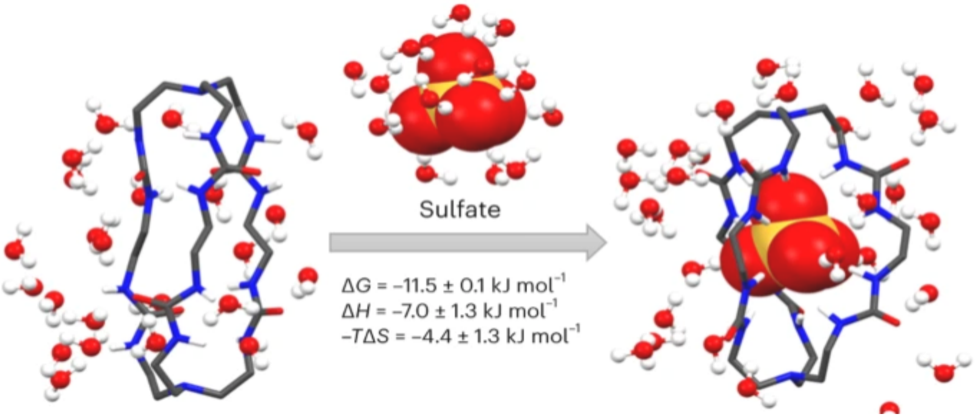
Chemistry made easy.

Timothy Quek



A sulfate ion being seamlessly encapsulated into a cage-like organic molecule via hydrogen bonds.
Nat. Chem. ***16****, 335–342 (2024).*

Hi there! I'm Timothy Quek, the Senior Lead Tutor and Head of JC Chemistry at Indigo Education Centre.

Chemistry is the foundation of everything around us. The better we understand it, the more we comprehend the world we live in. Without it, there would be no amino acids, nucleic acids, respiration, or photosynthesis — in fact, no life at all.

I'm a First-Class Honours (Highest Distinction) Chemistry graduate from NUS. Although my research journey didn't go as planned, teaching has always been my true calling. I find it incredibly rewarding to help students navigate chemistry's complexities and achieve breakthroughs in their learning.

Over the years, I've had the privilege of working with thousands of students. From these experiences, I've compiled and categorised the most frequently asked questions and key concepts to make learning easier and more efficient. My goal is not just to help students succeed academically, but to foster a deeper appreciation for chemistry.

Whether you're grappling with difficult topics or looking to expand your knowledge, I'm here to guide you in mastering chemistry.

"Nothing in life is to be feared, it is only to be understood." – Marie Curie

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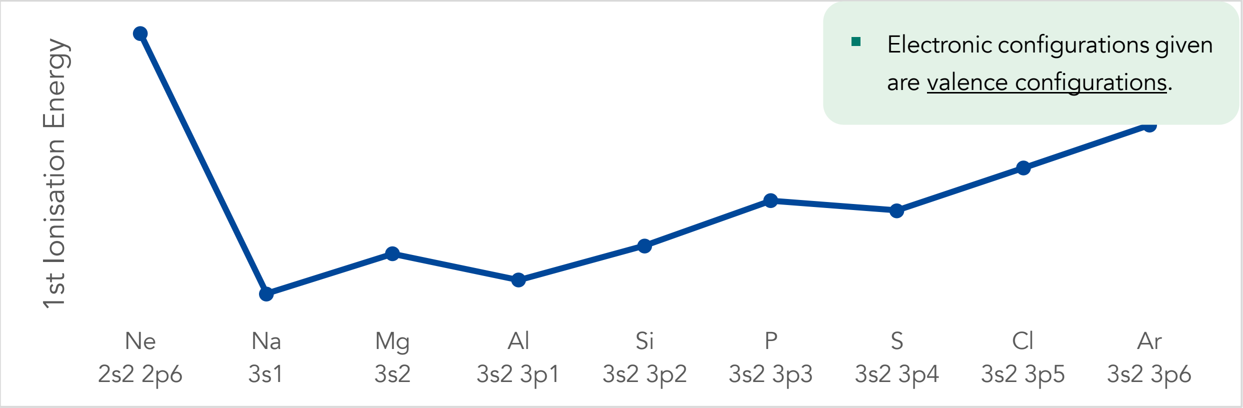
1 Atomic Structure

Interpreting Ionisation Energy Graphs Across the Period

1st Ionisation Energy Graph

1st Ionisation energy (IE) is defined as the energy required to remove 1 mol of electron from 1 mol of a gaseous atom to produce 1 mol of a singly charged gaseous cation.

1st IE of an element **X**: $\mathbf{X}(g) \longrightarrow \mathbf{X}^{+}(g) + e^{-}$



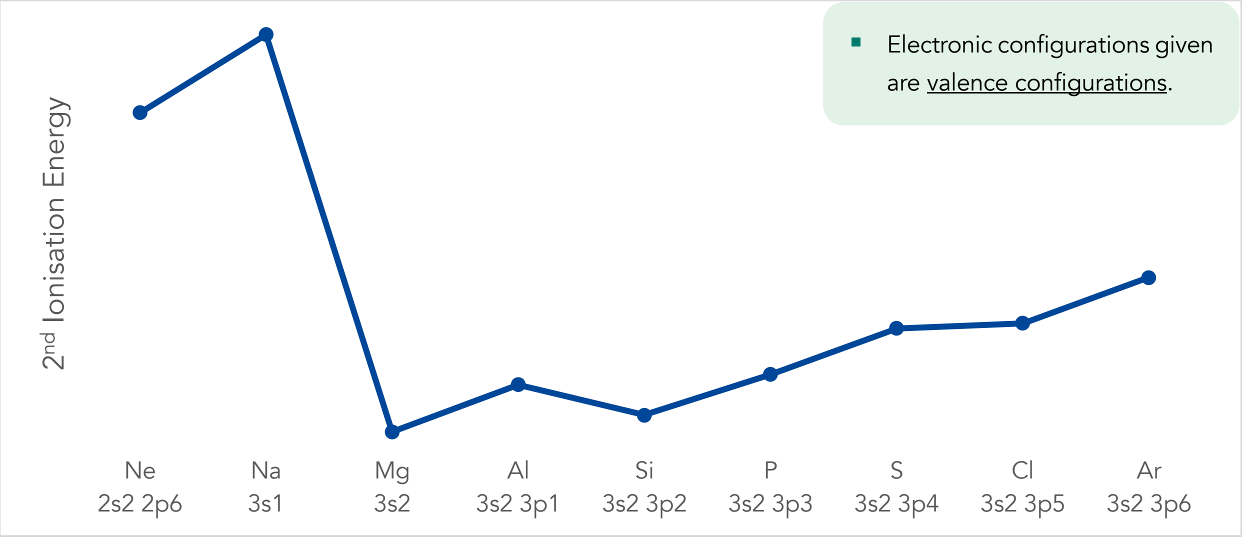
- Electronic configurations given are valence configurations.

Steep Decrease in 1st IE	From Group 18, Period 2 (Ne) to Group 1, Period 3 (Na), there is a steep decrease in 1st IE because: Significantly lesser energy is required to remove a valence electron from a higher energy quantum shell of the Group 1 element of a new period.
General Trend	Across the period (from Na to Ar), 1st IE increases because: • Nuclear charge (number of protons) increases. • Shielding effect (number of inner shell electrons) remains relatively constant; Na (3s^1) to Ar (3s^2 3p^6) have the same number of inner shell electrons. • Effective nuclear charge increases ⇒ electrostatic attraction between positively charged nucleus and valence electrons increases. • Energy required to remove valence electron increases.
Anomaly 1	From Group 2 to Group 13 (Mg to Al), 1st IE is lower than expected because: • Lesser energy is required to remove a valence electron from a higher energy 3p subshell of the Group 13 element.
Anomaly 2	From Group 15 to Group 16 (P to S), 1st IE is lower than expected because: • Lesser energy is required to remove a valence electron that experiences inter-electronic repulsion in the 3p orbital of the Group 16 element.

2nd Ionisation Energy Graph

2nd Ionisation energy (IE) is defined as the energy required to remove 1 mol of electron from 1 mol of a singly charged gaseous cation to produce 1 mol of a doubly charged gaseous cation.

2nd IE of an element **X**: $X^{+}(g) \longrightarrow X^{2+}(g) + e^{-}$



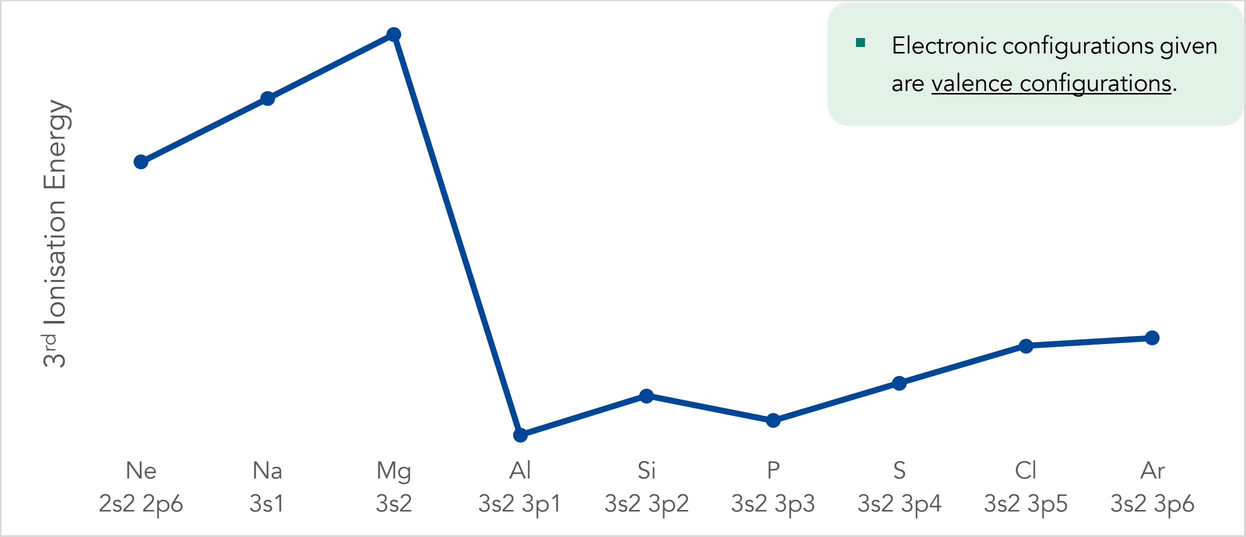
- Electronic configurations given are valence configurations.

Steep Decrease in 2nd IE	The steep decrease in 2nd IE is now from Na to Mg and not from Ne to Na (what we observed for 1st IE). This is because 2nd IE is removing a valence electron from Na^{+} ($2s^{2}$ $2p^{6}$) and from Mg^{+} ($3s^{1}$). • Significantly lesser energy is required to remove a valence electron from the higher energy quantum shell (n=3) from Mg^{+} ($3s^{1}$) than Na^{+} ($2s^{2}$ $2p^{6}$).
General Trend	From Mg to Ar, 2nd IE increases because: • Nuclear charge (number of protons) increases. • Shielding effect remains relatively constant; Mg^{+} ($3s^{1}$) to Ar^{+} ($3s^{2}$ $3p^{5}$) have the same number of inner shell electrons. • Effective nuclear charge increases ⇒ electrostatic attraction between positively charged nucleus and valence electrons increases. • Energy required to remove valence electron increases.
Anomaly 1	From Group 13 to Group 14 (Al to Si), 2nd IE lower than expected because: • Lesser energy is required to remove a valence electron from a higher energy 3p subshell of Si^{+} ($3s^{2}$ $3p^{1}$) than from Al^{+} ($3s^{2}$).
Anomaly 2	From Group 16 to Group 17 (S to Cl), 2nd IE is lower than expected because: • Lesser energy is required to remove a valence electron from Cl^{+} ($3s^{2}$ $3p^{4}$) that experiences inter-electronic repulsion in the 3p orbital than from S^{+} ($3s^{2}$ $3p^{3}$).

3rd Ionisation Energy Graph

3rd Ionisation energy (IE) is defined as the energy required to remove 1 mol of electron from 1 mol of a doubly charged gaseous cation to produce 1 mol of a triply charged gaseous cation.

3rd IE of an element **X**: $X^{2+}(g) \longrightarrow X^{3+}(g) + e^-$



- Electronic configurations given are valence configurations.

Steep Decrease in 3rd IE	The steep decrease in 3rd IE is now from Mg to Al and not from Na to Mg (what we observed for 2nd IE). This is because 3rd IE is removing a valence electron from Mg^{2+} ($2s^2$ $2p^6$) and from Al^{2+} ($3s^1$). • Significantly lesser energy is required to remove a valence electron from the higher energy quantum shell (n=3) from Mg^{2+} ($2s^2$ $2p^6$) than Al^{2+} ($3s^1$).
General Trend	From Al to Ar, 3rd IE increases because: • Nuclear charge (number of protons) increases. • Shielding effect remains relatively constant; Al^{2+} ($3s^1$) to Ar^{2+} ($3s^2$ $3p^4$) have the same number of inner shell electrons. • Effective nuclear charge increases ⇒ electrostatic attraction between positively charged nucleus and valence electrons increases. • Energy required to remove valence electron increases.
Anomaly 1	From Group 14 to Group 15 (Si to P), 3rd IE lower than expected because: • Lesser energy is required to remove a valence electron from a higher energy 3p subshell of P^{2+} ($3s^2$ $3p^1$) than from Si^{2+} ($3s^2$).
Anomaly 2	From Group 17 to Group 18 (Cl to Ar), 3rd IE is lower than expected because: • Lesser energy is required to remove a valence electron from Ar^{2+} ($3s^2$ $3p^4$) that experiences inter-electronic repulsion in the 3p orbital than from Cl^{2+} ($3s^2$ $3p^3$).

Relationship between the Steep Decrease in IE and n in nth IE

Steep decrease in **1**st IE occurred from Ne to Na (Group **1**).

Steep decrease in **2**nd IE occurred Na to Mg (Group **2**).

Steep decrease in **3**rd IE occurred from Mg to Al (Group 1**3**).

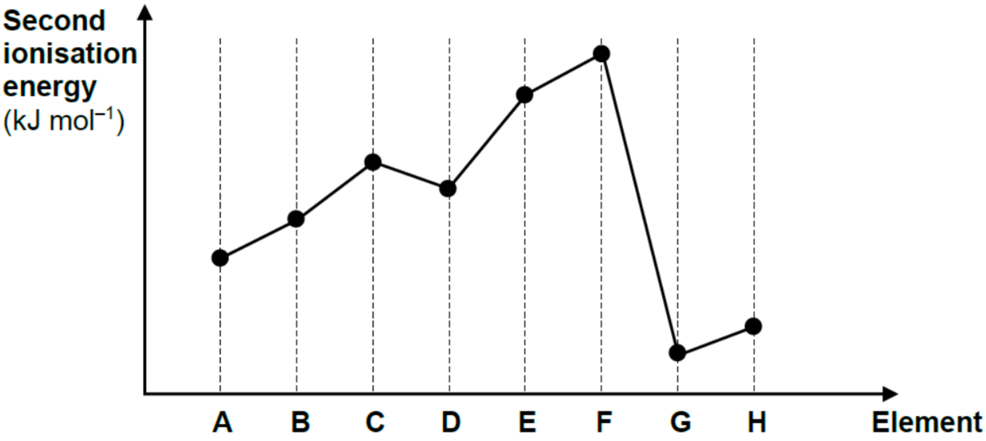
We can *predict* that the steep decrease in 4th IE will occur from Al to Si (Group 1**4**) and so on.

- This relationship only works for elements with atomic (proton) number less than 20 i.e., it does not work for transition elements.

Worked Example 1 [ASRJC/Prelim/2024/P1/Q2]

The graph shows the second ionisation energies of eight consecutive elements **A** to **H**, in Period 2 and 3 of the Periodic Table.

[Note that letters **A** to **H** are not the atomic symbols of the elements concerned.]



Which statements are correct?

1 **F** and **G** are in the same period in the Periodic Table.

2 The general increase from **A** to **F** is due to increasing atomic radius.

3 The small decrease from **C** to **D** is due to repulsion between paired electrons.

A 1 and 2 only B 1 and 3 only C 2 and 3 only D 3 only

Solution

Answer: **B**

Statement 1: Correct

Since this is 2nd IE, element **G** belongs to Group 2.

Since the elements are consecutive, we have:

Element	A	B	C	D	E	F	G	H
Period	2	2	2	2	2	3	3	3
Group	14	15	16	17	18	1	2	13
Identity	C	N	O	F	Ne	Na	Mg	Al

Statement 2: Incorrect

- Recall that for 2nd IE, we're removing an electron from the element's singly charged cation.

A$^+$ is C$^+$: $2s^2\ 2p^1$

F$^+$ is Na$^+$: $2s^2\ 2p^6$

2nd IE increases from **A** to **F** because nuclear charge increases, shielding effect remains relatively constant and hence, effective nuclear charge increases. Overall electrostatic attraction of nucleus to valence electron increases, more energy is required to remove valence electron.

Statement 3: Correct

C$^+$ is O$^+$: $2s^2\ 2p^3$

D$^+$ is F$^+$: $2s^2\ 2p^4$

2nd IE decreases slightly from **C** to **D** because:
Lesser energy is required to remove a valence electron that experiences interelectronic repulsion in the 2p orbital of **D**$^+$.

2 Chemical Bonding

Comparing boiling point and melting point of simple covalent molecules

To compare the boiling point (bp) and melting point (mp) of molecules **A** and **B**, start by checking the polarity of **A** and **B**.

- If **A** and **B** are both non-polar (both only have id-id), compare strength of id-id.
- If **A** and **B** are both polar OR one is polar and the other is non-polar, check if their difference in M_r is large.
  - If difference in M_r is large (more than 30), the molecule with the larger M_r has a stronger id-id and will have a higher mp/bp.
  - If difference in M_r is small (less than 30), the strength of intermolecular force of attraction is as follows: H-bonds (highest mp/bp) > pd-pd > id-id (lowest mp/bp)

Comparison between non-polar molecules (comparing id-id interactions)

C_3H_8 *vs* $CH(CH_3)_3$ *vs* $CH_3CH_2CH_2CH_3$

Since all three molecules are hydrocarbons and are hence non–polar, they only have id-id interactions, and we must compare their id-id interactions.

Instantaneous dipole-induced dipole (id-id) interaction is affected by two factors (listed in order of priority).

Factor 1: Strength of id-id (size of electron cloud)

Factor 2: Extensiveness/number of id-id (shape of the molecule; check this only if size of electron cloud is the same)

- Order of priority makes sense. Id-id interactions are intrinsically weak – it's logical that we compare strength first before extensiveness.

Factor 1: Strength of id-id (size of electron cloud)

The larger the electron cloud, the more polarisable it is, the larger the instantaneous dipole and hence stronger the id-id. The size of e cloud is proportional to the molecule's M_r.

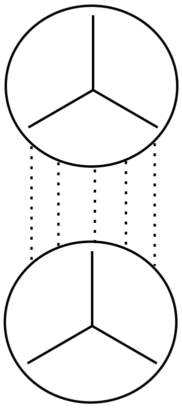
$CH(CH_3)_3$ and $CH_3CH_2CH_2CH_3$ have a larger and more polarisable electron cloud than C_3H_8 ⇒ stronger id-id than between the C_3H_8 molecules ⇒ more energy required to overcome the stronger id-id ⇒ $CH(CH_3)_3$ and $CH_3CH_2CH_2CH_3$ both have a higher bp and mp than C_3H_8.

Factor 2: Extensiveness of id-id (shape of molecule)

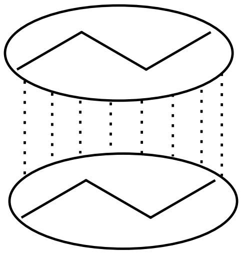
The shape of the molecule affects the number of id-id interactions that can be formed between a molecule. A molecule with a more elongated shape can form more id-id interactions than a molecule with a more spherical shape.

Since $CH(CH_3)_3$ and $CH_3CH_2CH_2CH_3$ have the same electron cloud size (strengths of id-id are the same), we compare their shapes.

$CH(CH_3)_3$ has a more spherical shape than $CH_3CH_2CH_2CH_3$ which has a more elongated shape. Therefore, $CH(CH_3)_3$ forms less extensive (smaller number of) id-id interactions which require less energy to break than the more extensive (greater number of) id-id interactions between $CH_3CH_2CH_2CH_3$.



$CH(CH_3)_3$



$CH_3CH_2CH_2CH_3$

Therefore, in terms of bp/mp, $CH_3CH_2CH_2CH_3 > CH(CH_3)_3 > C_3H_8$.

Comparison between polar molecules with a large difference in molecular mass

I-Br *vs* H_2O

difference in M_r between the molecules is more than 30

I-Br has a larger and more polarisable electron cloud ⇒ stronger id-id than the hydrogen bonds between the H_2O molecules ⇒ more energy required to overcome the stronger id-id ⇒ I-Br has a higher bp and mp than H_2O.

Comparison between polar molecules with a small difference in molecular mass

Determine which molecules are polar with H-bonds or polar with pd-pd or non-polar with only id-id.

The strength of the IMFOA is ranked accordingly: H-bond > pd-pd > id-id and the molecule with the strongest IMFOA will have the highest bp/mp (*vice versa*).

Polar molecule (H-bond) vs polar molecule (pd-pd) vs non-polar molecule (id-id)

NH_3 *vs* Cl-F *vs* N_2

difference in M_r between the molecules is less than 30

NH_3 is polar with H-bond, Cl-F is a polar molecule with pd-pd, N_2 is a non-polar molecule with only id-id.

Since the electron cloud sizes are similar, more energy is required to overcome the stronger H-bond between NH_3 molecules than the weaker pd-pd between Cl-F molecules and more energy is required to overcome the stronger pd-pd between Cl-F molecules than the weaker id-id between N_2 molecules.

In conclusion, in terms of bp/mp, NH_3 > Cl-F > N_2.

Polar molecule (H-bond) *vs* polar molecule (H-bond)

NH_3 *vs.* HF *vs.* H_2O

difference in M_r between the molecules is less than 30

All three molecules are polar with hydrogen bonds. We compare strength of hydrogen bonds to figure out which molecule has the strongest hydrogen bond and hence the highest bp/mp.

Hydrogen bond (H-bond) strength is affected by two factors (listed in order of priority):

Factor 1: extensiveness of H-bond (average number of H-bonds formed per molecule)

Factor 2: strength of H-bond (polarity of H-bond)

- Order of priority makes sense. Hydrogen bonds are incredibly strong – it's logical that we compare extensiveness first before strength.

Factor 1: Extensiveness of H-bond (average number of H-bonds formed per molecule)

The average number of H-bond that a molecule can form is decided by choosing the smaller value between the number of lone pairs on N/O/F on the molecule and the number of H atoms attached to N/O/F.

- Reason: Hydrogen bonds are formed between a lone pair of N/O/F and a H bonded to N/O/F. To determine the average number of H-bonds that can form, view it as a "balanced equation": lone pair + H ⟶ H-bond The number of H-bonds that can form depends on the limiting reagent *i.e.*, if a molecule has more lone pairs than H atoms, the number of H-atoms decide the number of H-bonds that can form (vice versa).

For e.g.,

- NH_3 has 3 Hs and 1 lone pair on N; it can form an average of 1 H-bond per molecule.
- HF has 1 H and 3 lone pairs on F; it can form an average of 1 H-bond per molecule.
- H_2O has 2 Hs and 2 lone pairs on O; it can form an average of 2 H-bonds per molecule.

Hence, between NH_3, HF and H_2O, H_2O forms the most extensive H-bonding and thus, requires the most amount of energy to break its H-bonds. H_2O has the highest bp/mp amongst the three.

Factor 2: Strength of H-bond (polarity of H-bond)

The polarity (strength) of H-bond is compared by looking at the electronegativity (EN) difference H and N/O/F.

Since F is the most EN, followed by O, then N, H-F bonds are the most polar (forms the strongest H-bonds), followed by O-F and N-F bonds are the least polar (forms the weakest H-bonds).

Therefore, HF has stronger H-bonds than NH_3 which requires more energy to break and hence HF has a higher bp/mp than NH_3.

In conclusion, in terms of bp/mp, $H_2O > HF > NH_3$

Drawing Difficult but Important Lewis Structures

A Prerequisite Knowledge for Drawing Lewis Structures:

1. *The first element in the molecular formula should be the central atom (unless the element is H), the rest of the elements will (usually) be the surrounding atoms.*
2. *Always bond the surrounding atoms one by one, taking careful note if the central atom is able (or unable) to expand octet.*
3. *Dative bonding is only thought of after considering single/double/triple bonds.*
4. *Radicals (unpaired electrons) can only exist if the total number of valence electrons is an odd number.*

Dinitrogen Monoxide, N_2O

As usual, the first element, N, is the central atom and the other N and O elements are made as surrounding atoms.

$$\mathrm{N}\quad\mathrm{N}\quad\mathrm{O}$$

Let's bond the surrounding O atom first; to make O stable, it needs two bonds. We give it a double bond.

$$\mathrm{N}\quad\mathrm{N{=}O}$$

Great! The first surrounding atom, O, is now stable.

Let's now satisfy the other surrounding atom, N, but there's a small issue, our central atom, N, can't expand octet (it's in Period 2 *i.e.*, no low-lying, vacant d orbitals to expand its octet configuration).

The only thing we can do now to satisfy the surrounding N atom is by giving it a single bond (a double/triple bond isn't possible because the central N atom expands octet).

$$\mathrm{N{-}N{=}O}$$

Now, before we end the structure off, let's think a little more.

The surrounding N atom is looking unstable (it only has 6 electrons). It needs two more electros but adding any other ordinary bonds causes central N to explode.

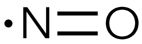
We use our "last resort" bond: a *dative covalent bond*.

- There should never be an atom in the structure with six electrons, you should be able to stabilise it by with a dative covalent bond.

Yes, there is another structure that could be drawn if you started off by stabilising the surr N atom first instead of the surr O atom.

Nitrogen Monoxide, NO

Following the same idea as drawing N_2O, NO will be drawn as such:



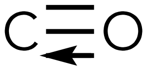
- An atom with 7 electrons *can* be stable, provided the total number of valence electrons is odd.

To verify the correctness of the radical (unpaired electron), count the total number of valence electrons: 5 + 6 = 11. An odd number validates the presence of a radical.

Carbon Monoxide, CO

Following the same idea as drawing N_2O, after bonding the O atom, we end up with:

We aren't done just yet! Realise that the C is non-octet with six valence electrons, we can and need to stabilise it by using a dative bond from O to C.

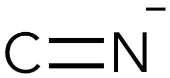


And that's it, both C and O have octet configurations and CO is looking stable.

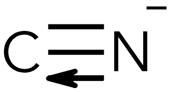
Cyanide, CN^-

When approaching structures with negative charges, the negative charge is assigned to the more electronegative element (spreading the charges evenly if we have to).

Applying this idea, we give N a negative charge and methodically follow the rules, we now have a structure that looks like:



Once again, we have a highly unstable six electron non-octet configuration O atom, we yet again must stabilise it by using a dative bond from N^- to C.



You *could* stop here as a **JC1** student, but if you're a JC2 student who has covered the chapter on halogenoalkanes, you'd know that the negative charge is on the C.

We can do that by expressing the dative bond as an ordinary single bond.

Expressing a dative bond as an ordinary single bond

To put it simply,

A dative covalent bond is a single bond with positive and negative charges.

$$A \rightarrow B \;=\; A \bullet \bullet B \;=\; \overset{+}{A} \bullet \times \overset{-}{B} \;=\; \overset{+}{A} — \overset{-}{B}$$

In the Figure above, • is the electron of **A** and **x** is the electron of **B**.

In a dative covalent bond (from **A** to **B**), **A** gives both of its • electrons to **B**, both electrons still essentially belong to **A** since they're still drawn as •.

An ordinary single bond is a bond with • and **x** and to convert a dative bond into an ordinary single bond, we need to make one of the • into a **x**.

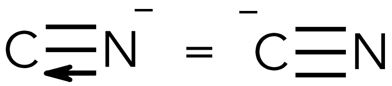
Hence,

In **A**'s perspective, it has lost an electron, and **A** gains a positive charge

In **B**'s perspective, it has gained an electron, and hence **B** gains a negative charge.

- To convert a dative bond into a single bond with charges,
  the head of the arrow of the dative bond leaves a negative charge on the atom that it is pointing towards.
  the tail of the arrow of the dative bond leaves a positive charge on the atom that it is pointing away.

Back to CN^- structure, converting the dative bond in CN^- to a single bond, will leave a negative charge on C and a positive charge on N (N is now neutral since it initially had a negative charge):



Hybridisation

Determining Hybridisation

If sum of lone pair and bond pair/sigma bonds/number of bonded atoms is:

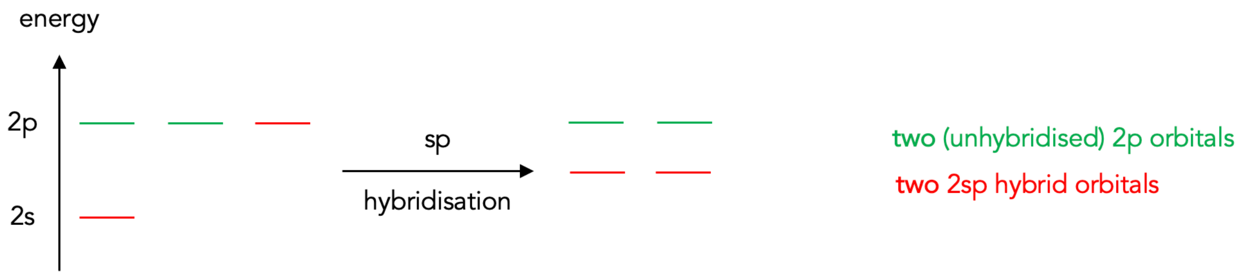
4 ⇒ sp^3 hybridised; 3 ⇒ sp^2 hybridised; 2 ⇒ sp hybridised

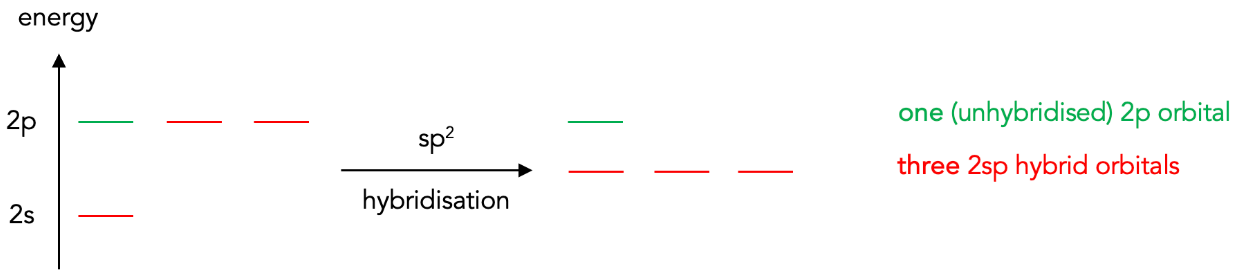
The Concept Behind Hybridisation

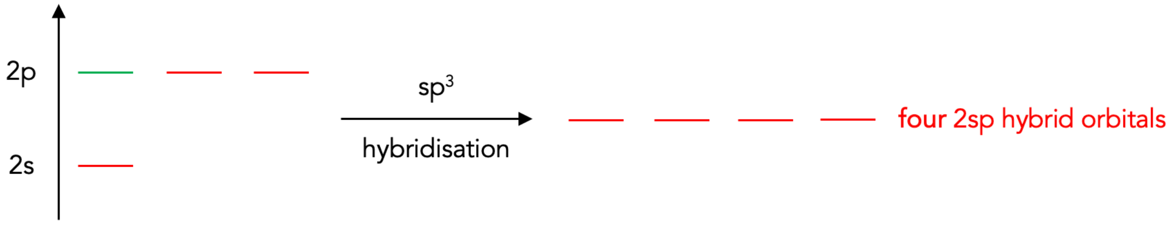
Before hybridisation, there is one s orbital and three p orbitals.

hybridisation	mixing of orbitals		number of hybrid orbitals formed	number of unhybridised p orbitals
	number of s orbitals mixed	number of p orbitals mixed		
sp	one	one	two sp hybrid orbitals	two
sp^2	one	two	three sp^2 hybrid orbitals	one
sp^3	one	three	four sp^3 hybrid orbitals	zero

<u>All</u> hybrid orbitals are <u>lower in energy than p orbitals</u> but <u>higher in energy than s orbitals</u>.







Assigning Electrons into Hybridised Orbitals

Focus on the number of σ bonds and π bonds attached to the atom of interest.

1. σ bonds must be formed from hybrid orbitals, π bonds must be formed from p orbitals. *i.e.,*
   if there are 'm' σ bonds ⇒ 'm' hybridised orbitals must have one electron each
   if there are 'n' π bonds, ⇒ 'n' p orbitals must have one electron each.
2. Lone pair of electrons go into vacant orbitals after settling σ and π bonds.

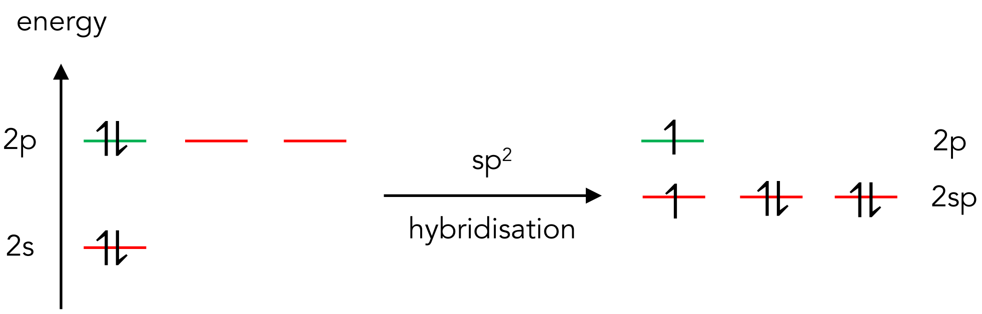
For e.g., Hybridisation of O atom in O=C=O.

O has 1 bond pair and 2 lone pairs so it is sp^2 hybridised *i.e.,* three sp^2 orbitals and one unhybridised p orbital.

O has one σ bond, one sp^2 orbital must have one electron (to form one σ bond)

O has one π bond, one p orbital must have one electron (to form one π bond).

The remaining two lone pairs of electrons will go into the empty orbital that remains, *i.e.,* the two sp^2 orbitals will accommodate a lone pair each.



Hybridisation of O in CO_2

- O has a starting configuration of $1s^2\ 2s^2\ 2p^4$ before it forms a compound.

Drawing Orbital Diagrams for Hybridised Orbitals

When drawing orbital diagrams, follow the series of steps:

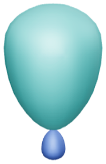
Step 1: Start by determining the hybridisation of the atom of focus.

Step 2: Assign electrons into all orbitals (hybridised and unhybridised) of that atom.

Step 3: Arrange the hybridised orbitals and unhybridised p orbitals in its correct geometry.

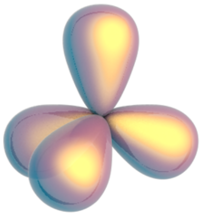
Important pointers:

- All hybridised orbitals (sp, sp^2, sp^3) have the same orbital shape:

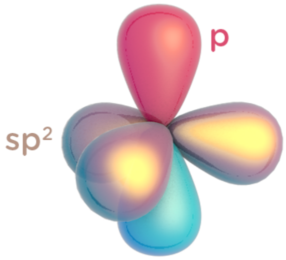


- p orbitals are perpendicular to hybridised orbitals.
- sp^3 hybridised orbitals are arranged tetrahedrally, sp^2 hybridised orbitals are arranged in a trigonal planar shape, and sp hybridised orbitals are arranged linearly.

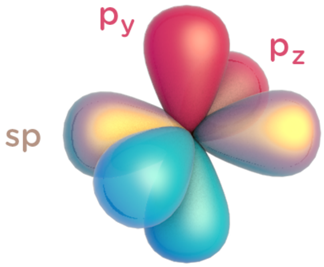
sp^3



sp^2



sp



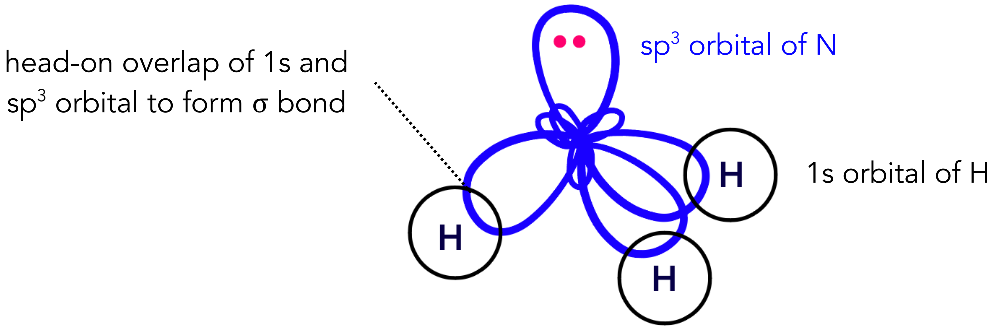
Worked Example 1 (Drawing the Orbital Diagram for N in NH_3)

Step 1: N has <u>3 bond pairs</u> and 1 lone <u>pair</u>. It is <u>sp^3 hybridised</u> with <u>four sp^3 orbitals</u>.

Step 2: N has 3 σ bonds ⇒ <u>one electron in each of the three sp^3 orbitals</u>.

The lone pair of electrons on N will be assigned to the remaining sp^3 orbital.

Step 3: The sp^3 orbitals of N will be arranged <u>tetrahedrally</u>.



- The node of each orbital of an atom must coincide perfectly because that is where the nucleus resides.

Worked Example 2 (Drawing the Orbital Diagram for C and O in $O=CH_2$)

Step 1: C has 3 bond pairs and 0 lone pairs.

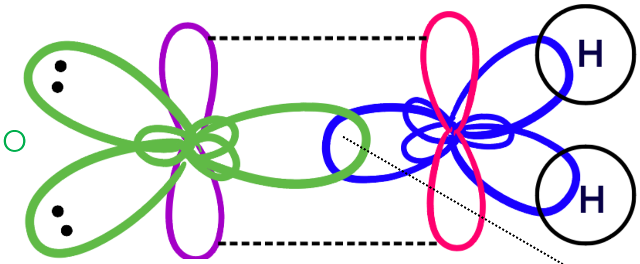
O has 1 bond pair and 2 lone pairs.

Both C and O are sp^2 hybridised with three sp^2 orbitals and one (unhybridised) p orbital.

Step 2: C has 3 σ bonds $\Rightarrow$ one electron in each of the three sp^2 orbitals. It also has 1 π bond $\Rightarrow$ one electron in one p orbital.

O has 1 σ bond $\Rightarrow$ one electron in one sp^2 orbital. It also has 1 π bond $\Rightarrow$ one electron in one p orbital. The 2 lone pair of electrons on O will be assigned to the remaining two sp^2 orbitals.

Step 3: The sp^2 orbitals of C and O will be arranged in a trigonal planar shape.



Worked Example 3 (Drawing the Orbital Diagram for C and O in O=C=O)

Step 1: C has 2 bond pairs and 0 lone pairs.

O has 1 bond pair and 2 lone pairs.

C is sp hybridised with two sp orbitals and two (unhybridised) p orbitals.

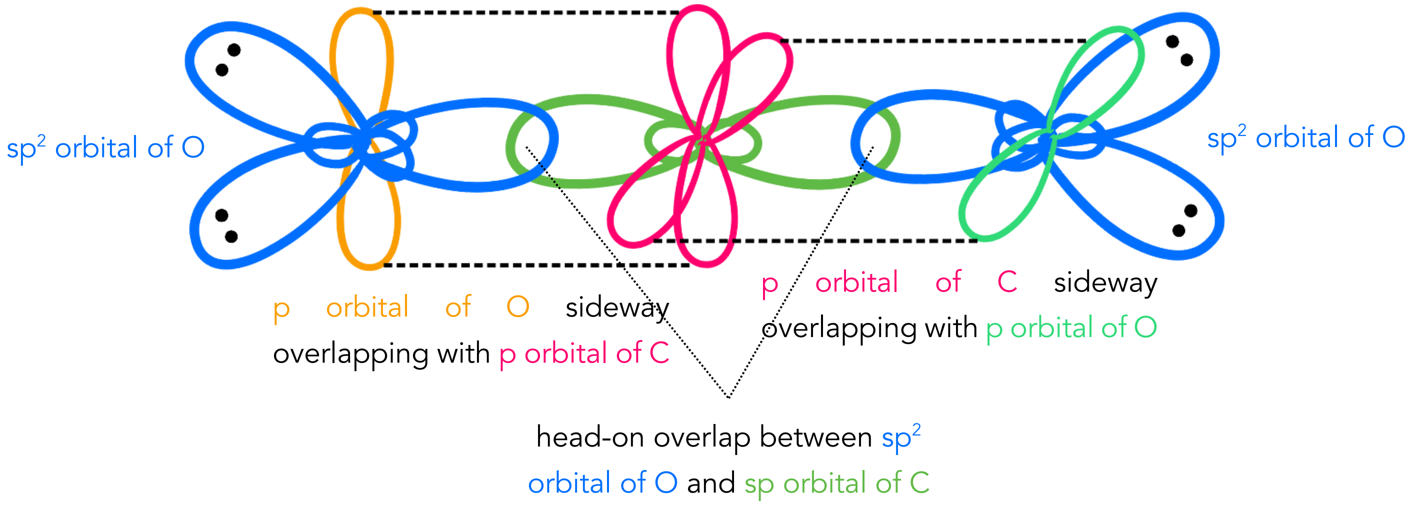
O is sp^2 hybridised with three sp^2 orbitals and one (unhybridised) p orbital.

Step 2: C has 2 σ bonds ⇒ one electron in each of the two sp orbitals. It also has 2 π bond ⇒ one electron in each of the two p orbitals.

O has 1 σ bond ⇒ one electron in one sp^2 orbital. It also has 1 π bond ⇒ one electron in one p orbital. The 2 lone pair of electrons on O will be assigned to the remaining two sp^2 orbitals.

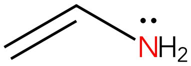
Step 3: The sp orbitals of C be arranged linearly.

The sp^2 orbitals of O will be arranged in a trigonal planar shape.

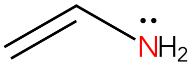
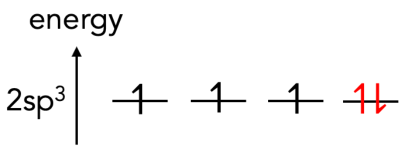
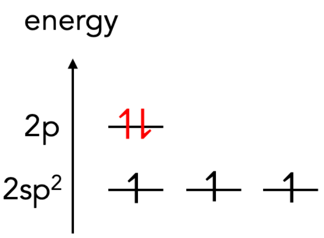


An Exception: Saturated Atoms with Lone Pair adjacent to π bonds (for JC2)

When there is a saturated atom with a lone pair of electrons directly bonded (adjacent) to a π bond (C≡C, C=C, benzene, C=O, C=N *etc.*), the lone pair will delocalise into that π bond (this is energetically favourable because it allows the system to be resonance stabilised) and for that to occur, that atom must be *sp*^{2} *hybridised. Why?*

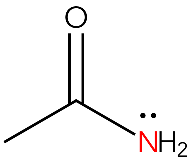
Let's use  *as an example.*

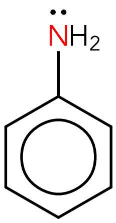
If we use our regular rules of hybridisation, **N** will be sp^3 hybridised but this means that **N** won't have a p orbital to contain the lone pair and hence delocalisation into the C=C π bond cannot occur – *this is disastrous* – remember, the lone pair of electrons wants to delocalise into the C=C π bond to create a resonance stabilised molecule.

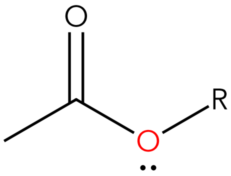
	
If N was sp^3 hybridised…	If N was sp^2 hybridised…
	

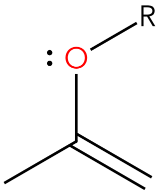
For delocalisation to occur, **N** wants its lone pair of electrons to be in a p orbital and hence, the **N** adopts the next immediate hybridisation that has a p orbital: *sp*^{2} *hybridisation*.

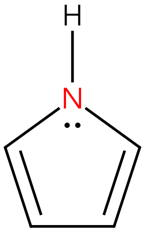
More examples of expected hybridisation being sp^3 but actual hybridisation being sp^2.











and many more…

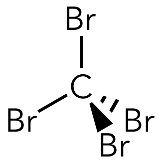
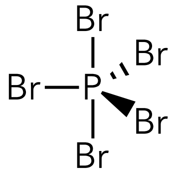
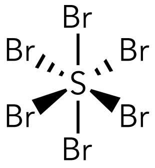
Molecular Polarity

A molecule is polar if there is a net dipole moment.

A Quick Way to Determine Molecular Polarity

The Recipe for Non-Polarity

- All hydrocarbons (molecules made up of C and H only) are non-polar.
- If a molecule has a basic shape (0 lone pairs) and its terminal atoms are all identical, the molecular is guaranteed to be non-polar.
- Some examples of such molecules:

$S=C=S$			
2 bond pairs **0 lone pairs**	4 bond pairs **0 lone pairs**	5 bond pairs **0 lone pairs**	6 bond pairs **0 lone pairs**

- Do not misuse this recipe: a molecule that has a basic shape with different terminal atoms does not necessarily mean it is polar. For e.g., PCl_3F_2 with a trigonal bipyramidal shape is non-polar if the 3 Cl atoms are equatorial plane and the 2 F atoms are axial.

Molecular Shapes that are always Polar

These shapes are:

- bent (2 bond pairs, 1 lone pair OR 2 bond pairs, 2 lone pairs)
- trigonal pyramidal (3 bond pairs, 1 lone pair)
- see-saw (4 bond pairs, 1 lone pair)
- T-shape (3 bond pairs, 2 lone pairs)
- square pyramidal (4 bond pairs, 2 lone pairs)

No matter what the surrounding atoms are, there will always be a net dipole moment.

- Please do not memorise this list of shapes. It's easily understandable (draw them out) why these shapes will always be polar.

3 Moles and Stoichiometry

Eudiometry (Combustion Data Questions)

Worked Example 1

10 cm^3 of a gaseous hydrocarbon, C_xH_y, was burnt in 130 cm^3 of oxygen. The total volume of the gaseous mixture after combustion was 120 cm^3. When the resultant gaseous mixture was passed over aqueous potassium hydroxide, the volume decreased by 20 cm^3. All volume measurements were taken at room temperature and pressure.

Determine the molecular formula of the hydrocarbon.

Solution

Background information

- For combustion data questions, we always assume complete combustion *i.e.*, O_2 is supplied in excess and the hydrocarbon is completely reacted at the end of reaction.
- When a hydrocarbon is completely combusted, the products are CO_2 and H_2O.

Step 1: Breaking down the data

"The total volume of the gaseous mixture after combustion was 120 cm^3."

Since O_2 is in excess, gaseous mixture contains unreacted O_2 and CO_2.

- There is no C_xH_y or H_2O in the gaseous mixture. C_xH_y is in limiting and H_2O is in the liquid state at r.t.p.

Therefore, 120 cm^3 is the volume of CO_2 and volume O_2 after combustion.

"When the resultant gaseous mixture was passed over aqueous potassium hydroxide, the volume decreased by 20 cm^3."

The gas that reacts with NaOH(aq) must be acidic ⇒ CO_2 reacts with NaOH(aq).

Therefore, 20 cm^3 is the volume of CO_2.

Hence, volume of O_2 = 120 – 20 = 100 cm^3

- Non-metal oxides (except CO, NO, H_2O) are acidic.

Step 2: Balance the combustion equation

<u>Construct a balanced equation</u> between C_xH_y and O_2. Balance **C**arbon atoms first, then **H**ydrogen atoms, and lastly **O**xygen atoms.

C	$C_xH_y(g) + O_2(g) \longrightarrow \mathbf{x}\ CO_2(g) + H_2O(\mathit{l})$
H	$C_xH_y(g) + O_2(g) \longrightarrow x\ CO_2(g) + \mathbf{\frac{y}{2}}\ H_2O(\mathit{l})$
O	$C_xH_y(g) + \left(\mathbf{\frac{2x + \frac{y}{2}}{2}}\right) O_2(g) \longrightarrow x\ CO_2(g) + \frac{y}{2}\ H_2O(\mathit{l})$ $C_xH_y(g) + \left(\mathbf{x + \frac{y}{4}}\right) O_2(g) \longrightarrow x\ CO_2(g) + \frac{y}{2}\ H_2O(\mathit{l})$

- There are $\left(2x + \frac{y}{2}\right)$ O atoms on the right.

Step 3: Construct an initial-change-final (ICF) table

Objective: Determine the change in the ICF table and compare it with the stoichiometric ratio of the equation.

Fill up the table by inputting the <u>initial volume</u> of C_xH_y and O_2 and <u>final volume</u> of C_xH_y, O_2 and CO_2 obtained in <u>Step 1</u>.

	$C_xH_y(g)$	+	$\left(x + \frac{y}{4}\right) O_2(g)$	⟶	$x\ CO_2(g)$	+	$\frac{y}{2}\ H_2O(\mathit{l})$
I / cm^3	10		130		0		–
C / cm^3	-10		-30		+20		–
F / cm^3	0		120 – 20 = 100		20		–

Step 4: Compare the change with the stoichiometric ratio

	$C_xH_y(g)$	+	$\left(x + \frac{y}{4}\right) O_2(g)$	$\longrightarrow$	$x\ CO_2(g)$	+	$\frac{y}{2} H_2O(l)$
stoichiometric ratio	1	:	$\left(x + \frac{y}{4}\right)$	:	x		–
|change|	10	:	30	:	20		–
	1	:	3	:	2		

- Ensure that the |change| for C_xH_y is simplified to 1 to match the stoichiometric ratio of 1.

$\therefore x = 2$ and $\left(x + \frac{y}{4}\right) = 3$

$y = 4$

The molecular formula of the hydrocarbon is C_2H_4.

Worked Example 2 (Volume Contraction) [TMJC/Prelim/2024/P1/Q8]

1 dm^3 of a gaseous hydrocarbon was mixed with excess oxygen. When the mixture undergoes complete combustion, the volume contracted by 2 dm^3. When the resultant mixture was passed through concentrated sodium hydroxide, the gas volume further decreased by 2 dm^3. All volumes were measured at room temperature and pressure.

What is the empirical formula of the hydrocarbon?

Solution

Background Information

- Question mentions that oxygen was in excess – we do not have to assume, unlike Worked Example 1.
- When a hydrocarbon is completely combusted, the products are CO_2 and H_2O.

Step 1: Breaking down the data

"When the mixture undergoes complete combustion, the volume contracted by 2 dm^3"

The sum of the change in the ICF table (step 3) will be **-2**.

"When the resultant mixture was passed through concentrated sodium hydroxide, the gas volume further decreased by 2 dm^3"

The gas that reacts with concentrated NaOH(aq) must be acidic ⇒ CO_2 reacts with NaOH(aq).

Therefore, 2 cm^3 is the volume of CO_2.

- Non-metal oxides (except CO, NO, H_2O) are acidic.

Step 2: Balance the combustion equation

Since the question did not provide the molecular formula of the hydrocarbon. let it be C_xH_y.

$$C_xH_y(g) + \left(\mathbf{x} + \frac{\mathbf{y}}{\mathbf{4}}\right) O_2(g) \longrightarrow x\, CO_2(g) + \frac{y}{2} H_2O(l)$$

- See Step 2 of Worked Example 1 if you forgot how to balance the combustion of a hydrocarbon.

Step 3: Construct an initial-change-final (ICF) table

Objective: Determine the change in the ICF table and compare it with the stoichiometric ratio of the equation.

Fill up the table by inputting the initial volume of C_xH_y and final volume of CO_2 in Step 1.

- The question did not provide the initial volume of O_2 (unlike Example 1).

	$C_xH_y(g)$	+	$\left(x + \frac{y}{4}\right) O_2(g)$	$\longrightarrow$	$x\ CO_2(g)$	+	$\frac{y}{2} H_2O(l)$
I / dm^3	1				0		–
C / dm^3	-1		?		+2		–
F / dm^3	0				2		–

Since we know the sum of the change = -2, the change for oxygen's volume must be -3.

	$C_xH_y(g)$	+	$\left(x + \frac{y}{4}\right) O_2(g)$	$\longrightarrow$	$x\ CO_2(g)$	+	$\frac{y}{2} H_2O(l)$
I / dm^3	1				0		–
C / dm^3	-1		**-3**		+2		–
F / dm^3	0				2		–

Step 4: Compare the change with the stoichiometric ratio

	$C_xH_y(g)$	+	$\left(x + \frac{y}{4}\right) O_2(g)$	$\longrightarrow$	$x\ CO_2(g)$	+	$\frac{y}{2}\ H_2O(l)$
stoichiometric ratio	1	:	$\left(x + \frac{y}{4}\right)$	:	x		–
|change|	1	:	3	:	2		–

- Ensure that the |change| for C_xH_y is simplified to 1 to match the stoichiometric ratio of 1.

$\therefore x = 2$ and $\left(x + \frac{y}{4}\right) = 3$

$y = 4$

The molecular formula of the hydrocarbon is C_2H_4.

The empirical formula of the hydrocarbon is CH_2.

Worked Example 3 (Combusted Species is in the Liquid State) [A-Levels/2010/P3/Q3]

0.10 cm^3 of liquid **J**, C_xH_yOH, was dissolved in an inert solvent and an excess of sodium metal added, 10.9 cm^3 of gas (measured at 293 K) was produced.

When 0.10 cm^3 of liquid **J** was combusted in an excess of oxygen in an enclosed vessel, the volume of gas (measured at 293 K) was reduced by 54.4 cm^3. The addition of an excess of NaOH(aq) caused a further reduction in gas volume of 109 cm^3 (measured at 293 K).

Use these data to calculate values for x and y in the molecular formula C_xH_yOH for **J**.

Step 1: Breaking down the data

*"When an excess of sodium metal was added to 0.10 cm^3 of liquid **J**, 10.9 cm^3 of gas was produced."*

$$C_xH_yOH(l) + Na(s) \longrightarrow C_xH_yO^-(l) + \tfrac{1}{2} H_2(g)$$

Amount of H_2 gas produced $= \frac{10.9}{24000} = 4.54167 \times 10^{-4}$ mol

Amount of C_xH_yOH in 0.10 cm^3 $= \frac{4.54167 \times 10^{-4}}{\frac{1}{2}} \times 1 = 9.0833 \times 10^{-4}$ mol

*"When 0.10 cm^3 of liquid **J** was combusted in an excess of oxygen… the volume of **GAS** was reduced by 54.4 cm^3"*

The sum of change in the ICF table (in mol) for O_2 and CO_2 is $-\frac{54.4}{24000} = -0.0022667$ mol

- The change is negative because the volume of gas was **REDUCED** by 54.4 cm^3.
- The decrease in 0.0022667 mol refers to the decrease in the amount of **GASES**, **NOT** liquid **J**.

"addition of an excess of NaOH(aq) caused a further reduction in gas volume of 109 cm^3"

The gas that reacts with NaOH(aq) must be acidic ⇒ CO_2 reacts with NaOH(aq).

Therefore, 109 cm^3 is the volume of CO_2.

Amount of CO_2 produced $= \frac{109}{24000} = 0.00454167$ mol

- Non-metal oxides (except CO, NO, H_2O) are acidic.

Step 2: Balance the combustion equation

$$C_xH_yOH(l) + \left(x + \frac{y+1}{4} - \frac{1}{2}\right) O_2(g) \longrightarrow x\,CO_2(g) + \frac{y+1}{2} H_2O(l)$$

- Total O atoms on RHS $= 2x + \frac{y+1}{2}$
- Since C_xH_yOH has 1 O, number of O atoms from $O_2 = 2x + \frac{y+1}{2} - 1$.

Step 3: Construct an initial-change-final (ICF) table

Objective: Determine the change in the ICF table and compare it with the stoichiometric ratio of the equation.

Fill up the table by inputting the <u>initial volume</u> of C_xH_yOH and <u>final volume</u> of CO_2 in <u>Step 1</u>.

- Since **J** is a liquid and not a gas unlike <u>Examples 1</u> and <u>2</u>, if we want to compare the **changes in volume of CO_2 and O_2** with **changes in mol of J** to obtain stoichiometric ratio, we need to **convert all units of volume to mol** before comparison. Hence, the ICF table is done in mol.
- The question did not provide the initial volume of O_2 (unlike <u>Example 1</u>).

	$C_xH_yOH(l)$	+	$\left(x + \frac{y+1}{4} - \frac{1}{2}\right) O_2(g)$	$\longrightarrow$	$x\ CO_2(g)$	+	$\frac{y+1}{2} H_2O(l)$
I / mol	9.0833×10^{-4}				0		
C / mol	-9.0833×10^{-4}		**?**		+0.00454167		
F / mol	0				0.00454167		

Since the sum of the change of O_2 and CO_2 = –0.0022667 mol, the change in moles of O_2 is:

	$C_xH_yOH(l)$	+	$\left(x + \frac{y+1}{4} - \frac{1}{2}\right) O_2(g)$	$\longrightarrow$	$x\ CO_2(g)$	+	$\frac{y+1}{2} H_2O(l)$
I / mol	9.0833×10^{-4}				0		
C / mol	-9.0833×10^{-4}		**–0.00680837**		+0.00454167		
F / mol	0				0.00454167		

Step 4: Compare the change with the stoichiometric ratio

	$C_xH_yOH(l)$	+	$\left(x + \frac{y+1}{4} - \frac{1}{2}\right) O_2(g)$	$\longrightarrow$	$x\ CO_2(g)$	+	$\frac{y+1}{2} H_2O(l)$
stoic. ratio	1	:	$\left(x + \frac{y+1}{4} - \frac{1}{2}\right)$	:	x		
|change|	9.0833×10^{-4}	:	0.00680837	:	0.0045417		
	1	:	7.49548	:	5		

- Ensure that the |change| for C_xH_yOH is simplified to 1 to match the stoichiometric ratio of 1.

$\therefore x = 5$ and $\left(x + \frac{y+1}{4} - \frac{1}{2}\right) = 7.49548$

$y = 10.9819 \approx 11$

The molecular formula of liquid **J** is $C_5H_{11}OH$.

4 Redox Reactions

Balancing Half-Equations

Balancing Half-Equations using EOHC

When balancing half-equations, we have learnt to balance the **E**lement first, followed by **O**xygen using H_2O, **H**ydrogen using H^+ ions, and **C**harge using electrons (EOHC).

For e.g., to obtain the molar ratio between Cl_2 and $Cr_2O_7^{2-}$ reacting in a redox equation, we would construct two half-equations using EOHC:

	oxidation: $Cl_2 \longrightarrow ClO_3^-$	reduction: $Cr_2O_7^{2-} \longrightarrow Cr^{3+}$
E	$Cl_2 \longrightarrow$ **2** ClO_3^-	$Cr_2O_7^{2-} \longrightarrow$ **2** Cr^{3+}
O	**6 H_2O** + $Cl_2 \longrightarrow 2\ ClO_3^-$	$Cr_2O_7^{2-} \longrightarrow 2\ Cr^{3+}$ + **7 H_2O**
H	$6\ H_2O + Cl_2 \longrightarrow 2\ ClO_3^-$ + **12 H^+**	**14 H^+** + $Cr_2O_7^{2-} \longrightarrow 2\ Cr^{3+} + 7\ H_2O$
C	$6\ H_2O + Cl_2 \longrightarrow 2\ ClO_3^- + 12\ H^+$ + **10 e^-**	**6 e^-** + $14\ H^+ + Cr_2O_7^{2-} \longrightarrow 2\ Cr^{3+} + 7\ H_2O$

To combine the half-equations, we multiply the oxidation half-equation by **3** and the reduction half-equation by **5** to make the number of electrons transferred the same.

The molar ratio between Cl_2 and $Cr_2O_7^{2-}$ is 3 : 5.

- Overall equation: **3** $Cl_2 + 34\ H^+$ + **5** $Cr_2O_7^{2-} \longrightarrow 6\ ClO_3^- + 10\ Cr^{3+} + 17\ H_2O$

Balancing Half-Equations using Changes in Oxidation States

EOHC can be *too slow* when we'd just want to obtain the molar ratio between two reacting species in a redox reaction.

Balancing half-equations using changes in oxidation states is *significantly* faster:

Step 1: Balance the element being reduced or oxidised.

Step 2: Balance oxidation states using electrons (an increase/decrease of oxidation state by **one** would mean a lost/gain of electrons by **one**)

	$Cl_2 \longrightarrow ClO_3^-$	$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$
Step 1	$Cl_2 \longrightarrow \mathbf{2}\ ClO_3^-$	$Cr_2O_7^{2-} \longrightarrow \mathbf{2}\ Cr^{3+}$
Step 2	$Cl_2 \longrightarrow \mathbf{2}\ ClO_3^- + \mathbf{10\ e^-}$ Oxidation state of Cl in Cl_2 increased from 0 to +5 in ClO_3^- ⇒ each Cl atom lost 5 e^-. Since there are 2 Cl atoms, 2 Cl atoms lose 10 e^-.	$\mathbf{6\ e^-} + Cr_2O_7^{2-} \longrightarrow 2\ Cr^{3+}$ Oxidation state of Cr in $Cr_2O_7^{2-}$ decreased from +6 to +3 in Cr^{3+} ⇒ each Cr atom gained 3 e^-. Since there are 2 Cr atoms, 2 Cr atoms gained 6 e^-.

To combine the half-equations, we multiply the oxidation half-equation by **3** and the reduction half-equation by **5** to make the number of electrons transferred the same.

The molar ratio between Cl_2 and $Cr_2O_7^{2-}$ is 3 : 5.

- Using EOHC took us four steps to obtain the molar ratio, this took us two.

Oxidation State, Electron Transfer, and Stoichiometric Ratio

The relationship between electron transfer and oxidation states

Consider this half-equation:

$$Cl_2 + 2\ e^- \longrightarrow 2\ Cl^-$$

Realise that 2 Cl atoms (in Cl_2) gain 2 electrons *i.e.*, 1 Cl atom gains 1 electron. Hence, the oxidation state (OS) of Cl will <u>decrease by 1</u> and indeed it does: <u>from 0 in Cl_2 to -1 in Cl^-</u>.

Consider another half-equation, but this time we'll <u>lose electrons</u> instead of <u>gain</u>.

$$Cr^{3+} \longrightarrow Cr^{6+} + 3\ e^-$$

Realise that 1 Cr^{3+} ions lose 3 e^-. Hence, the OS of Cr <u>increases by 3</u> and indeed it does: <u>from +3 in Cr^{3+} to +6 in Cr^{6+}</u>.

- The oxidation state of an element increases by the number of electrons lost.
  The oxidation state of an element decreases by the number of electrons gained.

Determining Stoichiometric Ratio between two reactants in a Redox reaction

Let's combine the half-equations in the example above.

reduction half-equation: $Cl_2 + 2\ e^- \longrightarrow 2\ Cl^-$

oxidation half-equation: $Cr^{3+} \longrightarrow Cr^{6+} + 3\ e^-$

To combine half-equations we make sure that the number of electrons transferred between reduction and oxidation is the same.

To do that, multiply the reduction half-equation by 3 and the oxidation half-equation by 2:

reduction half-equation: $3\ Cl_2 + 6\ e^- \longrightarrow 6\ Cl^-$

oxidation half-equation: $2\ Cr^{3+} \longrightarrow 2\ Cr^{6+} + 6\ e^-$

Combining the half-equations,

The stoichiometric ratio between Cl_2 and Cr^{3+} is 3 : 2.

- The stoichiometric ratio obtained in the overall equation is related to the numbers that was multiplied to the individual half-equations.

Calculating final oxidation state from stoichiometric ratio

Worked Example 1

0.0004 mol of aqueous sodium bromate(V), $NaBrO_3$ was found to react completely with 0.0012 mol hydroxylamine, NH_2OH. The half equation for reduction of bromate(V) ion is given:

$$BrO_3^-(aq) + 6\ H^+(aq) + 6\ e- \longrightarrow Br^-(aq) + 3\ H_2O(\mathit{l})$$

Determine the oxidation state of nitrogen in the product.

Solution

The stoichiometric ratio between BrO_3^- and NH_2OH is given to be 1:3, to determine the oxidation state of nitrogen in the product, we must work backwards.

From the given stoichiometric ratio, we must have multiplied the BrO_3^- reduction half-equation by 1 and the NH_2OH oxidation half-equation by 3.

- We saw this idea previously.

Since we multiplied the BrO_3^- reduction half-equation by 1, it shows that the stoichiometric number of electrons transferred between the half-equations is 6 x 1 = 6.

Since the oxidation half-equation of NH_2OH is not given, we construct our own:

Oxidation half-equation: $NH_2OH \longrightarrow y\ e^-$

y is the stoichiometric number of electrons that NH_2OH loses

Reduction half-equation (given): $BrO_3^- + 6\ H^+ + 6\ e^- \longrightarrow Br^- + 3\ H_2O$

We have deduced earlier that we multiplied oxidation half-equation by 3 and reduction half-equation by 1 to obtain a stoichiometric number of 6 electrons transferred *i.e.*,

$$(NH_2OH \longrightarrow y\ e^-) \times 3$$

$$(BrO_3^- + 6\ H^+ + 6\ e^- \longrightarrow Br^- + 3\ H_2O) \times 1$$

Therefore, $3\ y = 6 \times 1$

$y = 2$

NH_2OH loses 2 electrons and its oxidation state increases by 2, from -1 to +1.

The oxidation state of N in the product is +1.

Worked Example 2 (Disproportionation Reactions)

- Disproportionation: An element being oxidised and reduced i.e., its oxidation state decreases and increases after the reaction.

Use of the *Data Booklet* is relevant to this question.

30.0 cm^3 of 0.500 mol dm^{-3} $Br_2(aq)$ reacts completely with KOH(aq) to form 2.98g of KBr. The other products of this reaction are $KBrO_x$ and H_2O.

What is the value of x in the formula $KBrO_x$?

Solution

Determining the oxidation state (OS) of a reactant (or a product) in disproportionation (or comproportionation) is much simpler.

We leverage on the idea that oxidation state of the element (being reduced and oxidised) must be **conserved**.

- For e.g.,

$$10\ NO_2 + 8\ H_2O \longrightarrow 8\ NO_3^- + N_2 + 8\ H^+ + 4\ H_2O$$

Total OS of N in the reactants is 10(+4) = **+40**

Total OS of N in the products is 8(+5) + 1(0) = **+40**

We start by formulating an equation that includes the species containing the element undergoing redox, utilising the mole ratio given in the question.

Amount of $Br_2 = \frac{30}{1000} \times 0.5 = 0.015$

Amount of $Br^- = \frac{2.98}{119} = 0.025042$

$$Br_2 : Br^- \approx 3 : 5$$

$$3\ Br_2 \longrightarrow 5\ Br^- + BrO_x^-$$

Since total OS of Br must be conserved,

Total OS of Br in the reactant = 3(0) = 0

Total of OS of Br in the product must be 0 too. Since 5 Br^- has a total OS of -5, the OS of Br in BrO_x^- is +5.

Since O typically has an OS of -2 in a compound, **x = 3**.

- Oxygen has a -1 oxidation state in peroxide compounds. For e.g., BaO_2.

Determining Specific Oxidation States of Elements

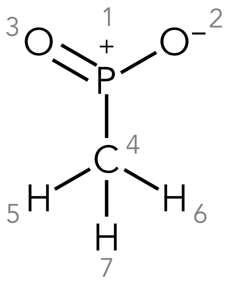
The specific oxidation state (OS) of an atom is dependent on its (relative) electronegativity and type of bonds (single, double or triple bond) it is involved in.

- The more electronegative element will 'pull' the bonding electrons of the less electronegative element towards itself.
- The more electronegative element acquires a negative oxidation state while the less electronegative element acquires a positive oxidation state.

	acquired oxidation state	
	less electronegative element	more electronegative element
single bond	+1	-1
double bond	+2	-2
triple bond	+3	-3
if negatively charged	-1	-1
if positively charged	+1	+1

Worked Example 1

Determine the oxidation states of all atoms in the molecule below (given that P is less electronegative than C).



Solution

Phosphorous-1 (P_1) P_1 is positively charged ⇒ gains **+1** P_1 is less EN than O_2 and is singly bonded ⇒ gains **+1** P_1 is less EN than O_3 and is doubly bonded ⇒ gains **+2** P_1 is less EN than C_4 and is singly bonded ⇒ gains **+1** Total OS of P_1 = (**+1**) + (**+1**) + (**+2**) + (**+1**) = **+5**.	Oxygen-2 (O_2) O_2 is negatively charged ⇒ gains -**1** O_2 is more EN than P_1 and is singly bonded ⇒ gains -1 Total OS of O_2 = (-**1**) + (-**1**) = -**2**
Oxygen-3 (O_3) O_3 is more EN than P_1 and is doubly bonded ⇒ gains -2 Total OS of O_3 = -**2**	Carbon-4 (C_4) C_4 is more EN than P_1 and is singly bonded ⇒ gains -**1** C_4 is more EN than H_5 and is singly bonded ⇒ gains -**1** C_4 is more EN than H_6 and is singly bonded ⇒ gains -**1** C_4 is more EN than H_7 and is singly bonded ⇒ gains -**1** Total OS of C_4 = (-**1**) + (-**1**) + (-**1**) + (-**1**) = -**4**
Hydrogen-5 (H_5) H_5 is less EN than C_4 and is singly bonded ⇒ gains **+1** Total OS of H_5 = **+1**	Hydrogen-6 (H_6) H_6 is less EN than C_4 and is singly bonded ⇒ gains **+1** Total OS of H_6 = **+1**
Hydrogen-7 (H_7) H_7 is less EN than C_4 and is singly bonded ⇒ gains **+1** Total OS of H_7 = **+1**	

5 Gaseous State

Combined Gas Law

Combined gas law questions involve changing one or more variables (pressure, volume, amount, temperature) and determining how the other variables get affected.

Worked Example 1 [AJC/Promo/2016/P1]

A ball is made of an air-filled plastic and has a volume of 40.0 cm^3.

A slightly dented ball of volume 38.5 cm^3 is filled with air at 27 °C and 106 kPa. To restore its spherical shape, the air inside the dented ball is heated to a constant temperature of 60 °C.

Assuming the air behaves ideally, what is the pressure of air at 60 °C when the shape is restored?

Solution

Step 1: Determine which variables were changed.

pressure (P)	volume (V)	temperature (T)	amount (n, in mol)
✓	✓	✓	constant

Step 2: Group constants and variables together in PV=nRT

$PV = \overline{n}RT$

- We use $\overline{\quad}$ to show that the variable is constant.

$\frac{PV}{T} = \overline{nR} = \text{constant}$

Therefore, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

- 1 and 2 refers to initial and final conditions respectively.

$\frac{(106)(38.5)}{27+273} = \frac{P_2(40)}{60+273} \quad \Rightarrow \quad P_2 = 113 \text{ kPa (3 sf)}$

- Volume and pressure were calculated in cm^3 and kPa because converting them into m^3 and Pa is unnecessary; the <u>conversion factors for division or multiplication would cancel out</u>. However, temperature must be in Kelvin because the unit conversion involves addition, which does <u>not cancel out</u>.

Worked Example 2 (Advanced Combined Gas Law) [RI/Prelim/2020/P1]

At 298 K, two vessels are connected by a stopcock. The 5 dm^3 vessel is filled with Ar at a pressure of 150 kPa and the 10 dm^3 vessel is filled with Xe at 350 kPa. The stopcock is then opened to allow the gases to mix at 298 K, resulting in a total pressure of $\mathbf{P}_{total}$ kPa.

Subsequently, the two vessels are heated to a temperature of **T** K and the total pressure at **T** K is 600 kPa.

Assuming that the gases do not react at all temperatures, what are the values of $\mathbf{P}_{total}$ and **T**?

Solution

This example is different from Worked Example 1 because there are two gases involved.

We use the first paragraph of information to determine $\mathbf{P}_{total}$. With $\mathbf{P}_{total}$, we find the temperature that the two vessels were heated to obtain a pressure of 600 kPa.

Step 1: Determine which variables were changed.

"The 5 dm^3 vessel is filled with Ar at a pressure of 150 kPa and the 10 dm^3 vessel is filled with Xe at 350 kPa. The stopcock is then opened to allow the gases to mix at 298 K, resulting in a total pressure of $\mathbf{P}_{total}$ kPa"

pressure (P)	volume (V)	temperature (T)	amount (n, in mol)
✓	✓	constant	constant

- More Ar or Xe was not introduced.

Step 2: Group constants and variables together in PV=nRT

$PV = \overline{nRT} = \text{constant}$

$P_1V_1 = P_2V_2$

Ar	Xe
$P_2 = \frac{P_1V_1}{V_2} = \frac{P_1V_1}{V_{total}} = \frac{(150)(5)}{15} = 50 \text{ kPa}$	$P_2 = \frac{P_1V_1}{V_2} = \frac{P_1V_1}{V_{total}} = \frac{(350)(10)}{15} = 233.33 \text{ kPa}$
$\mathbf{P}_{total} = P_2$ of Ar + P_2 of Xe = 50 + 233.33 = 283.33 KPa	

With P_{total} obtained, we find temperature **T** by repeating Steps 1 and 2.

Step 1: Determine which variables were changed.

*"Subsequently, the two vessels are heated to a temperature of **T** K and the total pressure at **T** K is 600 kPa."*

pressure (P)	volume (V)	temperature (T)	amount (n, in mol)
✓	constant	✓	constant

Step 2: Group constants and variables together in PV=nRT

$P\overline{V} = \overline{nR}T$

$\frac{P}{T} = \overline{\left(\frac{nR}{V}\right)} = \text{constant}$

Therefore, $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

- P_1 here is $\mathbf{P}_{total}$ and T_2 here is **T**.

$\frac{283.33}{298} = \frac{600}{T_2}$

T_2 = 631 K (3 s.f.)

6 Chemical Energetics

Constructing Energy Cycles

Worked Example 1 [YJC/Prelim/2016/P3/Q2]

Given the following enthalpy changes,

$Ca(s) + 2\ HCl(aq) \rightarrow CaCl_2(aq) + H_2(g)$ $\Delta H_1 = -622\ kJ\ mol^{-1}$

$CaCO_3(s) + 2\ HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g)$ $\Delta H_2 = -95\ kJ\ mol^{-1}$

$H_2(g) + \frac{1}{2}\ O_2(g) \longrightarrow H_2O$ $\Delta H_f\ (H_2O) = -622\ kJ\ mol^{-1}$

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_c\ (C) = -394\ kJ\ mol^{-1}$

calculate the enthalpy change of formation of calcium carbonate, $\Delta H_f\,(CaCO_3)$.

Solution

When constructing energy cycles, try to begin with the equation that has the greatest number of atoms (this prevents 'adding' species unnecessarily to both sides of an equation) and then connect equations to it by looking for species in common.

① We start the energy cycle off with ΔH_2 (equation with the greatest number of atoms).

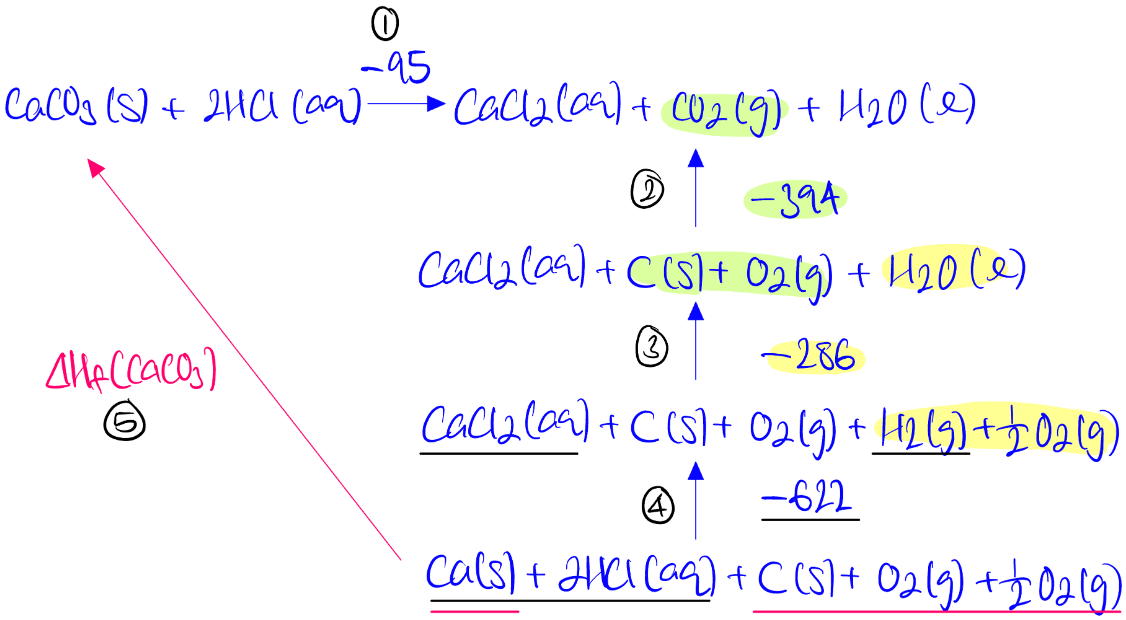
② The next equation we connect it to is $\Delta H_c\,(C)$ since both equations involve CO_2.

- You could also connect it to $\Delta H_f\,(H_2O)$.

③ Connect it to $\Delta H_f\,(H_2O)$ since both equations involve H_2O.

④ Connect it to ΔH_1 since both equations involve $CaCl_2$ and H_2.

⑤ Finally, we close the energy cycle by linking it up with $\Delta H_f\,(CaCO_3)$.



Apply Hess' Law (sum of anticlockwise arrows = sum of clockwise arrows):

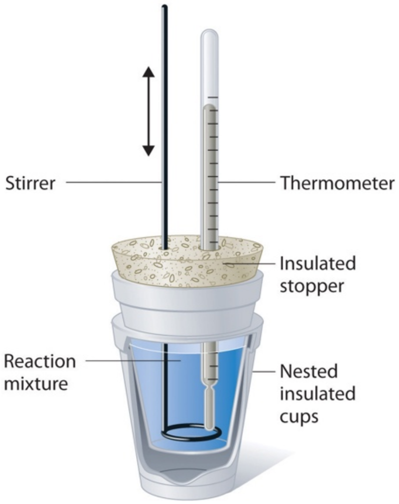
$(-394) + (-286) + (-622) = (-95) + \Delta H_f(CaCO_3)$

$\Delta H_f(CaCO_3) = -1207$ kJ mol^{-1}

- When constructing energy cycles, we usually connect equations from either the reactants (or products) of the starting equation and connect our way to the products (or reactants) of the starting equation.

Calorimetry

energy released (or absorbed) by reaction	=	energy absorbed (or released) by solution
$-\Delta H \times n$	=	$mc\Delta T$



Amount of energy released (or absorbed) by the chemical reaction is ΔH multiplied by the amount (in mol) of species reacted (or produced) in the chemical equation with a stoichiometric ratio of 1.

Worked Example 1

$$\mathbf{A} + 2\,\mathbf{B} \longrightarrow 3\,\mathbf{C} \qquad \Delta H = -50 \text{ kJ mol}^{-1}$$

Since 'per mol' in 'kJ per mol' refers to per mol of stoichiometric ratio, every 1 mol of **A** reacted with 2 mol of **B** to produce 3 mol of **C** releases 50 kJ of energy.

Energy released when 2 mol of **A** reacted = $-\Delta H \times n = -(-50) \times 2 =$ 100 kJ

BUT energy released when 2 mol of **B** reacted is NOT $-\Delta H \times n = -(-50) \times 2 =$ 100 kJ because the stoichiometric ratio of **B** is NOT **1**.

- The n in $-\Delta H \times n$ refers to the amount (in mol) of species reacted (or produced) in the chemical equation with a stoichiometric ratio of 1.

Worked Example 2

Consider standard enthalpy change of combustion of a gaseous hydrocarbon, C_4H_{10}:

- Standard enthalpy change of combustion of a species refers to 1 mol of a species is completely burnt in excess oxygen at standard conditions of 298 K and 1 bar.

$$C_4H_{10}(g) + \frac{13}{2} O_2(g) \longrightarrow 4\, CO_2(g) + 5\, H_2O(l)$$

The n in $-\Delta H \times n$ refers to the amount (in mol) of C_4H_{10} reacted in the equation since C_4H_{10} has a stoichiometric ratio of 1 in the chemical equation.

- The calorimetry formula assumes there is no heat gained from the calorimeter and heat transfer is 100% efficient.
- If there is heat gained from the calorimeter and the heat transfer is not 100% efficient, then the calorimetry formula is now:

$$E \times -\Delta H \times n = mc\Delta T + C\Delta T$$

  where *E* refers to the efficiency of heat transfer and C refers to heat capacity of the calorimeter.
- Heat capacity, C, is mass of calorimeter x specific heat capacity of calorimeter. i.e., C = mc

Questions that provide the Enthalpy Change of the Reaction

Worked Example 1 (Standard Enthalpy Change of Neutralisation)

Given that $\Delta H_{neutralisation}$ between H_2SO_4 and NaOH is -57.3 kJ mol^{-1}, calculate ΔT when 0.1 mol of H_2SO_4 reacts 0.3 mol of NaOH in a total volume of 100 cm^3 (specific heat capacity of solution = 4.18 J g^{-1} K^{-1}).

Solution

Step 1: Write out the chemical equation for the enthalpy change given

- Standard enthalpy change of neutralisation refers to 1 mol of water produced in the neutralisation reaction between an acid and a base under standard conditions of 298 K and 1 bar.

$\frac{1}{2} H_2SO_4 + NaOH \longrightarrow \frac{1}{2} Na_2SO_4 + H_2O$

Step 2: Figure out what n in $-\Delta H \times n = mc\Delta T$ refers to

As mentioned previously, n refers to the amount (in mol) of species reacted (or produced) with a stoichiometric ratio of 1.

In this question, n is *either* the number of moles of NaOH reacted *or* number of moles of H_2O produced.

Since H_2SO_4 is the limiting reagent, number of moles of NaOH reacted = 0.1 ÷ ½ = 0.2 mol = n

- 0.2 mol is also the number of moles of H_2O produced.

Step 3: Calculate change in temperature, ΔT

$-\Delta H \times n = mc\Delta T$

$-(+57.3) \times 10^3 \times 0.2 = 100 \times 4.18 \times \Delta T$

$\Delta T = +27.4$ K (or °C) (3 s.f.)

- ΔH is converted to **J** mol^{-1} because 4.18 is in **J** g^{-1} K^{-1}.
- m here refers to the mass of water since c is the specific heat capacity of water.
- A change in temperature of 1 °C is equivalent to 1 K.

Worked Example 2 (Chemical Reaction without a Species of Stoichiometric Ratio of 1)

Calculate the change in temperature when 0.1 mol of **A** reacts with 0.3 mol of **B** in a volume of 100 cm^3 of water (specific heat capacity of water = 4.18 J g^{-1} K^{-1})

$$2\,\mathbf{A} + 3\,\mathbf{B} \longrightarrow 4\,\mathbf{C} \qquad \Delta H_{\text{reaction}} = +50 \text{ kJ mol}^{-1}$$

Solution

~~Step 1: Write out the chemical equation for the enthalpy change given~~

Since the question has given us the chemical equation for the enthalpy change, we skip Step 1.

Step 2: Figure out what n in $-\Delta H \times n = mc\Delta T$ refers to

As mentioned previously, n refers to the amount (in mol) of species reacted (or produced) with a stoichiometric ratio of 1.

In this question, since the chemical equation does not have a species with a stoichiometric ratio of 1. We divide the chemical equation by 2 so that A has a stoichiometric ratio of 1:

$$1\,\mathbf{A} + \frac{3}{2}\,\mathbf{B} \longrightarrow 2\,\mathbf{C} \qquad \Delta H_{\text{reaction}} = +25 \text{ kJ mol}^{-1}$$

- You could *also* divide the chemical equation by 3 (or 4) to make **B** (or **C**) have a stoichiometric ratio of 1.
- The enthalpy change of the reaction would also divide by 2 since 'per mol' in 'kJ per mol' refers to per mol of stoichiometric ratio.

Now, n is the number of moles of **A** reacted.

Since **A** is the limiting reagent, number of moles of **A** reacted = 0.1 mol = n

Step 3: Calculate change in temperature, ΔT

$-\Delta H \times n = mc\Delta T$

$-(+50) \times 10^3 \times 0.1 = 100 \times 4.18 \times \Delta T$

$\Delta T = -12.0$ K (or °C) (3 s.f.)

- ΔH is converted to **J** mol^{-1} because 4.18 is in **J** g^{-1} K^{-1}.
- m here refers to the mass of water since c is the specific heat capacity of water.
- A change in temperature of 1 °C is equivalent to 1 K.

Questions that involve calculating Enthalpy Change of the Reaction

Worked Example

$$2\,\mathbf{A} + 3\,\mathbf{B} \rightarrow 4\,\mathbf{C}$$

0.03 mol of **A** reacts with 0.03 mol of **B** in a solution of 100 cm^3 which results in a temperature increase of 10 °C. Calculate the ΔH for the reaction (specific heat capacity of water = 4.18 J g^{-1} K^{-1}).

Solution

~~Step 1: Write out the chemical equation for the enthalpy change given~~

Since the question has given us the chemical equation for the enthalpy change, we skip Step 1.

Step 2: Figure out what n in $-\Delta H \times n = mc\Delta T$ refers to

As mentioned previously, n refers to the amount (in mol) of species reacted (or produced) with a stoichiometric ratio of 1.

In this question, since the chemical equation does not have a species with a stoichiometric ratio of 1. We divide the chemical equation by 2 so that **A** has a stoichiometric ratio of 1:

$$1\,\mathrm{A} + \frac{3}{2}\,\mathrm{B} \longrightarrow 2\,\mathrm{C}$$

- You could *also* divide the chemical equation by 3 (or 4) to make **B** (or **C**) have a stoichiometric ratio of 1.
- The enthalpy change of the reaction would also divide by 2 since 'per mol' in 'kJ per mol' refers to per mol of stoichiometric ratio.

Now, n is the number of moles of **A** reacted.

Since **B** is the limiting reagent, number of moles of **A** reacted = $\frac{0.03}{3}$ x 2 mol = 0.02 mol = n

Step 3: Calculate enthalpy change of the reaction, ΔH

- ΔH is in **J** mol^{-1} because 4.18 is in **J** g^{-1} K^{-1}
- m here refers to the mass of water since c is the specific heat capacity of water.
- A change in temperature of 1 °C is equivalent to 1 K.

$-\Delta H \times n = mc\Delta T$

$-\Delta H \times 0.02 = 100 \times 4.18 \times (+10)$

$\Delta H = -209\ 000 \text{ J mol}^{-1} = -209 \text{ kJ mol}^{-1}$

This is NOT the final answer.

Remember from Step 2 that ΔH= -209 kJ mol^{-1} refers to the following chemical equation:

$$1\text{ A} + \tfrac{3}{2}\text{ B} \longrightarrow 2\text{ C} \qquad \Delta H = -209 \text{ kJ mol}^{-1}$$

To obtain ΔH for **2 A + 3 B → 4 C**, we multiply ΔH = -209 kJ mol^{-1} by **2**.

Therefore,

$$2\text{ A} + 3\text{ B} \longrightarrow 4\text{ C} \qquad \Delta H = -209 \times 2 = -418 \text{ kJ mol}^{-1}$$

7 Reaction Kinetics

Understanding Concentration-time Graphs

Worked Example

The reaction **A** + **B** ⟶ **C** obeys the following rate equation: rate = $k[\mathbf{A}]^0[\mathbf{B}]$.

Three experiments were carried out using different concentrations of **A** and **B**.

Experiment	[**A**] / mol dm^{-3}	[**B**] / mol dm^{-3}
1	1.0	0.01
2	0.01	1.0
3	1.0	1.0

For each experiment, sketch a graph of [**A**] against time.

Solution

Experiment 1

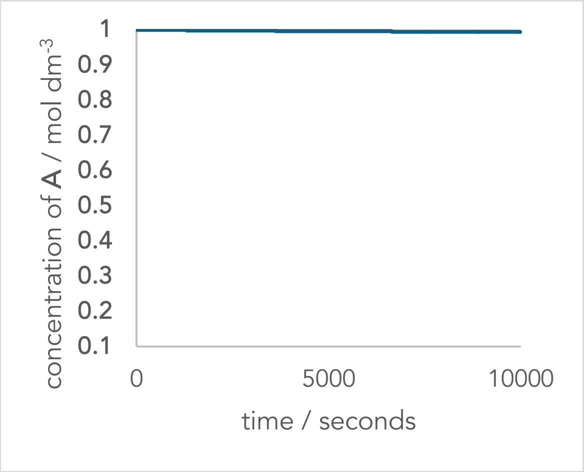
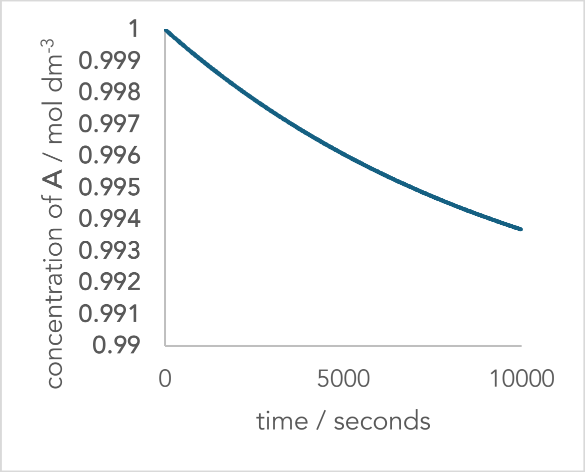
$$\text{rate} = k[\mathbf{A}]^0[\mathbf{B}]$$

Experiment	[**A**] / mol dm^{-3}	[**B**] / mol dm^{-3}
1	1.0	0.01

[**A**] is at least 10 times more than [**B**], **A** is in large excess and remains relatively constant throughout the reaction. This implies that any changes in rate (gradient of concentration-time graph) is solely due to changes in [**B**] throughout the reaction. Hence, [**A**]-time graph follows the order of reaction with respect to (wrt) [**B**].

Since the order of reaction is 1st wrt [**B**], graph of [**A**] against time follows a first-order reaction despite order wrt [**A**] being 0:

- A concentration-time graph for a first-order reaction is a downward sloping curve.

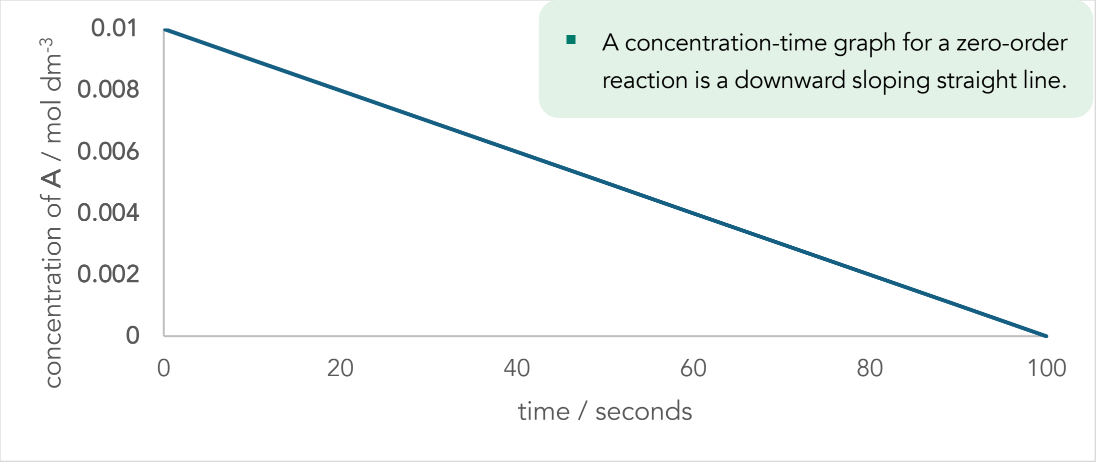
y-axis with **large** intervals (of 0.1)	y-axis with **small** intervals (of 0.001)
	
concentration of **A** *against time looks relatively constant when y–intervals are relatively large*	*concentration of* **A** *against time shows a first-order graph when y-intervals are relatively small*

Experiment 2

$$\text{rate} = k[\mathbf{A}]^0[\mathbf{B}]$$

Experiment	[**A**] / mol dm^{-3}	[**B**] / mol dm^{-3}
2	0.01	1.0

[**B**] is at least 10 times more than [**A**], **B** is in large excess and remains relatively constant throughout the reaction. This implies that any changes in rate (gradient of concentration-time graph) is solely due to changes in [**A**] throughout the reaction. Since the order of reaction wrt [**A**] is 0, graph of [**A**] against time follows a zero-order reaction:



- A concentration-time graph for a zero-order reaction is a downward sloping straight line.

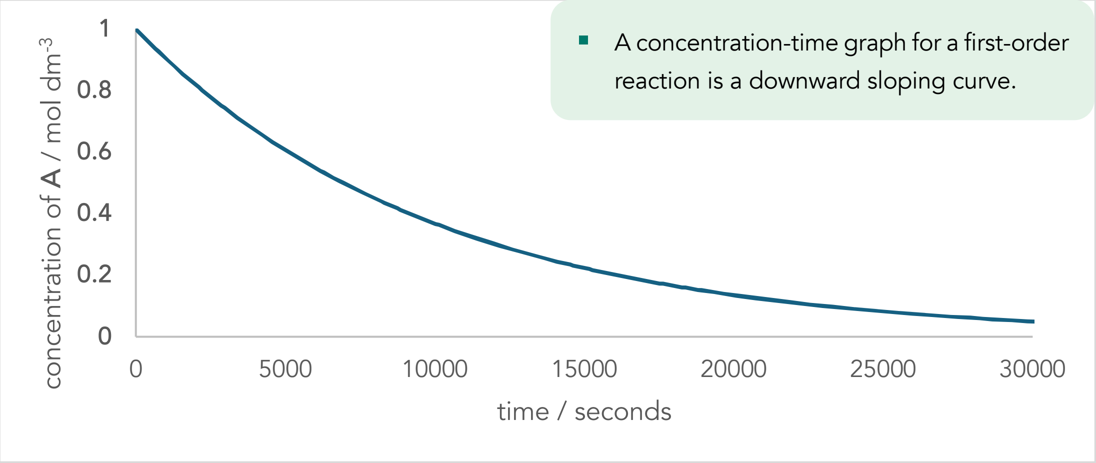
Experiment 3

$$\text{rate} = k[\mathbf{A}]^0[\mathbf{B}]$$

Experiment	[**A**] / mol dm^{-3}	[**B**] / mol dm^{-3}
3	1.0	1.0

Both [**A**] and [**B**] are not in large excess. Any changes in rate (gradient of conc-time graph) is now due to changes in both [**A**] and [**B**].

Since the order of reaction wrt [**A**] and [**B**] is 0 and 1 respectively, graph of [**A**] against time follows a combined order of 0+1 = 1.



- A concentration-time graph for a first-order reaction is a downward sloping curve.

Discontinuous Kinetics Data: Volume and Time

Tracked Species has Different Volumes

Worked Example

A student investigated the kinetics of the reaction between **A** and **B**.

$$\text{A} + \text{B} \longrightarrow \text{C}$$

The time taken for a green coloured **B** to completely decolourise was recorded.

Experiment	Vol of **A** / cm^3	Vol of **B** / cm^3	Vol of H_2O / cm^3	Time Taken / s
1	10	5	25	170
2	15	5	20	113
3	15	10	15	56.5

Deduce the rate equation for the reaction between **A** and **B**.

Solution

Step 1: Check if total volume of solution is constant in all experiments (see this section).

In this question, total volume of solution is constant at 40 cm^3 for all experiments.

- If total volume for an experiment was not 40 cm^3, we must adjust it to 40 cm^3 before proceeding. For *e.g.*, if the total volume for a certain experiment is 80 cm^3, we must halve the volume of every reagent. The time taken will **NOT** be halved because [reagents] before and after halving remains constant (if concentration does not change ⇒ rate does not change ⇒ time taken does not change).

Step 2: Convert time taken into rate by focusing on the tracked species.

In this question, the time taken is for **B** to completely decolourise. Therefore,

Experiment 1	Experiment 2	Experiment 3
It took **170s** for volume of **B** to decrease from **5 to 0 cm^3** ⇒ rate is proportional to $\left\lvert\frac{5-0}{0-170}\right\rvert = 0.02941\ cm^3\ s^{-1}$	It took **113s** for volume of **B** to decrease from **5 to 0 cm^3** ⇒ rate is proportional to $\left\lvert\frac{5-0}{0-113}\right\rvert = 0.04425\ cm^3\ s^{-1}$	It took **56.5s** for volume of **B** to decrease from **10 to 0 cm^3** ⇒ rate is proportional to $\left\lvert\frac{10-0}{0-56.5}\right\rvert = 0.1770\ cm^3\ s^{-1}$

Step 3: Compare between experiments to find the order of the reactants.

- To find the order with respect to (wrt) [**A**], compare experiments 1 and 2 (with **B** constant), when volume of **A** x 1.5, rate x ≈ 1.5 (from 0.02941 to 0.04425). Therefore, order wrt [**A**] is 1.
- To find the order wrt [**B**], compare experiments 2 and 3 (with **A** constant), when volume of **B** x 2, rate x ≈ 4 (from 0.04425 to 0.1770). Therefore, order wrt [**B**] is 2.
- rate = k[**A**][**B**]^2

Tracked Species has the Same Volume

Worked Example

A student investigated the kinetics of the reaction between **A** and **B**.

$$A + B \longrightarrow C$$

The time taken for a **fixed amount of brown-coloured C** to be produced was recorded.

Experiment	Vol of **A** / cm^3	Vol of **B** / cm^3	Vol of H_2O / cm^3	Time Taken / s
1	10	5	25	170
2	15	5	20	113
3	15	10	20	56.5

Deduce the rate equation for the reaction between **A** and **B**.

Solution

Step 1: Check if the total volume is constant in **all** experiments (see this section).

In this question, volume is constant at 40 cm^3 for all experiments.

- If total volume for an experiment was not 40 cm^3, we must adjust it to 40 cm^3 before proceeding. For *e.g.*, if the total volume for a certain experiment is 80 cm^3, we must halve the volume of every reagent. The time taken will NOT be halved because [reagents] before and after halving remains constant (if concentration does not change ⇒ rate does not change ⇒ time taken does not change).

Step 2: Convert time taken into rate by focusing on the tracked species.

In this question, the time taken is for a **FIXED** amount of (brown-coloured) **C** to be produced.

For simplicity, let the amount of **C** (n_C) produced be 0.1 mol (this value is *completely arbitrary*).

Therefore,

Experiment 1	Experiment 2	Experiment 3
It took **170s** for n_C to increase from **0 to 1 mol** ⇒ rate is proportional to $\left\lvert\frac{0.1-0}{0-170}\right\rvert$ = 5.88 x 10^{-4} cm^3 s^{-1}	It took **113s** for n_C to increase from **0 to 1 mol** ⇒ rate is proportional to $\left\lvert\frac{0.1-0}{0-113}\right\rvert$ = 8.85 x 10^{-4} cm^3 s^{-1}	It took **56.5s** for n_C to increase from **0 to 1 mol** ⇒ rate is proportional to $\left\lvert\frac{0.1-0}{0-56.5}\right\rvert$ = 1.77 x 10^{-3} cm^3 s^{-1}

- Since the numerator for all rates are the same and we're only concerned with relative rates (i.e., how the rate changes between experiments when the volume of a reactant is varied), we can conclude the relative rates for all experiments are proportional to $\frac{1}{\text{time taken}}$.

Step 3: Compare between experiments to find the order of the reactants.

- To find the order with respect to (wrt) [**A**], compare experiments 1 and 2 (with **B** constant), when volume of **A** x 1.5, rate x ≈ 1.5 (from 5.88 x 10^{-4} to 8.85 x 10^{-4}). Order wrt [**A**] is 1.
- To find the order wrt [**B**], compare experiments 2 and 3 (with **A** constant), when volume of **B** x 2, rate x ≈ 2 (from 8.85 x 10^{-4} to 1.77 x 10^{-3}). Therefore, order wrt [**B**] is 1.
- rate = k[**A**][**B**]

Why Must the Total Volume in All Experiments Be Constant in Discontinuous Kinetics Experiments?

Worked Example [NJC/Prelim/2016/P1/Q13/modified]

Using a colorimeter, the following reaction is studied by finding the time taken for a coloured reactant, **A**, to decolourise.

$$A + B \longrightarrow C + D$$

The following results are obtained:

Experiment	Volume of solution added / cm^3			Time Taken / s
	A	**B**	H_2O	
1	10	10	20	40
2	5	10	5	40
3	5	20	15	40

What is the rate equation for the reaction?

Solution

- Realise that the total volume in all experiments, except experiment 2, is 40 cm^3. Therefore, comparisons of volumes with experiment 2 are not valid.

  For e.g., when volume of **A** is doubled from 5 cm^3 (in experiment 2) to 10 cm^3 (in experiment 1), the concentration of **A** does <u>NOT</u> double.

- To understand this better, remember that volume and moles are proportional (larger volume added ⇒ more moles added). We can treat volume as moles.
- [A] in experiment 2 is proportional to $\frac{5}{5+10+5} = \frac{5}{20}$ and [A] in experiment 1 is proportional to $\frac{10}{10+20+10} = \frac{10}{40}$. See how when the volume of **A** is doubled from 5 cm^3 (in experiment 2) to 10 cm^3 (in experiment 1), [A] <u>does NOT double</u>.

- Hence, before comparing volumes with experiment 2, we must make the total volume of solution in experiment 2 to be 40 cm^3. We do that by doubling the volume of all species:

Experiment	Volume of solution added / cm^3			Time Taken / s
	A	B	H_2O	
2	5 x 2 = 10	10 x 2 = 20	5 x 2 = 10	40 (**unchanged**)

- Before doubling their volumes:
  [**A**] and [**B**] is proportional to $\frac{5}{20}$ and $\frac{10}{20}$ respectively.
- After doubling their volumes:
  [**A**] and [**B**] is proportional to $\frac{10}{40}$ and $\frac{20}{40}$ respectively.

- The time taken will not double because [**A**] and [**B**] does not double when their volumes are doubled; if concentrations of reactants remain the same, rate remains the same and hence time taken remains the same.
- Once the total volume in experiment 3 is the same as all other experiments, we employ the same working in the earlier worked example.
- The rate equation is rate = k[**A**].

First-Order Reactions and Half-Life

Rate Equation with Only One Reacting Species

Worked Example

Given that the rate equation for the reaction **A** ⟶ **B** is rate = k[**A**], calculate the half-life of **A** given that the rate constant is 0.004 s^{-1}.

Solution

Since there is only 1 reacting species in the reaction, $t_{\frac{1}{2}}$ of **A** = $\frac{\ln 2}{k}$.

$$t_{\frac{1}{2}} = \frac{\ln 2}{0.004}$$

$$= 173.287$$

$$= \mathbf{173\ s\ (3\ sf)}$$

Rate Equation with More Than One Reacting Species

Worked Example

Given that the rate equation for the reaction **A** + **B** ⟶ **C** is rate = k[**A**][**B**]^2, calculate the half-life of **A** given that the rate constant is 0.004 $mol^{-1}\ dm^{3}\ s^{-1}$ and that [**B**] is kept relatively constant throughout the reaction at 1.5 $mol\ dm^{-3}$.

Solution

- It is vital that [**B**] is kept relatively constant throughout the reaction so that as the reaction proceeds, any changes in rate will be solely due to changes in [**A**]. If the reaction is first order with respect to [**A**] is 1, the half-life of **A** will remain constant.
- If [**B**] was not kept relatively constant, the half-life of **A** will **NOT** remain constant even if the reaction is first order with respect to [**A**]. This is because both [**A**] and [**B**] contribute to the reaction rate, and the graph of [**A**] against time will reflect the combined order (1+1) of **A** and **B**.
- See the graphs in this section for a better understanding of this concept (notably Experiments 2 and 3).

Since [**B**] is relatively constant, and the reaction is first order with respect to [**A**], the half-life of [**A**] is constant.

Since the formula, $t_{\frac{1}{2}}$ of **A** = $\frac{\ln 2}{k}$ applies only to a reaction that is first order overall, we must modify the rate equation so that the **overall order is 1**:

rate = k[**A**][**B**]^2

Since [**B**] is relatively constant throughout the reaction,

rate = k'[**A**], where k' = k[**B**]^2

$t_{\frac{1}{2}}$ of **A** = $\frac{\ln 2}{k'}$

= $\frac{\ln 2}{k[B]^2}$

= $\frac{\ln 2}{0.004 \times 1.5^2}$

= 77.0164

= **77.0 s (3 sf)**

- The rate equation is first-order overall, $t_{\frac{1}{2}}$ of **A** = $\frac{\ln 2}{k}$ is applicable.

- The half-life of [**A**] is now dependent on [**B**]; if [**B**] changes in another experiment (but is still relatively constant throughout the reaction), the half-life of **A** will change.

8 Acid-Base Equilibrium

Calculating pH After an Acid-Base Reaction (Titration)

The general steps for calculating pH at different volumes added during titration are:

Step 1: Construct an "initial, change, final" (ICF) table to determine what species is left behind at the end of the acid-base reaction based on the limiting reagent.

Step 2: Depending on the species left behind, use different formulas to calculate pH. There are three possible cases:

a. weak acid (or weak base)
b. strong acid (or strong base)
c. buffer

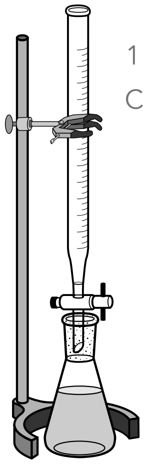
- An acidic (or basic salt) is just a weak acid (or weak base).

Worked Example

Calculate the pH of the solution when 25 cm^3, 0.5 mol dm^{-3} NaOH is titrated **with** 1.0 mol dm^{-3} CH_3COOH (K_a = 1.8 x 10^{-5} mol dm^{-3}) for each of the volumes added:

(i) 6.25 cm^3 **(ii)** 12.50 cm^3
(iii) 18.75 cm^3 **(iv)** 25.00 cm^3

- The species listed after "titrated with" or "titrated against" is in the burette.



Solution

(i) 6.25 cm^3 of 1 mol dm^{-3} CH_3COOH added to 25 cm^3, 0.5 mol dm^{-3} NaOH

Step 1: Construct ICF table.

(mol)	CH_3COOH	+	OH^-	⟶	CH_3COO^-	+	H_2O
I	$\frac{6.25}{1000}$ x 1 = 0.00625		$\frac{25}{1000}$ x 0.5 = 0.0125		0		–
C	−0.00625		−0.00625		+0.00625		–
F	0		0.00625		0.00625		

- Focus on '**F**' to calculate pH.

- Since CH_3COOH is an acid, and OH^- is a base and they are not conjugates, they undergo an acid-base reaction; acid-base reactions are always a full arrow.
- ICF table is done in mol (not mol dm^{-3}) becomes total volume changes. If volume is constant (change in moles is proportional to change in concentration), the ICF table can be done in mol dm^{-3}.
- Amount of CH_3COOH becomes 0 because it is the limiting reagent.

Step 2: Resultant solution contains strong base (OH^-) and weak base (CH_3COO^- is a basic salt).

THIS IS A STRONG BASE pH SCENARIO.

- Presence of OH^- (strong base) will suppress the dissociation of CH_3COO^- (weak base) in water. The position of dissociation equilibrium ($CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$) will lie very much to the left.
- Therefore, we ignore dissociation of CH_3COO^- (weak base) and **focus only on OH^-**.

To find the pH of OH^-, calculate pOH and then pH:

$$\text{pOH} = -\log_{10}[OH^-] = -\log_{10}\left(\frac{0.00625}{\frac{25+6.25}{1000}}\right) = 0.690$$

- Remember to convert amount of OH^- into $[OH^-]$!
- Amount of OH^- = 0.00625 mol
- Total volume of solution = (25 + 6.25) cm^3

pH = 14 – 0.69 = **13.3 (3 sf)**

$\text{pH} + \text{pOH} = \text{p}K_w = 14$ (at 25 °C)

If you're interested…

- Here's the proof to show that the dissociation of CH_3COO^- in the presence of OH^- is extremely minute and does not contribute significantly to the $[OH^-]$ in the solution.

(mol dm^{-3})	CH_3COO^-	+	H_2O	$\rightleftharpoons$	CH_3COOH	+	OH^-
I	$\frac{0.00625}{\left(\frac{25+6.25}{1000}\right)}$ = 0.200		-		0		$\frac{0.00625}{\left(\frac{25+6.25}{1000}\right)}$ = 0.200
C	-x		-		+x		+x
E	0.200 - x		-		x		0.2 + x

To find x, construct a K_b expression.

$$\frac{10^{-14}}{1.8 \times 10^{-5}} = K_b = \frac{x(0.2+x)}{0.2-x}$$

$[OH^-]$ dissociated from CH_3COO^- = x = 5.56×10^{-10} mol dm^{-3} which is highly insignificant to the 0.2 mol dm^{-3} of OH^- present at the end of the acid-base reaction.

(ii) 12.5 cm^3 of 1 mol dm^{-3} CH_3COOH added to 25 cm^3, 0.5 mol dm^{-3} NaOH

Step 1: Construct ICF table.

(mol)	CH_3COOH	+	OH^-	⟶	CH_3COO^-	+	H_2O
I	$\frac{12.5}{1000} \times 1$ = 0.0125		$\frac{25}{1000} \times 0.5$ = 0.0125		0		–
C	−0.0125		−0.0125		+0.0125		–
F	0		0		0.0125		

- Focus on 'F' to calculate pH.

- ICF table is done in mol (not mol dm^{-3}) becomes total volume changes. If volume is constant (change in moles is proportional to change in concentration), the ICF table can be done in mol dm^{-3}.
- Amounts of CH_3COOH and OH^- become 0 because their initial moles are stoichiometrically equivalent.

Step 2: Resultant solution contains only a weak base (CH_3COO^- is a basic salt).

THIS IS A WEAK BASE pH SCENARIO.

The weak base partially dissociates in water to release OH^- (basic salt hydrolysis).

To calculate pH, calculate $[OH^-]$ at equilibrium via an ICE table and a K_b expression:

(mol dm^{-3})	CH_3COO^-	+	H_2O	⇌	CH_3COOH	+	OH^-
I	$\frac{0.0125}{\left(\frac{25+12.25}{1000}\right)}$ = 0.33333		-		0		0
C	-x		-		+x		+x
E	0.33333 - x		-		x		x

- ICE table is in mol dm^{-3} because volume is constant when CH_3COO^- dissociates.

$\frac{K_w}{K_a}$

$$\frac{10^{-14}}{1.8 \times 10^{-5}} = K_b = \frac{x^2}{0.33333-x}$$

Since CH_3COO^- is a weak base, x << 0.33333 and 0.33333 - x ≈ 0.33333

$[OH^-] = x = 1.36082 \times 10^{-5}$ mol dm^{-3}

$pOH = -\log_{10}(1.36082 \times 10^{-5}) = 4.8662$

pH = 14 – 4.8662 = **9.13 (3 sf)**

$pH + pOH = pK_w = 14$ (at 25 °C)

(iii) 18.75 cm^3 of 1 mol dm^{-3} CH_3COOH added to 25 cm^3, 0.5 mol dm^{-3} NaOH

Step 1: Construct ICF table.

(mol)	CH_3COOH	+	OH^-	⟶	CH_3COO^-	+	H_2O
I	$\frac{18.75}{1000} \times 1$ $= 0.01875$		$\frac{25}{1000} \times 0.5$ $= 0.0125$		0		–
C	–0.0125		–0.0125		+0.0125		–
F	0.00625		0		0.0125		

- Focus on '**F**' to calculate pH.

- ICF table is done in mol (not mol dm^{-3}) becomes total volume changes. If volume is constant (change in moles is proportional to change in concentration), the ICF table can be done in mol dm^{-3}.
- A buffer is created because CH_3COOH is in excess.
- Amount OH^- becomes 0 mol because it is the limiting reagent.

Step 2: Resultant solution contains weak acid (CH_3COOH) with its conjugate base (CH_3COO^-).

THIS IS A <u>BUFFER</u> pH SCENARIO.

To find the pH of a buffer, use the buffer formula:

$$pH = pK_a + \log_{10}\frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$\log_{10}\frac{[base]}{[acid]}$$

- Base (or acid) is the buffer species with less (or more) H atoms.

$$pH = -\log_{10}(1.8 \times 10^{-5}) + \log_{10}\frac{\left(\frac{0.0125}{V}\right)}{\left(\frac{0.00625}{V}\right)}$$

where total volume, V = (18.75 + 25) cm^3

pH = **6.05 (3 sf)**

- The total volume will <u>always cancel off</u> in the $\frac{[base]}{[acid]}$ ratio because the buffer species will always share the same total volume (they are in the same solution).

(iv) 25 cm^3 of 1 mol dm^{-3} CH_3COOH added to 25 cm^3, 0.5 mol dm^{-3} NaOH

Step 1: Construct ICF table.

(mol)	CH_3COOH	+	OH^-	⟶	CH_3COO^-	+	H_2O
I	$\frac{25}{1000} \times 1$ = 0.0250		$\frac{25}{1000} \times 0.5$ = 0.0125		0		–
C	−0.0125		−0.0125		+0.0125		–
F	0.0125		0		0.0125		

- Focus on ‘**F**’ to calculate pH.

- ICF table is done in mol (not mol dm^{-3}) becomes total volume changes. If volume is constant (change in moles is proportional to change in concentration), the ICF table can be done in mol dm^{-3}.
- A buffer is created because CH_3COOH is in excess.
- Amount of OH^- becomes 0 mol because it is the limiting reagent.

Step 2: Resultant solution contains equal amounts of weak acid (CH_3COOH) with its conjugate base (CH_3COO^-).

THIS IS <u>MAXIMUM BUFFER CAPACITY (MBC)</u>.

To find the pH of a buffer, use the buffer formula:

$$pH = pK_a + \log_{10}\frac{[CH_3COO^-]}{[CH_3COOH]} \quad \boxed{\log_{10}\frac{[base]}{[acid]}}$$

- Base (or acid) is the buffer species with less (or more) H atoms.

$$pH = -\log_{10}(1.8 \times 10^{-5}) + \log_{10}\frac{\cancel{\left(\frac{0.0125}{V}\right)}}{\cancel{\left(\frac{0.0125}{V}\right)}}$$

where total volume, V = (25 + 25) cm^3

pH = **4.74 (3 sf)**

At MBC, pH = pK_a.

- The total volume will <u>always cancel off</u> in the $\frac{[base]}{[acid]}$ ratio because the buffer species will always share the same total volume (they are in the same solution).

MBC occurs when the volume of CH_3COOH added (25.0 cm^3) is <u>twice the equivalence point volume</u> (12.5 cm^3). This suggests a pattern:

When the <u>buffer region occurs after equivalence point</u>, <u>maximum buffer capacity</u> occurs at <u>twice the equivalence point volume</u>.

An Important Summary of pH Calculations from Titration

After studying the Worked Example, realise these three main points:

- The metal ion (Na^+) was ignored in the acid-base reaction. We generally ignore all metal ions in this topic unless stated otherwise, as they have low charge density (CD) and will not exhibit any acidic properties.

> ▪ In the Periodic Table chapter, we saw high charge density metal ions (Al^{3+}) that are acidic.

Additionally, in acid-base reactions involving strong acids (HCl, HBr, HI, HNO_3, H_2SO_4, HSO_4^-), we generally ignore their conjugate bases (Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, SO_4^{2-}) as they exhibit very weak basic properties (since $K_a \times K_b = K_w$, and the K_a of a strong acid is very large).

To summarise, we disregard these ions in this chapter:

ALL metal ions (unless stated otherwise)
and
Conjugate bases of strong acids (Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-})

- A buffer was only formed in the acid-base when CH_3COOH was in excess.

  To create a buffer via an acid-base reaction, the **weak species** (weak acid or weak base) must be added in **excess**.

  Since the reagent in the conical flask is only in excess before equivalence point (EP) and the reagent in the burette is only in excess after EP, this means that if the **weak species in titration is the conical flask (or burette)**, a **buffer occurs before (or after) EP**.

- If the buffer region takes place **after equivalence point**, MBC occurs at **twice of equivalence point volume**.

  If the buffer region takes place **before equivalence point**, MBC occurs at **half of equivalence point volume**.

The Four Main Types of Acid-Base Titrations

There are four main types of acid-base titrations, classified based on the strength of the acid and base involved, as well as whether the acid or base is in the burette or conical flask.

- We do not bother about strong acid–strong base titrations (overly simplistic) or weak acid–weak base titrations (overly complex).

For each type of acid-base titration (SA-WB, WB-SA, SB-WA, WA-SB), we will consider:

1. **Buffer Region & Maximum Buffer Capacity (MBC).**
    - Identify if the buffer region is before or after the equivalence point (EP).
    - Locate MBC.
2. **pH Calculations.**
    - Before, at, and after EP.

Titration of a Strong Acid Against a Weak Base

For e.g., titration of H_2SO_4 (strong acid) against NH_3 (weak base).

$$H^+ + NH_3 \longrightarrow NH_4^+$$

1. Since NH_3 is in the burette and is only in excess after EP,
    - A buffer (of NH_3 and NH_4^+) occurs **AFTER** EP.
    - MBC ($pH = pK_a$) occurs at **TWICE** of EP volume.

- To create a buffer via an acid-base reaction, the weak species must be in excess.

2.

	H^+ (flask)	+	NH_3 (burette)	⟶	NH_4^+	Type of pH Calculation
before EP	✓		✗		✓	**Strong acid** $pH = -\log_{10}[H^+]$
at EP	✗		✗		✓	**Acidic Salt (weak acid)** 1. Construct ICE table. 2. Calculate $[H^+]$ at equilibrium using K_a.
after EP	✗		✓		✓	**Buffer** $pH = pK_a + \log_{10}\frac{[NH_3]}{[NH_4^+]}$

✓ = *present after the acid-base reaction*
✗ = *absent (0 mol) after the acid-base reaction*

Titration of a Weak Base Against a Strong Acid

For e.g., titration of CH_3NH_2 (weak base) against HCl (strong acid).

$$CH_3NH_2 + H^+ \longrightarrow CH_3NH_3^+$$

1. Since CH_3NH_2 is in the flask and is only in excess before EP,
    - A buffer (of CH_3NH_2 and $CH_3NH_3^+$) occurs **BEFORE** EP.
    - MBC (pH = pK_a) occurs at **HALF** of EP volume.

- To create a buffer via an acid-base reaction, the weak species must be in excess.

2.

	CH_3NH_2 (flask)	+ H^+ (burette)	⟶ $CH_3NH_3^+$	Type of pH Calculation
before EP	✓	x	✓	**Buffer** $pH = pK_a + \log_{10}\frac{[CH_3NH_2]}{[CH_3NH_3^+]}$
at EP	x	x	✓	**Acidic Salt (weak acid)** 1. Construct ICE table. 2. Calculate $[H^+]$ at equilibrium using K_a.
after EP	x	✓	✓	**Strong acid** $pH = -\log_{10}[H^+]$

✓ = *present after the acid-base reaction*

x = *absent (0 mol) after the acid-base reaction*

Titration of a Strong Base Against a Weak Acid

For e.g., NaOH against CH_3COOH.

$$OH^- + CH_3COOH \longrightarrow CH_3COO^- + H_2O$$

1. Since CH_3COOH is in the burette and is only in excess after EP,
   - A buffer (of CH_3COOH and CH_3COO^-) occurs **AFTER** EP.
   - MBC ($pH = pK_a$) occurs at **TWICE** of EP volume.

- To create a buffer via an acid-base reaction, the weak species must be in excess.

2.

	OH^- (flask)	+	CH_3COOH (burette)	$\longrightarrow$	CH_3COO^-	+	H_2O	Type of pH Calculation
before EP	✓		✗		✓		–	**Strong base** $pOH = -\log_{10}[OH^-]$ $pH = pK_w - pOH$ *(At 25 °C, $pK_w = 14$)*
at EP	✗		✗		✓		–	**Basic Salt (weak base)** 1. Construct ICE table. 2. Calculate $[OH^-]$ at equilibrium using K_b. 3. $pOH = -\log_{10}[OH^-]$ $pH = pK_w - pOH$ *(At 25 °C, $pK_w = 14$)*
after EP	✗		✓		✓		–	**Buffer** $pH = pK_a + \log_{10}\frac{[CH_3COO^-]}{[CH_3COOH]}$

✓ = *present after the acid-base reaction*

✗ = *absent (0 mol) after the acid-base reaction*

Titration of a Weak Acid Against a Strong Base

For e.g., CH_3COOH against NaOH.

$$CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O$$

1. Since CH_3COOH is in the flask and is only in excess before EP,
    - A buffer (of CH_3COOH and CH_3COO^-) occurs **BEFORE** EP.
    - MBC (pH = pK_a) occurs at **HALF** of EP volume.

- To create a buffer via an acid-base reaction, the weak species must be in excess.

2.

	CH_3COOH (flask)	+	OH^- (burette)	⟶	CH_3COO^-	+	H_2O	Type of pH Calculation
before EP	✓		x		✓		–	**Buffer** $pH = pK_a + \log_{10}\frac{[CH_3COO^-]}{[CH_3COOH]}$
at EP	x		x		✓		–	**Basic Salt (weak base)** 1. Construct ICE table. 2. Calculate $[OH^-]$ at equilibrium using K_b. 3. $pOH = -\log_{10}[OH^-]$ $pH = pK_w - pOH$ *(At 25 °C, $pK_w = 14$)*
after EP	x		✓		✓		–	**Strong base** $pOH = -\log_{10}[OH^-]$ $pH = pK_w - pOH$ *(At 25 °C, $pK_w = 14$)*

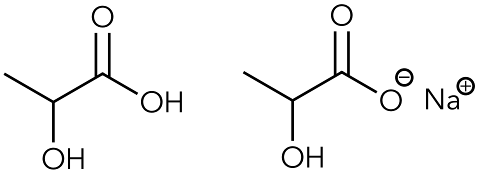
✓ = *present after the acid-base reaction*

x = *absent (0 mol) after the acid-base reaction*

Titrating a Buffer Solution Against a Strong Base

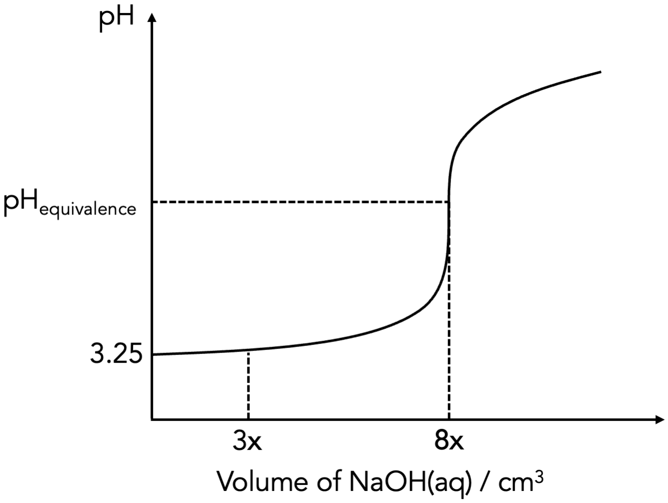
Worked Example 1 [RI/March CT/2024/Q1]

Lactic acid plays a role in several biochemical processes while sodium lactate is commonly used as a food preservative.



lactic acid sodium lactate

The initial pH of a lactic acid-sodium lactate solution is 3.25. To investigate the composition of the buffer solution, 25.0 cm^3 of this buffer solution is titrated with 1.0 mol dm^{-3} aqueous sodium hydroxide. The graph below shows the titration curve obtained.



Upon the addition of 3x cm^3 of aqueous sodium hydroxide, the buffer solution functions at its maximum buffering capacity. The equivalence point of titration is attained when 8x cm^3 of aqueous sodium hydroxide is added.

(a) Show that the ratio of [lactic acid] **:** [sodium lactate] is 4:1 in the original buffer solution.

(b) Determine the acid dissociation constant, K_a, of lactic acid.

Solution

(a) Show that the ratio of [lactic acid] **:** [sodium lactate] is 4:1 in the original buffer solution.

For simplicity, let lactic acid be H**A** and lactate ion (in sodium lactate) be **A**$^-$.

To determine the ratio of [H**A**] to [**A**$^-$], we need to obtain the amount of H**A** and **A**$^-$ in the buffer.

Determining the amount of lactic acid in the buffer solution

> *"The equivalence point of titration is attained when 8x cm^3 of aqueous sodium hydroxide is added."*

OH$^-$ (from NaOH) reacts with the acidic species of the buffer (lactic acid):

$$HA + OH^- \longrightarrow A^- + H_2O$$

- Acid–base reactions are always a full arrow (⟶).

Since equivalence point is reached after addition of 8x cm^3 of NaOH, amount of H**A** (in the buffer) is stoichiometrically equivalent to the amount of OH$^-$ (in 8x cm^3 of NaOH).

$$\text{Amount of } OH^- = \frac{8x}{1000} \times 1 \qquad \frac{\text{volume of NaOH in cm}^3}{1000\ \text{cm}^3} \times [\text{NaOH}] \text{ in mol dm}^{-3}$$

$$= 0.008x \text{ mol}$$

Since H**A** and OH$^-$ reacts in a 1:1 mole ratio, amount of H**A** (in the buffer solution) = 0.008x mol

Alternatively, we can do an initial–change–final table to visualise this better:

	HA	+	OH$^-$	⟶	A$^-$	+	H$_2$O
Initial / mol	?		$\frac{8x}{1000} \times 1 = 0.008x$		–		–
Change / mol	–0.008x		–0.008x		–		–
Final / mol	0		0		–		–

- H**A** and OH$^-$ must have completely reacted (final amount is 0 mol) at the end of the reaction because equivalence point is reached.
- We ignore **A**$^-$ here because we're focusing on finding the moles of HA.

Determining the amount of sodium lactate in the buffer solution

> *"Upon the addition of 3x cm^3 of aqueous NaOH, the buffer solution functions at its maximum buffering capacity."*

This means **after** HA reacts with the amount of NaOH in 3x cm^3, amount of HA and **A**$^-$ is **equal**.

We construct an initial–change–final table and let the initial amount of **A**$^-$ in the buffer be y mol:

	HA	+	OH$^-$	⟶	A$^-$	+	H_2O
Initial / mol	0.008x		$\frac{3x}{1000}$ x 1 = 0.003x		y		–
Change / mol	–0.003x		–0.003x		+0.003x		–
Final / mol	0.005 x		**0**		0.003x + y		–

- Always construct an ICF table to visualise an acid–base reaction better.
- Initial amount of **A**$^-$ is **NOT** zero; remember, we are adding 3x cm^3 of NaOH to a **buffer solution** containing HA and **A**$^-$.
- OH$^-$ must have reacted completely (final amount is 0 mol) because there is leftover HA (a buffer solution exists after the reaction) indicating that OH$^-$ was the limiting reagent.

Since amount of HA and **A**$^-$ is the same after the reaction,

$$0.005x = 0.003x + y$$

$$y = 0.002x$$

Amount of **A**$^-$ (in the buffer solution) = 0.002x mol

Determining the ratio of [lactic acid] : [sodium lactate] in the buffer solution

$$\frac{[HA]}{[A^-]} = \frac{\text{amount of HA}}{\text{amount of A}^-} = \frac{0.008x}{0.002x} = \frac{4}{1} \quad \textbf{(shown)}$$

- The ratio of their concentrations is equal to the ratio of their moles because the buffer species share the same volume of solution.

Solution

(b) Determine the acid dissociation constant, K_a, of lactic acid.

"The initial pH of a lactic acid-sodium lactate solution is 3.25"

It is well–known that the pH of a buffer can be simply obtain by using pH = $pK_a + \lg \frac{[A^-]}{[HA]}$

Since the pH is 3.25 and the ratio of $\frac{[HA]}{[A^-]} = 4$, we can easily solve for pK_a.

- The ratio of HA : A^- was shown in **(a)**.

$$pH = pK_a + \lg \frac{[A^-]}{[HA]}$$

$$\frac{[HA]}{[A^-]} = 4 \Rightarrow \frac{[A^-]}{[HA]} = \frac{1}{4}$$

$$3.25 = pK_a + \lg \frac{1}{4}$$

$pK_a = 3.85206$

$K_a = 1.41 \times 10^{-4}$ mol dm^{-3} **(3 s.f.)**

$K_a = 10^{-pK_a}$

9 Solubility Equilibrium

Selective Precipitation

Selective precipitation is a technique of <u>separating ions in an aqueous solution</u> by using a reagent that <u>precipitates one or more of the ions</u>, while <u>leaving other ions in solution</u>.

Effectiveness of Selective Precipitation

Worked Example 1 [RI/Tutorial 16/Q6]

The numerical values of the solubility products of BaF_2 and CaF_2, at 25 °C, are 1.84×10^{-7} and 3.45×10^{-11} respectively.

A student accidentally mixed 25.0 cm^3 of 0.100 mol dm^{-3} $CaCl_2$ solution with 25.0 cm^3 of 0.100 mol dm^{-3} $BaCl_2$ solution. To separate the two metal ions, he added just enough solid KF to precipitate the maximum amount of CaF_2 from the mixture, without precipitating BaF_2.

(a) Determine the concentration of F^- in the solution at the end of the separation.

(b) Determine the concentration of Ca^{2+} remaining in the solution.

(c) Calculate the percentage of Ca^{2+} remaining in the solution and comment on the effectiveness of the separation.

Solution

(a) At the end of the separation, <u>maximum amount of CaF_2 has precipitated</u> without precipitating BaF_2. This would mean that ionic product (IP) of BaF_2 is only <u>slightly below</u> its K_{sp} and hence,

$$\text{IP of } BaF_2 = K_{sp} \text{ of } BaF_2$$

$$[Ba^{2+}][F^-]^2 = 1.84 \times 10^{-7}$$

$$[Ba^{2+}] \text{ initial upon mixing} = \frac{\frac{25}{1000} \times 0.1}{\frac{25+25}{1000}} \quad \boxed{\frac{\text{moles of } Ba^{2+}}{\text{total volume upon mixing}}}$$

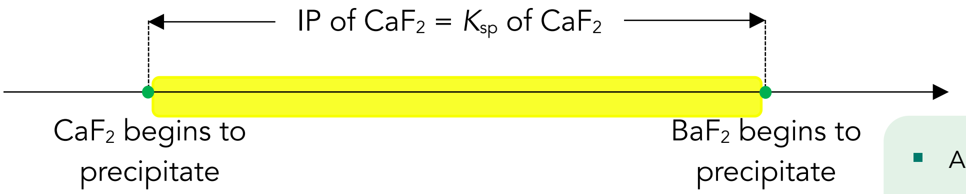
$$= 0.05 \text{ mol dm}^{-3}$$

$$(0.05)\,[F^-]^2 = 1.84 \times 10^{-7}$$

$$[F^-] = 1.918333 \times 10^{-3}$$

$$= \mathbf{1.92 \times 10^{-3}\ mol\ dm^{-3}\ (3\ sf)}$$

(b) As CaF_2 precipitates from solution, IP of CaF_2 decreases until it matches its K_{sp}. This means that when $[F^-]$ is between "CaF_2 begins to precipitate" and "BaF_2 begins to precipitate", **IP of CaF_2 will always be equal to its K_{sp}:**



- As BaF_2 begins to ppt, IP of BaF_2 = K_{sp} of BaF_2 too.

Therefore, to calculate $[Ca^{2+}]$ remaining in the solution when BaF_2 begins to precipitate:

$$\text{IP of } CaF_2 = K_{sp} \text{ of } CaF_2$$

$$[Ca^{2+}][F^-]^2 = 3.45 \times 10^{-11}$$

$$[Ca^{2+}](1.918333 \times 10^{-3})^2 = 3.45 \times 10^{-11}$$

$$[Ca^{2+}] = 9.374996 \times 10^{-6}$$

$$= \mathbf{9.37 \times 10^{-6}\ mol\ dm^{-3}\ (3\ sf)}$$

- For pptⁿ to occur, IP > K_{sp}.
- As pptⁿ proceeds, IP decreases and eventually matches K_{sp}, reaching a stable equilibrium.

- A very small value of $[Ca^{2+}]$ is expected. We have precipitated the maximum amount of CaF_2.

(c) $[Ca^{2+}]$ initial upon mixing $= \dfrac{\frac{25}{1000} \times 0.1}{\frac{25+25}{1000}}$

$$\frac{\text{moles of } Ca^{2+}}{\text{total volume upon mixing}}$$

$= 0.05\ mol\ dm^{-3}$

% of Ca^{2+} remaining in solution $= \dfrac{9.374996 \times 10^{-6}}{0.05}$

$$\frac{[Ca^{2+}] \text{ after maximum precipitation}}{\text{initial } [Ca^{2+}]}$$

$= 0.01874999\ \%$

$= \mathbf{0.0187\ \%\ (3\ sf)}$

99.98% (100% – 0.01874999%) of Ca^{2+} has been removed from the solution via precipitation. The separation is extremely effective.

Comparing Effectiveness of Selective Precipitation

Worked Example 2 [RI/March CT/2024/Q2]

The following are the solubility products of silver chloride and bromide, and thallium chloride and bromide at 298 K.

Compound	$AgCl$	$AgBr$	$TlCl$	$TlBr$
K_{sp} / mol^2 dm^{-6}	2.0×10^{-10}	4.1×10^{-13}	1.7×10^{-4}	3.4×10^{-6}

Two experiments on selective precipitation were conducted: one with silver nitrate and the other with thallium(I) nitrate. Deduce if the addition of solid thallium(I) nitrate will result in a more or less effective separation of the halide ions in a 1 dm^3 solution containing 0.10 mol of $NaCl$ and 0.15 mol of $NaBr$ as compared to adding solid silver nitrate.

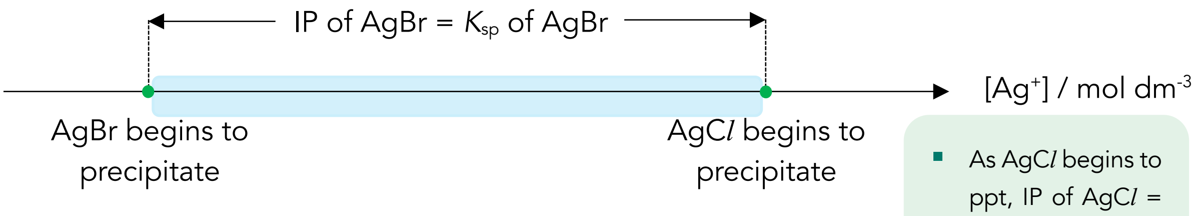
Solution

Important Prerequisite*: to have read and understood Worked Example 1.*

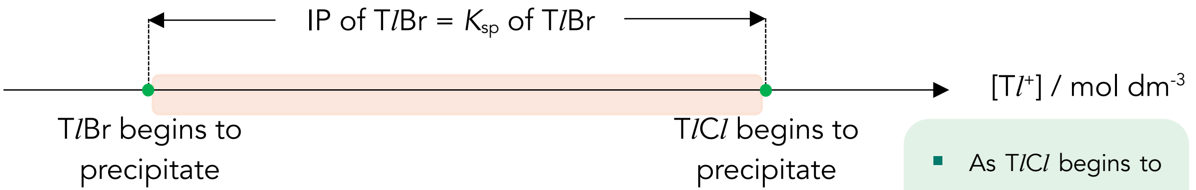
In both experiments, the bromide salts ($AgBr$ and $TlBr$) will precipitate first and the chloride salts ($AgCl$ and $TlCl$) precipitate after.

- Since the chloride and bromide salts have the same cation:anion ratio (1:1), the salt with the lower K_{sp} is the less soluble salt and will likely ppt first.
- Alternatively, you can prove this by calculating $[Ag^+]$ required for $AgCl$ (or $TlCl$) and $AgBr$ (or $TlBr$) to ppt and realise that $[Ag^+]$ for $AgCl$ to ppt is larger than $[Ag^+]$ for $AgBr$ to ppt.

The smaller $[Br^-]_{left}$ when the chloride salts begin to precipitate, the better the separation.



- As $AgCl$ begins to ppt, IP of $AgCl$ = K_{sp} of $AgCl$ too.



- As $TlCl$ begins to ppt, IP of $TlCl$ = K_{sp} of $TlCl$ too.

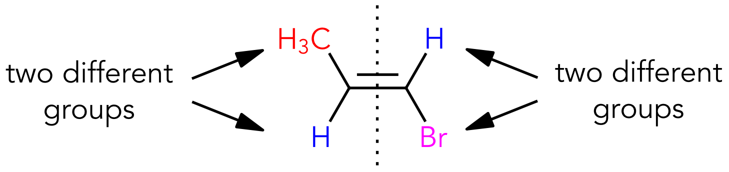
<table>
<tr><th colspan="3">Selective precipitation of…</th></tr>
<tr><th>AgBr and AgC<i>l</i></th><th rowspan="2"><i>vs</i></th><th>T<i>l</i>Br and T<i>l</i>C<i>l</i></th></tr>
<tr><td>$[\text{Br}^-]_{\text{left}}$ when AgC<i>l</i> ppts
$= \dfrac{K_{sp}(\text{AgBr})}{[\text{Ag}^+]\ \text{when AgC}l\ \text{ppts}}$
$= \dfrac{K_{sp}(\text{AgBr})}{K_{sp}(\text{AgC}l) \div [\text{C}l^-]}$
$= \dfrac{4.1 \times 10^{-13}}{(2 \times 10^{-10}) \div 0.1}$
$= 2.05 \times 10^{-4}$ mol dm^{-3}</td><td>$[\text{Br}^-]_{\text{left}}$ when T<i>l</i>C<i>l</i> ppts
$= \dfrac{K_{sp}(\text{T}l\text{Br})}{[\text{Ag}^+]\ \text{when T}l\text{C}l\ \text{ppts}}$
$= \dfrac{K_{sp}(\text{T}l\text{Br})}{K_{sp}(\text{T}l\text{C}l) \div [\text{C}l^-]}$
$= \dfrac{3.4 \times 10^{-6}}{(1.7 \times 10^{-4}) \div 0.1}$
$= 2.00 \times 10^{-2}$ mol dm^{-3}</td></tr>
<tr><td colspan="3">• Since $[\text{Br}^-]_{\text{left}}$ when AgC<i>l</i> ppts is smaller, the addition of solid thallium(I) nitrate results in a <u>less effective separation</u>.
• Realise that calculating $[\text{Br}^-]_{\text{left}}$ essentially involves K_{sp} of the bromide salt by the K_{sp} of the chloride salt. Therefore, the greater the difference in magnitude between the solubility products, the smaller the value of $[\text{Br}^-]_{\text{left}}$.
• The $K_{sp}(\text{AgBr})$ is ~488 times smaller than $K_{sp}(\text{AgC}l)$ while the $K_{sp}(\text{T}l\text{Br})$ is 50 times smaller than $K_{sp}(\text{T}l\text{C}l)$.</td></tr>
</table>

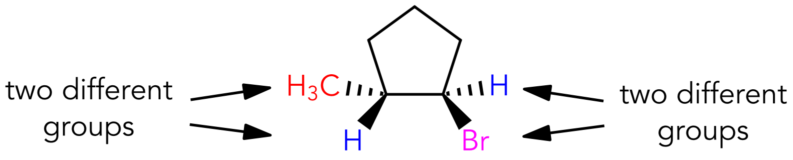
10 Isomerism

Stereoisomerism: Cis-Trans Isomerism

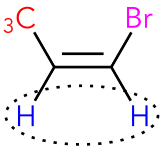
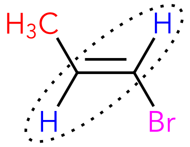
Criteria for Cis-Trans Isomerism

1. Restricted rotation (RR) about a bond (typically C=C, but **single bonds can have RR too**)
2. **Two** different groups on each atom of the bond with RR.

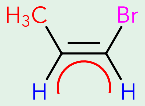




Distinguishing Cis-Trans Isomers in Alkenes

If the two identical groups are on the...	
Same side of C=C π bond	**Opposite side** of C=C π bond
Cis Isomer	***Trans*** Isomer
	

- These two molecules are isomers, no form of bond rotation can make them equivalent.
- An easy to remember the cis notation is that if the identical groups are on the same side of the C=C π bond, a rotated alphabet C is formed:

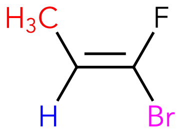


- Realise that cis-trans isomers differ by a 180° flip of the groups on one carbon of the C=C π bond.

Alkenes that Satisfy the Cis-Trans Criteria Without Identical Groups

The following molecule exhibits cis-trans isomerism because it satisfies the criteria, but we struggle to draw the other stereoisomer because there are no identical groups.

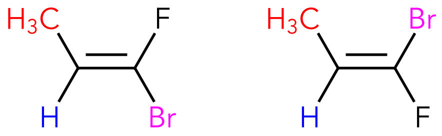
For e.g.,



If you're interested…

- Molecules that satisfy the criteria for cis-trans but do not have identical groups are called *E-Z* isomers.

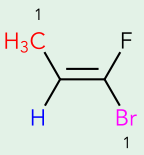
We can still draw the other stereoisomer! Remember that if a molecule satisfies the cis-trans criteria, we can draw the other stereoisomer by simply doing a 180° flip of the groups on one carbon of the C=C π bond:



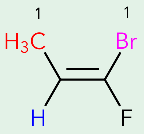
We **can't use the "*cis*" and "*trans*" nomenclature here** because there are no identical groups, but we know that they are still stereoisomers (same molecular formula, different spatial arrangement of atoms) of each other.

If you're interested…

- To know which isomer is *E* or *Z*, we rank the two groups on each carbon according to their atomic numbers of the atom directly attached to the carbon (for e.g., Cl > F).
- If both groups that are ranked 1 are on the same side of the π bond, the molecule is the Z-isomer and if they are on the opposite side of the π bond, the molecule is the E-isomer.



E-isomer

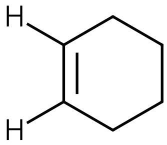
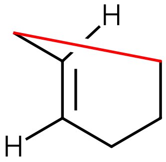


Z-isomer

A Must-Know Exception to the Cis-Trans Alkene Criteria

Theoretically, it's possible to draw cis- and trans- cyclohexene since the C=C π bond fulfils the criteria for cis-trans isomerism.

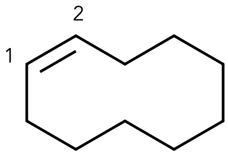
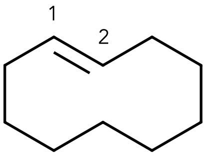
But, *in reality*, the trans-cyclohexene is impossibly strained:

Cis-cyclohexene	Trans-cyclohexene
	 extremely unstable due to ring strain

For this reason, for **ring sizes 7 and below, C=C in rings will not be able to exhibit cis-trans isomerism**; the *trans* form is **too strained**.

At ring sizes of 8 and above, the trans– isomer becomes possible.

For e.g., in cyclodecene (dec = 10 carbons)

Cis-cyclodecene	*Trans*-cyclodecene
	

Cis-Trans Isomers in Ring Systems

Cis-trans isomerism can exist in ring systems too. They fulfil the criteria for *cis-trans* isomerism:

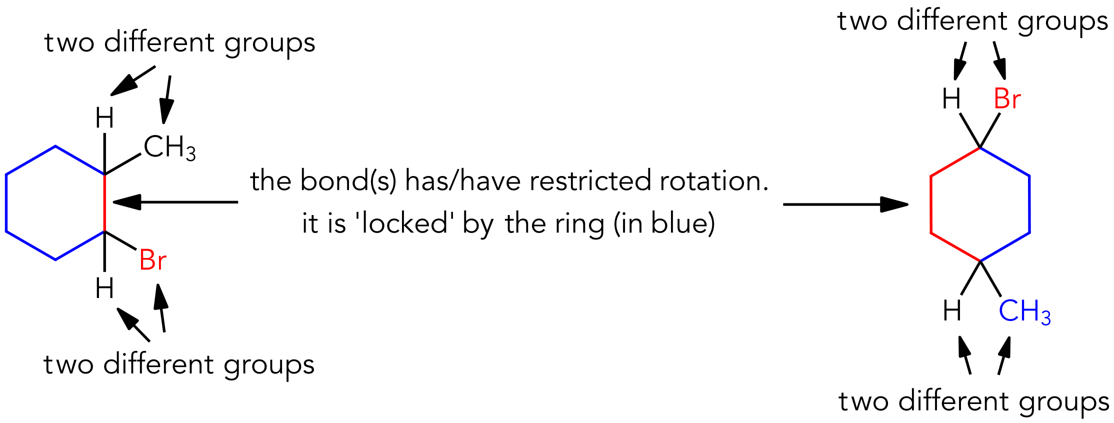
1. Restricted rotation (RR) about a bond
2. **Two** different groups on each atom of the bond with RR.

- We saw this earlier.

Cis-trans isomerism in rings have one more criterion:

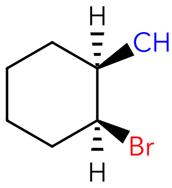
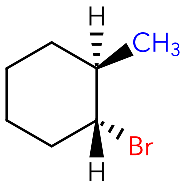
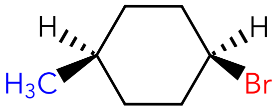
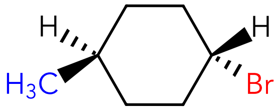
3. The two carbons **must have at least one group in common**.

For e.g., 1-Bromo-2-methylcyclohexane and 1-Bromo-4-methylcyclohexane:



- 1-bromo-3-methylcyclohexane can exhibit cis-trans isomerism in its ring too.

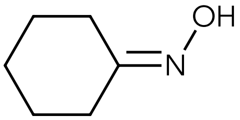
Distinguishing Cis-Trans Isomers in Ring Systems

	If the two identical groups are…	
	both **above or below the ring**	on **opposite sides** of the ring
	Cis Isomer	***Trans*** Isomer
1-Bromo-2-methylcyclohexane		
1-Bromo-4-methylcyclohexane		

- The two identical groups are the hydrogen atom (H).
- The carbon atoms with two different groups need not be adjacent to each other on the ring.
- Wegded and hashed bonds **MUST** be shown because the carbon is chiral.

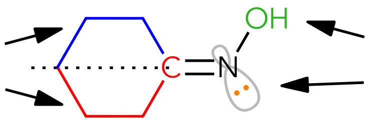
Worked Example 1 (A Lone pair of Electrons Can Act as a Group) [RI/Prelim/2022/P3/Q5]

Explain whether *N*-Hydroxycyclohexanimine exhibits *cis-trans* isomerism.



Solution

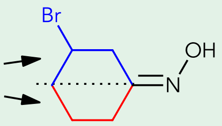
No. Despite the C=N π bond having restricted rotation, and the N atom of the C=N having two different groups, the C atom of C=N has two identical groups bonded to it:



these two groups are identical

these two groups (-OH and lone pair) are different

- If there was a substituent attached to either side of the six-membered ring, the two groups attached to C will now be different and the molecule can exhibit *cis-trans* isomerism:

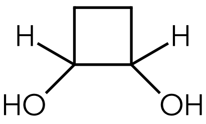


these two groups are now different

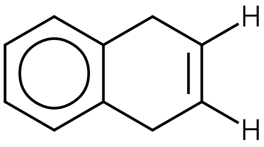
Worked Example [AJC/Prelim/2019/P1/Q19]

Which of the following compounds exhibit *cis-trans* isomerism?

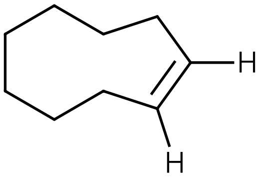
1



2



3



A 1 only **B** 1 and 3 only **C** 2 and 3 only **D** 1, 2 and 3

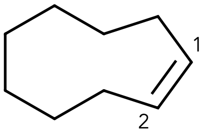
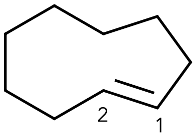
Solution

Answer: **B**

Molecule **1** can exhibit *cis-trans* isomerism in its ring structure because the criteria for *cis-trans* isomerism in ring systems is satisfied.

Molecule **2** cannot exhibit *cis-trans* isomerism in its C=C because of ring strain.

Molecule **3** can exhibit *cis-trans* isomerism in its C=C because the C=C is in a ring size more than 8 and does not have significant ring strain in its trans isomer:

Cis isomer	*Trans* isomer
	

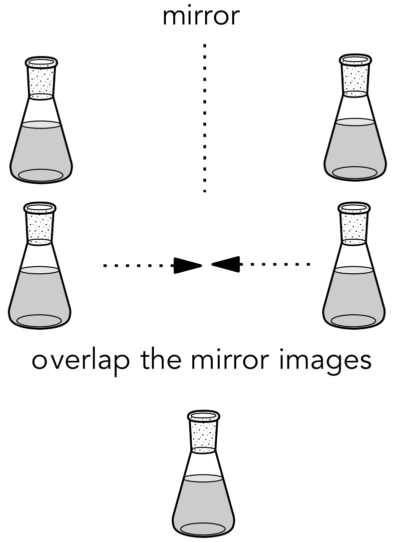
Stereoisomerism: Enantiomerism

What Are Enantiomers?

Enantiomers are a pair of stereoisomers that are non-superimposable mirror images of each other *i.e.*, the mirror image of the molecule cannot be rotated around and perfectly overlapped with the original.

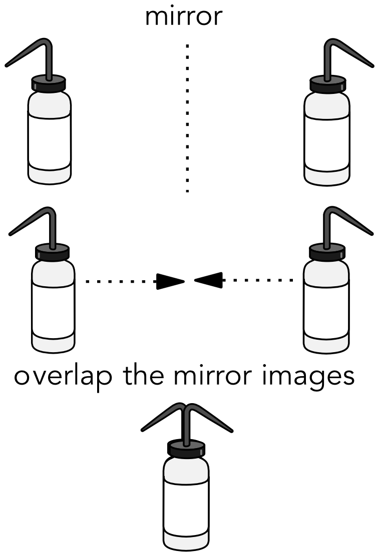
Chirality

Imagine a conical flask held in front of a mirror. If you could take the mirror image and overlap it onto the original conical flask they would coincide exactly. This is called being **superimposable**. In other words, the conical flask and its mirror image are identical. Hence, the conical flask is **achiral** (not chiral).



the mirror images overlap perfectly
this flask is NOT chiral

Now, imagine a wash bottle held in front of a mirror. If you could take the mirror image and overlap it onto the original wash bottle, they would NOT coincide exactly. The mirror images are now **non-superimposable**. The wash bottle and its mirror image are different. Hence, the wash bottle is chiral.



the mirror images do NOT overlap perfectly
this wash bottle is chiral

Summarising Chirality

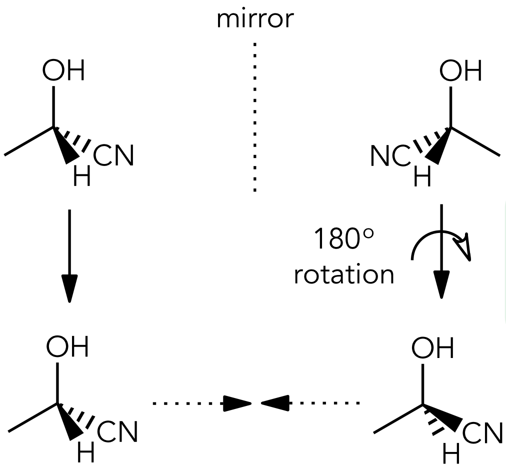
- Any structure that has no plane of symmetry is chiral and can exist as two different mirror image forms. These different mirror image forms are called **enantiomers**.
- To deduce if a molecule has no plane of symmetry (chiral), we *usually* look out for a carbon atom carrying four different groups (a **chiral centre**).
- If a molecule has…
  - only **ONE** chiral centre, it has no plane of symmetry (the molecule is chiral).
  - **TWO or more** chiral centres, it *might* have a plane of symmetry (the molecule is achiral). A molecule that is achiral despite having chiral centers is a called a **meso compound**.

Drawing Enantiomers

The Fundamental but Slow Approach to Drawing Enantiomers

The blue carbon is chiral in $CH_3CH(OH)CN$ because it is bonded to four different groups.

To draw its mirror image, wedged and hashed bonds **MUST** be shown on the chiral carbon (understand why).



- The rotation was done to show that the mirror images are **non-superimposable**.

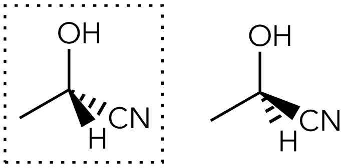
the mirror images do NOT overlap perfectly
one CN is above the plane and the other CN is below

The More Advanced and Faster Approach to Drawing Enantiomers

Realise that enantiomers differ only in the **spatial arrangement of CN and H** — one has CN below and H above the plane, while the other has CN above and H below.

Therefore, a quicker method to draw enantiomers is to place the **mirror plane on the plane of the paper (making it flat) instead of using a vertical mirror plane** to create the mirror image.

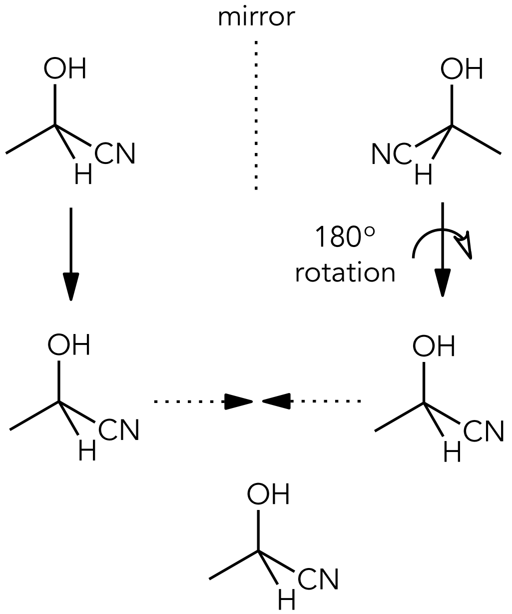
Drawing the mirror image with a flat mirror plane is simpler because we only need to swap the wedged groups with hashed groups and vice versa:



mirror plane
is plane of paper

Chiral Carbons Require Wedged and Hashed Bonds

This is the **WRONG WAY** to show enantiomers. Without using (three-dimensional) wedged and hashed bonds on the chiral carbon, the two mirror–imaged structures **appear superimposable**, which is **incorrect**:



In two dimensions, mirror images can overlap perfectly.
However, in three-dimensional reality, they cannot.

Drawing Out Multiple Stereoisomers (Enantiomers and *Cis-Trans*)

Calculating Total Number of Stereoisomers

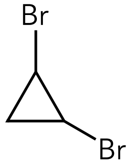
The total number of stereoisomers is calculated using 2^{a+b} where a is the **number of chiral carbon atoms** and b is the **number of *cis-trans*** ALKENES.

- The number of *cis-trans* rings has **already been accounted** for after considering chiral carbons.

For e.g., 1-bromo-2-chlorocyclobutane has 2^{2+0} stereoisomers where *cis-trans* rings are **already included** in the **four** stereoisomers.

Worked Example

Draw out all the stereoisomers for 1,2-dibromocyclopropane:

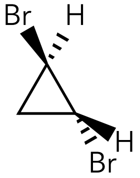


Solution

Since there are two chiral carbons and no cis-trans C=C, we have $\mathbf{2^2 = 4}$ stereoisomers.

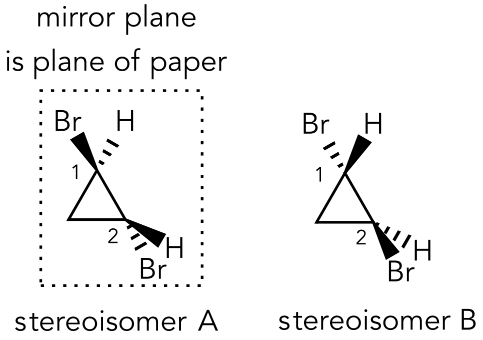
Ensure that **ALL** chiral carbons have wedged and hashed bonds; the choice of which groups to depict as wedged or hashed is **flexible**, but chemists typically keep ring bonds flat (solid lines) for simplicity.

Let's draw the first stereoisomer:



- Remember, you can choose which groups to place above (wedged) or below the plane (hashed)!

And then draw its enantiomer,

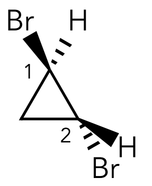


Two stereoisomers down, ***two more to go***.

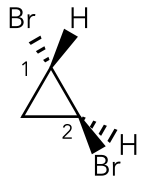
Before drawing the last two stereoisomers, note that when we drew stereoisomer **B**, we simply went to both chiral carbons (C_1 and C_2) of stereoisomer **A** and **swap** its wedged and hashed groups.

To draw the other two stereoisomers (**C** and **D**), instead of swapping the groups on both chiral carbons on **A**, we only swap the groups on one chiral carbon:

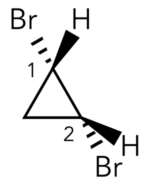
- To draw **C**, swap the groups on chiral carbon-1 and leave chiral carbon-2 unchanged.
- To draw **D**, swap the groups on chiral carbon-2 and leave chiral carbon-1 unchanged.



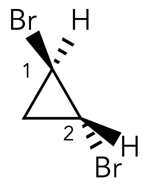
stereoisomer A



stereoisomer B



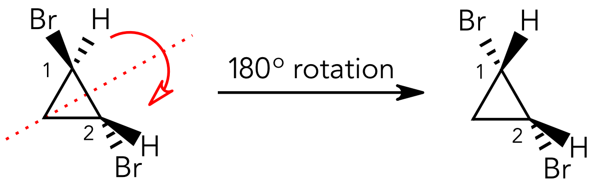
stereoisomer C



stereoisomer D

Notice that stereoisomers **C** and **D** are mirror images of each other, with both chiral carbons having their groups swapped.

However, **C** has an internal plane of symmetry and is therefore not chiral. This means that **D**, the mirror image of **C**, is not an enantiomer of **C** but rather the **SAME MOLECULE** as **C**.

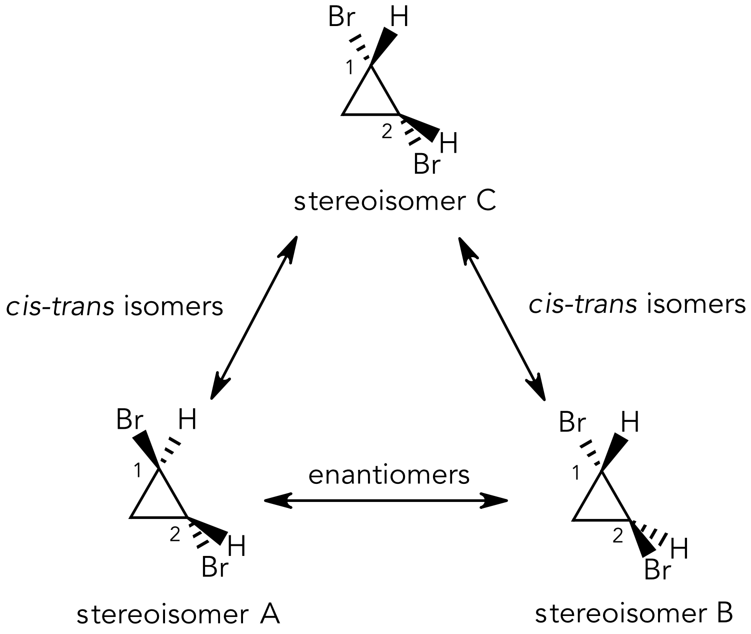


stereoisomer D

stereoisomer C

- Stereoisomer **C** is a meso compound i.e., a molecule with chiral carbons, despite having an internal plane of symmetry.

In conclusion, there are only $2^2 - 1 = 3$ stereoisomers since **one of the stereoisomers is achiral and does not have an enantiomer**. The three stereoisomers are:



- Realise that stereoisomers **C** and **A** (also **C** and **B**) are *cis-trans* isomers.

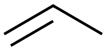
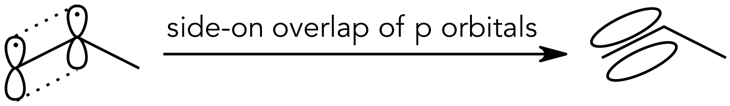
11 Resonance & Delocalisation

Understanding π Bonds, π Electrons and p Orbitals

π Bonds and π Electrons

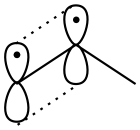
A **π bond** is formed by the side-on overlap of two adjacent and parallel p orbitals.

For e.g., propene:

Skeletal formula	**p orbital diagram**
	

A **π electron** is an electron that occupies a p orbital that is participating in a side-on overlap with other adjacent p orbitals.

For e.g., there are two π electrons in propene.

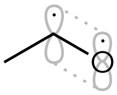
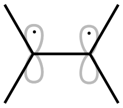
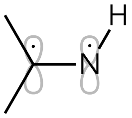


- There is one electron in each p orbital and both p orbitals are side-on overlapping with each other.

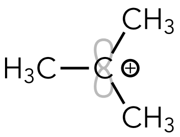
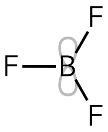
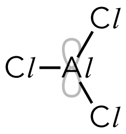
p Orbitals

Some examples of p orbitals are:

- p-orbitals of a π bond (e.g., C=C, C=O, C=N, etc.)

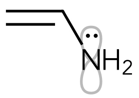
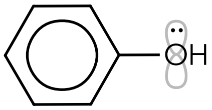
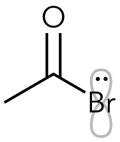
CH_3CO	$(CH_3)_2C=C(CH_3)_2$	$(CH_3)_2C=NH$
		

- an empty p orbital (e.g., in a carbocation, or on boron or aluminium in their compounds)

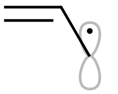
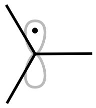
$(CH_3)_3C^+$	BF_3	$AlCl_3$
		

- Since a carbocation is sp^2 hybridised and has 3 σ bonds, the p orbital is vacant (it houses the positive charge).

- a p orbital with a lone pair of electrons (e.g., a saturated atom adjacent to a π bond)

$H_2C=CH-NH_2$	C_6H_5-OH	CH_3COBr
		

- a half-filled p orbital (e.g., a radical)

$H_2C=CH-CH_2^{\bullet}$	$(CH_3)_3C^{\bullet}$
	

- Since a carbon radical is sp^2 hybridised and has 3 σ bonds, the lone electron (radical) is found in the p orbital.

The Criterion for Delocalisation

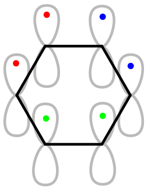
Delocalisation refers to the movement of **π** electrons.

For delocalisation to occur, there must be **three or more** p orbitals consecutively/adjacently placed, and are all parallel to each other.

The Three Categories of Delocalisation & Resonance

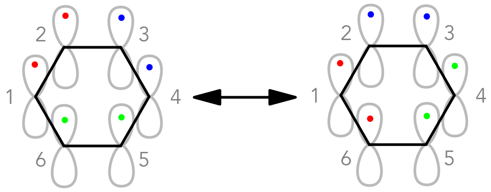
Category 1: π bond adjacent to another π bond

Benzene (Alternating π Bonds in a Ring Structure)

Skeletal structure	p orbital diagram
	

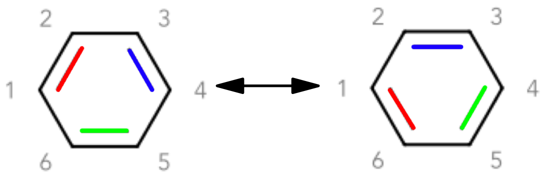
Since benzene has at least three p orbitals adjacent and parallel to each other, delocalisation of its π electrons can occur.

One π electron hops into the **adjacent p orbital** to its left (or right), and pushes out the π electron into the next adjacent p orbital. This process repeats.



- π electron in C_1 hops into the p orbital of C_6, pushing that π electron into the p orbital of C_5. This process repeats. Eventually, the π electron of C_2 then hops into the p orbital of C_1.

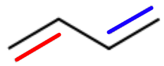
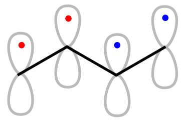
Delocalisation results in benzene adopting two different structures:



These different structures are called **resonance structures**.

- A double-headed arrow (delocalisation arow) is used to show that a molecule can adopt multiple structures.

Buta-1,3-diene (Alternating π Bonds in an Open Non-Polar Structure)

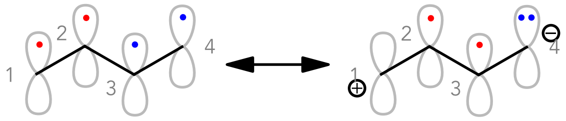
Skeletal structure	p orbital diagram
	

Again, the criterion for delocalisation is met and π electrons can delocalise (move).

In this example, after delocalisation,

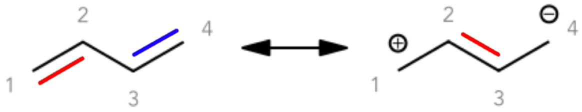
- C_1 loses an electron ⇒ gains a positive charge.
- C_4 gains an electron ⇒ gains a negative charge.

- The π electrons can delocalise in either direction.

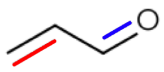
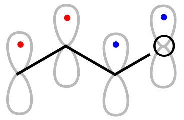


- π electron in C_1 hops into the p orbital of C_2, pushing that π electron into the p orbital of C_3 and the π electron of C_3 hops into the p orbital of C_4.
- The π electron of C_4 is **unable to hop into the p orbital of C_1** because the p orbitals of C_4 and C_1 are **not adjacent**.

Delocalisation results in buta-1,3-diene adopting two different structures:



3-Buten-2-one (Alternating π Bonds in an Open Polar Structure)

Skeletal structure	p orbital diagram
	

Again, the criterion for delocalisation is met and π electrons can delocalise (move).

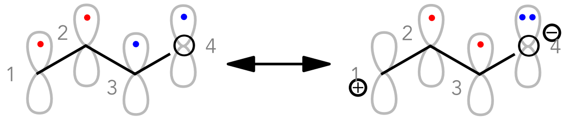
This is a slightly different scenario from buta-1,3-diene because the structure contains a more electronegative oxygen element (i.e., the structure is polar).

Unlike buta-1,3-diene, the π electrons MUST **delocalise towards the more electronegative element**. In this context, towards the oxygen atom.

- Oxygen is more electronegative than carbon.

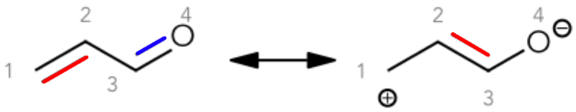
Similarly, after delocalisation,

- C_1 loses an electron ⇒ gains a positive charge.
- O_4 gains an electron ⇒ gains a negative charge.



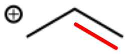
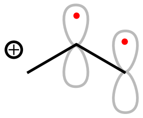
- π electron in C_1 hops into the p orbital of C_2, pushing that π electron into the p orbital of C_3 and the π electron of C_3 hops into the p orbital of O_4.
- The π electron of O_4 is **unable to hop into the p orbital of C_1** because the p orbitals of O_4 and C_1 are **not adjacent**.

Delocalisation results in 3-Buten-2-one adopting two different structures:



Category 2: π bond adjacent to an empty p orbital (typically carbocations)

Allyl Cation, $^{+}CH_2CH{=}CH_2$ (a C=C π bond adjacent to a carbocation)

Skeletal structure	p orbital diagram
	

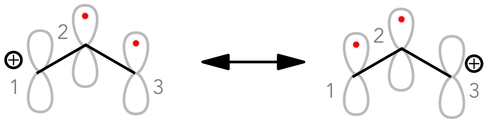
- Since a carbocation is sp^2 hybridised and has 3 σ bonds, the p orbital is vacant (it contains the positive charge).

Since $^{+}CH_2CH{=}CH_2$ has at least three p orbitals adjacent and parallel to each other, delocalisation of its π electrons can occur.

The π electrons delocalise towards the positively charged carbon due to electrostatic attraction between the positively charged carbon and the negatively charged π electrons.

Similarly, after delocalisation,

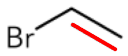
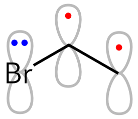
- C_1 gains an electron ⇒ gains a negative charge. Since C_1 was initially positively charged, it turns electrically neutral.
- C_3 loses an electron ⇒ gains a positive charge.



- π electron in C_3 hops into the p orbital of C_2, pushing that π electron into the empty p orbital of C_1.

Category 3: π bond adjacent to saturated atom with a lone pair in p orbital

Vinyl Bromide, $BrCH{=}CH_2$

Skeletal structure	p orbital diagram
	

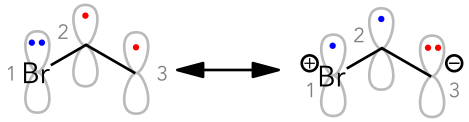
- A saturated atom with at least one lone pair of electrons adjacent to π bond will always be sp^2 hybridised so that its lone pair of electrons reside in a p orbital.
  For e.g., H_2**N**-$CH{=}CH_2$, H**O**-$CH{=}CH_2$, ***Cl***–C_6H_5 etc.
- This allows for side-on overlap with the p orbitals of the π bond, enabling delocalisation of π electrons to occur, rendering extra stability in the molecule.

Since $BrCH{=}CH_2$ has at least three p orbitals adjacent and parallel to each other, delocalisation of its π electrons can occur.

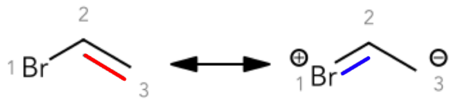
The delocalisation of π electrons must be **towards the π bond**. If the π electrons delocalised away from the π bond, it leaves three electrons in the p orbital of Br, but an orbital can only accommodate two electrons.

After delocalisation,

- C_3 gains an electron ⇒ gains a negative charge.
- Br_1 loses an electron ⇒ gains a positive charge.

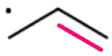
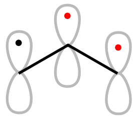


- **One** π electron in Br_1 hops into the p orbital of C_2, pushing that π electron into the p orbital of C_3.



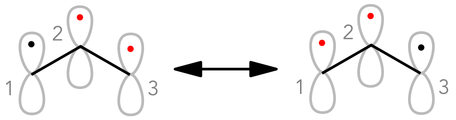
Category 4: π bond adjacent to a radical (p orbital with lone electron)

2–Propenyl, $^{\bullet}CH_2CH{=}CH_2$

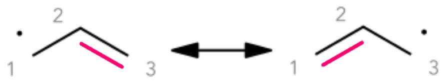
Skeletal structure	p orbital diagram
	

Since $^{\bullet}CH_2CH{=}CH_2$ has at least three p orbitals adjacent and parallel to each other, delocalisation of its π electrons can occur.

The delocalisation of π electrons in a radical is significantly different from what we have seen in categories 1 to 3. Instead of the π electrons 'hopping' from one p orbital to the next adjacent p orbital, the π electrons swap positions instead.

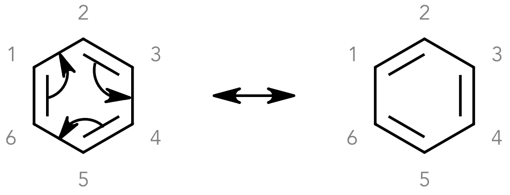
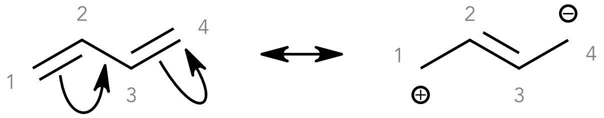
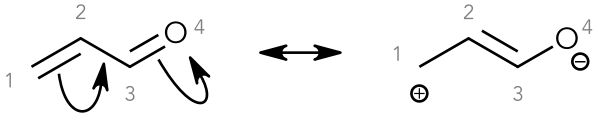
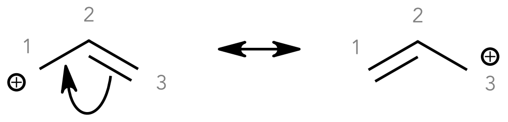
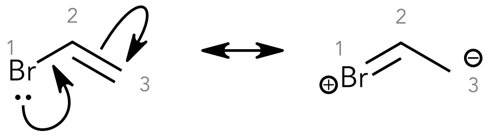
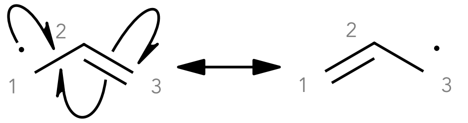


- The π electron in C_1 swaps position with the π electron in C_2, the π electron in C_2 then swaps with C_3.



Drawing Curly Arrows to Represent Resonance Structures

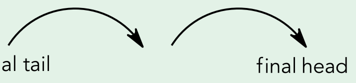
Let's draw the arrows for the resonance structures that we previously saw.

<table>
<tr><th>π bond adjacent to another π bond</th><th>π bond adjacent to an empty p orbital (usually carbocation)</th></tr>
<tr><td rowspan="5">Example 1

Example 2

Example 3
 </td><td>Example 4
 </td></tr>
<tr><th>π bond adjacent to saturated atom with a lone pair of electrons</th></tr>
<tr><td>Example 5
 </td></tr>
<tr><th>π bond adjacent to radical</th></tr>
<tr><td>Example 6
 </td></tr>
</table>

From the curly arrows drawn, we note the following:

- Half-headed arrows are used **ONLY** for radicals.

- When **breaking a π bond**, the **tail** of the arrow **starts from the bond**.
- When **forming a π bond**, the **head** of the arrow **lands in the middle of two atoms**.
- The initial **tail** leaves a positive charge; the final **head** leaves a negative charge (examples 2–5). It also applies to example 1 but the arrows form a closed loop and hence the atoms do not receive a net charge.
- When a **lone pair of electrons form a π bond**, the **tail** of the arrow **starts from the lone pair** (Example 5).



More Examples

<table>
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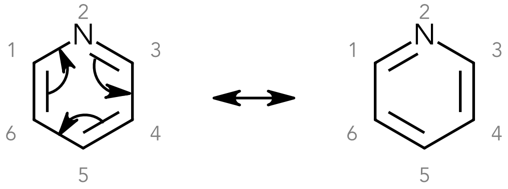
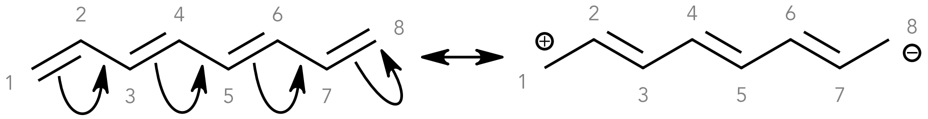
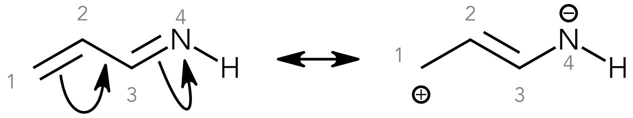
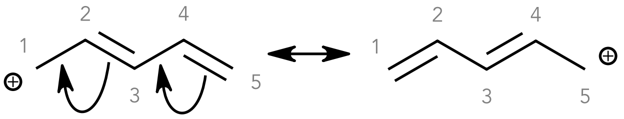
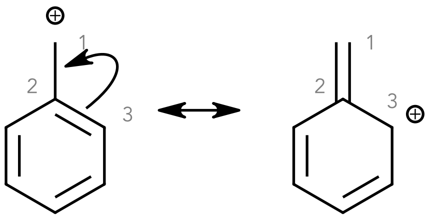
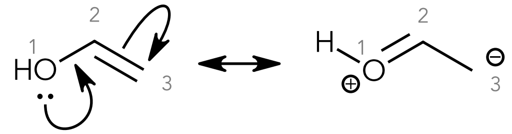
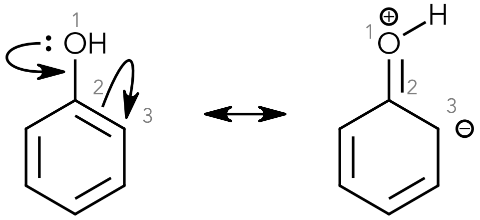
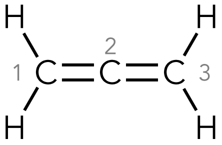
<tr><td colspan="2">   </td></tr>
<tr><th>π bond adjacent to an empty p orbital</th><th>π bond adjacent to saturated atom with a lone pair of electrons</th></tr>
<tr><td>  </td><td>  </td></tr>
</table>

Misconceptions in Resonance: Structures that Don't Have Delocalisation

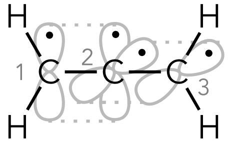
Misconception 1: Allenes

Allenes are molecules with π bonds that are **consecutive** (not alternating like in Resonance Category 1)



- Recall that the criterion for delocalisation is at least three adjacent and **parallel** p orbitals.

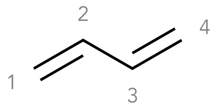
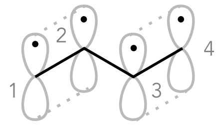
Not all p orbitals in allene are **parallel**; only two are:



there are only two adjacent and parallel p orbitals not three in the allene

Allene has π bonds formed by side-on overlap of p orbitals. Since the central carbon (C_2) forms two π bonds—one with C_1 and one with C_3—it must use two different p orbitals. However, the p orbitals on the **same atom** are **perpendicular** (e.g., p_x and p_y), so there are only two adjacent and parallel p orbitals, not three. Hence, there's no delocalisation of π electrons.

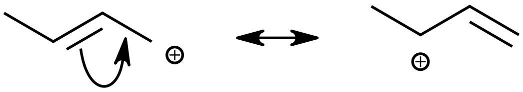
Compare allene with a molecule that has alternating π bonds, buta-1,3-diene:

Skeletal structure	p orbital diagram
	

In buta-1,3-diene, no single atom forms two π bonds, unlike in allene. Each atom forms only one π bond. However, because the π bonds are alternating with single bonds, at least three adjacent atoms each have a p orbital that can align parallel to one another. This allows for delocalisation of π electrons.

Misconception 2: Carbocations Adjacent to a π bond with N or O

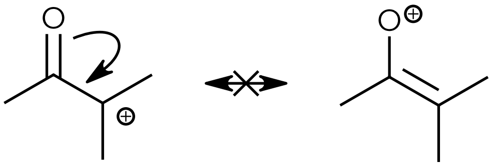
We saw earlier in resonance category 2 that π electrons can delocalise into an empty p orbital of a carbocation:



The carbon atom with the positive charge has only 6 valence electrons, meaning it does not achieve an octet. While this non-octet configuration is unstable, it can still exist because carbon is not highly electronegative.

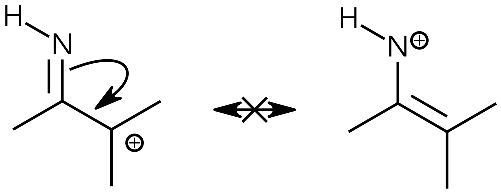
However, if delocalisation were to occur in the structure below and the positive charge shifts to the oxygen atom, this leaves oxygen with only 6 valence electrons — a non-octet configuration. Since oxygen is highly electronegative, it strongly prefers a full octet.

A non-octet oxygen with a positive charge is extremely unstable and unlikely to occur:



highly unstable
non-existent structure

To summarise, if there is a carbocation adjacent to a π bond that contains an electronegative element (O or N), **delocalisation of π electrons into the empty p orbital of the carbon does not occur**. Here is one more example:

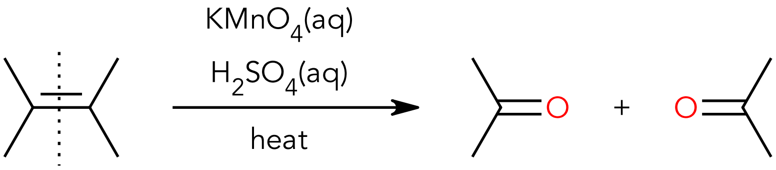


highly unstable
non-existent structure

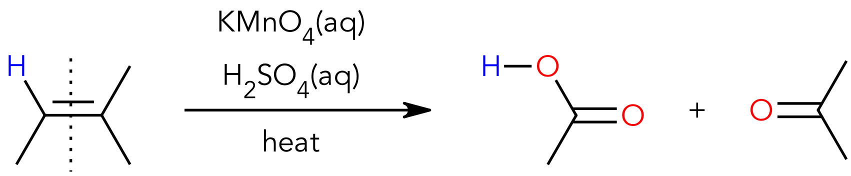
12 Oxidation of Organic Compounds

Oxidation of Alkenes (Oxidative Cleavage)

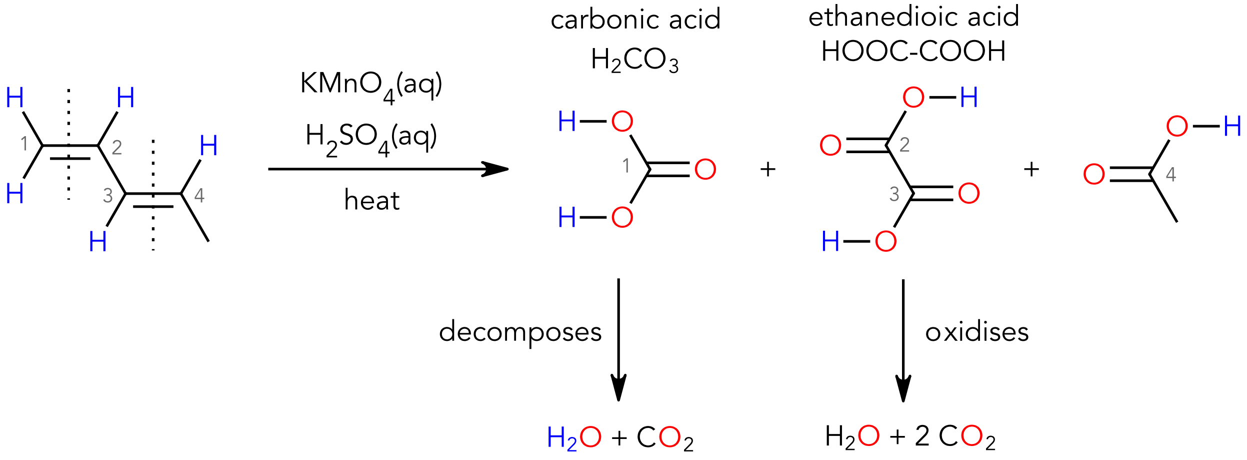
Alkenes can be oxidised with acidified $KMnO_4$ (not $K_2Cr_2O_7$) through a reaction named Oxidative Cleavage. The C=C alkene functional group cleaves in this process and two oxygen (O) atoms are inserted between the carbon atoms of the C=C:



If there are any hydrogen atoms (H) attached directly to the C=C, an O atom must be also inserted between the C and H atoms of that C–H bond:



IMPORTANT: Certain products from oxidative cleavage can either further decompose or oxidise to produce carbon dioxide gas and water:



- Two -OH groups attached to the same atom (for e.g., H_2CO_3) is unstable and spontaneously eliminates water to form a π bond.
- $H_2CO_3 \longrightarrow CO_2 + H_2O$ is **not oxidation** because there is no change in the oxidation state of C. It remains at +4.

- HOOC–COOH $\longrightarrow 2\ CO_2 + H_2O$ is **oxidation** because the oxidation state of C in HOOC–COOH increased from +3 to +4 in CO_2.

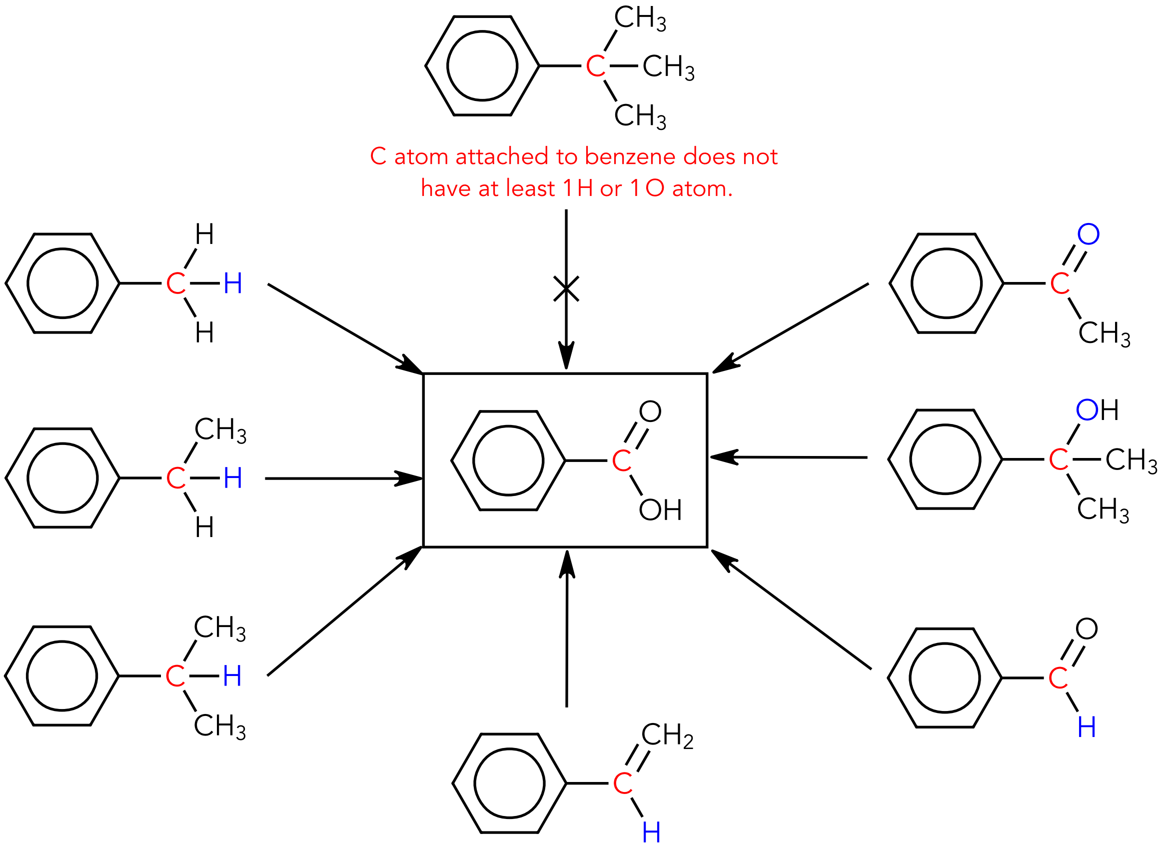
Oxidation of Side Chains on Benzene (Side Chain Oxidation)

Alkylbenzenes can be oxidised with acidified $KMnO_4$ (not $K_2Cr_2O_7$) through a reaction named Side Chain Oxidation.

The Criterion for Side Chain Oxidation

The carbon atom (C) directly attached to benzene must have at least one hydrogen atom (H) **OR** one oxygen atom (O) attached to it.

If that criterion is met, the C atom directly attached to benzene oxidises to COOH.



C atom attached to benzene does not have at least 1 H or 1 O atom.

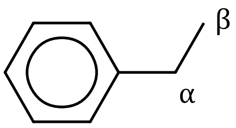
- The reagent and conditions for side chain oxidation is $KMnO_4(aq)$, $H_2SO_4(aq)$, heat
- If NaOH(aq) was used instead of $H_2SO_4(aq)$, $C_6H_5\text{-}COOH$ reacts further with NaOH to form $C_6H_5\text{-}COO^-Na^+$:

$$C_6H_5\text{-}COOH + NaOH \longrightarrow C_6H_5\text{-}COO^-Na^+ + H_2O$$

Fate of Carbon Atoms Not Attached to Benzene During Oxidation

Hwa Chong Institution Students

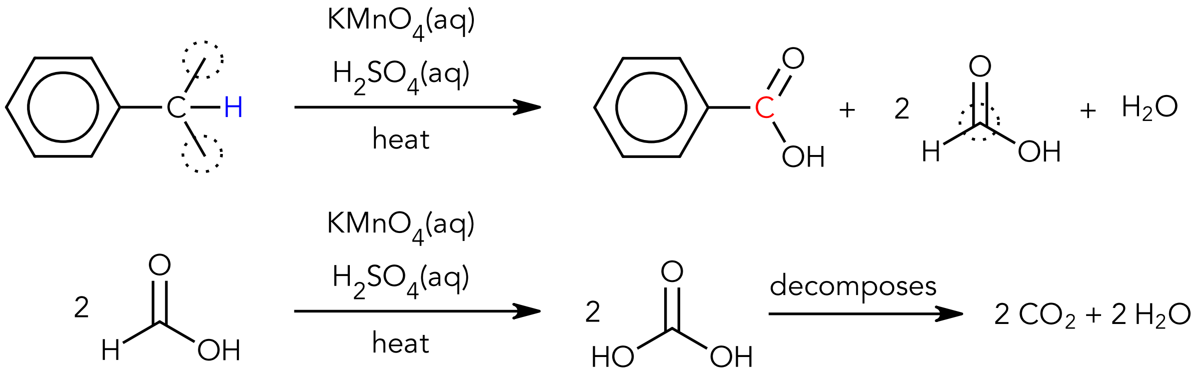
For added clarity to the explanations, we will call the carbon directly bonded to the benzene ring the α–carbon and the carbon adjacent to the α–carbon as β–carbon:



If the β-carbon atom has:

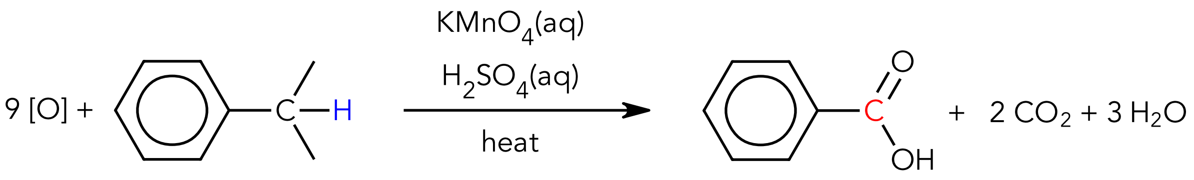
- at least 2 H atoms, it oxidises to carboxylic acid:

Example 1



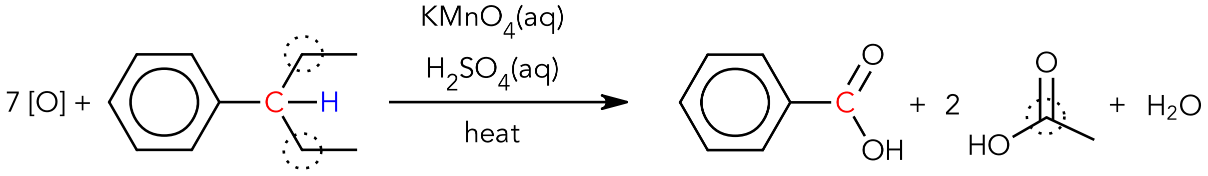
- Remember that methanoic acid (HCOOH) further oxidises to H_2CO_3 which then decomposes (NOT oxidises) to form CO_2 and H_2O. This was seen under Oxidative Cleavage of Alkenes.

Overall equation:

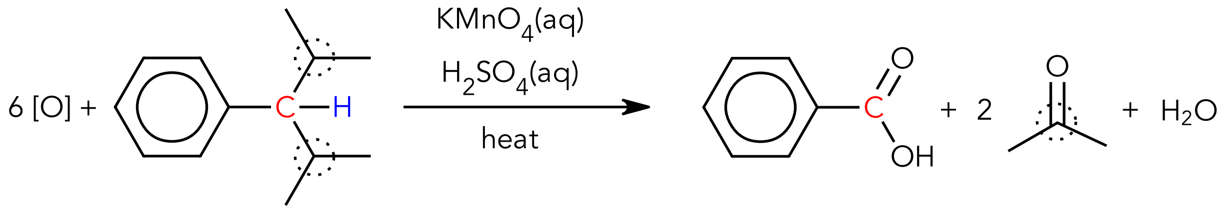


- When balancing the overall equation for side chain oxidation, balance the elements in the following order:
  C, H (using H_2O molecules), O (using [O] to denote oxidation)
- The H element was already balanced in Step 1 as shown by one water molecule as the side product.

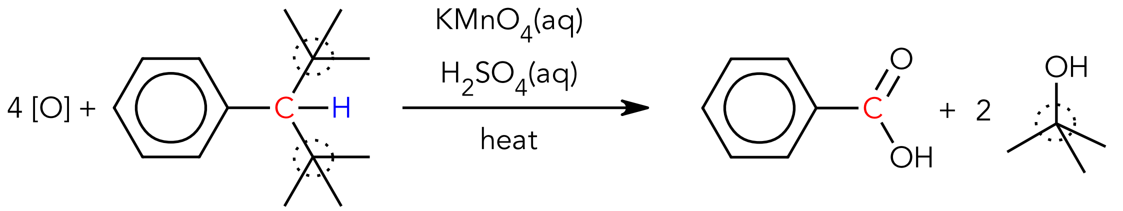
Example 2



- only 1 H atom, it oxidises to ketone:

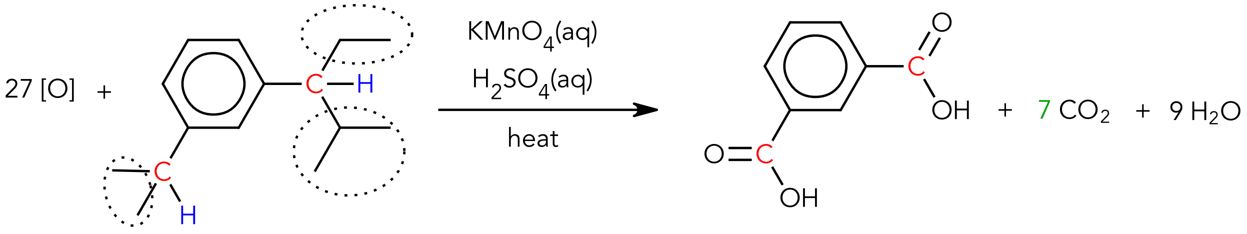


- no H atoms, it oxidises to a tertiary alcohol:



All Other Students

Carbon atoms <u>not directly attached to benzene</u> become <u>carbon dioxide gas</u>:

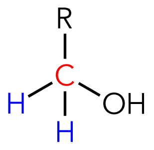
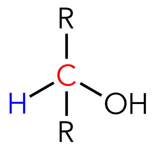
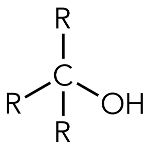


- When balancing the overall equation for side chain oxidation, balance the elements in the following order:
  C, H (using H_2O molecules), O (using [O] to denote oxidation)

Oxidation of Alcohols

An alcohol can oxidise if the (saturated) carbon bonded to the hydroxyl (–OH) group has at least one hydrogen atom.

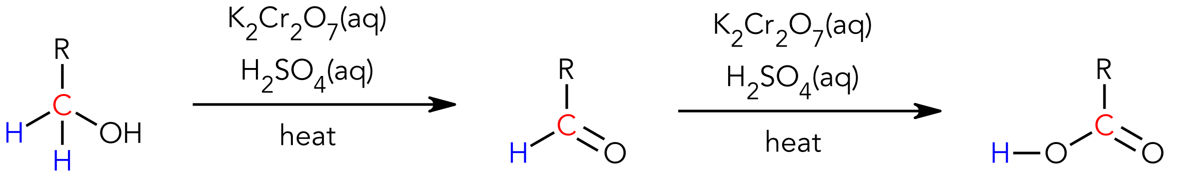
Therefore, a primary and secondary alcohol can oxidise, and a tertiary alcohol cannot:

		
primary alcohol (1° ROH)	secondary alcohol (2° ROH)	tertiary alcohol (3° ROH)

where R is a carbon atom (alkyl or aryl group).

Oxidation of Primary Alcohols

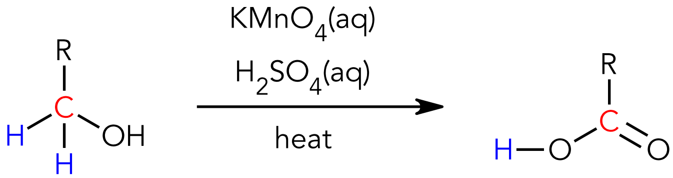
Since a 1° ROH has two hydrogen atoms attached to its C (bonded to –OH), it can undergo a two-step oxidation with **potassium dichromate, $K_2Cr_2O_7$,** *first* to an aldehyde, *then* to carboxylic acid:



aldehyde (CHO)

carboxylic acid (COOH)

If a stronger oxidising agent, $KMnO_4$ is used, the 1° ROH oxidises all the way to carboxylic acid **bypassing** the formation of the aldehyde:



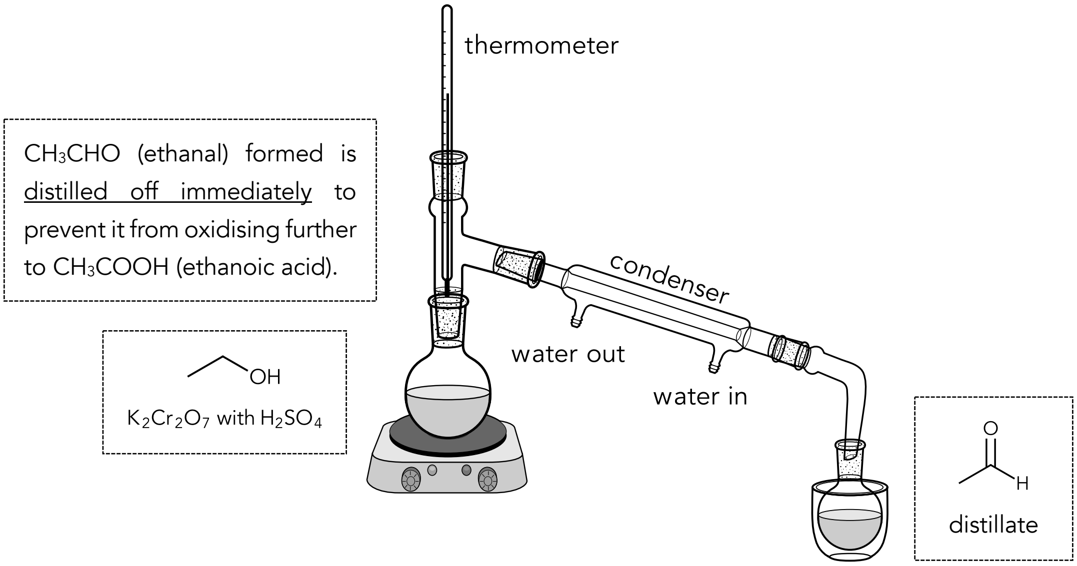
carboxylic acid (COOH)

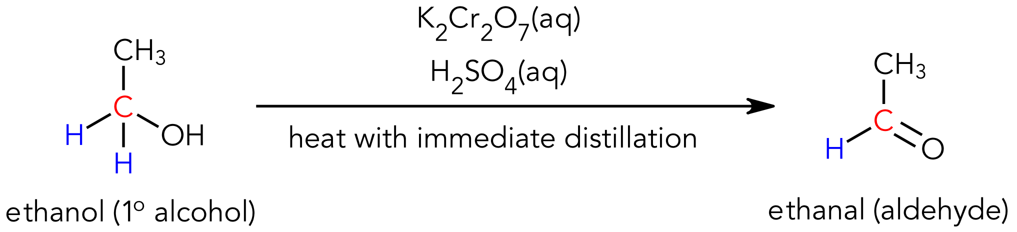
- The number of hydrogen atoms attached to the carbon bonded to the hydroxy (–OH) group indicates the number of times the alcohol can oxidise.

Synthesising an Aldehyde from a Primary Alcohol

If an aldehyde is to be synthesised from a primary alcohol, **immediate distillation** must be done with hot, acidified **$K_2Cr_2O_7$(aq)**, to allow the aldehyde to ***escape*** from the round bottom flask and to be collected as a distillate.

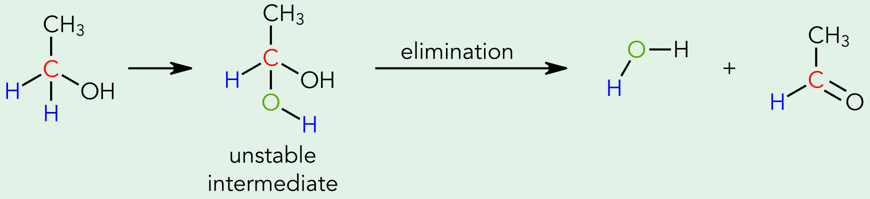
- Remember: $KMnO_4$(aq), H_2SO_4(aq), heat cannot be used to obtain an aldehyde because it oxidises the primary alcohol immediately to carboxylic acid, bypassing the formation of an aldehyde.


CH_3CHO (ethanal) formed is distilled off immediately to prevent it from oxidising further to CH_3COOH (ethanoic acid).



If you're interested…

- When a 1° alcohol oxidises, an oxygen atom gets inserted into the C-H bond of the C bonded to OH.
- This produces an unstable intermediate (2 –OH groups attached to the same C atom) which then spontaneously eliminates water with the simultaneous formation of a π bond:



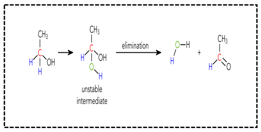
Synthesising a Carboxylic Acid from a Primary Alcohol

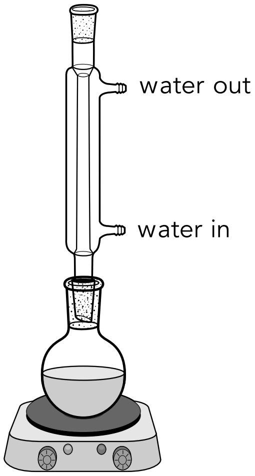
If a carboxylic acid is to be synthesised from a primary alcohol, either **heating with reflux with acidified $K_2Cr_2O_7(aq)$** OR **hot, acidified $KMnO_4(aq)$** would work.

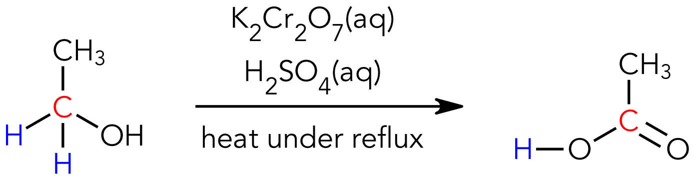
Method 1: $K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, Heat Under Reflux

Heating under reflux prevents the aldehyde from escaping by using a vertically placed condenser which condenses the aldehyde vapour back into the flask. This ensures the aldehyde undergoes complete oxidation with acidified $K_2Cr_2O_7$ to carboxylic acid.

CH_3CHO (ethanal) vapour condenses in the condenser and returns to the flask, allowing further oxidation to CH_3COOH (ethanoic acid).





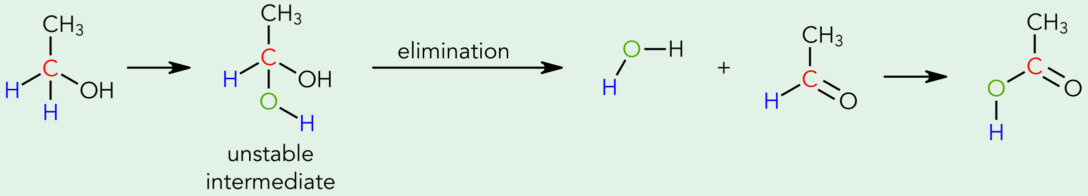


ethanol (1° alcohol)

ethanoic acid (carboxylic acid)

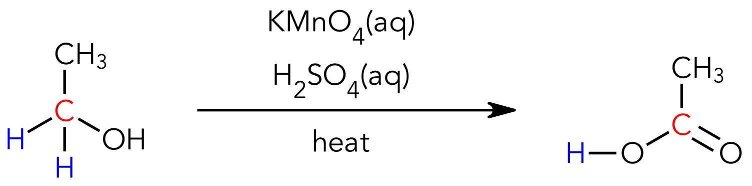
If you're interested…

- To oxidise the aldehyde further into carboxylic acid, another oxygen atom gets inserted into the C-H bond of the ketone (the other undisturbed C-H bond in the primary alcohol at the beginning):



Method 2: $KMnO_4(aq)$, $H_2SO_4(aq)$, heat

Since hot, acidified $KMnO_4$ fully oxidises primary alcohols to carboxylic acid (and does not form the aldehyde intermediate), reflux is unnecessary.



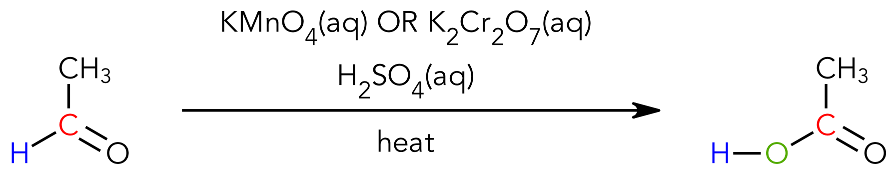
ethanol (1° alcohol) ethanoic acid (carboxylic acid)

- Some schools write heat under reflux for <u>most</u> organic reactions to improve yield.

Oxidation of Aldehydes

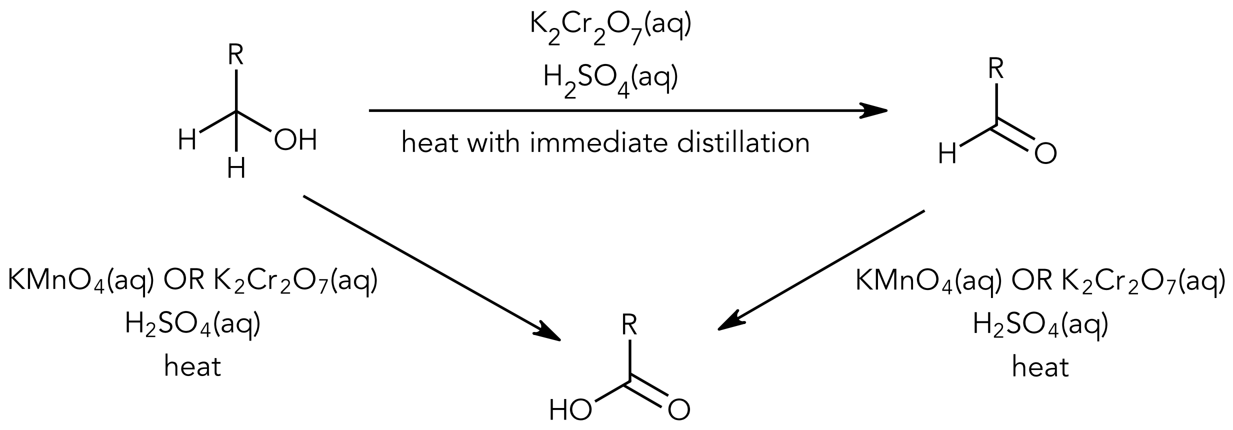
Since an aldehyde has only <u>one</u> hydrogen atom attached to its C (doubly bonded to O), it can only undergo a <u>one-step oxidation</u> to a carboxylic acid. Hence, reflux is unnecessary.

Hence, reflux is unnecessary, and either acidified $K_2Cr_2O_7$ **OR** acidified $KMnO_4$ can be used:



ethanal (aldehyde) ethanoic acid (carboxylic acid)

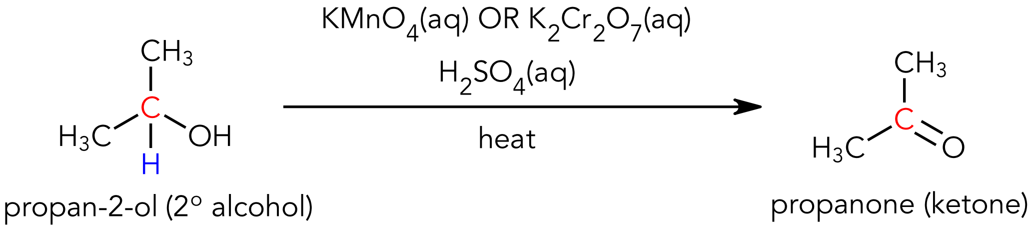
An Overview of Primary Alcohol Oxidation



Oxidation of Secondary Alcohols

Since a 2° ROH has only <u>one</u> hydrogen atom attached to its C (bonded to –OH), it can only undergo a <u>one-step oxidation</u> to a ketone.

Hence, reflux is unnecessary, and either acidified $K_2Cr_2O_7$ **OR** acidified $KMnO_4$ can be used:



propan-2-ol (2° alcohol)

propanone (ketone)

13 Hydrolysis

The Five Functional Groups That Can Hydrolyse

Hydrolysis is a chemical reaction where a molecule of water breaks one or more chemical bonds; "hydro" = water and 'lysis' = break. When a functional group is hydrolysed, a bond is broken between two atoms and a H_2O molecule is inserted in between them.

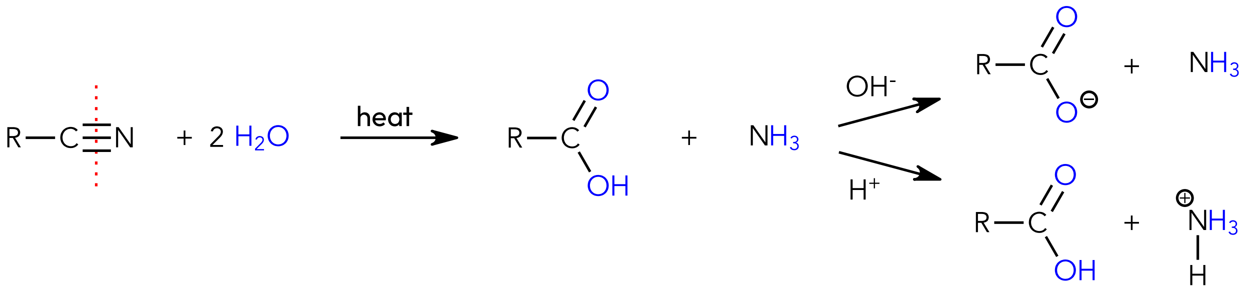
- Sometimes, two H_2O molecules are added in (nitrile hydrolysis).

The hydrolysis products then FURTHER UNDERGO AN ACID-BASE REACTION depending on whether the hydrolysis occurs under an acidic or basic medium:

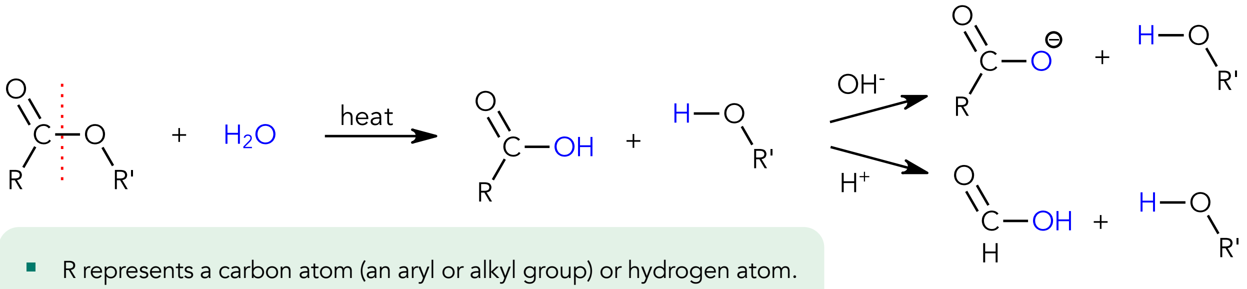
Acidic medium: $H_2SO_4(aq)$, heat	**Basic medium: NaOH(aq), heat**
Basic products (NH_3, RNH_2, R_2NH, R_3N) protonate (gain H^+): $R_2NH + H^+ \longrightarrow R_2NH_2^+$	Acidic products (R-COOH, HX) deprotonate (lose H^+): $R\text{-}COOH + OH^- \longrightarrow RCOO^- + H_2O$

The five functional groups that can hydrolyse: nitriles, alkyl halides, esters, amides, acyl halides

Nitrile Hydrolysis

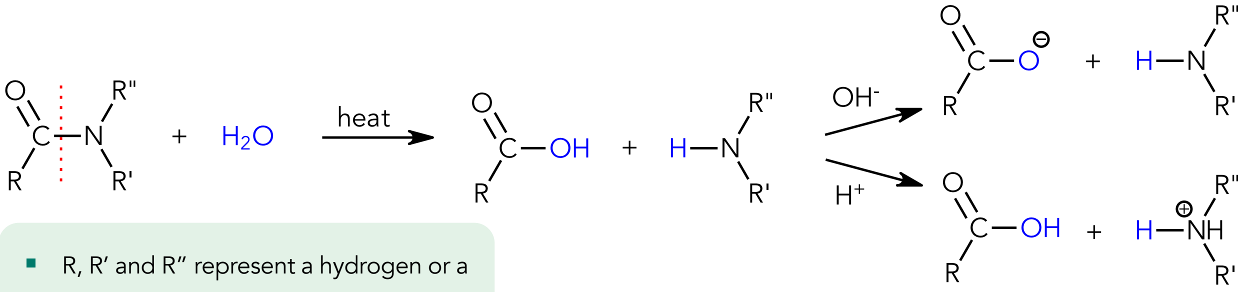


Ester Hydrolysis



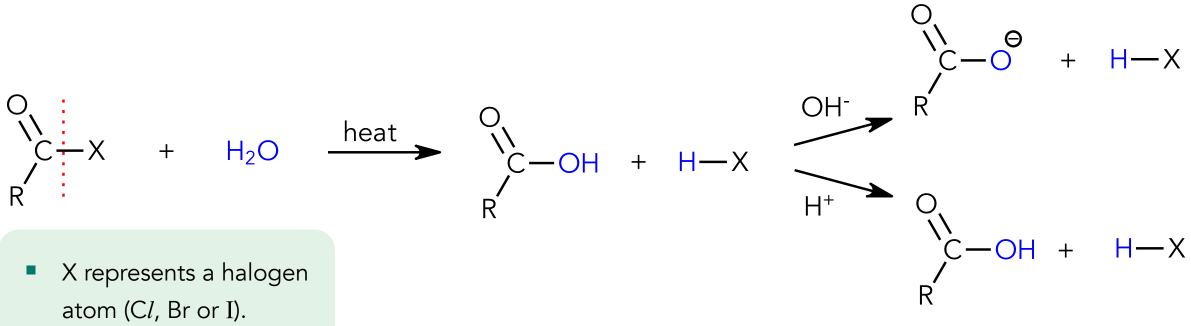
- R represents a carbon atom (an aryl or alkyl group) or hydrogen atom. R' represents a carbon atom (an aryl or alkyl group).

Amide Hydrolysis



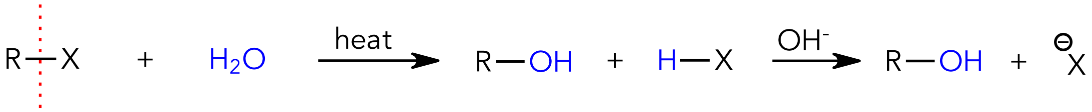
- R, R′ and R″ represent a hydrogen or a carbon atom (an aryl or alkyl group).

Acyl Halide Hydrolysis



- X represents a halogen atom (C*l*, Br or I).

Alkyl Halide (Halogenoalkane) Basic Hydrolysis



- X represents a halogen atom (C*l*, Br or I).

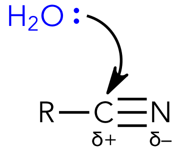
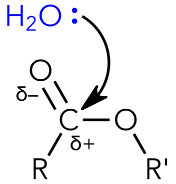
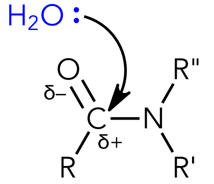
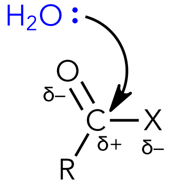
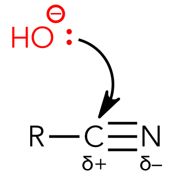
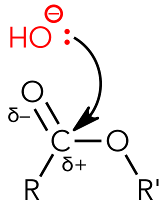
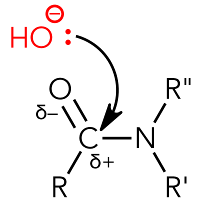
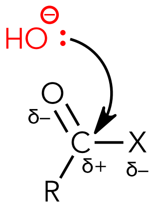
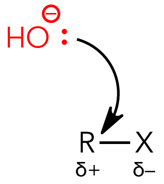
I was *very hesitant* to say that alkyl halides undergo hydrolysis. When R-X reacts with NaOH(aq) via nucleophilic substitution, the products are R-OH and X^-, resembling those of basic hydrolysis.

Hence, we sometimes say alkyl halides can hydrolyse. However, they cannot undergo acidic hydrolysis—only a (nucleophilic substitution) reaction with NaOH(aq) under heat.

The Fundamental Principle of Hydrolysis

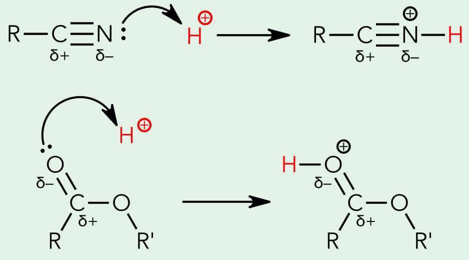
Nitriles, esters, amides and acyl halides can hydrolyse because the carbon atom is electron-deficient and is susceptible to nucleophilic attack by H_2O: nucleophile (in acidic hydrolysis) and :OH^- nucleophile (in basic hydrolysis).

- In basic hydrolysis, NaOH(aq), heat; two nucleophiles are present: OH^- and H_2O (solvent).
- OH^- is a stronger nucleophile than H_2O due to the presence of the negative charge that makes the lone pair of electrons on O more electron rich.

	nitriles	esters	amides	acyl halides	alkyl halides
acidic hydrolysis					no reaction
basic hydrolysis					

If you're interested…

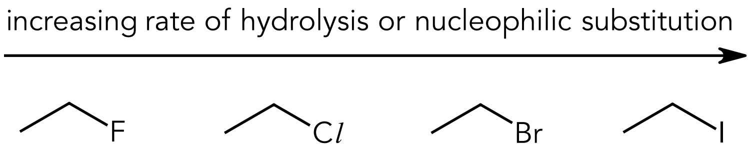
- Water is a **VERY** weak nucleophile because oxygen's high electronegativity makes it less willing to donate its lone pair to an electrophile. This is why most oxygen-based nucleophiles used are negatively charged such as OH^-, RO^-.
- In acidic hydrolysis, the lone pair of electrons of the functional group attacks a H^+ (protonates), making the carbon atom a lot more electron-deficient (positive charge withdraws electron density away from the carbon) and susceptible to attack by the weak nucleophile, water.
- For e.g.,



lone pair of electrons on the saturated O does not attack H^+ because it is delocalised into the adjacent C=O π bond and is less available for donation.

Comparing Rate of Hydrolysis

Rate of Hydrolysis of Halogenoalkanes



When comparing rate of hydrolysis between different C-X bonds, focus on **extent of orbital overlap** (*i.e.*, bond length and subsequent bond strength).

The poorest extent of orbital overlap (2p-5p in C-I) will hydrolyse the **fastest** and the greatest extent of orbital overlap (2p-3p in C-C*l*) will hydrolyse the **slowest**.

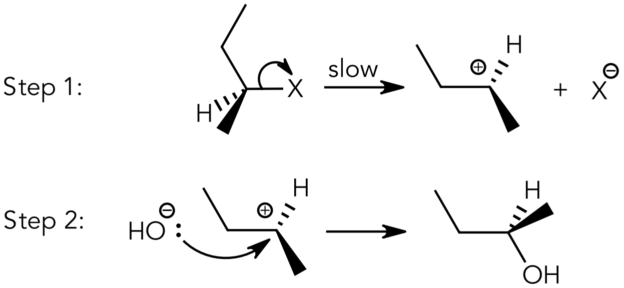
- Nucleophilic substitution is the mechanism that halogenoalkanes undergo with a nucleophile. Hydrolysis is a broader term that encompasses various mechanisms (nucleophilic substitution, nucleophilic acyl substitution, etc.)

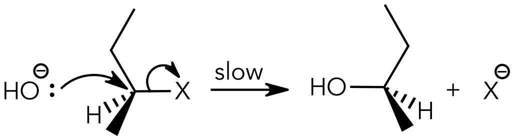
A Highly Common Misconception

*Isn't fluorine the **most electronegative halogen** and hence the carbon atom is the **most electron-deficient** and should undergo nucleophilic substitution the **fastest**?*

Despite the C in C-F of a fluoroalkane being very electron-deficient (F is the most electronegative halogen and hence very electron-withdrawing), the C-F bond is **too strong and will not break**.

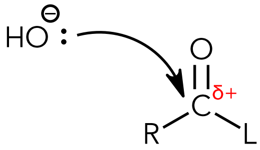
This is logical; whether you're looking at S_N1 or S_N2, both nucleophilic substitution mechanisms break of C-**X** bond in the **slow step** (rate-determining step) and how electron-deficient the C atom is doesn't matter if the C-X bond simply requires too much energy to break.


Unimolecular Nucleophilic Substitution (S_N1)


Bimolecular Nucleophilic Substitution (S_N2)

Rate of Hydrolysis of Carboxylic Acid Derivatives

When comparing the rate of hydrolysis of carboxylic acid derivatives, focus on the **electron-deficiency of the carbonyl carbon atom** undergoing nucleophilic attack.

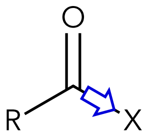
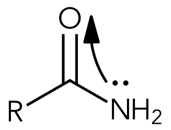
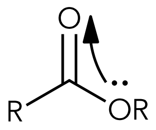


where L = -OH, -OR, $-NH_2$, -NHR, $-NR_2$, -X

The more electron-deficient the carbonyl carbon atom is, the faster the rate of hydrolysis.

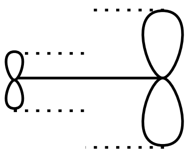
Acyl Halides *vs* Esters and Amides

- The carbonyl carbon of acyl chlorides is more electron-deficient than esters and amides and **hydrolyses faster**.
- The –X group (in acyl halides) is **electron withdrawing (by inductive)**, while the –OR (in ester) and $–NH_2$ (in amide) groups are **electron donating (by resonance)**:

<table>
<tr><th>Acyl halides</th><th>Amides</th><th>Esters</th></tr>
<tr><td> </td><td> </td><td> </td></tr>
<tr><td>Halogen (X) is more electronegative than carbon, exerting an electron-withdrawing inductive effect that outweighs its electron-donating resonance effect.</td><td colspan="2">Lone pair of electrons on N or O delocalises into C=O π bond, exerting an electron-donating resonance effect that outweighs its electron-withdrawing inductive effect.</td></tr>
</table>

Why Do Halogens Exert an Overall Electron-Withdrawing Effect in Acyl Halides?

- Despite halogens having a lone pair of electrons that can delocalise into the adjacent C=O π bond, the 2p orbital from the carbon atom (of the C=O π bond) overlaps inefficiently with the larger p orbitals from the halogen (3p for chlorine, 4p for bromine, 5p for iodine).

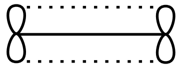


inefficient overlap between
orbitals of different size (e.g., 2p-3p)

- This results in a weaker electron-donating resonance effect that is outweighed by its electron-withdrawing inductive effect.

Why Do –NH_2 and –OR Exert an Overall Electron-Donating Effect in Amides and Esters?

- Despite nitrogen and oxygen being able to exert an electron-withdrawing inductive effect (both are more electronegative than the carbon atom its bonded to), the 2p orbital from the carbon atom (of the C=O π bond) overlaps efficiently with the 2p orbitals of nitrogen or oxygen because the p orbitals are of the same size.

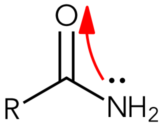


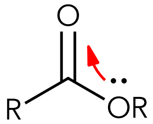
efficient overlap between
orbitals of similar size (e.g., 2p-2p)

- This results in a stronger electron-donating resonance effect that outweighs its electron-withdrawing inductive effect.

Esters *vs* Amides

- The carbonyl carbon of esters is more electron-deficient than amides and **hydrolyses faster**.
- The lone pair of electrons on the N atom in $–NH_2$ delocalises into the C=O π bond to a greater extent than the lone pair of electrons on the O atom in –OR because nitrogen is less electronegative than oxygen and is more willing to give up its lone pair for delocalisation.





- This means that the $–NH_2$ group exerts a **stronger electron-donating resonance effect** than the –OR group and hence, the carbonyl carbon of an amide will be less electron-deficient.

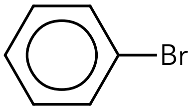
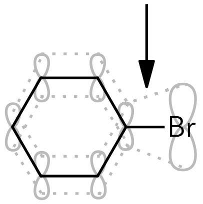
To summarise, the rate of hydrolysis is ranked in the following manner:

Acyl Halides >> Esters > Amides

Halogenoarenes and Phenols Are Resistant to Nucleophilic Reactions (Hydrolysis)

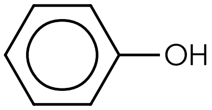
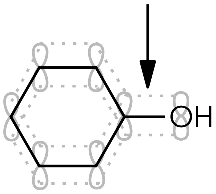
Halogenoarenes are resistant to nucleophilic reactions because of the partial double bond (PDB) character in the C–X bond that requires a lot of energy to break.

This PDB character arises from the continuous side-on overlap of the p orbital of the halogen and the p orbital of the benzene π electron cloud that allows the lone pair of electrons on the halogen to delocalise into the benzene π electron cloud.

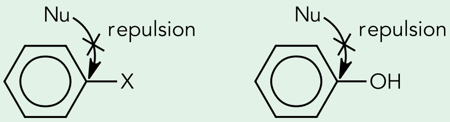
Skeletal structure	p orbital diagram
	partial double bond in C-Br 

- Inefficient overlap between bromine's 4p orbital and carbon's 2p orbital still results in PDB formation.

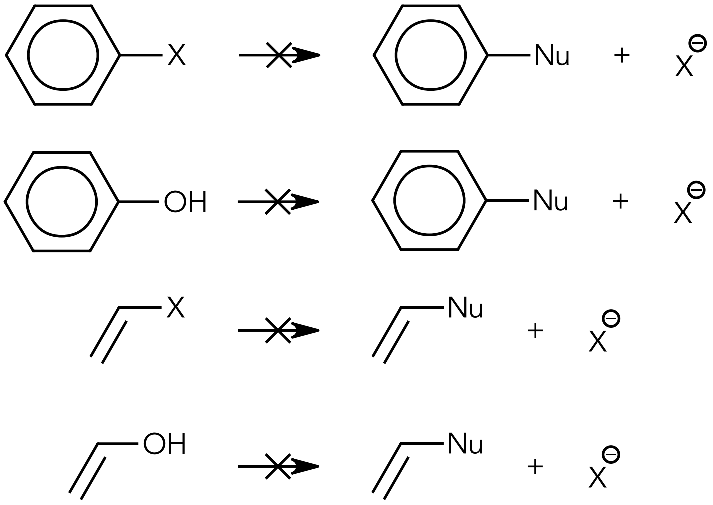
This concept is seen in phenols as well; the lone pair of electrons on O in –OH delocalises into the adjacent benzene's π electron cloud, giving the C–O bond PDB character.

Skeletal structure	p orbital diagram
	partial double bond in C-O 

- **Another reason** for why phenols and halogenoarenes are resistant to nucleophilic reactions is because the carbon atom being attacked is not electron-poor as it is part of the electron-rich benzene π electron cloud that repels any incoming nucleophiles:



To summarise, whenever there is a saturated atom with a lone pair adjacent to a **carbon–based** π electron system (alkene or benzene), the PDB character makes the bond **unbreakable** and hence **inert** to any reaction that attempts to break that bond:



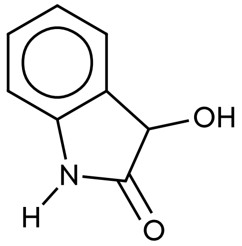
Hydrolysis and Subsequent Oxidation

Reagents like "$KMnO_4$(aq), H_2SO_4(aq), heat" **or** "$K_2Cr_2O_7$(aq), H_2SO_4(aq), heat" can **hydrolyse and oxidise** (heating with a strong acid causes acidic hydrolysis) a reactant.

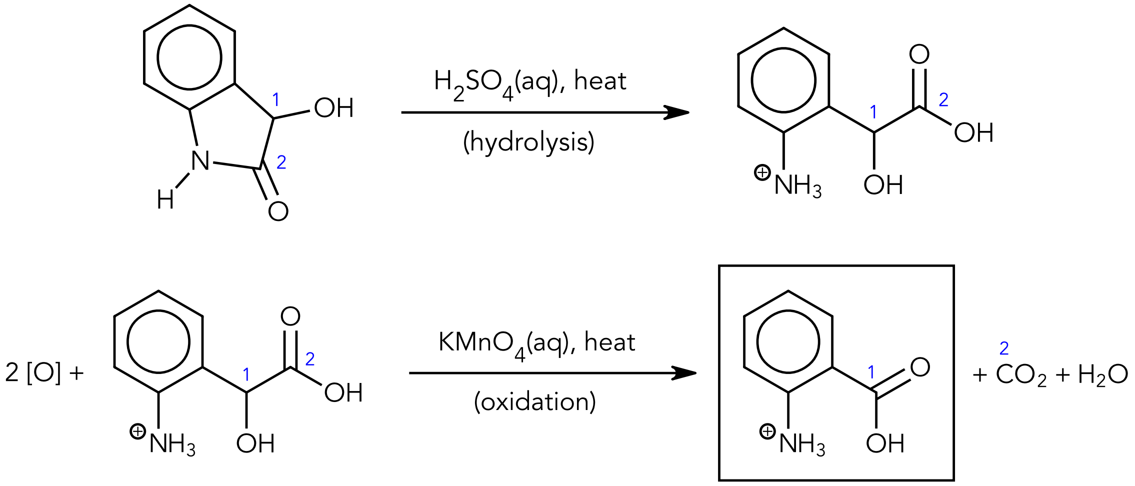
If a reactant can hydrolyse **and** oxidise, always remember to hydrolyse first BEFORE oxidation.

Worked Example (Common Exam Question)

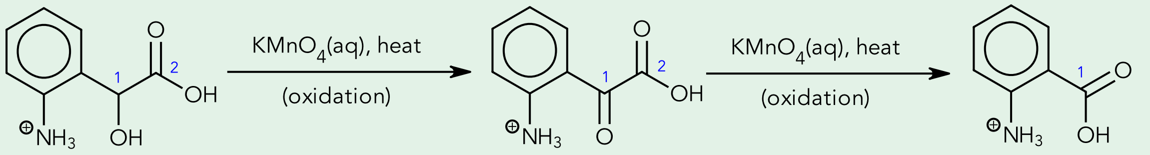
Draw the product(s) when the following reactant is subjected to



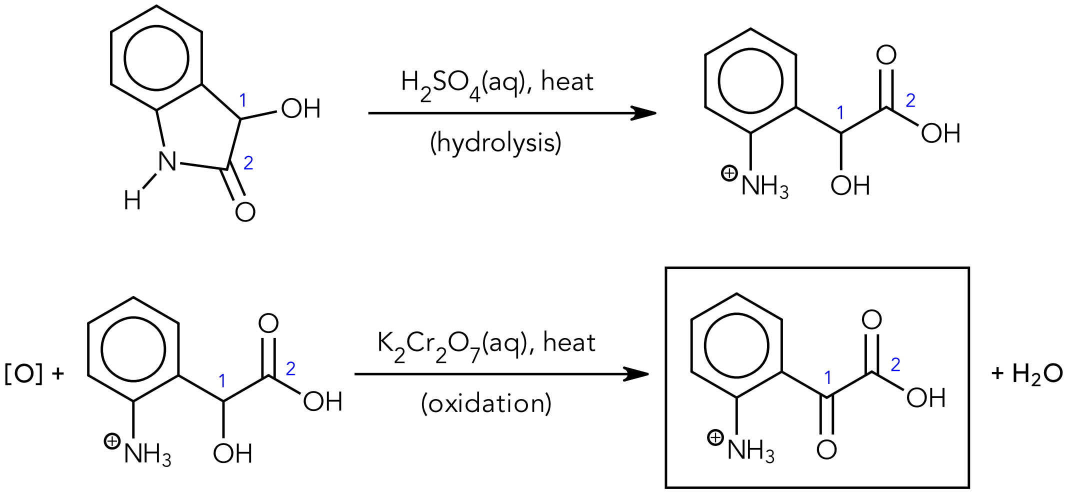
(a) $KMnO_4$(aq), H_2SO_4(aq), heat



- $KMnO_4$(aq) can **side-chain oxidise alkylbenzenes, oxidise 1° and 2° alcohols, oxidatively cleave alkenes**.
- Always consider side-chain oxidation **LAST**. In this example, $KMnO_4$ oxidises the 2° alcohol to a ketone first, which then undergoes side-chain oxidation after to form benzoic acid:



(b) $K_2Cr_2O_7$(aq), H_2SO_4(aq), heat



- $K_2Cr_2O_7$(aq) can only oxidise alcohols.
- Balance organic oxidation half-equations by first balancing C, then H using H_2O, finally O using [O].

14 Determining the Type of an Organic Reaction

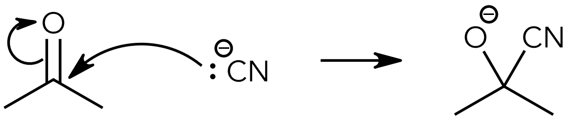
To identify the correct type of organic reaction, we must recognise key similarities in their reaction mechanisms.

There are **ten** types of organic reactions:

Nucleophilic Addition	Nucleophilic Substitution	Nucleophilic Acyl Substitution	Electrophilic Addition	Electrophilic Substitution
Nucleophilic Addition	Acid–base	Elimination	Condensation	Hydrolysis

Nucleophilic Addition

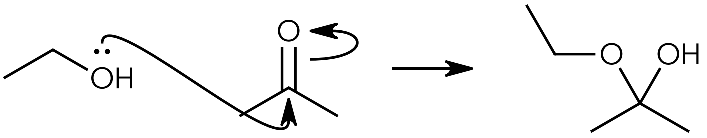
To correctly identify nucleophilic addition, look out for a nucleophile forming a bond with an unsaturated carbon atom (bonded to a more electronegative element) that results in the π bond breaking towards the more electronegative element:



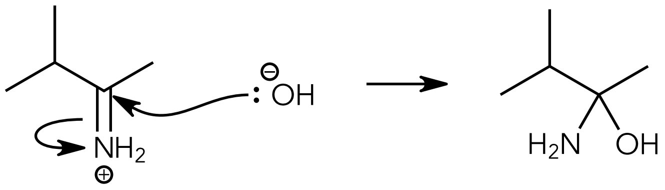
- Realise that the unsaturated carbon changes its shape after the reaction, from trigonal planar to tetrahedral.

Examples of Nucleophilic Addition

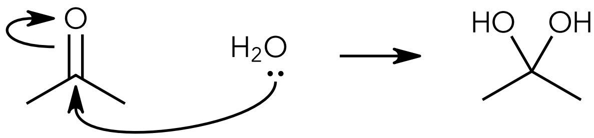
Example 1



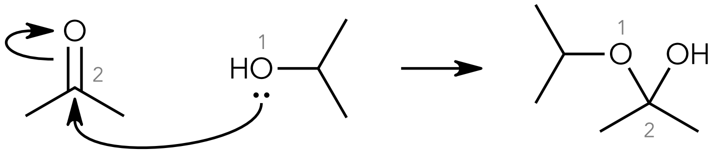
Example 2



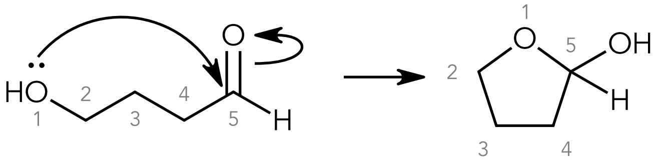
Example 3



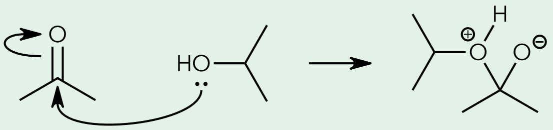
Example 4



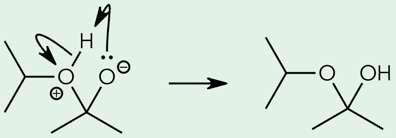
Example 5



- All the arrows drawn only represent the **first step of the reaction**; they do not form the product immediately. For e.g., the arrows drawn in Example 4 gives:



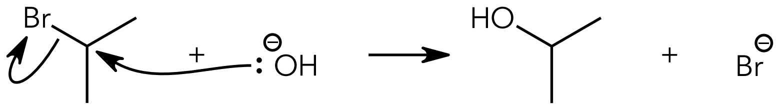
The intermediate then undergoes an (intramolecular) acid–base reaction:



Nucleophilic Substitution

Nucleophilic substitution is the replacement of a group with a nucleophile at a saturated atom (typically carbon atoms).

To recognise nucleophilic substitution (S_N1 or S_N2), look out for a nucleophile forming a single bond with a saturated atom (typically carbon) and a single bond of the saturated atom breaks:

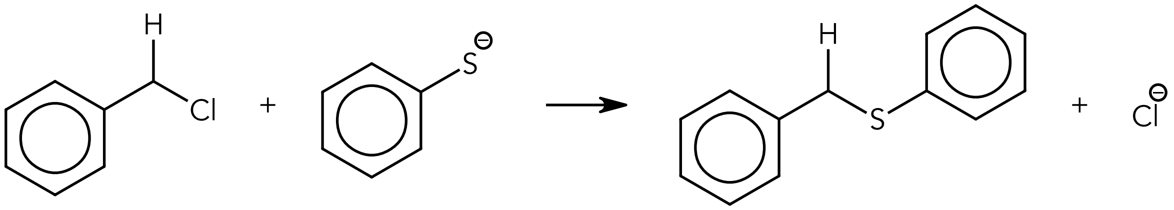


- We're assuming that the nucleophilic that attacks the C bonded to Br in $(CH_3)_2CHBr$ experiences little steric hindrance and hence proceeds via S_N2.
- Unlike nucleophilic addition, the carbon that reacted **did not undergo a change its molecular shape**; it remained tetrahedral.

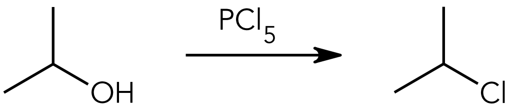
Examples of Nucleophilic Substitution

Some examples will be intentionally unbalanced– focus on the reactant and product that show it's a nucleophilic substitution.

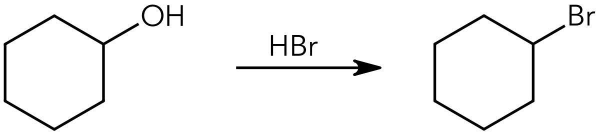
Example 1



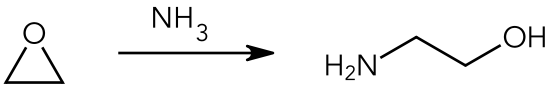
Example 2



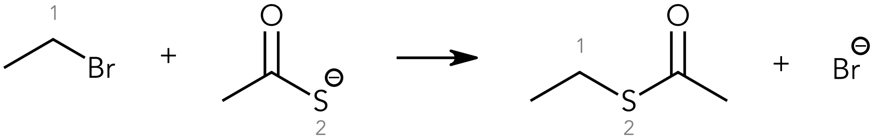
Example 3



Example 4



Example 5

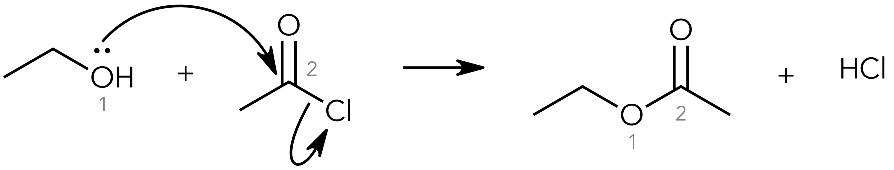


- Curly arrows were not drawn for the examples because the nucleophilic substitution could proceed via S_N1 or S_N2. As long we can recognise that it's a nucleophilic substitution reaction, that's sufficient.

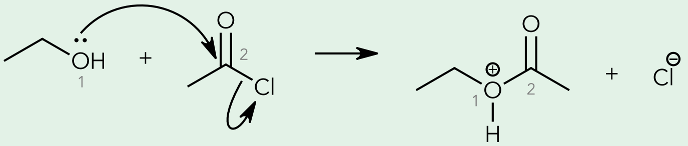
Nucleophilic Acyl Substitution

Nucleophilic acyl substitution (NAS) is similar to nucleophilic substitution, the only difference is that NAS is the replacement of a group with a nucleophile at an **acyl carbon** (*usually* a carbonyl).

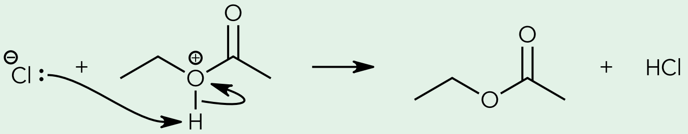
To recognise NAS, look out for a nucleophile forming a single bond with an unsaturated atom and a single bond of that unsaturated atom breaks.



- The curved arrows shown are a simplified representation to show bond breaking. The correct mechanism involves the C=O π bond breaking first. But don't worry about the details for now; just be able to realise that this reaction is nucleophilic acyl substitution.
- Also note that the (simplified) curved arrows drawn here don't give the final product *directly*. The curved arrows drawn should have instead given:



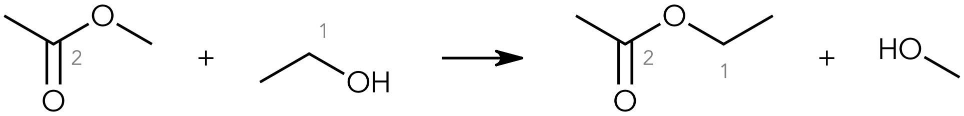
The Cl^- then undergoes an acid–base reaction with the intermediate:



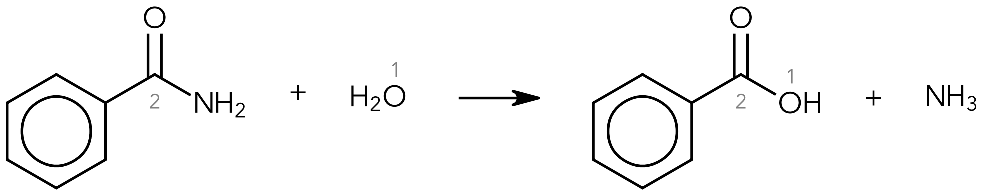
Examples of Nucleophilic Acyl Substitution

Some examples will be intentionally unbalanced– focus on the reactant and product that show it's a nucleophilic substitution.

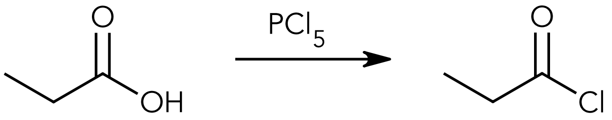
Example 1



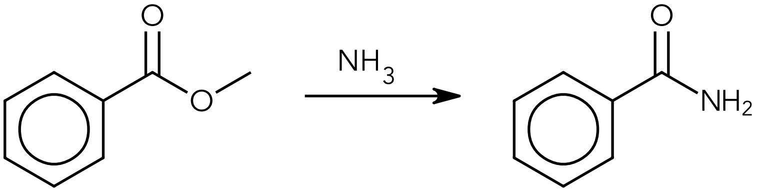
Example 2



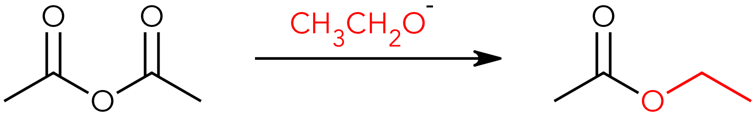
Example 3



Example 4



Example 5



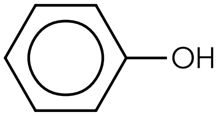
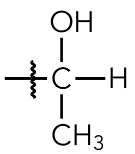
15 Structural Elucidation

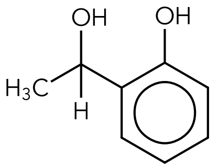
The Phenol Tri–Substitution Reaction

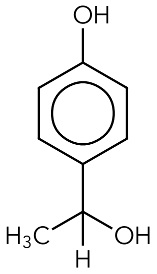
Worked Example [RI/March CT/2024/Q5]

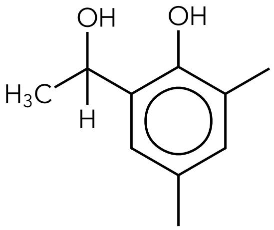
J ($C_{10}H_{14}O_2$) forms a violet complex with neutral aqueous iron(III) chloride. **J** reacts with hot aqueous alkaline iodine to give a yellow precipitate and does not decolourise aqueous bromine. Upon heating **J** with acidified potassium dichromate(VI), **K** ($C_{10}H_{12}O_2$) is produced. **J** reacts with PCl_3 to form **L**.

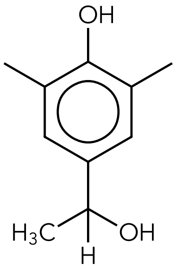
Deduce, with reasoning, the structures of compounds **J** to **L**.

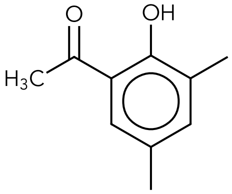
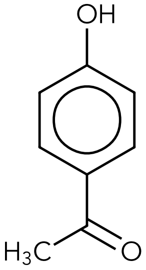
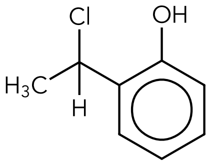
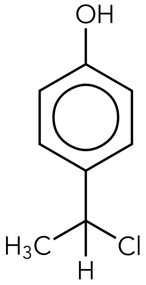
	Observation	Deduction	Additional Notes
1	**J** ($C_{10}H_{14}O_2$) forms a violet complex with neutral aqueous iron(III) chloride	Double Bond Equivalents (DBE) $= 10 + 1 - \frac{14}{2} = \mathbf{4}$ J is a phenol: 	Since **J** has 4 DBE and a benzene ring, the rest of **J** is saturated (only single bonds). - DBE refers to the number of π bonds and rings. - Since benzene ring consists of 3 π bonds and 1 ring, its DBE is 4. - DBE formula: $\mathbf{C + 1 - \frac{H}{2} + \frac{N}{2}}$ *where C is no. of **C**arbon atoms, **H** is total no. of **H**alogen and **H**ydrogen atoms, and N is no. of **N**itrogen atoms.*
2	**J** reacts with hot aqueous alkaline iodine to give a yellow precipitate	**J** contains $-COCH_3$ or $-CH(OH)CH_3$ Type of reaction: Oxidation	From observation 1, since the rest of **J** is saturated, **J** does <u>not</u> contain $-COCH_3$. J has $-CH(OH)CH_3$:  $-\overset{OH}{\underset{CH_3}{C}}-H$ - We need to decide whether to attach the group to the 2nd, 3rd or 4th position relative to OH on phenol.

<table>
<tr>
<td rowspan="2">3</td>
<td>**J** does not decolourise aqueous bromine</td>
<td>Phenol can undergo 2,4,6–tri substitution with $Br_2(aq)$, since there was **no reaction**, the 2nd, 4th, 6th positions relative to OH on phenol are **occupied** with substituents.</td>
<td>We now know that a partial structure of **J** is either:


or


- **J** has 10 carbon atoms ($C_{10}H_{14}O_2$), its incomplete structure requires 2 more carbons.</td>
</tr>
<tr>
<td colspan="3">- The rest of the information provided (4 and 5) will not help us deduce the structure of **J**.
- Here’s what we know so far to complete the partial structure of **J**:
1. It requires 2 more carbons.
2. These carbon atoms are saturated (DBE of 4 has been reached); hence, they are $-CH_3$ groups.
3. These carbons **must be placed** on two of the positions of 2nd, 4th, and 6th relative to OH on phenol.
Therefore, **J** is:


or

 </td>
</tr>
</table>

4	Upon heating **J** with acidified potassium dichromate(VI), **K** ($C_{10}H_{12}O_2$) is produced	Since **J** is a secondary alcohol, **K** is a ketone. Type of reaction: **Oxidation**	Based on **J**'s structure, **K** is either:  or 
5	**J** reacts with PCl_3 to form **L**	Since **J** is a secondary alcohol, **L** is a secondary halogenoalkane. Type of reaction: **Nucleophilic substitution**	This reaction converts –OH to –C*l*. **L** is either  or 

- When writing deductions, remember to include
    1. Type of reaction
    2. Functional groups
    3. Structural features (e.g., –CH(OH)CH_3 present, 2nd, 4th, 6th positions relative to OH is occupied etc.)

16 Electrochemistry

When tackling electrochemistry questions, it's crucial to first identify which of the three scenarios the question is based on. Ask yourself:

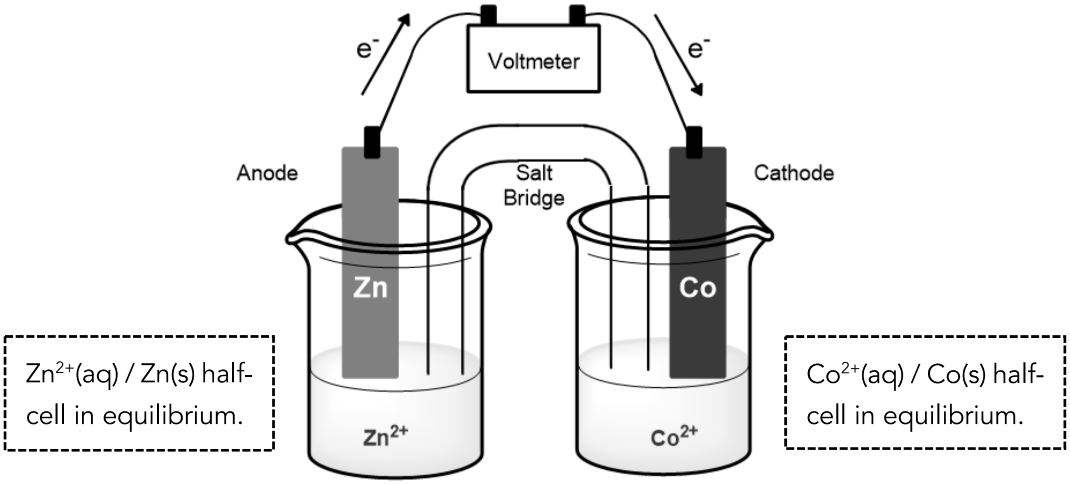
> *"Is this about an electrochemical cell, an electrolytic cell, or is it simply asking whether a spontaneous redox reaction can occur?"*

Recognising the scenario will help you choose the right concepts and approach.

Electrochemical Cells (Batteries)

An **electrochemical cell is a battery** made up of two half-cells connected by a wire and a salt bridge that generates electricity because of a spontaneous reaction that occurs.

- A spontaneous reaction is a reaction that happens without any external energy (heat or electricity) supplied to the system.



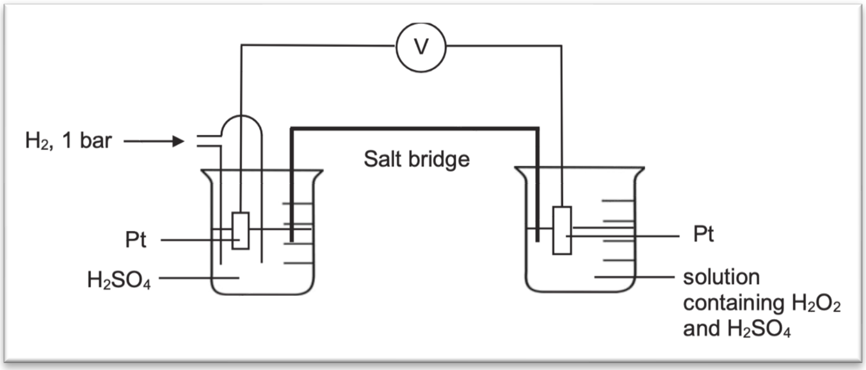
An electrochemical cell of Zn^{2+}/Zn and Co^{2+}/Co half-cells

The half-cell that undergoes reduction or oxidation is dependent on their respective electrode potentials values, E°.

Choosing the Correct Set of Half-Equations

To choose the correct half-equation: every single species in the half-equation must be in the half-cell.

Example 1 [ACJC/Prelim/2020/P1/Q19]



$2\ H^+ + 2\ e^- \rightleftharpoons H_2$

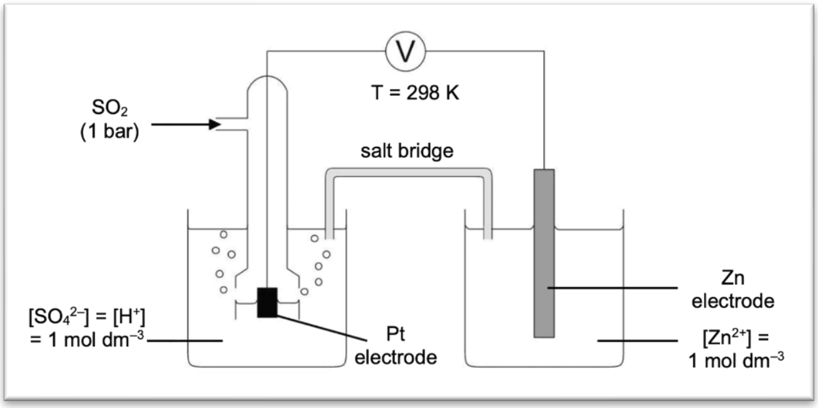
H^+ and H_2 are present in the half–cell.

$H_2O_2 + 2\ H^+ + 2\ e^- \rightleftharpoons 2\ H_2O$

H_2O_2, H^+ and H_2O are present in the half–cell.

- The half–equations can be found in the *Data Booklet*.
- SO_4^{2-} ion here is a spectator ion that is involved in the reduction/oxidation reaction.

Example 2 [RI/Prelim/2019/P1/Q28]



$SO_4^{2-} + 4\ H^+ + 2\ e^- \rightleftharpoons SO_2 + 2H_2O$

SO_4^{2-}, H^+, SO_2 and H_2O are present in the half–cell.

$Zn^{2+} + 2\ e^- \rightleftharpoons Zn$

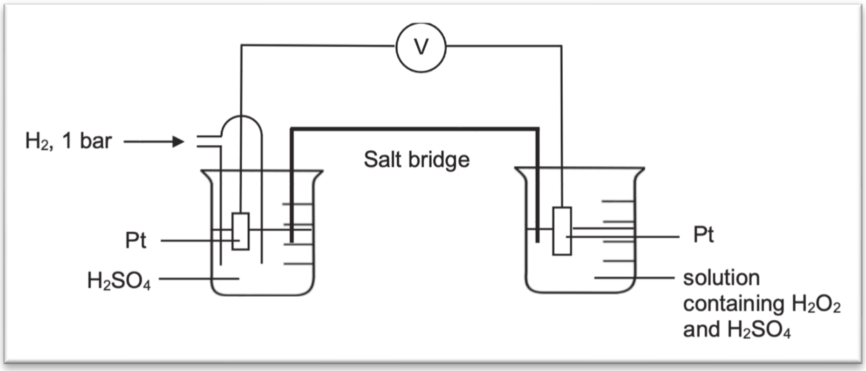
Zn^{2+} and Zn are present in the half–cell.

- The half–equations can be found in the *Data Booklet*.

Analysing Half–Cells: Which One is Oxidised or Reduced?

The main principle: **The half-cell with the more positive E° value undergoes reduction.**

Example 1 [ACJC/Prelim/2020/P1/Q19]



H^+/H_2 half–cell		**H_2O_2/H_2O half–cell**	
$2\ H^+ + 2\ e^- \rightleftharpoons H_2$	$E^\circ = 0.00$ V	$H_2O_2 + 2\ H^+ + 2\ e^- \rightleftharpoons 2\ H_2O$	$E^\circ = +1.77$ V

According to the *Data Booklet*, $E^\circ(H^+/H_2) = 0.00$ V and $E^\circ(H_2O_2/H_2O) = +1.77$ V. Since H_2O_2/H_2O has a more positive E° value, it undergoes reduction and is hence, the cathode.

- The electrode at which oxidation occurs is the anode; the electrode at which reduction occurs is the cathode.

Cathode half-equation: $H_2O_2 + 2\ H^+ + 2\ e^- \longrightarrow 2\ H_2O$

Anode half-equation: $H_2 \longrightarrow 2\ H^+ + 2\ e^-$

- Full arrows are used now, as reduction (or oxidation) has been determined.

Overall equation: $H_2O_2 + H_2 \longrightarrow 2\ H_2O$

Electron flow direction: From H^+/H_2 to H_2O_2/H_2O

Standard cell potential: $E^\circ_{cell} = E^\circ_r - E^\circ_o = +1.77 - 0.00 = \mathbf{+1.77\ V}$

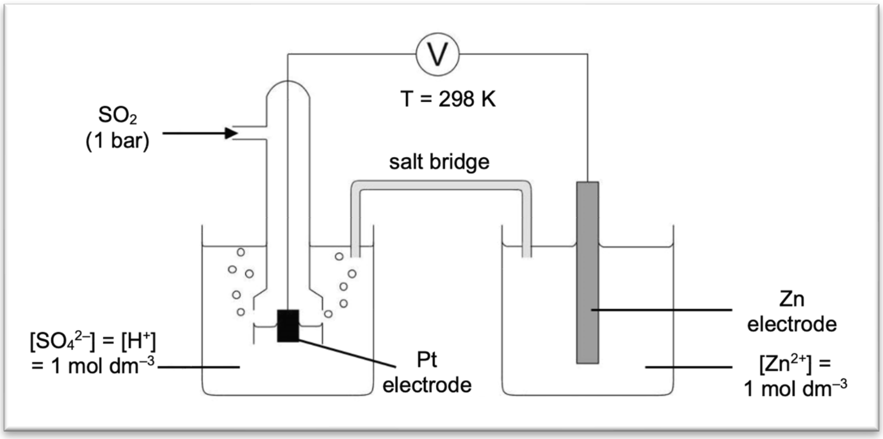
- A double A battery is usually +1.50 V.

- Electrons will always flow from anode (oxidation = loss of electrons) to cathode (reduction = gain of electrons).

Polarity of electrodes: Anode (H^+/H_2) is negative; cathode (H_2O_2/H_2O) is positive.

- Since the anode releases electrons and is the source of electrons, it has an excess of negatively charged electrons, this makes it the negative terminal.
- In an electrochemical cell (battery), the anode is (–) while the cathode is (+) [only for electrochemical cells].

Example 2 [RI/Prelim/2019/P1/Q28]



SO_4^{2-}/SO_2 half–cell		Zn^{2+}/Zn half–cell	
$SO_4^{2-} + 4\,H^+ + 2\,e^- \rightleftharpoons SO_2 + 2H_2O$	$E^\circ = +0.17$ V	$Zn^{2+} + 2\,e^- \rightleftharpoons Zn$	$E^\circ = +1.77$ V

According to the *Data Booklet*, $E^\circ(SO_4^{2-}/SO_2) = +0.17$ V and $E^\circ(Zn^{2+}/Zn) = +1.77$ V. Since Zn^{2+}/Zn has a more positive E° value, it undergoes reduction and is hence, the cathode.

Cathode half-equation: $Zn^{2+} + 2\,e^- \longrightarrow Zn$

Anode half-equation: $SO_2 + 2\,H_2O \longrightarrow SO_4^{2-} + 4\,H^+ + 2\,e^-$

Overall equation: $Zn^{2+} + SO_2 + 2\,H_2O \longrightarrow Zn + SO_4^{2-} + 4\,H^+$

Electron flow direction: From SO_4^{2-}/SO_2 to Zn^{2+}/Zn

Standard cell potential: $E^\circ_{cell} = E^\circ_r - E^\circ_o = +1.77 - (+0.17) = \mathbf{+1.60\ V}$

Polarity of electrodes: Anode (SO_4^{2-}/SO_2) is negative; cathode (Zn^{2+}/Zn) is positive.

Electrolytic Cells (This Is NOT a Battery!)

Electrolytic cells are **fundamentally different** from electrochemical cells.

An electrolytic cell uses a battery (an electrochemical cell) connected to electrodes, which then attract ions from the electrolyte to drive a **non-spontaneous** reduction or oxidation reaction.

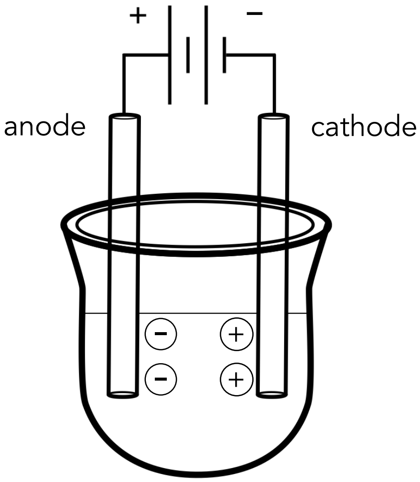
Essentially, we're using electricity to break down the electrolyte.

- An electrolytic cell requires an external source of current; an electrochemical cell **is** the source of current.

The Approach to an Electrolytic Cell

Begin by looking at how the electrodes are connected to the battery:

- The electrode connected to the negative terminal of the battery is the **negative** terminal and **attracts cations** (from the electrolyte) for **reduction**. Hence, this is the **cathode**.
- The electrode connected to the positive terminal of the battery is **positive** terminal and **attracts anions** (from the electrolyte) for **oxidation**. Hence, this is the **anode**.
- **Electrically neutral** molecules (H_2O) are **not attracted** and are present at both electrodes.



- In an electrochemical cell, the anode is the negative terminal; cathode is the positive terminal.
- Reduction and oxidation still occur at the cathode and anode respectively.

Dealing with concentrated electrolytes

Worked Example 1 [YIJC/Prelim/2023/P3/Q4]

A solution of concentrated NaCl is electrolysed, using platinum electrodes.

Write relevant half-equations for the reactions occurring during the electrolysis.

Solution

Step 1: Determine the respective species that migrate to the cathode and anode

At the cathode: Na^+, H_2O; At the anode: Cl^-, H_2O

- This can be *difficult.*

Step 2: Determine the half–equations at the cathode and anode

- Since reduction occurs at the cathode, species migrated to the cathode must be found on the **left side** of the half–equation in the *Data Booklet*.
- Since oxidation occurs at the anode, species migrated to the anode must be found on the **right side** of the half–equation in the *Data Booklet*.

At the cathode	At the anode
$Na^+ + e^- \rightleftharpoons Na$	$Cl_2 + 2\,e^- \rightleftharpoons 2\,Cl^-$
$2\,H_2O + 2\,e^- \rightleftharpoons H_2 + 2\,OH^-$	$O_2 + 4\,H^+ + 4\,e^- \rightleftharpoons 2\,H_2O$

Step 3: Determine which species gets preferentially reduced/oxidised at the cathode/anode

At the cathode, the half–equation with the **more positive E° gets reduced**; at the anode the half–equation with the **more negative (less positive) E° gets oxidised**.

At the cathode	At the anode
$Na^+ + e^- \rightleftharpoons Na$ $E^\circ = -2.71$ V $2 H_2O + 2 e^- \rightleftharpoons H_2 + 2 OH^-$ $E^\circ = -0.83$ V	$Cl_2 + 2 e^- \rightleftharpoons 2 Cl^-$ **$E^\circ = +1.36$ V** $O_2 + 4 H^+ + 4 e^- \rightleftharpoons 2 H_2O$ $E^\circ = +1.23$ V
• E° of −2.71 V corresponds to Na^+ under **standard conditions of 1 mol dm^{-3}**, but since conc. NaCl electrolyte is used, $[Na^+]$ is **more than 1 mol dm^{-3}**. • At $[Na^+] > 1$ mol dm^{-3}, equilibrium position of $Na^+ + e^- \rightleftharpoons Na$ lies more to the **RIGHT**. • Hence, E value of Na^+/Na becomes significantly more positive than −2.71V: $Na^+ + e^- \rightleftharpoons Na$ **$E >> -2.71$ V** • However, since the E° value of H_2O/H_2 is significantly more positive than −2.71 V, H_2O is **STILL** preferentially reduced over Na^+.	• E° of +1.36 V corresponds to Cl^- under **standard conditions of 1 mol dm^{-3}**, but since conc. NaCl electrolyte is used, $[Cl^-]$ is **more than 1 mol dm^{-3}**. • At $[Cl^-] > 1$ mol dm^{-3}, equilibrium position of $Cl_2 + 2 e^- \rightleftharpoons 2 Cl^-$ lies more to the **LEFT**. • Hence, E value of Cl_2/Cl^- becomes significantly more negative than +1.36 V: $Cl_2 + 2 e^- \rightleftharpoons 2 Cl^-$ **$E << +1.36$ V** • The new E value will likely be more negative than +1.23 V and hence, Cl^- gets preferentially oxidised over H_2O.
$2 H_2O + 2 e^- \longrightarrow H_2 + 2 OH^-$	**$2 Cl^- \longrightarrow Cl_2 + 2 e^-$**
Overall equation: $2 H_2O + 2 Cl^- \longrightarrow H_2 + 2 OH^- + Cl_2$	

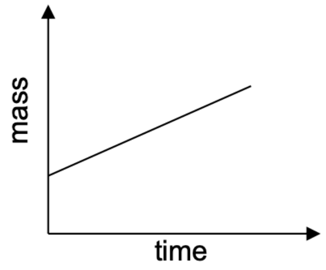
- Standard electrode potentials, E°, are **FIXED**. However, electrode potentials, E, vary if the concentration of the ions in the half–equation differ from the standard condition of 1 mol dm^{-3}.
- If E° values of the two half-equations are relatively close (around 0.2 V apart), changes in E due to a concentrated electrolyte can influence which species is preferentially discharged (oxidised or reduced).
- Concentrated electrolytes usually affects the outcome at the anode, not the cathode i.e., if dilute NaCl (1 mol dm^{-3}) was electrolysed, O_2/H_2O has a more negative E° value than Cl_2/Cl^- and H_2O will now be preferentially oxidised at the anode. The species preferentially reduced at the cathode remains unchanged.

Dealing with reactive electrodes

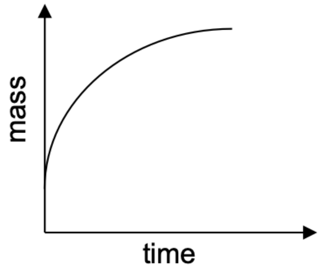
Example 2 [RVHS/Prelim/2021/P1/Q19]

Electrolysis of aqueous copper(II) sulfate was carried out using copper electrodes and a steady current. Which graph shows the change in mass of the cathode with time?

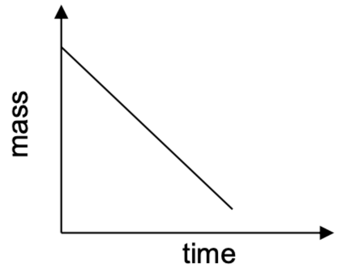
A



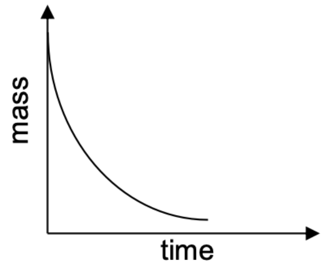
C



B



D



Solution

Step 1: Determine the respective species that migrate to the cathode and anode

At the cathode: Cu^{2+}, H_2O; At the anode: SO_4^{2-}, H_2O

Step 2: Determine the half–equations for the species at the cathode and anode

- Since reduction occurs at the cathode, species migrated to the cathode must be found on the **left side** of the half–equation in the *Data Booklet*.
- Since oxidation occurs at the anode, species migrated to the anode must be found on the **right side** of the half–equation in the *Data Booklet*.

At the cathode	At the anode
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$

Step 3: Determine which species gets preferentially reduced/oxidised at the cathode/anode

At the cathode, the half–equation with the **more positive E° gets reduced**; at the anode the half–equation with the **more negative (less positive) E° gets oxidised**.

At the cathode		At the anode	
$\mathbf{Cu^{2+}} + 2\,e^- \rightleftharpoons Cu$	$E^\circ = +0.34$ V	$S_2O_8^{2-} + 2\,e^- \rightleftharpoons 2\,\mathbf{SO_4^{2-}}$	$E^\circ = +2.01$ V
$2\,\mathbf{H_2O} + 2\,e^- \rightleftharpoons H_2 + 2\,OH^-$	$E^\circ = -0.83$ V	$O_2 + 4\,H^+ + 4\,e^- \rightleftharpoons 2\,\mathbf{H_2O}$	$E^\circ = +1.23$ V
		$Cu^{2+} + 2\,e^- \rightleftharpoons \mathbf{Cu}$	$E^\circ = +0.34$ V

- Since reactive Cu electrodes are used, they will compete with the half–equations at the anode because metals can oxidise!
- Reactive metal electrodes **will never** compete with the half–equations at the cathode because metals can **never be reduced**.

Since E° of Cu^{2+}/Cu is more positive than –0.83 V, Cu^{2+} is preferentially reduced over H_2O.	Since E° of Cu^{2+}/Cu is more negative (less positive) than +2.01 V and +1.23 V, Cu is preferentially oxidised over H_2O and SO_4^{2-}.
$Cu^{2+} + 2\,e^- \longrightarrow Cu$	$Cu \longrightarrow Cu^{2+} + 2\,e^-$
No overall equation.	

- Cu^{2+} ions from the electrolyte that is reduced at the cathode is **replenished** by oxidation of Cu at the anode.
- The blue colour intensity of the electrolyte remains the same during electrolysis.

Since Cu^{2+} ions are reduced at the cathode to Cu, a reddish–brown solid is deposited on the copper cathode, causing the mass of the cathode to increase over time:

The answer is either options **A** or **C**.

Option **C** is incorrect because the deposition of Cu(s) on the cathode should occur at a constant rate, meaning the mass–-time graph should have a constant gradient. There's no logical reason for a faster rate of copper deposition at the beginning.

Answer: A

Spontaneous Redox Reactions

Students frequently mix this concept up with electrolytic/electrochemical cells. The goal is to see whether a redox reaction will occur spontaneously when substance **A** is added to substance **B**.

Deducing the reduction half–equation

Worked Example 1 [ACJC/Prelim/2024/P1/Q28]

Use of the Data Booklet is relevant to this question.

By considering E° values, which aqueous species will oxidise Sn^{2+} to Sn^{4+}?

1 H_2O_2, H^+

2 I_2

3 V^{3+}

A 1, 2 and 3 B 1 and 2 only C 2 and 3 only D 1 only

Solution

Step 1: Choosing the correct set of half–equations

Since Sn^{2+} is being **oxidised** to Sn^{4+}, find the half–equation with Sn^{2+} on the **right side** of the half–equation in the *Data Booklet*:

$$Sn^{4+} + 2\,e^- \rightleftharpoons Sn^{2+} \qquad E^\circ_o = +0.15\text{ V}$$

- This E° is E°_o because Sn^{2+} is being oxidised.

To see if the aqueous species can oxidise Sn^{2+}, it must be **reduced**. To choose the correct half–equation, these species must be on the **left side** of the half–equation in the *Data Booklet*:

$$H_2O_2 + 2\,H^+ + 2\,e^- \rightleftharpoons 2\,H_2O \qquad E^\circ_r = +1.77\text{ V}$$

$$I_2 + 2\,e^- \rightleftharpoons 2\,I^- \qquad E^\circ_r = +0.54\text{ V}$$

$$V^{3+} + e^- \rightleftharpoons V^{2+} \qquad E^\circ_r = -0.26\text{ V}$$

- All the E° values here are E°_r because these species are being reduced.

- Choosing the correct set of half-equations to determine a spontaneous redox reaction is very different.
- In electrochemical cells, the half–cell that undergoes reduction is the half–equation with the more positive E° value and *vice versa*.
- In electrolytic cells, the species that undergoes reduction is the species that migrates to the cathode with a more positive E° value and *vice versa*.

Step 2: Checking if the redox reaction is spontaneous using E°_{cell}

Calculating E°_{cell} for the oxidation of Sn^{2+} with…		
H_2O_2 and H^+	$E^\circ_{cell} = E^\circ_r - E^\circ_o = +1.77 - (+0.15) > 0$	$E^\circ_{cell} > 0 \Rightarrow$ redox is spontaneous
I_2	$E^\circ_{cell} = E^\circ_r - E^\circ_o = +0.54 - (+0.15) > 0$	$E^\circ_{cell} > 0 \Rightarrow$ redox is spontaneous
V^{3+}	$E^\circ_{cell} = E^\circ_r - E^\circ_o = -0.26 - (+0.15) < 0$	$E^\circ_{cell} < 0 \Rightarrow$ redox is non-spontaneous

Answer: B

Deducing reduction and oxidation half–equations

Worked Example 2 [VJC/Prelim/2024/P1/Q29]

Use of the Data Booklet is relevant to this question.

Which of the following are chemically stable when left to stand in the atmosphere?

1 An aqueous solution of potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$

2 An aqueous solution of chromium(II) chloride, $CrCl_2$

3 A mixture of aqueous sodium hydroxide, NaOH and iron(II) sulfate, $FeSO_4$

A 1, 2 and 3 B 1 and 2 only C 2 and 3 only D 1 only

Solution

Understanding the question:

"chemically stable…" ⇒ **non–spontaneous** redox reaction

"…left to stand in the atmosphere" ⇒ exposed to **oxygen gas** in the air

Step 1: Choosing the correct set of half–equations

This step is a slightly trickier than Example 1; the question did not tell us how oxygen gas reacts – does it undergo oxidation or reduction?

Firstly, find the half–equations in the *Data Booklet* that contains O_2:

$$O_2 + 4\,H^+ + 4\,e^- \rightleftharpoons 2\,H_2O \qquad E^\circ = +1.23\text{ V}$$

$$O_2 + 2\,H_2O + 4\,e^- \rightleftharpoons 4\,OH^- \qquad E^\circ = +0.40\text{ V}$$

$$O_2 + 2\,H^+ + 2\,e^- \rightleftharpoons H_2O_2 \qquad E^\circ = +0.68\text{ V}$$

$$O_2 + H_2O + 2\,e^- \rightleftharpoons HO_2^- + OH^- \qquad E^\circ = –0.08\text{ V}$$

Since O_2 can only be found on the left–hand side of our half–equations, it shows that oxygen gas can only undergo **reduction**.

Among these four half–equations, we select the one with the **most positive** E° value. The most positive E° value means that O_2 has the strongest tendency to be reduced to that specific species (in this context, H_2O):

$$O_2 + 4\,H^+ + 4\,e^- \rightleftharpoons 2\,H_2O \qquad E_r^\circ = +1.23\text{ V}$$

- This E° is E_r° because O_2 is being reduced.

Step 2: Checking if the redox reaction is spontaneous using E_{cell}°

We still have one more half–equation to deduce, which must be oxidation, since O_2 is reduced. Hence, the species to reduce O_2 must be found on the right side of the half–equation:

The Oxidation Half–Equations	
$K_3[Fe(CN)_6]$	K^+ and $[Fe(CN)_6]^{3-}$ **cannot be oxidised**– they can only be reduced as they appear only on the **left–hand side** of their half–equations: $K^+ + e^- \rightleftharpoons K$ $[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$ **Option 1 is** **correct**. O_2 is unable to react with $K_3[Fe(CN)_6]$. Hence, its aqueous solution is chemically stable.

The Oxidation Half–Equations (continued)	
$CrCl_2$	According to the *Data Booklet*, Cr^{2+} can either be oxidised to Cr^{3+} or reduced to Cr. *Of course*, we focus on its oxidation: $Cr^{3+} \rightleftharpoons \mathbf{Cr^{2+}} + e^-$ $\quad E^\circ_o = -0.41$ V Cl^- can only be oxidised: $Cl_2 + 2e^- \rightleftharpoons \mathbf{Cl^-}$ $\quad E^\circ_o = +1.36$V Cr^{2+} is **oxidised** to Cr^{3+} by O_2: $E^\circ_{cell} = E^\circ_r - E^\circ_o = +1.23 - (-0.41) > 0$. Cl^- **cannot be oxidised** by O_2: $E^\circ_{cell} = E^\circ_r - E^\circ_o = +1.23 - (+1.36) < 0$ Since Cr^{2+} can be oxidised by O_2, $CrCl_2$ is chemically unstable ⇒ **Option 2 is incorrect**.
NaOH and $FeSO_4$ - Fe^{2+} reacts with OH^- to form $Fe(OH)_2$.	According to the *Data Booklet*, $Fe(OH)_2$ can only be oxidised: $Fe(OH)_3 + e^- \rightleftharpoons \mathbf{Fe(OH)_2}$ $\quad E^\circ_o = +0.36$V $Fe(OH)_2$ is **oxidised** $Fe(OH)_3$ by O_2: $E^\circ_{cell} = E^\circ_r - E^\circ_o = +1.23 - (+0.36) > 0$. Since $Fe(OH)_2$ can be oxidised by O_2, $Fe(OH)_2$ is chemically unstable ⇒ **Option 3 is incorrect**.

- These E° values are E°_o because they're being oxidised (by O_2).

Answer: D