Units for activation energy : J mol-1
- In a reaction where gas is produced, what 2 variables can be measured, which **together** can be used to monitor rate? And how wld u measure them?

6

 $\textbf{Together} \rightarrow \textbf{can plot graph} \rightarrow \textbf{Vol of gas against time}$ 

- Frictionless, graduated gas syringe
- Stopwatch, start stopwatch only when reactants are added in a sealed, closed system

#### Energetics

#### • Explain the deviation of experimental lattice energy from theoretical lattice energy.

Theoretical value assumes ions exist as discrete point charges.

Cation:

- High charge : size ratio
- Higher charge per unit volume
- Higher charge density
- Greater polarising power

Cation distorts the electron cloud of anion. There is covalent character in the ionic bond.

• State sign of change in Gibbs free energy and explain without reference to any calculation Cannot do calculation  $\rightarrow$  cannot be like high temp -> T $\Delta$ S larger than  $\Delta$ H. This is still calculation Explain based on the meaning of the sign.

- Reaction (eg dissolution) is spontaneous
- U calculated that the minimum temperature for dissolution of NH4Cl to dissolve in liquid water is 207K. Why is this only a theoretical value?

Strategy: look within the details, at the reaction. Can the reaction occur at this temperature? Is it too high or too low? Reason?

207K = -66 degrees. Too low. Water exists as solid ice. Reaction (dissolution) cannot occur.

- Explain 2 reasons why entropy change is large and positive.
  - 1. Dir: Inc # of gaseous particles, inc level of disorderliness
  - 2. Mag: enthalpy < 0. As rxn proceeds, T increases, KE increases. Even more disorderly.
- Why is it impossible to measure enthalpy of KHCO3 (s)?
  - Concept: enthalpy is experimentally measured using a calorimeter, with thermometer in a liquid
  - Impossible to measure temperature of a solid
- Exo: Combustion, Neutralisation
- Endo: Photosynthesis, Thermal decomposition
- Suggest an other process than requires energy in electrolysis cell → if got eg carbonate, think of thermal decomposition
- Equilibrium doesn't mean [rxt] = [pdt]. Equilibrium occurs where Gibbs free energy is minimum (most stable).

Chemical Equilibrium

- Explain the conditions used in the Haber process for manufacturing ammonia.
- Temperature is low to favour forward exothermic reaction, but not too low, such that rate of reaction is sufficiently fast enough.
- Pressure is high to favour forward reaction which reduces the total amount of gaseous particles, but not too high, such that cost of maintenance of equipment is not too high.
- Catalyst is used to speed up the reaction.
- What does small Kc value imply?

Small Kc  $\rightarrow$  small numerator (product)  $\rightarrow$  position of equilibrium lies on the left  $\rightarrow$  forward reaction is not favored

• State the Le Chatelier's Principle

It states that when a system **at equilibrium** is subjected to a change, it will **shift its position of equilibrium** to partially oppose the change, in order to **re-establish the equilibrium**.

# • Adding inert gas

If volume is constant, increase in total pressure does not affect partial pressures. (Concentration of reactants is constant)

# • Changing temp

favor endo/exo reaction > to absorb/release heat > partially change temperature

 N<sub>2</sub> + O<sub>2</sub> → 2NO. How does composition of reaction mixture change when total volume increases by 5 times?

Total pressure decreases <u>by 5 times (give numerical value when qn gives u numbers)</u>. Partial pressures decrease by 5 times. No change in number of gas particles (partial pressure decreases by the same extent), so no change in POE.

• Predict how Kp changes when total volume changes

ALWAYS RMB THAT KP IS ONLY DEPENDENT ON TEMPERATURE SO IT'S CONSTANT.

# Thermodynamics

• Explain the significance of the sign of entropy change.

Positive, implies increase in level of disorderliness.

• Explain why Gibbs free energy at non standard condition more negative than GFE at standard condition

GFE linked to POE. say smth like "POE shifts **further** right". (initially GFE<0, so POE was already at the right)

• Phase change  $\rightarrow$  change in entropy

Eg solid to liquid: gas moves more freely in liquid state as compared to being in fixed positions in solid state.

Acid base equilibria

compare acid strength of HOCI and HOBr
 Acid dissociation → forms conjugate base
 CI more electronegative
 Disperse negative charge on -OCI conjugate base more
 Conjugate base more stable
 HOCI more acidic

- Explain, with an equation, why pH of mixture is 7.6 when equal amount of strong base is added to equal amount of weak acid (both monobasic/monoprotic).
  - Qn wants u to *explain* why pH>7, not calculate pH to be 7.6
  - Insert hydrolysis eqn of salt → OH<sup>-</sup>. (the eqn that qn wants isn't acid + base → salt + water, but rather an eqn to prove that salt is basic. Remember hydrolysis is reversible).
  - Weak acid and strong base react according to stoichiometric ratio. Only salt is
    present. Salt is conjugate base of weak acid. It is more basic than water. Further explain
    the equation: conjugate base undergoes partial hydrolysis in water to produce some
    OH<sup>-</sup>.
- Arrhenius acid: releases H+ VS Bronsted Lowry acid: donates H+

• State a similarity in *acidic behaviour* of HCl and HClO

# Both monobasic

"Acidic behaviour"  $\rightarrow$  type of acid  $\rightarrow$  strength, type of basicity

• Indicator explanation

The pH range of the indicator coincides with (or is within) the sharp change in pH at equivalence point

#### Electrochemical cell

• Name an advantage of the fuel cell over a conventional battery Used electrolyte in fuel cell can be replaced with fresh electrolyte so that battery does not run out of power

• Why need membrane to allow selected ions to pass through <u>Maintain electrical neutrality</u> so that electrical energy continues to flow

- State and explain polarity of half-cell A when battery is discharging, given that during discharge, battery supplies electricity.
  - Identify electrolysis or electrochem. Supply electricity  $\rightarrow$  electrochemical cell.
  - E° of half cell A is more positive than E° of half cell B. (Need to explain why [R] occurs here).
  - Reduction occurs at half cell A
  - Electrode is cathode, so it is positive.

• What is a disadvantage of increasing current through an electrolytic cell (electroplating). Non-uniform plating, rough surface on plated electrode.

What material should be used as electrode

Platinum, as it is inert.

- Given 2 half cells have the same electrode potential, which is the more powerful oxidant at high pH?
- 1. A + 4H+  $\rightarrow \dots$
- 2.  $B + 2H + \rightarrow \dots$

Definitions:

- Oxidising ability = oxidising power
- Oxidant = the species oxidises others (oxidising agent)

As eqm 1 has more H+, increase in pH leads to larger fall in H+. POE of 1 shift left more. Tendency to be reduced decreases more for 1. Oxidising power falls more for A. A is a less powerful oxidant.

- keywords: **tendency** to be reduced, oxidising strength
- Why is Fel2 produced, but not Fel3?
  - past mistake: used half eqn Fe -> Fe3+. Should use Fe2+ -> Fe3+. Step by step process:
     Fe2+ + I2 -> FeI3, show that E cell <0. If you use Fe->Fe3+, E cell >0, not showing why
     FeI3 is NOT produced (at all).
- Why need to constantly stir the beaker? 4Cl- + 4Ag + O2 + 4H+  $\rightarrow$  4AgCl + 2H2O

Got gas, Need to ensure gas constantly diffuses through membrane (cuz it's used as a reactant.

Scenario: U calculated standard E cell, and u expect a certain observation, but the question
presents u with a contrasting observation. Trust ur instincts and ur calculated E cell, think of why
actual E cell is not your calculated value: non-standard conditions! (not 1.0 moldm-3, not 298K,
not 1 bar)

• Why is KCI solution kept concentrated?

(CI- is oxidised to AgCI). AgCI is solid! So that decrease in [CI-] is insignificant, E0 cell remains constant

Explain how anodising plates Al2O3 onto Al

Anodising is a surface treatment to plate Al2O3 onto Al, by placing Al metal at the anode in an electrolysis set-up.

Anodising:
 Anode: impure metal
 Cathode: pure metal (eg Cu)
 Electrolyte: Cu2+ cu2 it is needed for reduction at cathode

[O] 2AI + 3H2O  $\rightarrow$  Al2O3 + 6e + 3H2O + 6H+ [R] 2H+ + 2e  $\rightarrow$  H2 Must be acidic medium to produce H2

Solubility equilibria

• State the order of  $K_{sp}$  of AgCl, AgBr and AgI  $K_{sp \text{ of } AgCl} > K_{sp \text{ of } AgBr} > K_{sp \text{ of } Agl}$ AgCl is most soluble

• Explain why in dilute HNO<sub>3</sub>, only AgCl is soluble Complex ion effect  $\rightarrow$  decrease [Ag<sup>+</sup>]  $\rightarrow$  decrease ionic product  $\rightarrow$  soluble means IP<K<sub>sp</sub>

$$\begin{split} & \mathsf{K}_{\mathsf{sp of AgCl}} \! > \! \mathsf{K}_{\mathsf{sp of AgBr}} \! > \! \mathsf{K}_{\mathsf{sp of Agl}} \\ & \mathsf{In dilute HNO}_3, \, [\mathsf{Ag}(\mathsf{NH}_3)_2]^* \, \mathsf{complex ions are formed} \\ & \mathsf{Decrease in } [\mathsf{Ag}^+] \\ & \mathsf{Ionic product decrease} \\ & \mathsf{Only IP of AgCl fell below } \mathsf{K}_{\mathsf{sp}} \! \to \! \mathsf{only AgCl dissolved} \\ & \mathsf{IP of AgBr and Agl still greater than } \mathsf{K}_{\mathsf{sp}} \! \to \! \mathsf{remain undissolved} \end{split}$$

Explain why in concentrated HNO<sub>3</sub>, only AgCI and AgBr are soluble
 Concentrated → more complex ions formed → further decrease in Ag+ conc → further decrease in IP
 Both IP<Ksp for AgCI and AgBr</li>
 IP still > Ksp for AgI so AgI is still undissolved

• AgCl is soluble in excess  $NH_3$  but not Agl. Explain why. \*\*Need to explain the effect of  $NH_3$  first: Addition of  $NH_3$  reduces  $[Ag^+]$  because  $[Ag(NH_3)_2]^+$  complex is formed.

Then go on to explain IP and  $K_{sp}$ 

Transition metal

• Solution changes from (colour) to (colour) when a bidentate ligand is added. Suggest an explanation for this observation and write an equation [2].

1m for equation, 1m for explanation. Therefore the explanation should NOT be the long ass d-splitting shit. Ligand exchange occurred, bidentate ligand displaced original ligand

• Why Cul is white [2]

Fully filled d orbitals, no d-d transition, <u>no photons absorbed</u>, <u>appears white</u>. (<u>no need details on</u> <u>promotion of electrons and complementary shit</u>)

• Explain why transition metal can form ions of variable oxidation states

(Many diff oxidation states  $\leftarrow$  varying number of lost electrons  $\leftarrow$  electrons are lost from 4s and 3d subshells)

4s and 3d <u>orbitals</u> have **similar energy levels** > after 4s electrons are removed, 3d electrons can also be removed **to form stable ions**, giving rise to various oxidation states

- Why is transition metal significantly denser than s-block metal
- (1) Why denser

Larger atomic mass and smaller atomic radius

# (2) Why significantly denser

# TE metal can contribute both 3d and 4s electrons to sea of delocalised electrons > stronger metallic bonding

More atoms of larger atomic mass packed per unit volume > significantly larger density

• Why can a molecule act as a ligand

The **lone pair of electrons** on the molecule form dative bonds with **energetically accessible d orbitals** of cation.

• How does transition metal act as a heterogeneous catalyst

Cuz qn specified transition metal, not just any old molecule, must say **availability of 3d and 4s electrons in transition metal** allow reactant molecules to adsorb onto active sites ...

How do transition metals act as catalysts

- Heterogeneouscatalyst: got ions of partially filled d subshells, can accept electrons from reactants to act as heterogeneous catalyst
- Homogeneous catalyst: have variable oxidation states, can act as homogeneous catalysts

• Use E0 values to explain how Fe2+ acts as a **homogeneous** catalyst In ur equations, need to show state symbols to show Fe2+ is in same phase as reactants (cuz homogeneous)

• Why got difference in energy of d orbitals in presence of ligand vs isolated Interelectronic repulsion  $\rightarrow all$  electrons in d orbitals have higher energy than in isolated TM

• VS Why  $d_{z2}$  and  $d_{x2-y2}$  have higher energy than  $d_{xy}$ , etc Orientation of orbitals + degree of repulsion:

 $d_{z2}$  and  $d_{x2-y2}$  are oriented along the x, y, z axes  $\rightarrow$  face direct repulsion from lp electrons of ligand  $d_{xy}$ , etc oriented between axes, face less repulsion

• Explaining electrons filling lower energy d orbitals then moving to higher energy d orbitals VS electrons filling all orbitals singly before pairing up

Use the term "it is more energetically favourable..."

- Difference in properties of TM compounds compared to other compounds
  - Physical properties:
    - Higher bp, mp
    - Higher density
  - Chemical properties:
    - Coloured compounds (cuz of empty 3d orbital)
    - Catalytic behaviour (cuz of empty 3d orbital)
    - Can form complexes (also cuz of empty 3d orbitals)

#### Period 3

- Describe what you would observe when u add chlorides to water.
  - NaCl: no hydrolysis occurs, only hydration
  - MgCl2: dissolves in water with slight hydrolysis
  - AICI3: dissolves in water with appreciable hydrolysis
  - SiCl4: dissolves in water and completely hydrolyses to produce white fumes of HCl (g) which dissolves to give HCl (aq)
- Explain the trend in pH of chlorides.
  - NaCl: undergoes hydration due to low charge density
  - MgCl2: undergoes partial hydrolysis, cuz Mg2+ has higher charge density than Na+
  - AICI3: undergoes appreciable hydrolysis, cuz AI3+ has higher charge density than Mg2+
  - SiCl4 & PCl5: <u>complete hydrolysis</u> cuz blah vacant 3d orbitals.
- Describe the reactions when u add oxides to water
  - Na2O: NaOH is a strong base, dissociates completely in water to produce OH-, giving a strongly alkaline solution
  - MgO: Mg(OH)2 is sparingly soluble in water, producing some OH-, giving a weakly alkaline solution
  - Al2O3, SiO2: no reaction with water
  - P4O10: H3PO4 is a weak acid, dissociates partially in water to produce some H+, giving a weakly acidic solution
  - SO3: H2SO4 is a strong acid, dissociates completely in water to produce H+, giving a strongly acidic solution

Oxides: discuss about products; dissociation; strength of acidity/basicity Chlorides: discuss about reactants; hydrolysis/hydration; extent of hydrolysis

• Explain why CCl4 and SiCl4 react differently with water

Si possesses vacant energetically accessible d orbitals that can accept lone pair of electrons from  $H_2O$  while C doesn't. (SiCl4 can undergo hydrolysis to form SiO2)

• Explain why FeCl3 is acidic

write equation and yap about polarising power, polarise electron cloud of H2O, weaken O-H bond to explain why [Fe(H2O)6]2+ hydrolyses

• Explain what it means for an oxide to be amphoteric, and explain why a metal oxide is amphoteric.

Concept: Type of oxide <--- type of bonding

- Amphoteric oxides react with both acids and bases.
- Oxide is a metallic oxide > ionic > basic (think of Na2O) > reacts with acids
- Cation has high charge density > X—O bond has covalent character > acidic (think of CO2) > reacts with bases

Notes

- Ca(OH)2 is aqueous (limewater)
- Sulfur's standard state is S8

Isomerism

- State the 2 structural features required for an alkene to undergo cis-trans isomerism / explain how isomerism arises
- 1. Restricted rotation about C=C bond
- 2. <u>2 different groups attached to each carbon atom in C=C</u>
- Explain if cis or trans-isomer has higher boiling point

cis: polar, pdpd VS trans: nonpolar, idid Cis isomer higher bp

• Explain if cis or trans-isomer has higher melting point

Cis: more bulky > poorer packing efficiency > less intermolecular FOA per unit vol > lower mp

• Why is there optical inactivity in a solution of 2 enantiomers

The enantiomers are of <u>same concentration</u>

Is a racemic mixture

Rotation effect on plane polarized light by each enantiomer is equal and opposite, offset e/o.

• Why is there optical inactivity in a solution of meso compound

The rotation effect on plane polarized light by each half of the meso compound is equal and opposite, offset e/o.

# • Why only 1 enantiomer can react with enzyme

# Lock and key hypothesis

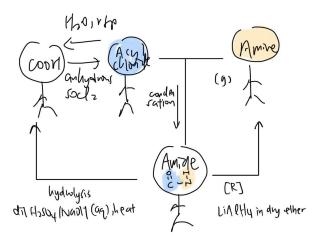
Other enantiomer (cis/trans isomer) is in wrong orientation/has different 3D shape.

Summary of reagents & conditions

Functional group	Characteristics	Reagents
Alkane	-	<ul> <li>alkane → RX: limited X2 (CCl4), UV light</li> <li>Not the best way in a synthesis qn to synthesize RX, as you cannot control where the X is attached</li> </ul>
Alkene	-	alkene $\rightarrow$ RX: HX (g) /X <sub>2</sub> (g) / X <sub>2</sub> (CCl4) rtp • Markonikov's rule: H attaches to carbon with <i>more</i> H (gang!!) • Better way to synthesize RX
		alkene → ROH: 1. concentrated h2so4, rtp 2. add h2o, heat
		alkene $\rightarrow$ diol: KMnO4 (aq), dil. H2SO4, cold
		alkene → cooh: KMnO4 (aq), dil. H2SO4, heat ● If carbon has a H, add O
		Alkene $\rightarrow$ alkane: H <sub>2</sub> (g), Pt (s), rtp / Ni (s), heat • Cannot LiAlH <sub>4</sub> and NaBH4 cuz C=C repels H <sup>-</sup>
RX	need ethanolic to produce nucleophile nuc sub needs heat Rong Xuan needs HOT ALCOHOL to drink	$RX \rightarrow ROH$ : NaOH (aq), heat "hot NaOH (aq)"
		<ul> <li>RX → alkene: ethanolic KOH, heat</li> <li>Zeitsev's rule: remove H from the carbon with the least H (if the gang goes, I go!)</li> </ul>
		$RX \rightarrow nitrile:$ ethanolic NaCN, heat
		<ul> <li>RX → amine: excess ethanolic NH<sub>3</sub>, heat in sealed tube</li> <li>If excess RX, polysubstitution of amine will occur</li> </ul>
		nitrile $\rightarrow$ cooh: dil H2SO4 (aq), <b>heat</b>
		nitrile $\rightarrow$ coo-: dil NaOH (aq), <b>heat</b>
		$ \begin{array}{l} \mbox{nitrile} \rightarrow \mbox{amine:} \ H_2 \ (g), \ Pt \ (s) \ / \ LiAlH_4 \ in \ dry \ ether, \ rtp \\ \bullet \ \ NaBH_4 \ is \ too \ weak \ (NaBH4 \ reserved \ for \ only \ carbonyls) \end{array} $
ROH	Need $H_2SO_4$ as	$ROH \rightarrow salt: Na (s)$
	dehydrating agent to draw out the water	ROH $\rightarrow$ alkene: excess concentrated H <sub>2</sub> SO <sub>4</sub> , heat

	Anhydrous →	$ROH \rightarrow RX:$ HX (g) / anhydrous $PX_{3}$ / anhydrous $\textbf{PCI}_{3}$ / anhydrous $\textbf{SOCI}_{2},$ rtp	
		$ROH \rightarrow aldehyde: K_2Cr_2O_7$ (aq), dil $H_2SO_4$ (aq), heat with distillation (condenser is placed at an angle, to separate aldehyde from reactant, to prevent cooh from forming)	
		$ROH \rightarrow ketone / cooh: KMnO_4 (aq), dil H_2SO_4 (aq), heat / K_2Cr_2O_7 (aq), dil H_2SO_4 (aq), heat under reflux (condenser is placed vertically, to ensure complete rxn)$	
		ROH $\rightarrow$ ester: cooh, <b>conc</b> H <sub>2</sub> SO <sub>4</sub> , heat / RCOCI, rtp	
		Ester $\rightarrow$ RX: dil H2SO4/NaOH (aq), <b>heat</b>	
Arene	Need lewis acid catalyst	Benzene $\rightarrow$ nitrobenzene: conc HNO <sub>3</sub> , conc H <sub>2</sub> SO <sub>4</sub> , 30/60/90 <sup>o</sup> C	
	Alkylbenzene can be	Xxx, anhydrous FeCl <sub>3</sub>	
	oxidised if at least 1 O/H → cooh	<ul> <li>Nitrobenzene → phenylamine:</li> <li>1. Sn in conc HCl, heat</li> <li>2. Excess NaOH (aq)</li> <li>Phenylamine ion is basic, will react with HCl in (1), so need NaOH to turn NH4+ to NH3</li> </ul>	
Phenol	Phenoxide is a better nucleophile attracter	<ul> <li>Phenol → ester: NaOH (aq) (phenoxide is acidic, so use a base), RCOCI, rtp</li> <li>Weak nucleophile, doesnt react with cooh</li> <li>Need NaOH to form phenoxide</li> </ul>	
	Doesnt undergo nucleophilic substitution	Phenol $\rightarrow$ NO <sub>2</sub> /Br substituents: conc/dil HNO <sub>3</sub> / Br <sub>2</sub> (aq)/(I)	
Carbonyl		Carbonyl $\rightarrow$ hydroxynitrile: HCN, trace NaCN, cold	
		Hydroxynitrile → amine: LiAlH <sub>4</sub> in dry ether / H <sub>2</sub> (g), Pt (s) • NaBH <sub>4</sub> cannot	
		Hydroxynitrile $\rightarrow$ cooh: H2SO4 (aq), <b>heat</b> (hydrolysing CN bond, so need H2O)	
		Hydroxynitrile $\rightarrow$ coo-: NaOH (aq), <b>heat</b>	
		Carbonyl $\rightarrow$ alcohol: LiAlH <sub>4</sub> in dry ether / ethanolic NaBH <sub>4</sub> / H <sub>2</sub> (g), Pt (s), rtp	
cooh	Cooh and acyl chloride are cousins, cannot react with each other	Cooh → acyl chloride: anhydrous PCl <sub>3</sub> / SOCl <sub>2</sub> • Similar to ROH (OH → Cl) • No water cuz water will turn acyl chloride back to cooh	
	<ul> <li>Cooh + amine is an acid base rxn, not condensation</li> </ul>		
		Acyl chloride $\rightarrow$ cooh: h2o, rtp	
		Acyl chloride $\rightarrow$ ester: ROH, rtp / phenol, NaOH (aq), rtp	
		Acyl chloride $\rightarrow$ amide: amine (g), rtp / NH3 (g), rtp	

		Amine cannot be aqueous, if not acyl chloride will hydrolyse
Nitrogen		Amine $\rightarrow$ amide: acyl chloride, rtp
compounds	compounds	Amide $\rightarrow$ cooh: dil H <sub>2</sub> SO <sub>4</sub> (aq), <b>heat</b>
		Amide → amine: LiAlH₄ in dry ether • Amide is similar to COOH
	<ul> <li>Phenylamine → bromo substituted: Br<sub>2</sub> (aq)/(I)</li> <li>similar to phenol</li> <li>VS phenol: phenylamine cannot use HNO<sub>3</sub> to undergo electrophilic substitution because phenylamine is basic, will undergo acid-base</li> </ul>	
		Protein $\rightarrow$ amino acid: conc NaOH/HCl, heat under reflux for a prolonged period



Summary of explanations

Question	Idea	Keywords
Why is a specific product formed more / in greater abundance / formed preferentially Explain acidity	Stability	<ul> <li>electron donating / electron withdrawing groups</li> <li>increase / decrease electron density</li> <li>more stable molecule / carbocation / conjugate base</li> <li>disperse / intensify the positive / negative charge</li> </ul>
Is mixture optically active	Optical activity	<ul> <li>trigonal planar carbocation</li> <li>attack 2 sides with equal probability</li> <li>form equal proportions of products</li> <li>racemate</li> </ul>
	Bonds	<ul> <li>p orbital overlaps laterally</li> <li>lone pair delocalised into pi electron cloud</li> <li>partial double bond character</li> </ul>

Bulky

Org chem

• State the role of H+ in step 1

Must only look at step 1, not the whole reaction Whole reaction: H+ is regenerated, catalyst Step 1: Bronsted Lowry acid

• Explain why SO3 can act as an electrophile

Sulfur is bonded to electronegative oxygen atoms, electron deficient.

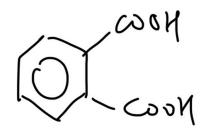
• Use the concept of electronegativity, electronic and steric effects, and delocalisation to explain why a product is formed / not formed.

The electronic effect means resonance.

Write about stability of intermediate if cannot explain using reactant steric hindrance.

Conditions for resonance: at least 3 sp2 hybridized atoms

- Intermediate is resonance stabilized by C=O. Lone pair of electrons on carbon with negative charge delocalised into electronegative O atom.
- Name this



priority should be given to COOH. Benzene should be the substituent. Benzene (or benzal) -1, 2-dioic acid

• Why is a racemic mixture formed (different from why it is optically inactive) (radical) has trigonal planar arrangement, (chlorine) attacks from either top or bottom with equal probability

- Resonance: at least 3 sp2 hybridized atoms
  - remember C might have H
  - lone pair of electrons is considered as an electron region
  - o radical is not considered as an electron region, it resides in unhybridized p orbital
- When naming cis trans isomers, need the dash after cis-
- Why isomer with 3- position is least likely to be formed if the substituent at the benzene ring is 2,4-directing?

2-4 directing means it increases electron density at 2 and 4 positions. **Intermediate of isomer is less stable** 

Alkanes

• Explain what is meant by homolytic fission

When a <u>covalent bond</u> undergoes homolytic fission, it <u>breaks evenly</u>. <u>One electron</u> from the bond goes to each atom. <u>2 radicals are formed</u>.

• Explain what is meant by sp hybridization with reference to the C atom in CS<sub>2</sub>.

Before: 1s and 1p orbital mix

After: shape around C is linear. There are 2 sp hybrid orbitals and 2 unhybridized p orbitals. (total 4 always)

• Explain how electrons are arranged in sp<sup>2</sup> sulfur atom so that bonding in CS<sub>2</sub> can occur. Orbitals that take part in bonding  $\rightarrow$  has **unpaired electron** Orbitals that do not take part in bonding  $\rightarrow$  has **lone pair** Plonk number of valence electrons

Qn has 2 parts: how electrons are arranged + how bonding occurs

- 1. 2 lp in 2 hybrid sp<sup>2</sup> orbitals, 1 unpaired electron in 1 hybrid sp<sup>2</sup> orbital, 1 unpaired electron in unhybridized p orbital.
- Sp<sup>2</sup> hybrid orbital with unpaired electron undergoes head on overlap with C sp hybrid orbital to form sigma bond. Unhybridized p orbital undergoes sideway overlap with p orbitals of C to form pi bond.
- Explain why alkanes are very unreactive.
- 1. C–C and C–H bonds are nonpolar  $\rightarrow$  do not attract electrophiles and nucleophiles
- 2. C–C and C–H bonds are very strong, hard to break  $\rightarrow$  large amt of energy needed
- Explain why more xx monosubstituted halogenoalkane are formed than expected.

Alkyl radical has <u>more electron donating alkyl groups</u> > **disperse positive charge on carbocation** > <u>more stable</u> > preferentially formed

• Why does reaction occur at a high rate even after exposure to light has stopped.

\_\_\_ Radicals produced initiate *chain* reactions of *propagation* which form more radicals for reaction to proceed.

• Why does FRS occur in high temperature, rather than electrophilic addition? ⇒ Why does FRS need high temp? Which **step** of FRS?

High temperature (heat/UV) is needed to provide sufficient energy in the initiation stage, for X-X bonds to break and form X radicals

Alkenes

Why are more highly substituted alkenes produced more readily

more <u>electron donating</u> alkyl groups greater <u>electron density</u> in C=C bond more stable alkene

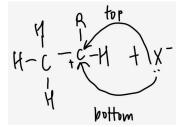
> Why is xxx product from electrophilic addition (alkene + H2O and alkene + HX) formed in <u>greater</u> <u>abundance</u>?

#### Ans: Carbocation stability

Carbocation has more electron-donating alkyl groups > further reduces electron deficiency of carbocation > carbocation is more stable > carbocation is preferentially formed > major product formed

 Why is the product of electrophilic addition of alkene optically inactive although it contains a chiral carbon?

Explain why equal yield of enantiomers: In step 2 of the mechanism, the nucleophile has <u>equal likelihood</u> to attack the <u>trigonal planar</u> carbocation from either side of the plane, hence 2 enantiomers are formed in equal proportion.



Standard explanation: This forms a racemic mixture. The effect on plane polarized light by each enantiomer is equal and opposite, which cancel each other out and result in net zero optical activity. Hence mixture is optically inactive.

#### Arenes

Why can't benzene react with weak electrophiles and undergo electrophilic addition like alkenes?

For benzene, there are 6 delocalised pi electrons which cause benzene to have resonance stability (also used to answer why benzene undergoes substitution instead of addition). Hence the pi electrons are less available for reaction. Hence benzene requires a stronger electrophile.

Why is xxx product from electrophilic substitution formed in greater abundance?

Same idea as alkene, compare carbocation stability.

Side note: draw carbocation without the benzene ring

Xx degree carbocation has more electron donating alkyl groups, which further reduce the electron deficiency of the carbocation, hence it is more stable, more preferentially formed.

• Explain difference in reactivity/conditions for these 2 reactions. (focus on the reactant)

Scenario 1) More electron donating alkyl groups > increases electron density of benzene more > benzene more reactive, more susceptible to electrophilic attack

Scenario 2) Substituent is a stronger activator > increases electron density of benzene more > increases reactivity of benzene more > milder conditions needed

• Why got 2,4-directing effect if the substituent is an EDG?

Substituent is electron donating group > increase electron density at 2nd & 4th positions relative to substituent > if the reactant is at 3rd carbon, **carbocation** is **least stable** 

 If substituent is at 1st carbon, why is reactant more likely to be at the 4th carbon instead of the 2nd carbon?

Steric hindrance, substituent is bulky

• Why need anhydrous condition

Water will react with AICI<sub>3</sub> (no need to state product)

- Describe the 2 roles of AICI3
- 1) Lewis acid
- 2) Catalyst

Halogen derivatives

• Why is product from Sn1 nuc substitution of 3° halogenoalkane optically inactive

Carbocation is <u>trigonal planar</u>, the nucleophile can attack from above and below in <u>equal probability</u>. Optical isomers formed in <u>equal proportion</u>, effect on plane polarised light are equal and opposite. No net effect on pp light.

• Why product from Sn2 nuc sub is optically active

[direction of nucleophilic attack]

Nucleophile attacks electron deficient carbon from opposite side of leaving group, produce only one enantiomer

• Why 3° halogenoalkane will undergo Sn1 nuc subst instead of Sn2

#### Why Sn1: carbocation stability

The carbocation is 3°, has 3 electron-donating alkyl groups which reduce its electron deficiency, very stable.

Why not Sn2: steric hindrance

It has 3 bulky alkyl groups, carbon experiences large steric hindrance, hard for the nucleophile to attack carbon from rear end.

• Why got low yield of products from Sn1 nuc sub Polysubstitution, \_\_\_ is a stronger nucleophile than \_\_\_

• Explain order of reactivity of chloroethane, bromoethane and iodoethane.

Method: focus on bond strength. Hierarchy of explanation: BE>electronegativity. Their explanations contradict so umm don't write abt electronegativity.

Strength: C-CI > C-Br > C-I (Decreasing orbital overlap) Reactivity: C-CI < C-Br < C-I(weaker bond => more reactive)

During slow step, energy is needed to break C–X bond Compare bond strength, quote bond energy values Nuc subst occurs more readily

- Explain why halogenoarenes and halogenoalkenes do not undergo nucleophilic substitution
- p orbitals of (halogen) overlaps with  $\pi$  electron cloud of benzene/p orbitals of C=C bond
- lone pair on X atom delocalised into electron cloud via resonance
- There is partial double bond character in C-X bond
- C–X bond is stronger, cannot be broken to form X- ions
- Suggest safety precaution when handling PCI5

White fume HCI (g) produced, toxic Use fume hood

Phenols

Why is phenol more acidic than alcohol and water?

(compare stability of anion after dissociation of phenol aka conjugate base)

P orbital of oxygen (in conjugate base of phenol) overlaps with the electron cloud of benzene ring Lone pair electrons is delocalised into benzene ring via resonance Negative charge of conjugate base of phenol is dispersed Conjugate base of phenol is more stable than conjugate base of alcohol and water

• Explain effect of electron withdrawing substituent on acid strength of phenol

EWG disperses negative charge on ion more than normal phenoxide ion This ion is more stable Acid dissociation of this phenol occurs to a greater extent -> greater acidity

(opposite for electron donating group)

 Explain why phenols do not undergo nucleophilic substitution like alcohols to form halogenoalkanes

P orbital of oxygen overlaps with electron cloud of benzene ring Lone pair of electrons delocalises into benzene ring via resonance There is partial double bond character in C–OH bond, stronger, difficult to break

Explain why phenols do not react with CA to undergo condensation and form ester like alcohols

P orbital of oxygen overlaps with electron cloud of benzene ring Lone pair of electrons delocalises into benzene ring via resonance  $\rightarrow$  **less available** to attack electron-deficient Carbon in COOH Weaker nucleophile

• Explain why phenols are more reactive towards electrophilic substitution than benzene Phenol got OH, benzene dh

delocalisation of lone pair of electron on oxygen into benzene ring (resonance effect) \*\*\*OH does NOT donate electrons!\*\*\*

OH group increases electron density in ring Phenol is more susceptible to electrophilic attack Milder conditions required, position of electrophile is 2,4 cuz of OH directing effect

Carbonyls

Why do carbonyl compounds undergo nucleophilic addition
 Carbonyl carbon is partial positively charged -> it is electron deficient -> susceptible to attack by nucleophiles

(C=O -> C-OH so addition)

 Why is racemic mixture formed when an asymmetrical carbonyl compound undergoes nucleophilic addition with HCN

The nucleophile can attack trigonal planar carbonyl carbon from above or below in equal probability. Equal proportion of enantiomers is formed, their rotation effects on plane polarised light are equal and opposite and cancel each other out. racemic mixture is formed, and is optically inactive.

- Why are aldehydes more reactive than ketones
- 1) Steric factor: aldehyde only has 1 bulky alkyl group, ketone has 2. Less steric hindrance in aldehyde.
- 2) Electronic factor: aldehyde only 1 electron-donating alkyl group, ketones have 2. Carbonyl carbon in aldehyde is more electron deficient.
- Why is LiAlh4 a stronger reducing agent than NaBH4

Either: Al is less electronegative (more electropositive) than boron (H is then electronegative) -> larger electronegativity difference -> Al-H bond broken more easily

Or: Al-H bond is longer and weaker so broken more easily than B-H

• Why is NaCN in slightly acidic conditions used \*\*\* NaCN undergoes **complete** dissolution (soluble salt). HCN <-> H+ + CN-

- (slightly acidic instead of too acidic → POE not too to the left) High enough conc of CN- to attack carbonyl C in rate-determining step
- (acidic instead of not acidic → POE not too to the right) And got HCN to for step 2 of mechanism

Carboxylic acids

• Why CA have higher BP than alcohol

CA hv electron withdrawing oxygen (in C=O) -> (Carbon is more electropositive) -> OH bond in CA is more polarized -> stronger H bond

- Compare the ease of hydrolysis of acyl chloride and RX
- acyl chloride more easily hydrolysed
- acyl chloride has electronegative O & Cl, RX only has Cl
- carbon atom in acyl chloride is more electron deficient
- more susceptible to nucleophilic attack

#### Nitrogen compounds

- *G*Explain basicities of amines
- Basicity = availability of lone pair of electrons on N to accept H+
- Higher electron density  $\rightarrow$  LP of electrons more available to accept H+  $\rightarrow$  more basic
- Increasing basicity: amide, phenylamine, methylamine
- Methylamine with electron withdrawing group:
  - Electron density of nitrogen atom decrease
  - LP of electrons are less available to accept H+ (proton)
- Phenylamine:
  - Delocalisation of electrons into pi electron cloud of adjacent benzene ring via resonance
  - LP less available to accept H+
- Amide (CONH)
  - Lone pair of electrons on N delocalised into electron-withdrawing C=O group
  - LP not available to accept proton

#### Why phenylamines undergo E sub more readily than benzene

Amine group is electron donating, LP on nitrogen delocalised into benzene ring, increases electron density.

#### • Why are amides neutral (ie why not basic)

Continuous sideway overlap of p orbitals on adjacent atoms (C and N) LP on nitrogen delocalises into C=O bond, not available to accept H+

#### Melting point of amino acid is higher than xxx

Amino acid exists as zwitterion, more energy needed to overcome stronger hydrogen bonding

#### • α-COOH is more acidic than side chain COOH

 $\alpha$  COOH closer to electron withdrawing  $\alpha$ -NH<sub>3</sub><sup>+</sup>, so the negative charge on  $\alpha$  COO- conjugate base is more dispersed, more stable, more reactive in donating H<sup>+</sup>

#### α- NH<sub>3</sub><sup>+</sup> is more acidic than side chain NH<sub>3</sub><sup>+</sup>

Closer to electron withdrawing  $\alpha$  COOH, disperse electron density on  $\alpha$  NH<sub>2</sub> more, lone pair on NH<sub>2</sub> is less available to donate. Smaller orbital overlap, weaker N-H bond, NH<sub>3</sub><sup>+</sup> donates H<sup>+</sup> more readily Nh3 less basic  $\rightarrow$  conjugate acid nh4+ more acidic

Environment

What are the health effects of carbon monoxide

CO binds more strongly to haemoglobin than O2, reducing ability of haemoglobin to carry oxygen

• Suggest a harmful effect of NO<sub>2</sub>, other than its role as catalyst in formation of acid rain It forms ozone in the lower atmosphere, causing respiratory problems.

• What compound catalyses formation of acid rain NO2 catalyst SO3 + H2O  $\rightarrow$  H2SO4

• What reactions occur in catalytic converters  $NO + CO \rightarrow N_2 + CO_2$  $NO_2 + C \rightarrow N_2 + CO_2$ 

Removal of CO: CO +  $\frac{1}{2}$  O2  $\rightarrow$  CO2 Removal of hydrocarbons: CxHy + O2  $\rightarrow$  H2O + CO2 (balance)

- Explain, with the aid of an equation, why oxides of nitrogen are present in engine exhaust.
  - Engine exhaust: under high temperature in combustion engine,
  - Explain: atmospheric N<sub>2</sub> reacts with O<sub>2</sub>
  - $\circ \quad \text{Eqn: } \mathsf{N}_2 + \mathsf{O}_2 \to \mathsf{2NO}$
- Give the equations for the depletion effect of CFCs on the ozone layer (which also causes skin cancer)

CFCs stand for chloroflurocarbons

 $\begin{array}{l} \mathsf{CF3Cl}+\mathsf{UV}\to\mathsf{Cl}\bullet+\bullet\mathsf{CF3}\\ \mathsf{Cl2} \text{ as } \underline{\mathsf{catalyst}}, \text{ regenerated}\\ \mathsf{Cl}\bullet+\mathsf{O3}\to\mathsf{Cl}\mathsf{O}\bullet+\mathsf{O2}\\ \mathsf{Cl}\mathsf{O}\bullet+\mathsf{O}\to\mathsf{Cl}\bullet+\mathsf{O2} \end{array}$ 

C–Cl bonds break > produce Cl radicals > Cl radicals destroys ozone

• What are safe alternatives to CFCs

Anything that won't produce chlorine radicals C–F & C-H bonds strong, won't break

Why is CFCI3 used as a refrigerant

chemically inert + liquefies easily under pressure, vaporizes easily when pressure is released -> cools substances down

C–Cl, C–F bonds strong > unreactive, stable

# Distinguishing tests

Fn group	Rxn	Reagents & Conditions	Obs
Alkene	Electrophilic addition	Br2 in CCl4, room temp	Orange red Br2 decolourised
		Br2 (aq), <u>room temp</u>	Orange Br2 decolourised
	Vig [O]	KMnO4 (aq), H2SO4 (aq), heat	Decolorization of purple KMnO4
			If terminal alkene: Effervescence due to CO2 (g) formed, turns limewater white
	Mild [O]	KMnO4 (aq), NaOH (aq), cold	Decolorization of purple KMnO4, brown ppt of MnO2 formed
Halogenoalkane	Nuc sub	<ol> <li>NaOH (aq), heat</li> <li>Excess dilute HNO3 (Remove OH-, prevent formation of brown Ag<sub>2</sub>O)</li> <li>AgNO3 (aq)</li> <li>MEMORISEEE !!!</li> <li>eqn: RX + NaOH -&gt; ROH + NaX X- + Ag+ -&gt; AgX</li> <li>(halogenoarene and halogenoalkene do not give ppt due to resonance/p orbital overlap)</li> </ol>	Chloroalkane: White Bromoalkane: Cream Iodoalkane: Yellow
		<ol> <li>Same as above</li> <li>Ethanolic AgNO3, heat</li> </ol>	Chloroalkane; - White ppt (AgCl) formed in 5-8 min Bromoalkane: - Cream ppt (AgBr) formed in 3-5 min Iodoalkane: - Yellow ppt (AgI) formed almost immediately

Alcohol	Redox	Na (s)	Effervescence of colourless H2 gas extinguishes burning splint with a pop
		ROH + Na-> RO-Na+ + ½ H2	
	Nucleophilic substitution	Anhydrous PCI5, room temp ROH + PCI5 -> RCI + POCI3 + HCI	Effervescence of <mark>white fumes</mark> HCI (g) observed
		Anhydrous SOCl2, room temp ROH + SOCl2 -> RCl + SO2 + HCl	-ve obs: no eff. Xno observation
	Triiodomethane test (oxidation)	I2, NaOH (aq), warm RCH(OH)(CH3) + 4I2 + 6OH- → RCOO- + CHI3 + 5I- + 5H2O	Yellow precipitate of CHI3 observed
		1 ROH : 1 CHI3	
Phenol	Redox	Na (s) ROH + Na-> RO-Na+ + ½ H2	Effervescence of colourless H2 gas extinguishes burning splint with a pop
			Using sodium to distinguish between alcohol and phenol: <b>rate of formation</b> of H2 gas is faster in phenol cuz more acidic
	Electrophilic substitution	Br2 (aq), rtp	Orange Br2 decolourised and white ppt of tri-brominated phenol is formed
		Tri sub $\rightarrow$ 1 phenol : 3 Br <sub>2</sub> (aq)	
	Complex formation	Neutral FeCl3 (aq)	Violet complex
	Redox		
Carbonyls	Condensation	2,4-DNPH	<mark>Orange</mark> ppt
All aldehydes	Oxidation	KMnO4/K2Cr2O7 (aq), H2SO4 (aq), heat (cannot write heat under reflux/heat with distillation cuz it is conducted using test tubes)	Purple -> colourless Orange -> green
All aldehydes	Oxidation	Tollens' reagent Ammonical $[Ag(NH_3)_2]^+$ , heat	Grey ppt of Ag (silver mirror)
		$\begin{array}{l} \textbf{RCOH} + 2[Ag(NH_3)_2]^+ + 3OH \rightarrow ROCO_+ \\ + 2Ag + 4NH3 + 2H2O \\ \textbf{(ONE aliphatic aldehyde produces} \\ \textbf{TWO Ag (s)!!!)} \end{array}$	
Aliphatic aldehydes			

	Oxidation	Fehling's solution (alkaline $Cu^{2+}$ complex), heat ROCH + 2 $Cu^{2+}$ + 5 $OH^-$ -> ROCO- + $Cu_2O$ + 3 $H_2O$	Brick red ppt of Cu <sub>2</sub> O -ve: remains blue
Methyl carbinol group (RCOCH3)	Triiodomethane test [O]	I <sub>2</sub> (aq), NaOH (aq), heat Like alcohol, CA is formed, undergoes acid base rxn	Yellow ppt of CHI3
Carboxylic acid	Nucleophilic substitution	Anhydrous PCI5, room temp	Effervescence of white fumes HCI (g)
	substitution	Anhydrous SOCI2, room temp	observed -ve obs: no eff. Ⅹno observation
	Acid base	Na2CO3 (aq) / NaHCO3 (aq)	Effervescence of co2 gas which forms white ppt with limewater
	Oxidation	Acidified kmno4	Decolorise purple solution for presence of hco2h or (co2h)2
Acyl halide	Hydrolysis	Limited H2O (I), room temp	White fumes of HCI (g)
	QA	AgNO3 (aq), rtp	Coloured ppt formed
Amide	Hydrolysis	NaOH (aq), heat Or HCl (aq), heat	Pungent, alkaline gas evolved which turns moist red litmus paper blue
Phenylamine	E sub	Br2 (aq), rtp	Orange aq Br2 decolourised, white ppt formed
		Br2 in CCl4, rtp	Orange red Br2 decolourised

Legend: Unique to functional group

Alkane/Cycloalkane/Arene? vs Alkene

- Electrophilic addition: add Br2 dissolved in CCl4 solvent
  - Alkene: orange-red Br2 decolourised
    - Alkane: Br2 remained orange-red
- Vigorous oxidation: add acidified KMnO4, dilute H2SO4 (aq), heat
  - Alkene: purple KMnO4 decolourised
  - Alkane: KMnO4 remained purple

Alkene with terminal C vs Alkene with non-terminal C

• Vigorous oxidation: KMnO4, dilute H2SO4 (aq), heat

- Alkene with terminal C: Decolourisation of purple KMnO4 + Effervescence due to CO2 gas produced which turns limewater white
- Alkene with non-terminal C: Decolourisation of purple KMnO4

Benzene vs Alkylbenzene

• Oxidation (Benzene cannot be oxidized)

Alkylbenzenes

- Oxidation
  - Pri Alkylbenzene: decolourise, no effervescence
  - Sec Alkyl: decolourise, have effervescence due to CO2 produced, which turns limewater white
  - Tertiary Alkyl C (no H/O): KMnO4 remains purple

Halogenoalkane vs other functional groups

Types of halogenoalkanes

Aldehyde vs Ketone

- Oxidation: add acidified KMnO4, dil H2SO4 (aq), heat
  - Aldehyde: decolourises purple KMnO4
  - Ketone: KMnO4 remains purple

Pri/Sec alcohol vs Tertiary alcohol

- Oxidation
  - Pri/sec alcohol: decolourise
  - Tertiary alcohol: KMnO4 remains purple

Alcohol vs alkene using oxidation Alkene: doesnt oxidise with K2Cr2O7 Alcohol: doesnt oxidise with cold