1 The Basic Oxygen steel-making process is a method of preparing steel from carbon-rich molten pig iron. The process is basic because chemical bases are added to remove impurities. One such impurity is phosphorus pentoxide, P_4O_{10}. Calcium oxide, CaO, is added to remove it and the only product of the reaction is the salt, calcium phosphate, $Ca_3(PO_4)_2$.

How many moles of CaO reacted with one mole of P_4O_{10} in this reaction?

A 1

B 1.5

C 3

D 6

2 Two moles of an oxidising agent, XO_4^- in the presence of excess acid oxidised 96 dm^3 of nitrogen dioxide gas at room temperature and pressure to NO_3^-.

What is the number of moles of electrons accepted by one mole of XO_4^-?

A 1 **B** 2 **C** 3 **D** 4

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

The ion $\mathbf{T}^+$ contains 28 electrons and 35 neutrons.

Which of the following statements about $\mathbf{T}^+$ or **T** is correct?

A **T** and Ga^{3+} are isoelectronic species.

B The elemental form of **T** can be oxidised by chlorine.

C The electronic configuration of $\mathbf{T}^+$ ion is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^9\,4s^1$.

D The angle of deflection of $^{27}Al^{3+}$ is approximately three times that of $\mathbf{T}^+$ in an electric field.

4 Which of the following species has a different bond angle from the rest?

A ICl_3 **B** SF_3^+ **C** ClO_3^- **D** N_2H_4

5 What will happen to the volume of a bubble of air submerged in water under a lake at 10.0 °C and 2.00 atm if it rises to the surface where the temperature is 20.0 °C and the pressure is 1.00 atm?

A The volume will increase by a factor of 2.00.

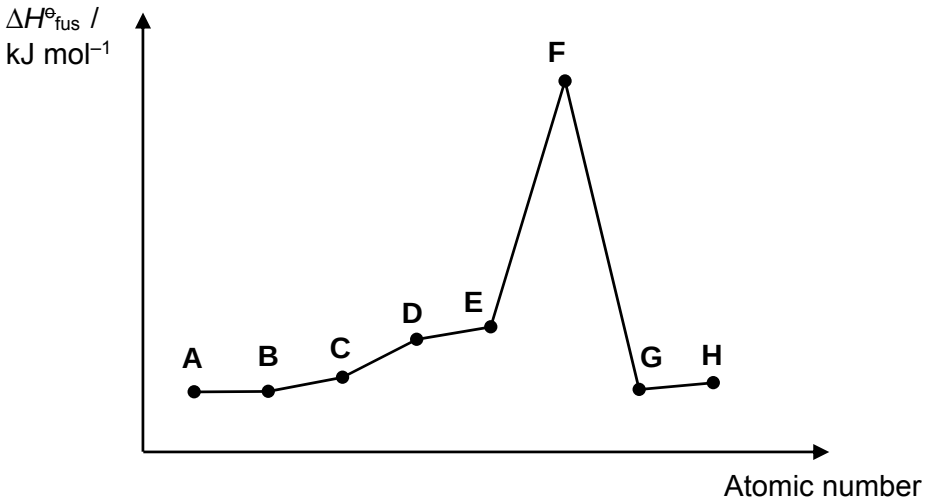
B The volume will increase by a factor of 2.07.

C The volume will decrease by a factor of 2.00.

D The volume will decrease by a factor of 1.93.

6 The graph below shows the variation in the standard enthalpy change of fusion, $\Delta H^{\ominus}_{fus}$ for 8 consecutive elements from period 2 to 3 in the periodic table.

Standard enthalpy change of fusion is the heat absorbed when one mole of a substance changes its state from solid to liquid under standard conditions.



Which of the following statements is true based on the information deduced from the above graph?

A The chlorides become more acidic from **A** to **C**.

B An oxide of **E** dissolves in water to form an alkaline solution.

C Element **G** has a higher first ionisation energy than element **F** and **H**.

D Element **D** has a lower electrical conductivity as compared to element **F**.

7 Some enthalpy changes of combustion are given below.

	ΔH_c / kJ mol^{-1}
CO(g)	–283
H_2(g)	–286
CH_3OH(*l*)	–715

What is the enthalpy change of the following reaction, in kJ mol^{-1}?

$$CO(g) + 2H_2(g) \longrightarrow CH_3OH(l)$$

A –146

B +146

C –140

D +140

8 The reaction of nitrogen monoxide and hydrogen gas

$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$$

is thought to involve the following steps:

I $NO + NO \rightleftharpoons N_2O_2$ (fast)

II $N_2O_2 + H_2 \longrightarrow H_2O + N_2O$ (slow)

III $N_2O + H_2 \longrightarrow N_2 + H_2O$ (fast)

Which of the following about the reaction is true?

A H_2 acts as the catalyst.

B The rate equation for the reaction is rate = $k[N_2O_2][H_2]$.

C The overall order of the reaction is 3.

D Increasing the concentration of NO does not change the rate of reaction.

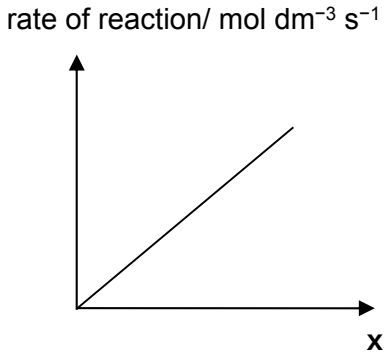
9 Hydrogen peroxide reacts with acidified iodide ions liberating iodine according to the equation below:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \longrightarrow I_2(aq) + 2H_2O(l)$$

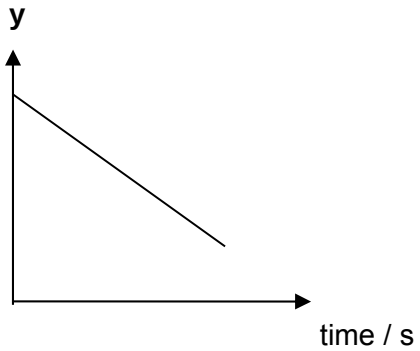
The kinetics of this reaction was investigated and it was found to have the following rate equation: rate = $k[H_2O_2][I^-]$

Two series of experiments were conducted, giving rise to **Graph A** and **Graph B**.

Graph A



Graph B

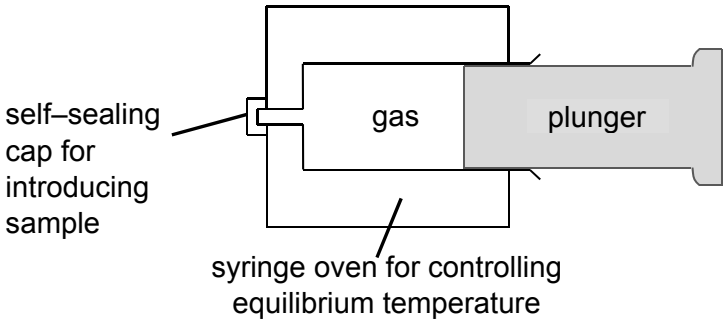


Which of the following shows the correct labelling of the x-axis for **Graph A** and y-axis for **Graph B**?

	x-axis	y-axis
A	$[H_2O_2][I^-]$ / mol^2 dm^{-6}	$[H^+]$ / mol dm^{-3}
B	$[H^+]$ / mol dm^{-3}	$[H_2O_2]$ / mol dm^{-3}
C	$[H_2O_2][I^-]$ / mol^2 dm^{-6}	$[I^-]$ / mol dm^{-3}
D	$[H^+]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}

10 A gaseous dimer, **Z**, is introduced into an empty gas syringe which has a movable, tightly–fitting plunger. The gas is allowed to expand until equilibrium is reached at a controlled temperature at which 20 % of **Z** dissociates into its monomer **W**.

$$\mathbf{Z}(g) \rightleftharpoons 2\mathbf{W}(g)$$



Which of the following statements is correct?

A The forward reaction is exothermic.

B The value of the equilibrium constant, K_p is 0.167 atm.

C The pressure inside the syringe at equilibrium will be higher than the atmospheric pressure.

D The dissociation of dimer **Z** will be favoured when the plunger is pushed back into the equilibrium mixture.

11 The acid dissociation constants for the diprotic acid, malonic acid $H_2C_3H_2O_4$ are K_{a1} = 1.5 x 10^{-3} and K_{a2} = 2.0 x 10^{-6}.

What is the K_b for $HC_3H_2O_4^-$?

A $K_w \times K_{a1}$

B $K_w \times K_{a2}$

C K_w / K_{a1}

D K_w / K_{a2}

12 Hardness in tap water can be determined by titrating a sample against a reagent which forms complex ions with dissolved metal ions. The indicator for this titration requires the pH to be maintained at about 10.

Which of the following, in aqueous solution, could be used to maintain the pH at about 10?

A 10 cm^3 of 2.0 g dm^{-3} of sodium hydroxide neutralised by 10 cm^3 of 0.025 mol dm^{-3} of ethanoic acid

B 5 cm^3 of 1.7 g dm^{-3} of ammonia neutralised by 10 cm^3 of 0.025 mol dm^{-3} hydrochloric acid

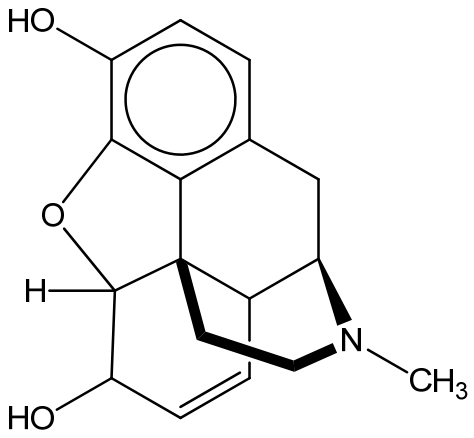
C 20 cm^3 of 0.05 mol dm^{-3} of hydrochloric acid neutralised by 5 cm^3 of 1.7 g dm^{-3} ammonia

D 10 cm^3 of 0.05 mol dm^{-3} of ethanoic acid neutralised by 5 cm^3 of 2.0 g dm^{-3} of sodium hydroxide

13 The solubility product of some sparingly soluble lead compounds are shown below. Which compound will have the lowest concentration of Pb^{2+}(aq) ions in a saturated solution?

	compound	numerical value of solubility product (at 25 ^oC)
A	lead(II) fluoride	2.7×10^{-8}
B	lead(II) bromide	4.0×10^{-5}
C	lead(II) iodide	7.1×10^{-9}
D	lead(II) sulfate	1.6×10^{-8}

14 Morphine is a powerful narcotic painkiller which could be isolated from opium poppy. Though it relieves pain effectively, it can cause addiction so readily that it should only be used in the cases where other pain medications are inadequate.



morphine

Which of the following claims about morphine is true?

1 There are 5 chiral carbons present in the molecule.

2 There are 7 C–C bonds formed by sp^3 – sp^3 overlap.

3 The molecule cannot exhibit cis-trans isomerism at the C=C double bond.

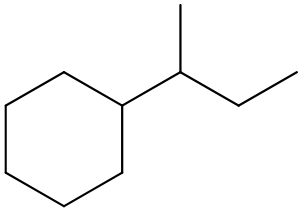
A 1 only

B 2 only

C 2 and 3 only

D 1, 2 and 3

15 Compound **L** reacts with limited chlorine gas in the presence of sunlight.



compound **L**, $C_{10}H_{20}$

Assuming that only mono-chlorination takes place and ignoring the relative rates of abstraction of the different type of hydrogen atom, which of the following statements is **incorrect**?

A The maximum number of chlorinated products formed is 8.

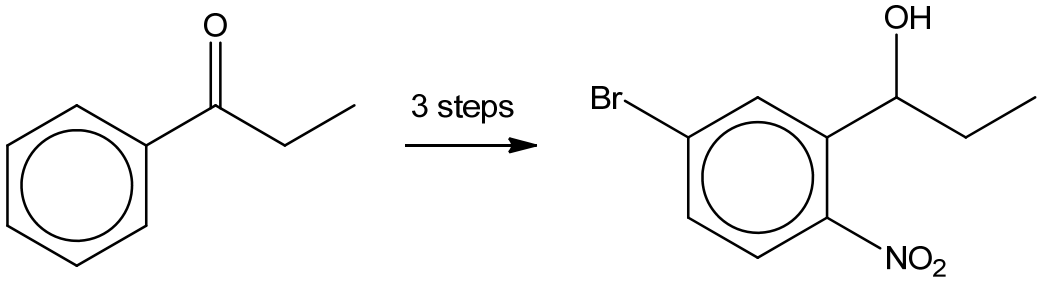
B $C_{20}H_{38}$ is present in small quantities in the products.

C Homolytic fission occurs in both initiation and propagation step.

D The ratio of primary to secondary to tertiary chloroalkanes formed is 3:6:2.

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

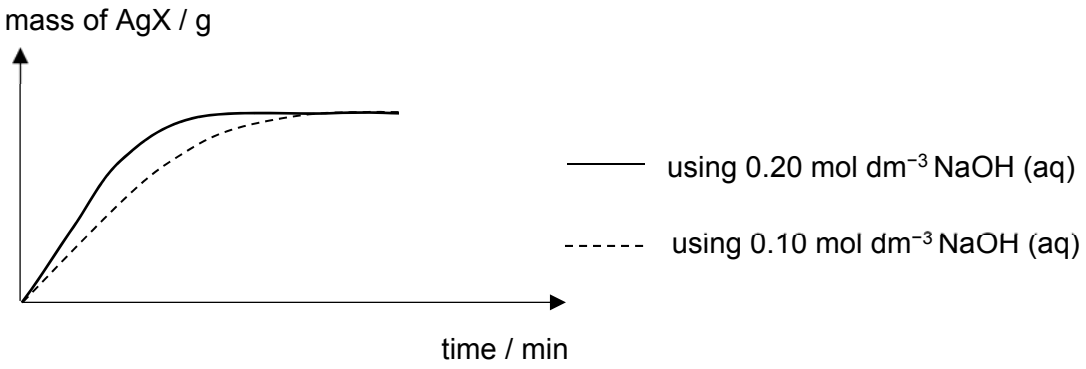
The following transformation takes place in three steps.



Which of the following shows the best choice of reagents and conditions to carry out the transformation?

	step 1	step 2	step 3
A	H_2, Pt	conc HNO_3, conc H_2SO_4	Br_2, $FeBr_3$
B	Br_2, $FeBr_3$	H_2, Pt	conc HNO_3, conc H_2SO_4
C	H_2, Pt	Br_2, $FeBr_3$	conc HNO_3, conc H_2SO_4
D	Br_2, $FeBr_3$	conc HNO_3, conc H_2SO_4	H_2, Pt

17 A halogen-containing compound, **U**, is heated with 2 different concentrations of aqueous sodium hydroxide. After acidifying the mixture and adding excess aqueous silver nitrate, the mass of silver halide formed is analysed over a period of time. The following graph for the mass of silver halide precipitate against time was obtained.



Which of the following is the likely structure of **U**?

A

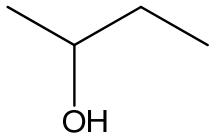
B

C

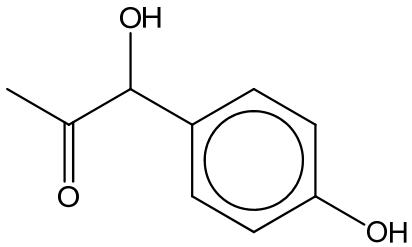
D

18 The following two compounds react with alkaline aqueous iodine to form yellow precipitate of tri-iodomethane as one of the products.

What is the ratio of sodium hydroxide used to react with 1 mol of compound **V** and 1 mol of compound **W** respectively?



compound **V**



compound **W**

	compound **V**	compound **W**
A	4	4
B	4	6
C	6	4
D	6	5

19 A fresh salad with tomatoes may contain compound $CH_3CH_2CH_2CH{=}CHCHO$ which provides an aroma for tomatoes. What will be the final product, **P** in this sequence of reactions?

$$CH_3CH_2CH_2CH{=}CHCHO \xrightarrow[\text{then } H_2O]{NaBH_4 \text{ in } CH_3OH} \mathbf{O} \xrightarrow[\text{heat}]{K_2Cr_2O_7/H^+} \mathbf{P}$$

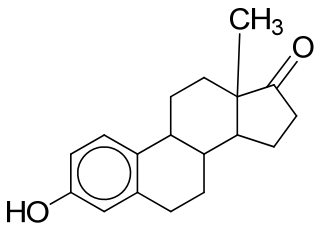
A $CH_3CH_2CH_2CH{=}CHCOOH$

B $CH_3CH_2CH_2CH_2CH_2COOH$

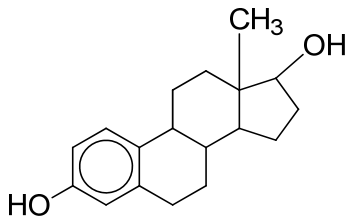
C $CH_3CH_2CH_2CH{=}CHCH_2OH$

D $CH_3CH_2CH_2COOH$

20 Two female sex hormones are oestrone and oestradiol.



oestrone



oestradiol

Which of the following reagents could be used to distinguish between the two hormones?

1 $SOCl_2$

2 $KMnO_4/H^+$

3 $LiAlH_4$ in dry ether

A 1, 2 and 3

B 1 and 2 only

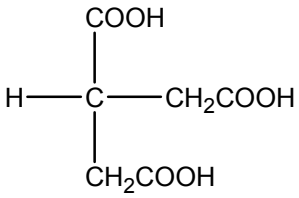
C 2 and 3 only

D 1 only

21 Ethanoic acid can be made by direct carbonylation of methanol, in presence of a rhodium catalyst.

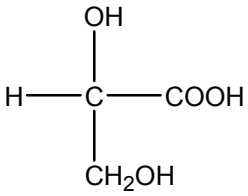
$$CH_3OH + CO \xrightarrow{\text{rhodium catalyst}} CH_3COOH$$

Which of the following can produce compound **S** using a similar method?

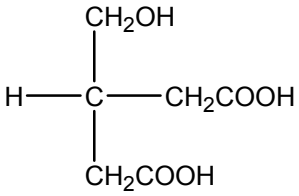


compound **S**

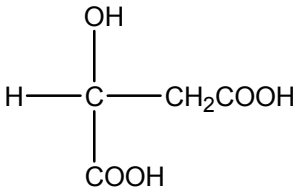
A



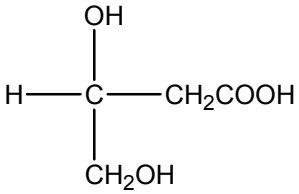
B



C



D



22 Benzylamine has the formula $C_6H_5CH_2NH_2$ and is a common precursor in organic synthesis.

Which of the following statements about benzylamine is correct?

1 It reacts with excess CH_3CH_2Cl to form the compound, $C_{13}H_{22}NCl$.

2 It reacts with CH_3COOH to form $C_6H_5CH_2NHCOCH_3$.

3 It can be distinguished from $CH_3CH_2NH_2$ by the use of aqueous bromine.

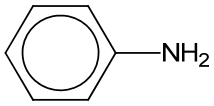
A 1, 2 and 3

B 1 and 2 only

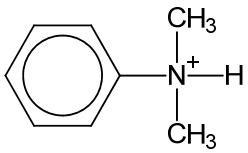
C 1 only

D 2 and 3 only

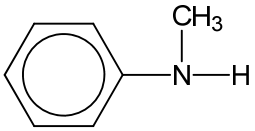
23 The structures of some nitrogen containing compounds are shown below.



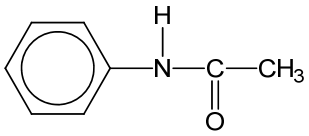
compound **H**



compound **I**



compound **J**



compound **K**

What is the order of increasing basicity of the nitrogen containing compounds?

	least basic →			most basic
A	**I**	**H**	**K**	**J**
B	**I**	**K**	**H**	**J**
C	**I**	**K**	**J**	**H**
D	**K**	**I**	**J**	**H**

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

Which statements about the elements chlorine, bromine and iodine are correct?

1 The oxidising power decreases from chlorine to iodine.

2 The bond length of the molecule increases from chlorine to iodine.

3 The magnitude of the first electron affinity increases from chlorine to iodine.

A 1 and 2 only

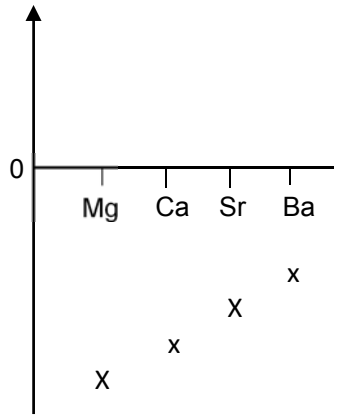
B 1 and 3 only

C 2 and 3 only

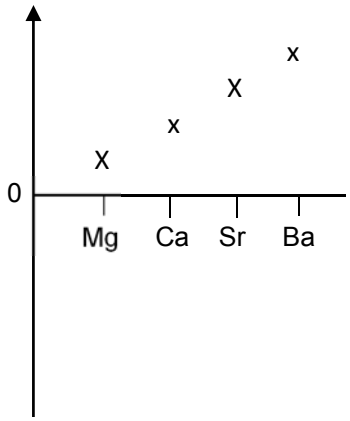
D 1, 2 and 3

25 Which diagram correctly shows the trend in a property of the Group 2 elements Mg, Ca, Sr, Ba?

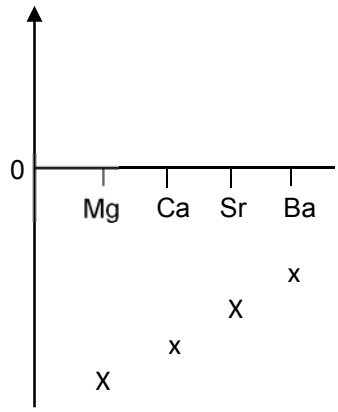
A ΔH_{hyd}, the enthalpy change of hydration of $M^{2+}(g)$



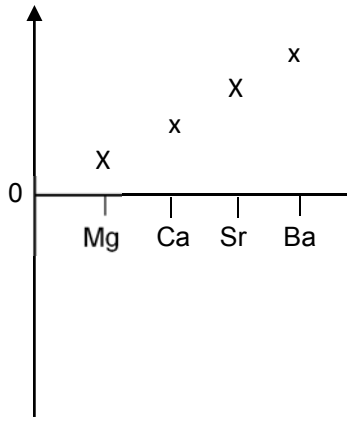
B *I*, the first ionisation energy



C $E^{\ominus}$, the standard electrode potential of $M^{2+}(aq)|M(s)$ electrode



D Electronegativity value



26 Three half cells are constructed as follows.

Half cell **I**: an electrode of metal **Q** in a 1.0 M solution of $\mathbf{Q}^+$(aq) ions

Half cell **II**: an electrode of metal **R** in a 1.0 M solution of $\mathbf{R}^+$(aq) ions

Half cell **III**: an electrode of Cu metal in a 1.0 M solution of Cu^{2+}(aq) ions

The half cells are connected in pairs, as shown below, to form a series of galvanic cells. For each cell, the polarity of the electrodes and the voltage generated are recorded.

half cells used	positive electrode	negative electrode	voltage (V)
I and **III**	Cu	**Q**	0.57
II and **III**	Cu	**R**	1.10
I and **II**	**Q**	**R**	0.53

Which one of the following lists the metals in order of **increasing** strength as reducing agents?

A **R**, **Q**, Cu

B **Q**, Cu, **R**

C Cu, **R**, **Q**

D Cu, **Q**, **R**

27 Some standard redox potential ($E^{\ominus}$) values are given in the table below.

electrode reaction	$E^{\ominus}$/ V
$Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq)$	+0.77
$Sn^{4+}(aq) + 2e \rightleftharpoons Sn^{2+}(aq)$	+0.15
$Ce^{4+}(aq) + e \rightleftharpoons Ce^{3+}(aq)$	+1.45

Which of the following reactions would occur under standard conditions?

1 $Ce^{4+}(aq) + Fe^{2+}(aq) \longrightarrow Ce^{3+}(aq) + Fe^{3+}(aq)$

2 $Sn^{2+}(aq) + 2Fe^{3+}(aq) \longrightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$

3 $2Ce^{4+}(aq) + Sn^{2+}(aq) \longrightarrow 2Ce^{3+}(aq) + Sn^{4+}(aq)$

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

28 A current was passed through two cells connected in series. The first cell contained molten sodium chloride while the other contained a molten aluminium salt.

What would be the mass of aluminium liberated from the other cell if 4.6g of sodium was liberated from the first cell?

A 0.9 g

B 1.8 g

C 2.7 g

D 3.6 g

29 Which of the following does **not** act as a ligand in the formation of complexes?

A SCN^-

B Cl^-

C AlH_4^-

D $C_2O_4^{2-}$

30 A reaction scheme starting from aqueous copper(II) sulfate solution is shown below. Both **X** and **Y** are copper-containing species.

$$CuSO_4(aq) \xrightarrow[\text{I}]{NH_3(aq)} \mathbf{X} \xrightarrow[\text{II}]{\text{excess } NH_3(aq)} \mathbf{Y} \xrightarrow[\text{III}]{Na_4edta(aq)} [Cu(edta)]^{2-}(aq)$$

Which of the following statements is true?

1 NH_3 acts as a ligand in reaction I.

2 Reaction II is a redox reaction.

3 The entropy of the system increases when reaction III occurs.

A 1 only

B 3 only

C 1 and 3 only

D 1, 2 and 3 only

1	D	**11**	C	**21**	D
2	B	**12**	B	**22**	C
3	B	**13**	D	**23**	B
4	A	**14**	D	**24**	A
5	B	**15**	D	**25**	A
6	C	**16**	B	**26**	D
7	C	**17**	A	**27**	A
8	C	**18**	D	**28**	B
9	A	**19**	A	**29**	C
10	B	**20**	D	**30**	B

1 The Basic Oxygen steel-making process is a method of preparing steel from carbon-rich molten pig iron. The process is basic because chemical bases are added to remove impurities. One such impurity is phosphorus pentoxide, P_4O_{10}. Calcium oxide, CaO, is added to remove it and the only product of the reaction is the salt, calcium phosphate, $Ca_3(PO_4)_2$.

How many moles of CaO reacted with one mole of P_4O_{10} in this reaction?

A 1

B 1.5

C 3

D 6

$P_4O_{l0} + 6CaO \rightarrow 2Ca_3(PO_4)_2$

Given that Ca_3PO_4 is the only product, write the balanced equation between P_4O_{10} and CaO to form Ca_3PO_4. Based on mole ratio, 6 moles of CaO is required to completely react with one mole of P_4O_{l0}.

Answer: **D**

2 Two moles of an oxidising agent, XO_4^- in the presence of excess acid oxidised 96 dm^3 of nitrogen dioxide gas at room temperature and pressure to NO_3^-.

What is the number of moles of electrons accepted by one mole of XO_4^-?

A 1 **B** 2 **C** 3 **D** 4

$n(NO_2) = 96/24 = 4$

$NO_2 + H_2O \rightarrow NO_3^- + 2H^+ + e$

$XO_4^- \equiv NO_2$

2 : 4

1 : 2

2 mol of NO_2 donate 2 mol of e which is accepted by 1 mol of XO_4^-

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

The ion **T**$^+$ contains 28 electrons and 35 neutrons.

Which of the following statements about **T**$^+$ or **T** is correct?

A **T** and Ga^{3+} are isoelectronic species.

B The elemental form of **T** can be oxidised by chlorine.

C The electronic configuration of **T**$^+$ ion is $1s^22s^22p^63s^23p^63d^94s^1$.

D The angle of deflection of $^{27}Al^{3+}$ is approximately three times that of **T**$^+$ in an electric field.

Since ion **T**$^+$ contains 28 electrons, element **T** is copper which contains 29 electrons.

Option A is wrong as Ga^{3+} has 28 electrons, hence **T** and Ga^{3+} do not have the same number of electrons.

Option B is correct as Cu can be oxidised to Cu^{2+} by chlorine.

$Cu^{2+} + 2e \rightleftharpoons Cu \quad E^{\ominus} = +0.34\ V$

$Cl_2 + 2e \rightleftharpoons 2Cl^- \quad E^{\ominus} = +1.36\ V$

$E^{\ominus}_{cell} = +1.36 - (+0.34) = +1.02\ V$

Option C is wrong as the electronic configuration of **T**$^+$ ion is $1s^22s^22p^63s^23p^63d^{10}$.

Option D is wrong as the angle of deflection of $^{27}Al^{3+}$ is not approximately three times that of **T**$^+$ in an electric field.

The angle of deflection depends on the charge-to-mass ratio of the particles.

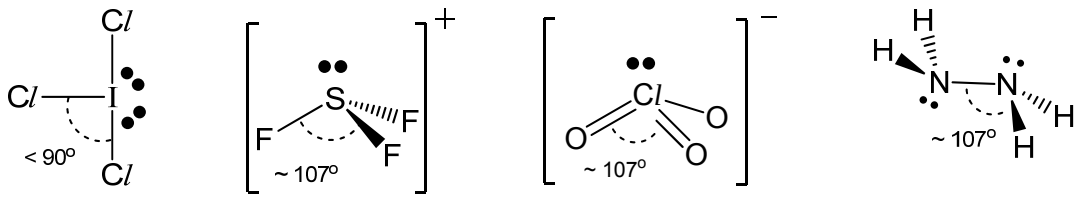
Angle of deflection of $Al^{3+} = k(\frac{3}{27}) = 0.111\ k$

Angle of deflection of **T**$^+$ $= k(\frac{1}{64}) = 0.0156\ k$

Answer: **B**

4 Which of the following species has a different bond angle from the rest?

A ICl_3 **B** SF_3^+ **C** ClO_3^- **D** N_2H_4



Answer: **A**

5 What will happen to the volume of a bubble of air submerged in water under a lake at 10.0 °C and 2.00 atm if it rises to the surface where the temperature is 20.0 °C and the pressure is 1.00 atm?

A The volume will increase by a factor of 2.00.

B The volume will increase by a factor of 2.07.

C The volume will decrease by a factor of 2.00.

D The volume will decrease by a factor of 1.93.

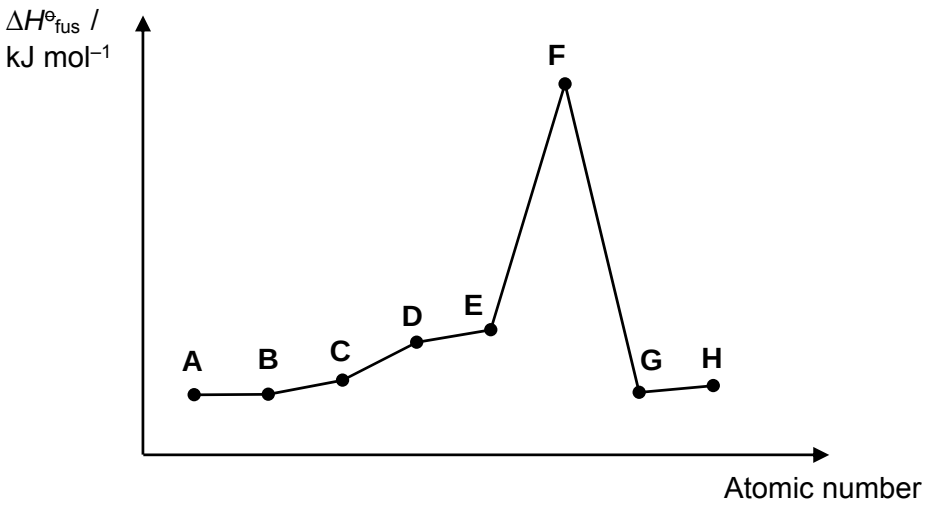
Answer : **B**

$P_1V_1/T_1 = P_2V_2/T_2$
$2(V_1)/ (273+10) = 1 (V_2) / (273 + 20)$

$V_2 = 293 \times (2) \times V_1 / 283 = 2.07\ V_1$

6 The graph below shows the variation in the standard enthalpy change of fusion, $\Delta H^{\ominus}_{fus}$ for 8 consecutive elements from period 2 to 3 in the periodic table.

Standard enthalpy change of fusion is the heat absorbed when one mole of a substance changes its state from solid to liquid under standard conditions.



Which of the following statements is true based on the information deduced from the above graph?

A The chlorides become more acidic from **A** to **C**.

B An oxide of **E** dissolves in water to form an alkaline solution.

C Element **G** has a higher first ionisation energy than element **F** and **H**.

D Element **D** has a lower electrical conductivity as compared to element **F**.

Since **F** is an element from period 2 to 3, and it has the largest $\Delta H^{\ominus}_{fus}$ (the rest of the elements have much lower $\Delta H^{\ominus}_{fus}$), **F** must be Si. Si has a giant covalent structure with high melting point and $\Delta H^{\ominus}_{fus}$.

So **A** is fluorine, **B** is neon, **C** is sodium, **D** is magnesium, **E** is aluminium, **G** is phosphorus and **H** is sulfur.

Option A is wrong as sodium chloride is a neutral chloride and there is no chloride of fluorine (fluorine reacts with chlorine to form chlorine fluoride instead). There is no reaction between neon and chlorine.

Option B is wrong as aluminium oxide is insoluble in water.

Option C is correct as phosphorus has a higher first ionisation energy than silicon and sulfur.

Option D is wrong as magnesium has a higher electrical conductivity as compared to silicon.

Answer: **C**

7 Some enthalpy changes of combustion are given below.

	ΔH_c / kJ mol^{-1}
CO(g)	–283
H_2(g)	–286
CH_3OH(*l*)	–715

What is the enthalpy change of the following reaction?

$$CO(g) + 2H_2(g) \longrightarrow CH_3OH(l)$$

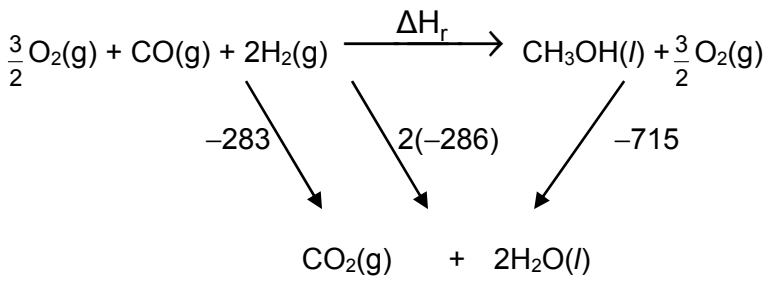
A –146

B +146

C –140

D +140

Answer: C



By Hess' law: $\Delta H_r = \Delta H_c$ *(reactants)* - ΔH_c *(products)*

= –283 + 2(–286) – (–715) = **–140** kJ mol^{-1}

8 The reaction of nitrogen monoxide and hydrogen gas

$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$$

is thought to involve the following steps:

I $NO + NO \rightleftharpoons N_2O_2$ (fast)

II $N_2O_2 + H_2 \longrightarrow H_2O + N_2O$ (slow)

III $N_2O + H_2 \longrightarrow N_2 + H_2O$ (fast)

Which of the following about the reaction is true?

A H_2 acts as the catalyst.

B The rate equation for the reaction is rate = $k[N_2O_2][H_2]$.

C The overall order of the reaction is 3.

D Increasing the concentration of NO does not change the rate of reaction.

Answer: C

A is incorrect as there is insufficient information to deduce that H_2 is the catalyst.

B is incorrect.

Based on the slow step:

Rate = k $[N_2O_2]$ $[H_2]$

However, N_2O_2 is not present in the final equation, this show that it is an intermediate and should not be present in the rate equation.

Based on step I,

$[N_2O_2]$ α $k'[NO]^2$

Rate = $k'[NO]^2[H_2]$

C is correct.

Based on the rate equation, overall order is 3.

D is incorrect. Since NO is present in the rate equation, increasing the concentration will increase the rate of reaction

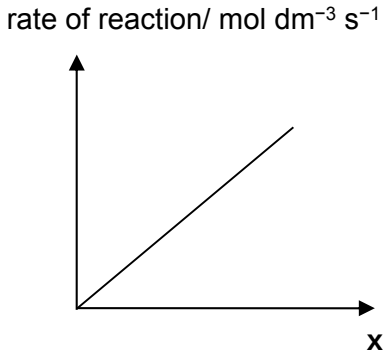
9 Hydrogen peroxide reacts with acidified iodide ions liberating iodine according to the equation below:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \longrightarrow I_2(aq) + 2H_2O(l)$$

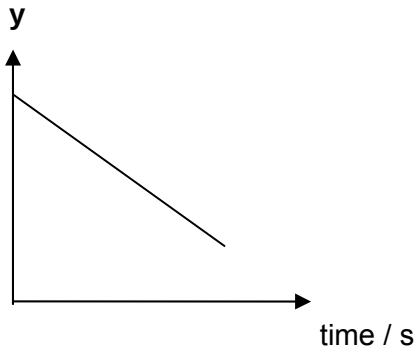
The kinetics of this reaction was investigated and it was found to have the following rate equation: rate = k $[H_2O_2]$ $[I^-]$

Two series of experiments were conducted, giving rise to **Graph A** and **Graph B**.

Graph A



Graph B



Which of the following shows the correct labelling of the x-axis for **Graph A** and y-axis for **Graph B**?

	x-axis	y-axis
A	$[H_2O_2]$ $[I^-]$ / mol^2 dm^{-6}	$[H^+]$ / mol dm^{-3}
B	$[H^+]$ / mol dm^{-3}	$[H_2O_2]$ / mol dm^{-3}
C	$[H_2O_2]$ $[I^-]$ / mol^2 dm^{-6}	$[I^-]$ / mol dm^{-3}
D	$[H^+]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}

Answer: A

Graph A:

As the rate eqn is rate = k $[H_2O_2]$ $[I^-]$

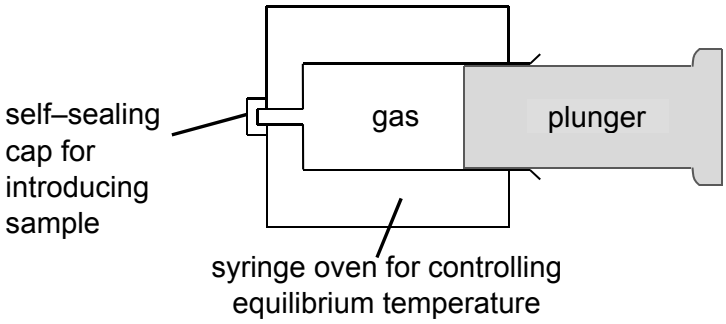
If y = mx , then y axis = rate

x-axis is $[H_2O_2]$ $[I^-]$

Graph B: It shows a zero order concentration-time graph (constant rate/grad), it is first order wrt to $[H_2O_2]$ and $[I^-]$. It is zero order wrt to $[H^+]$.

10 A gaseous dimer, **Z**, is introduced into an empty gas syringe which has a movable, tightly–fitting plunger. The gas is allowed to expand until equilibrium is reached at a controlled temperature at which 20 % of **Z** dissociates into its monomer **W**.

$$\mathbf{Z}(g) \rightleftharpoons 2\mathbf{W}(g)$$



Which of the following statements is correct?

A The forward reaction is exothermic.

B The value of the equilibrium constant, K_p is 0.167 atm.

C The pressure inside the syringe at equilibrium will be higher than the atmospheric pressure.

D The dissociation of dimer **Z** will be favoured when the plunger is pushed back into the equilibrium mixture.

Answer: **B**

Option A

The dissociation of a dimer only involves "bond breaking" and thus is an endothermic process.

Option B

Let the initial amount (mol) of **X** be 'a'

	$\mathbf{X}(g)$	$\rightleftharpoons$	$2\mathbf{W}(g)$
Initial/mol	a		0
Change/mol	–0.2a		+0.4a
Eqm/mol	0.8a		0.4a

P_W = (0.4a / 1.2a) x 1 atm = 1/3 atm

P_X = (0.8a / 1.2a) x 1 atm = 2/3 atm

$K_p = P_W^2 / P_X = (1/3)^2 / (2/3) = 1/6$ atm = 0.167 atm

Option C

The final pressure inside the syringe will have to be the same as atmospheric pressure (1 atm) to ensure that the syringe stops moving.

Option D

Pushing the plunger back will decrease volume, and thus cause the pressure of the system to increase.

Based on Le Chatelier's Principle, equilibrium position will shift to the left which has lesser gaseous particles to reduce the pressure. Thus association of **W** is favoured.

11 The acid dissociation constants for the diprotic acid, malonic acid $H_2C_3H_2O_4$ are K_{a1} = 1.5 x 10^{-3} and K_{a2} = 2.0 x 10^{-6}.

What is K_b for $HC_3H_2O_4^-$?

A $K_w \times K_{a1}$

B $K_w \times K_{a2}$

C K_w / K_{a1}

D K_w / K_{a2}

Answer: **C**

$H_2C_3H_2O_4 \rightleftharpoons HC_3H_2O_4^- + H^+$ K_{a1} = 1.5 x 10^{-3}

$HC_3H_2O_4^- \rightleftharpoons C_3H_2O_4^{2-} + H^+$ K_{a2} = 2.0 x 10^{-6}

Measurement for K_b, $HC_3H_2O_4^-$ would be acting as a base accepting proton

$HC_3H_2O_4^- + H^+ \rightleftharpoons H_2C_3H_2O_4$

$K_w = K_{a1(H_2C_3H_2O_4)} \times K_{b(HC_3H_2O_4^-)}$ ($H_2C_3H_2O_4$ and $HC_3H_2O_4^-$ are conjugate acid-base pair)

$K_{b(HC_3H_2O_4^-)} = K_w / K_{a1(H_2C_3H_2O_4)}$

12 Hardness in tap water can be determined by titrating a sample against a reagent which forms complex ions with dissolved metal ions. The indicator for this titration requires the pH to be maintained at about 10.

Which of the following, in aqueous solution, could be used to do this?

A 10 cm^3 of 2.0 g dm^{-3} of sodium hydroxide neutralised by 10 cm^3 of 0.025 mol dm^{-3} of ethanoic acid

B 5 cm^3 of 1.7 g dm^{-3} of ammonia neutralised by 10 cm^3 of 0.025 mol dm^{-3} hydrochloric acid

C 20 cm^3 of 0.05 mol dm^{-3} of hydrochloric acid neutralised by 5 cm^3 of 1.7 g dm^{-3} ammonia

D 10 cm^3 of 0.05 mol dm^{-3} of ethanoic acid neutralised by 5 cm^3 of 2.0 g dm^{-3} of sodium hydroxide

Answer: **B**

To maintain solution at pH10 we need basic buffer which is made of weak base and its salt

Option (A) is made of sodium hydroxide (strong acid) and sodium ethanoate salt

Option (B) is made of ammonia and ammonium chloride (weak base and its salt)

Option (C) is made of hydrochloric acid and ammonium chloride

Option (D) is made up of ethanoic acid and sodium ethanoate

13 The solubility product of some sparingly soluble lead compounds are shown below. Which compound will have the lowest concentration of Pb^{2+} (aq) ions in a saturated solution?

	compound	numerical value of solubility product (at 25 °C)
A	lead(II) fluoride	2.7×10^{-8}
B	lead(II) bromide	4.0×10^{-5}
C	lead(II) iodide	7.1×10^{-9}
D	lead(II) sulfate	1.6×10^{-8}

For the lead halides, $K_{sp} = [Pb^{2+}][X^-]^2$ where X = F, Br or I

Let $[Pb^{2+}]$ be x mol dm^{-3}

Hence $[X^-]$ is 2x mol dm^{-3}

Ksp is hence $4x^3$

For $PbBr_2$, $[Pb^{2+}] = 0.0215$ mol dm^{-3}

For PbF_2, $[Pb^{2+}] = 1.89 \times 10^{-3}$ mol dm^{-3}

For PbI_2, $[Pb^{2+}] = 1.21 \times 10^{-3}$ mol dm^{-3}

For $PbSO_4$, $K_{sp} = [Pb^{2+}][SO_4^{2-}]$.

Hence $[Pb^{2+}] = \sqrt{K_{sp}}$

$[Pb^{2+}] = 1.26 \times 10^{-4}$ mol dm^{-3}

Answer: **D**

14 Morphine is a powerful narcotic painkiller which could be isolated from opium poppy. Though it relieves pain effectively, it can cause addiction so readily that it should only be used in the cases where other pain medications are inadequate.

morphine

Which of the following claims about morphine is true?

1 There are 5 chiral carbons present in the molecule.

2 There are 7 C–C bonds formed by sp^3 – sp^3 overlap.

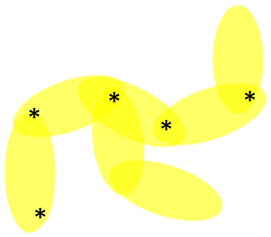
3 The molecule cannot exhibit cis-trans isomerism at the C=C double bond.

A 1 only

B 2 only

C 2 and 3 only

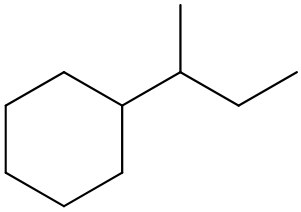
D 1, 2 and 3



There are 5 chiral carbons present in the molecule, indicated by the asterisks and there are 7 C–C bonds formed by sp^3 – sp^3 overlap, highlighted in the diagram. The molecule cannot exhibit cis-trans isomerism at the C=C double bond as the trans isomer could not exist.

Answer: **D**

15 Compound **L** reacts with limited chlorine gas in the presence of sunlight.



compound **L**, $C_{10}H_{20}$

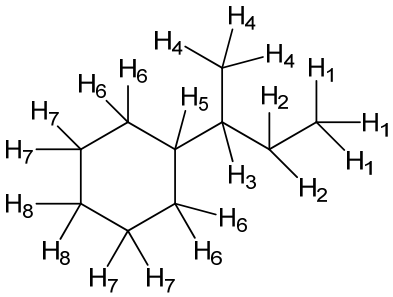
Assuming that only mono-chlorination takes place and ignoring the relative rates of abstraction of the different type of hydrogen atom, which of the following statements is **incorrect**?

A The maximum number of chlorinated products formed is 8.

B $C_{20}H_{38}$ is present in small quantities in the products.

C Homolytic fission occurs in both initiation and propagation step.

D The ratio of primary to secondary to tertiary chloroalkanes formed is 3:6:2.

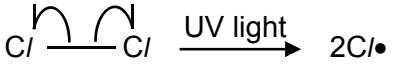


Option A is correct. The maximum number of chlorinated products formed is 8.

Option B is correct. Since compound **L** has the molecular formulae of $C_{10}H_{20}$, it can form a radical with the molecular formula of $C_{10}H_{19}$ in the first step of propagation. Hence two radicals of $C_{10}H_{19}$ can react in the termination step to form $C_{20}H_{38}$ as one of the side products.

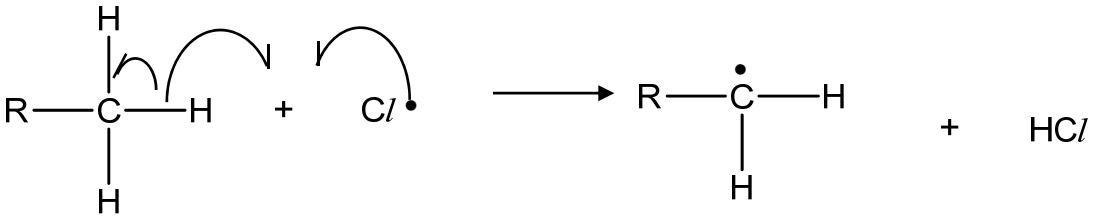
Option C is correct. Homolytic fission occurs in both initiation and propagation step.

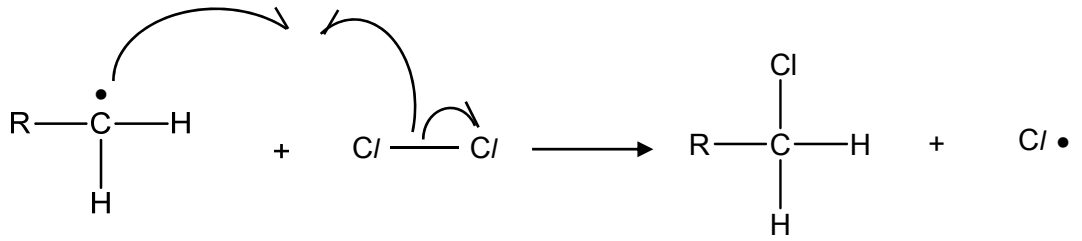
<u>Initiation step:</u>



<u>Propagation step:</u>

Let R be the rest of the molecule.





Option D is incorrect.

When H_1 and H_4 atoms are substituted (total of 6 hydrogen atoms), primary chloroalkanes will be formed.

When H_2, H_6, H_7 and H_8 atoms are substituted (total of 12 hydrogen atoms), secondary chloroalkanes will be formed.

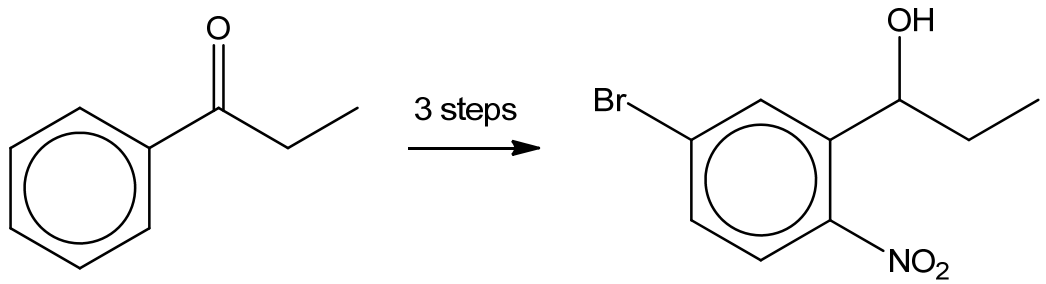
When H_3 and H_5 atoms are substituted (total of 2 hydrogen atoms), tertiary chloroalkanes will be formed.

Hence the ratio of primary to secondary to tertiary chloroalkanes formed is 6:12:2 => 3:6:1 instead of 3:6:2.

Answer: **D**

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

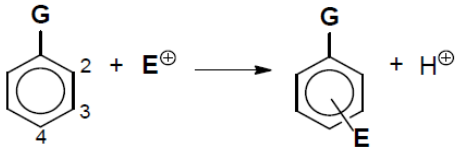
The following transformation takes place in three steps.



Which of the following shows the best choice of reagents and conditions to carry out the transformation?

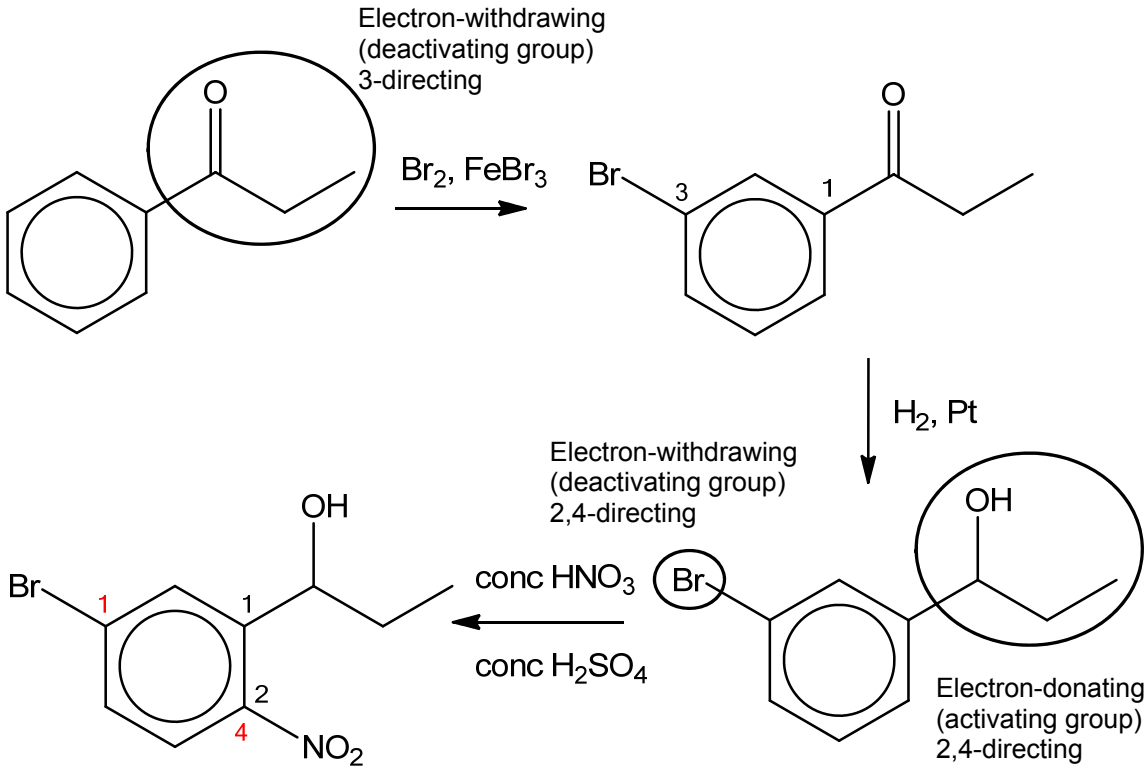
	step 1	step 2	step 3
A	H_2, Pt	conc HNO_3, conc H_2SO_4	Br_2, $FeBr_3$
B	Br_2, $FeBr_3$	H_2, Pt	conc HNO_3, conc H_2SO_4
C	H_2, Pt	Br_2, $FeBr_3$	conc HNO_3, conc H_2SO_4
D	Br_2, $FeBr_3$	conc HNO_3, conc H_2SO_4	H_2, Pt

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



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

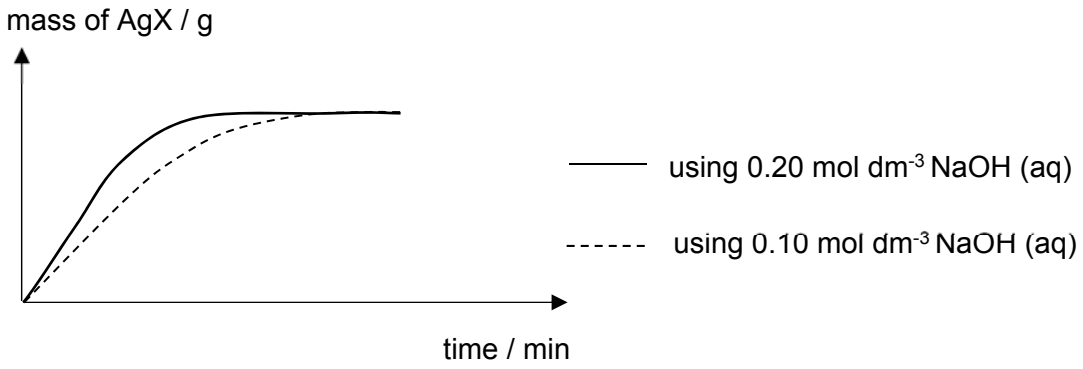
The circled groups will be needed to decide the correct way of transformation in this question.



Note that $-NO_2$ group is an electron-withdrawing group and strong deactivating, it will direct incoming electrophile to the 3rd position relative to itself.

Answer: **B**

17 A halogen-containing compound, **U**, is heated with 2 different concentrations of aqueous sodium hydroxide. After acidifying the mixture and adding excess aqueous silver nitrate, the mass of silver halide formed is analysed over a period of time. The following graph for the mass of silver halide precipitate against time was obtained.



Which of the following is the likely structure of **U**?

A **B**

C **D**

The gradient of the graph gives the rates of reaction.

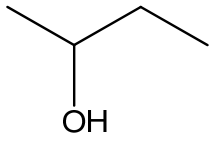
The graph shows that the rate of formation of the ppt increases when $[OH^-]$ increases from 0.10 M to 0.20 M. Hence the nucleophilic substitution of the alkyl halide involves OH^- in the slow step. (i.e. Compound U can undergo SN2 mechanism, so it must be primary or secondary alkyl halide)

A is a secondary alkyl halide, so its rate of reaction is affected by $[OH^-]$.
B is a tertiary alkyl halide, so its rate of reaction is not affected by $[OH^-]$.
C is a vinyl halide (halogen atom bonded to alkene functional group), so it is resistant to nucleophilic substitution.
D is a chloride salt, so it form silver halide ppt immediately.

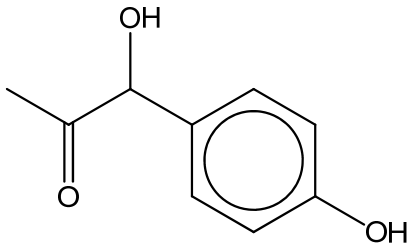
Answer: **A**

18 The following two compounds react with alkaline aqueous iodine to form yellow precipitate of tri-iodomethane as one of the products.

What is the ratio of sodium hydroxide used to react with 1 mol of compound **V** and 1 mol of compound **W** respectively?

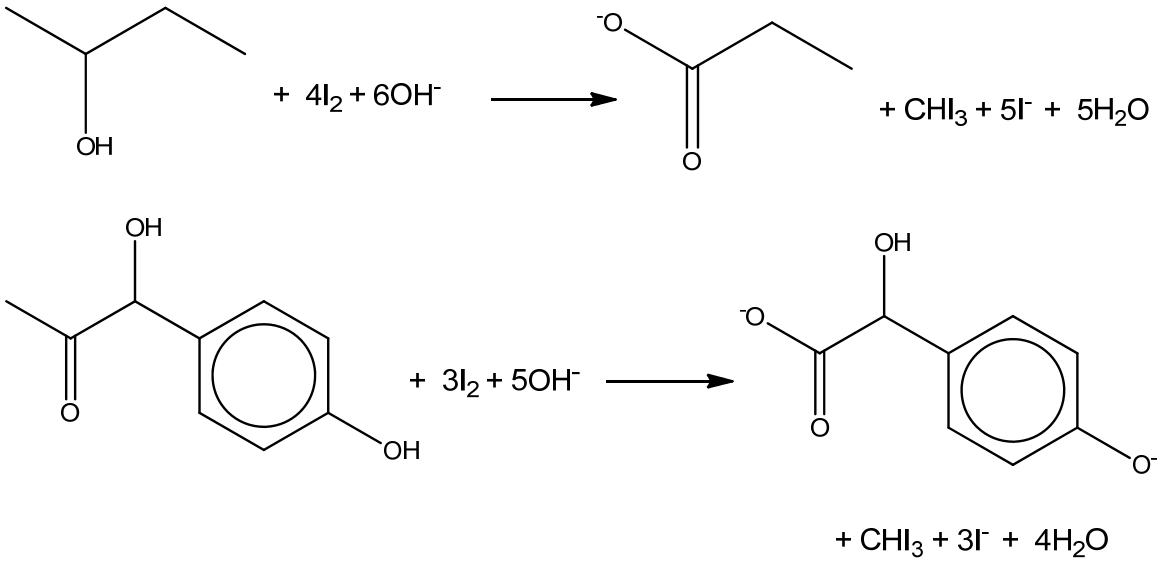


compound **V**



compound **W**

	compound **V**	compound **W**
A	4	4
B	4	6
C	6	4
D	6	5



Hence the ratio of sodium hydroxide used to react with 1 mol of compound **V** and 1 mol of compound **W** respectively is 6: 5.

Note that phenol is acidic enough to react with sodium hydroxide, but not alcohol.

Answer: **D**

19 A fresh salad with tomatoes may contain compound $CH_3CH_2CH_2CH{=}CHCHO$ which provides an aroma for tomatoes. What will be the final product, **P** in this sequence of reactions?

$$CH_3CH_2CH_2CH{=}CHCHO \xrightarrow[\text{then } H_2O]{NaBH_4 \text{ in } CH_3OH} \mathbf{O} \xrightarrow[\text{heat}]{K_2Cr_2O_7/H^+} \mathbf{P}$$

A $CH_3CH_2CH_2CH{=}CHCOOH$

B $CH_3CH_2CH_2CH_2CH_2COOH$

C $CH_3CH_2CH_2CH{=}CHCH_2OH$

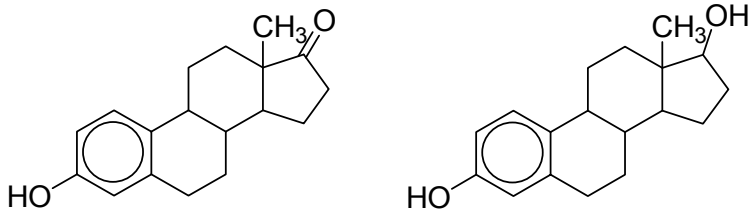
D $CH_3CH_2CH_2COOH$

In $CH_3CH_2CH_2CH{=}CHCHO$ the aldehyde group undergoes reduction by $NaBH_4$ to form primary alcohol group in P, $CH_3CH_2CH_2CH{=}CHCH_2OH$. The primary alcohol group in P is then oxidized to acid group in **Q** $CH_3CH_2CH_2CH{=}CHCOOH$ by $K_2Cr_2O_7/H^+$, heat

C=C is not reduced by $NaBH_4$ and not oxidized by $K_2Cr_2O_7/H^+$, heat

Answer: **A**

20 Two female sex hormones are oestrone and oestradiol.



oestrone oestradiol

Which of the following reagents could be used to distinguish between the two hormones?

1 $SOCl_2$

2 $KMnO_4/H^+$

3 LiA/H_4 in dry ether

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

Answer: **D** (1 only is correct)

Option 1 (Correct)

$SOCl_2$ reacts with the secondary alcohol group in oestradiol to give white fumes of HCl. Oestrone does not have the secondary alcohol group.

Option 2 (Wrong)

Both can react with $KMnO_4$ due to the alkyl side chain of benzene, in addition to the secondary alcohol group in oestradiol.

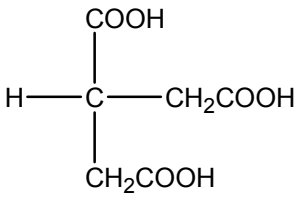
Option 3 (Wrong)

While $LiAlH_4$ reacts with the ketone group in oestrone and not with oestradiol, there is no way to distinguish based on absence of visible change.

21 Ethanoic acid can be made by direct carbonylation of methanol, in presence of a rhodium catalyst.

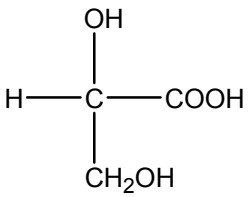
$$CH_3OH + CO \xrightarrow{\text{rhodium catalyst}} CH_3COOH$$

Which of the following can produce compound **S** using a similar method?

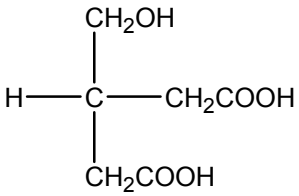


compound **S**

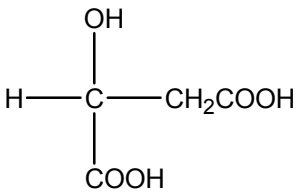
A

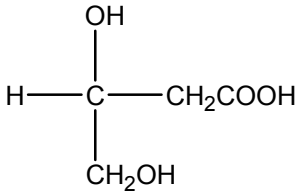


B



C

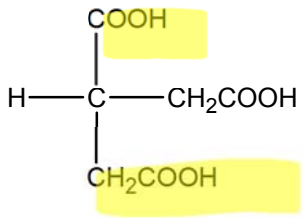


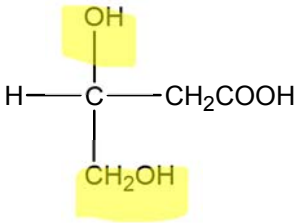
D 

Answer: D

Pattern recognition of adding a CO between the C and O atom.

$$CH_3OH + CO \xrightarrow{\text{rhodium catalyst}} CH_3COOH$$

To form compound S, 



22 Benzylamine has the formula $C_6H_5CH_2NH_2$ and is a common precursor in organic synthesis.

Which of the following statements about benzylamine is correct?

1 It reacts with excess CH_3CH_2Cl to form the compound, $C_{13}H_{22}NCl$.

2 It reacts with CH_3COOH to form $C_6H_5CH_2NHCOCH_3$.

3 It can be distinguished from $CH_3CH_2NH_2$ by the use of aqueous bromine.

A 1, 2 and 3

B 1 and 2 only

C 1 only

D 2 and 3 only

1 is correct

Benzylamine undergoes nucleophilic substitution with CH_3CH_2Cl to form a quarternary ammonium salt.

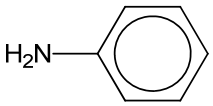
2 is incorrect

Benzylamine reacts with CH_3COOH to form an ionic salt.

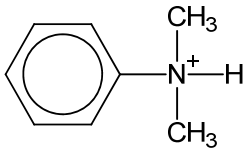
3 is incorrect

Both cannot decolourise bromine. Phenylamine will decolourise bromine but not benzylamine.

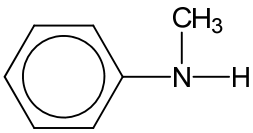
23 The structures of some nitrogen containing compounds are shown below.



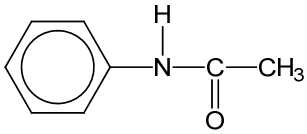
compound **H**



compound **I**



compound **J**



compound **K**

What is the order of increasing basicity of the nitrogen containing compounds?

	least basic →			most basic
A	**I**	**H**	**K**	**J**
B	**I**	**K**	**H**	**J**
C	**I**	**K**	**J**	**H**
D	**K**	**I**	**J**	**H**

Methyl group is electron donating and it increases the electron density on nitrogen in J

Lone pair of electrons on nitrogen in H is delocalised into the benzene ring , hence it is less available for accepting a proton.

K is a neutral compound as the lone pair of electrons on nitrogen is delocalised into C=O group.

I is an acidic compound due to salt hydrolysis, hence it is least basic.

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

Which statements about the elements chlorine, bromine and iodine are correct?

1 The oxidising power decreases from chlorine to iodine.

2 The bond length of the molecule increases from chlorine to iodine.

3 The magnitude of the first electron affinity increases from chlorine to iodine.

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

Option 1 (Correct)

Down the group from chlorine to iodine, increasing shielding effect results in lower effective nuclear charge, hence less ability to attract electrons resulting in decreasing oxidizing power down the group

Option 2 (Correct)

Down the group, size of atoms increases resulting in less effective orbital overlap between two halogen atoms in a covalent bond and hence longer bond length of the molecule

Option 3 (Incorrect)

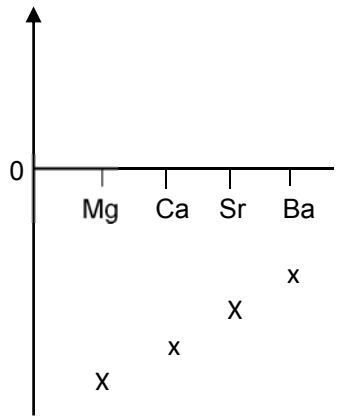
$X(g) + e^- \longrightarrow X^-(g)$

The magnitude of first electron depends on the effective nuclear charge which decreases as the shielding effect increases down the group from chlorine to iodine

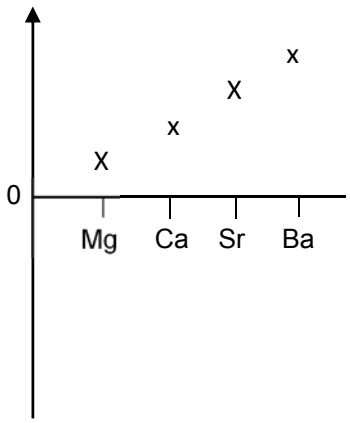
Answer: **A**

25 Which diagram correctly shows the trend in a property of the Group 2 elements Mg, Ca, Sr, Ba?

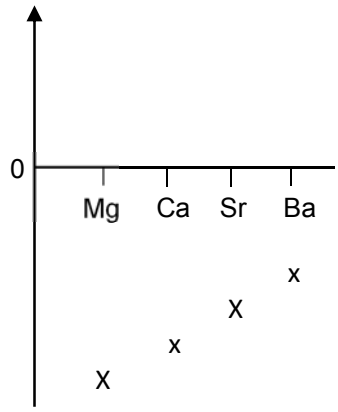
A ΔH_{hyd}, the enthalpy change of hydration of $M^{2+}(g)$



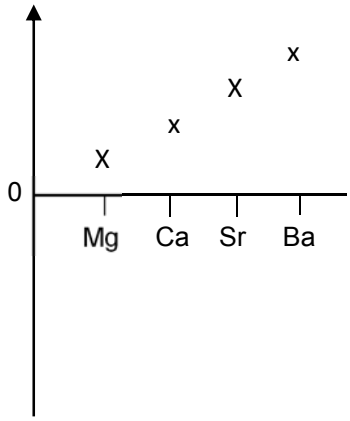
B *I*, the first ionisation energy



C $E^{\ominus}$, the standard electrode potential of $M^{2+}(aq)|M(s)$ electrode



D Electronegativity value



Enthalpy change of hydration is proportional to charge/radius of cation and it is an attraction force hence exothermic

As cation radii, increases from Mg^{2+} to Ba^{2+}, the enthalpy change of hydration becomes less exothermic.

Answer: **A**

26 Three half cells are constructed as follows.

Half cell **I**: an electrode of metal **Q** in a 1.0 M solution of $\mathbf{Q}^{+}(aq)$ ions

Half cell **II**: an electrode of metal **R** in a 1.0 M solution of $\mathbf{R}^{+}(aq)$ ions

Half cell **III**: an electrode of Cu metal in a 1.0 M solution of $Cu^{2+}(aq)$ ions

The half cells are connected in pairs, as shown below, to form a series of galvanic cells. For each cell, the polarity of the electrodes and the voltage generated are recorded.

half cells used	positive electrode	negative electrode	voltage (V)
I and **III**	Cu	**Q**	0.57
II and **III**	Cu	**R**	1.10
I and **II**	**Q**	**R**	0.53

Which one of the following lists the metals in order of **increasing** strength as reducing agents?

A **R**, **Q**, Cu

B **Q**, Cu, **R**

C Cu, **R**, **Q**

D Cu, **Q**, **R**

Answer: D

In a galvanic cell the reducing agent is oxidised; oxidation occurs at the anode; the anode is the negative electrode. In each cell the stronger reducing agent is at the negative electrode.

According to the data relative strength of the reducing agents are:

For half cells:

II and IV **Q** > Cu;

III and IV **R** > Cu;

II and III **R** > **Q**

Hence, the order of increasing strength of the reducing agents is Cu < **Q** < **R**

27 Some standard redox potential ($E^{\ominus}$) values are given in the table below.

electrode reaction	$E^{\ominus}$/ V
$Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq)$	+0.77
$Sn^{4+}(aq) + 2e \rightleftharpoons Sn^{2+}(aq)$	+0.15
$Ce^{4+}(aq) + e \rightleftharpoons Ce^{3+}(aq)$	+1.45

Which of the following reactions would occur under standard conditions?

1 $Ce^{4+}(aq) + Fe^{2+}(aq) \longrightarrow Ce^{3+}(aq) + Fe^{3+}(aq)$

2 $Sn^{2+}(aq) + 2Fe^{3+}(aq) \longrightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$

3 $2Ce^{4+}(aq) + Sn^{2+}(aq) \longrightarrow 2Ce^{3+}(aq) + Sn^{4+}(aq)$

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

Answer: A

Checking for reactions 1,2 and 3:

Reaction 1: $E^{\ominus}_{cell}$= +1.45 – 0.77 = +0.68V

Reaction 2: $E^{\ominus}_{cell}$= +0.77 – 0.15 = +0.62 V

Reaction 3: $E^{\ominus}_{cell}$= +1.45 – 0.15 = +1.3V

All the values are >0, hence the reactions are all spontaneous.

28 A current was passed through two cells connected in series. The first cell contained molten sodium chloride while the other contained a molten aluminium salt.

What would be the mass of aluminium liberated from the other cell if 4.6g of sodium was liberated from the first cell?

A 0.9 g

B 1.8 g

C 2.7 g

D 3.6 g

Answer: B

Amt of electrons transferred in the two electrolytic cells is the same.

[R]: $Na^{+} + e \rightarrow Na$ (s)

Amt of sodium = 4.6/23 = 0.2 mol

Amt of electrons = 0.2 mol

[R]: $Al^{3+} + 3e \rightarrow Al$ (s)

Amt of electrons transferred = 0.2 mol

Amt of Al = 0.2/3 = 0.06667 mol

Mass of Al = 0.06667 x 27 = 1.8g

29 Which of the following does **not** act as a ligand in the formation of complexes?

A SCN^-

B Cl^-

C AlH_4^-

D $C_2O_4^{2-}$

Out of all the species present, AlH_4^- has no available lone pairs of electrons for donation to form a dative covalent bond as all the electrons are used for bonding.

Answer: **C**

30 A reaction scheme starting from aqueous copper(II) sulfate solution is shown below. Both **X** and **Y** are copper-containing species.

$$CuSO_4(aq) \xrightarrow[\text{I}]{NH_3(aq)} \mathbf{X} \xrightarrow[\text{II}]{\text{excess } NH_3(aq)} \mathbf{Y} \xrightarrow[\text{III}]{Na_4edta(aq)} [Cu(edta)]^{2-}(aq)$$

Which of the following statements is true?

1 NH_3 acts as a ligand in reaction I.

2 Reaction II is a redox reaction.

3 The entropy of the system increases when reaction III occurs.

A 1 only

B 3 only

C 1 and 3 only

D 1, 2 and 3 only

In reaction I, NH_3 is acting as a weak base to generate OH^- a to form the ppt **X.** NH3 only acts as a ligand in reaction II.

In reaction II, it is a ligand exchange reaction, hence there is no change in the oxidation state of the metal centre.

$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$

Oxidation state of the Cu centre is still +2.

In reaction III, edta displaces the NH_3 and H_2O ligands.

$[Cu(NH_3)_4(H_2O)_2]^{2+} + edta^{4-} \rightleftharpoons [Cu(edta)]^{2-} + 4NH_3 + 2H_2O$

There is an increase in the number of particles from 2 to 7 after the reaction and hence the entropy of the system increases in reaction III.

Answer: **B**

Answer **all** the questions in the spaces provided.

1 A mixture contains two white solids **X**CO_3 and **Y**SO_4 where **X** and **Y** could be either magnesium, zinc or barium. The following investigations were carried out to determine the identity of **X** and **Y**.

(a) When the mixture of solids was treated with excess dilute hydrochloric acid, a colourless gas was evolved and some, but not all, of the mixture dissolved.

The resulting mixture was filtered. To the filtrate, dilute aqueous ammonia was added dropwise till in excess. The white precipitate formed was insoluble in excess aqueous ammonia.

Deduce the identity of elements **X** and **Y**, showing your reasoning clearly.

……..

……..

……..

……..

……..

…… [3]

(b) Group 2 carbonates decompose according to the following equation:

$$ZCO_3(s) \longrightarrow ZO(s) + CO_2(g)$$

element	magnesium	calcium	barium
enthalpy change for the reaction, ΔH_r / kJ mol^{-1}	+101	+178	+269

(i) Use the data above to state and explain the trend in the thermal stability of the Group 2 carbonates.

……

……

……

……

……

…… [3]

(ii) Lithium carbonate, a Group 1 carbonate, decomposes on heating.

Use relevant data from the Data booklet to calculate relative charge densities of the above cations and hence deduce which of the above ΔH_r values in the table is likely to be the nearest to that of lithium carbonate.

[2]

(c) Patients with digestive tract problems are sometimes asked to take an x-ray after they have swallowed a "barium meal", consisting of a suspension of $BaSO_4$ in water.

(i) Write an expression for the solubility product, K_{sp} for $BaSO_4$, including its units.

…… [2]

(ii) The numerical value of K_{sp} is 1.30×10^{-10}. Calculate $[Ba^{2+}(aq)]$ in a saturated solution of $BaSO_4$.

[1]

(iii) Although Ba^{2+} ions are toxic, the $[Ba^{2+}(aq)]$ in a saturated solution of $BaSO_4$ is too low to cause any problems of toxicity.

The numerical value of K_{sp} for $BaCO_3$ (5×10^{-10}) is not significantly higher than that of $BaSO_4$, but $BaCO_3$ is **very** poisonous if ingested. Suggest a reason why this might be so.

……

…….. [1]

(iv) $BaSO_4$ is commonly prepared in the laboratory by combining aqueous solutions containing Ba^{2+} and SO_4^{2-}.

Determine if $BaSO_4$ will form when equal volumes of 2.00×10^{-2} mol dm^{-3} aqueous $Ba(NO_3)_2$ and 4.00×10^{-2} mol dm^{-3} aqueous Na_2SO_4 are mixed.

[2]

[Total: 14]

2 A student conducted two separate electrolysis using inert electrodes under room temperature and pressure.

electrolysis reaction	electrolyte	volume of gas collected at anode / cm^3	duration
1	concentrated hydrochloric acid	150	10 minutes
2	aqueous sodium sulfate	37.5	

(a) **(i)** Write the half-equation with state symbols for the reaction occurring at the anode for electrolysis reaction **1**.

…….. [1]

(ii) Calculate the current that was used in electrolysis reaction **1**.

[2]

(b) **(i)** Write the half-equation with state symbols for the reaction occurring at the anode for electrolysis reaction **2**.

…….. [1]

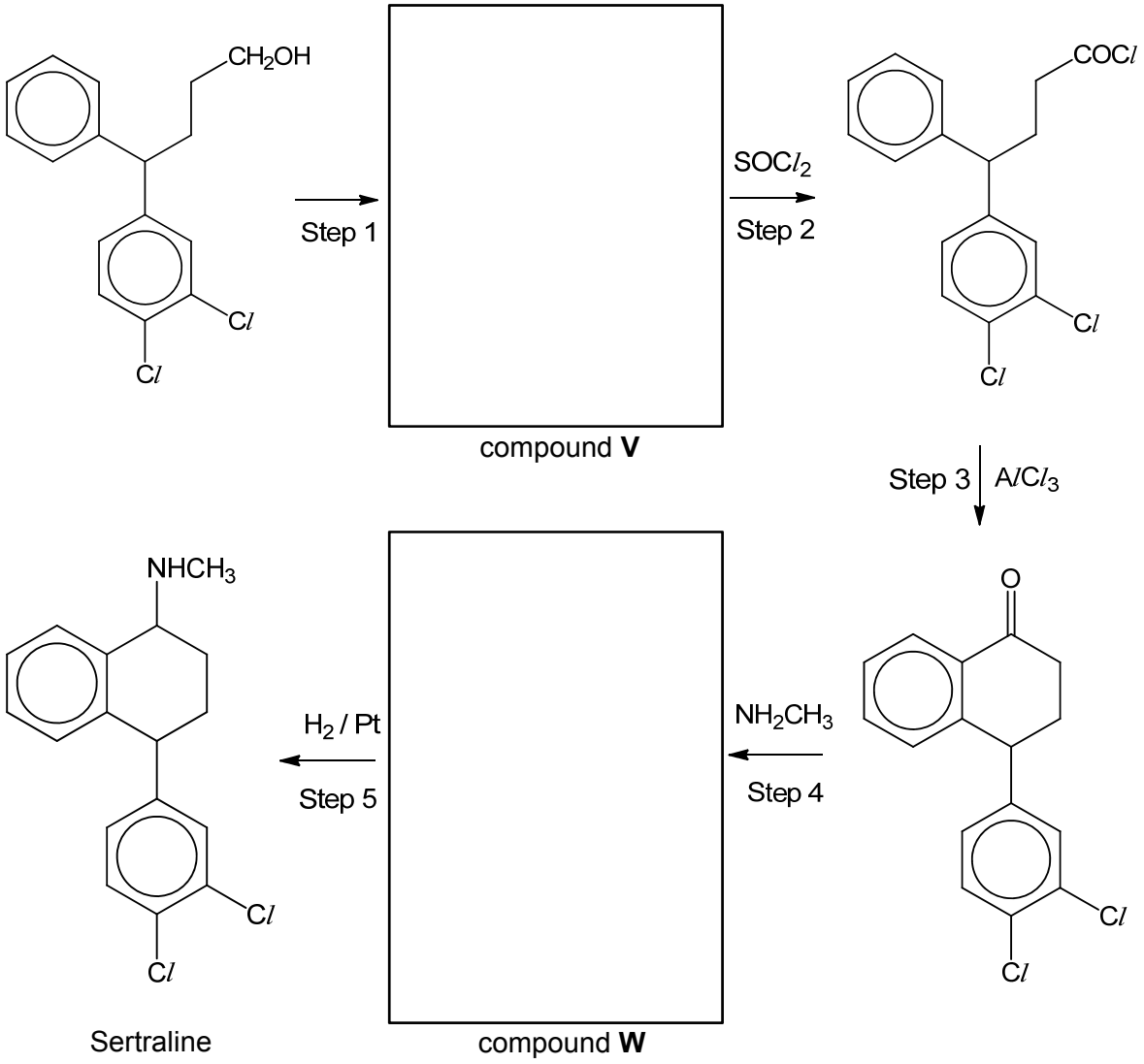
(ii) Determine the current used in electrolysis reaction **2**.

[2]

[Total: 6]

3 Sertraline is an antidepressant used to treat depression, obsessive compulsive disorder, post-traumatic stress disorder and related conditions. This medication can help to improve mood, mental alertness, energy level and sleep pattern for the patients. Sertraline works by helping to restore the balance of serotonin, a neurotransmitter in the brain which regulates anxiety, mood and happiness.

A proposed synthesis route of sertraline is shown below.

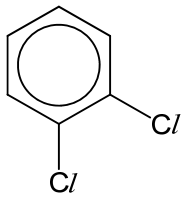


(a) State the reagents and conditions needed for step 1 and draw the structure of compound **V** in the box above.

..... [2]

(b) Electrophilic substitution takes place in step 3 where $AlCl_3$ acts as a Lewis acid catalyst and reacts with the acyl chloride functional group to generate the electrophile.

Write an equation to show the generation of the electrophile and hence draw the mechanism for the reaction that occurs in step 3.

You may use R to represent 

in Sertraline for part **(b)** and part **(d)**.

[3]

(c) State the type of reaction taking place in step 4 and draw the structure of compound **W** in the box above.

…… [2]

(d) Sertraline exists as a mixture of stereoisomers. Draw the structures of the stereoisomers of Sertraline.

[2]

[Total: 9]

4 **(a)** The change in colour from blue to pink of the cobalt complexes has been the basis of cobalt chloride indicator papers for the detection of the presence of water.

The two differently coloured cobalt(II) complex ions, $Co(H_2O)_6^{2+}$ and $CoCl_4^{2-}$, exist together in equilibrium in solution in the presence of chloride ions. This is represented by the equation below.

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

An experiment is conducted to investigate the effects on the equilibrium position by imposing a series of changes on the system. The shift in equilibrium position can be indicated by any colour change of the solution.

species	**colour**
$Co(H_2O)_6^{2+}$ (aq)	pink
$CoCl_4^{2-}$ (aq)	blue
initial equilibrium mixture containing $Co(H_2O)_6^{2+}$ and $CoCl_4^{2-}$	purple

After a 3.00 cm^3 sample of an initial equilibrium mixture was placed in three separate boiling tubes, a different substance was added to each tube, as indicated in Table 4.1.

(i) Complete Table 4.1 by predicting:
- the change in concentration, if any, of each ions in solution compared to the initial solution, after a new equilibrium position is reached.
- the colour change, if any, that takes place from the initial purple-coloured solution.

Table 4.1

Substance added	Change in concentration from initial solution to new equilibrium (increase, decrease, unchanged)			Colour change (pink, blue or unchanged)
	$[Co(H_2O)_6]^{2+}$	Cl^-	$[CoCl_4]^{2-}$	
$H_2O(l)$				
Concentrated HCl				
$AgNO_3(aq)$				

[3]

(ii) Another experiment was conducted to investigate the effect of temperature on the same equilibrium mixture. When 3.00 cm^3 of the original equilibrium mixture in a test tube was placed in an ice bath, the solution became pink.

Determine whether the forward reaction, as illustrated by the equation above, is exothermic or endothermic. Use Le Châtelier's Principle to justify your answer.

……

……

……

……

…….. [2]

(b) At room temperature, a solution of sodium tartrate, $Na_2C_4H_4O_6$, does not react with hydrogen peroxide. When heated in a water bath, the reaction mixture reacts giving a very slow stream of carbon dioxide.

When a few drops of an aqueous pink cobalt(II) salt are added, the colour of the solution soon turns green and a vigorous effervescence of carbon dioxide takes place.

When the reaction stops, the pink colour is restored.

The half equation for the oxidation of tartrate ions is given as shown:

$$C_4H_4O_6^{2-}(aq) + 8OH^-(aq) \longrightarrow 4CO_2(g) + 6H_2O(l) + 10e^-$$

(i) In alkaline medium, H_2O_2 exists as hydroperoxide ions, HO_2^-. Construct a balanced half equation for the reduction of HO_2^- to OH^-.

…….. [1]

(ii) Write a balanced ionic equation for the reaction between tartrate ions and hydroperoxide ions.

…….. [1]

(iii) Suggest why there is no reaction observed when tartrate ions and hydroperoxide ions are mixed at room temperature even though the reaction is energetically feasible.

……

……..[1]

(iv) Explain why a slow stream of carbon dioxide is observed when reaction mixture is heated in a water bath.

……

……

…….. [2]

(v) State the identity of the aqueous ions responsible for the green colour.

…….. [1]

(vi) Use your answer in **(b)(v)** to describe the catalysed two-step reactions involving aqueous cobalt ions with the tartrate ions and hydroperoxide ions.

……

……

……

…….. [2]

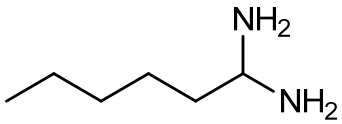
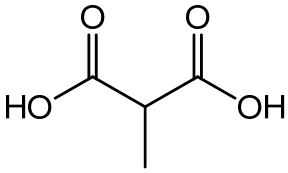
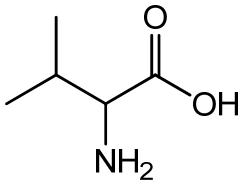
[Total: 13]

5 **(a)** Amino acids are biologically-important organic compounds containing both amine ($-NH_2$) and carboxylic acid (-COOH) functional groups.

To consider the effect of having both an amine and a carboxylic acid functional group on the same molecule, amino acids can be compared with other organic compounds such as diamines and dicarboxylic acids.

Amino acids have significantly higher melting points than diamines and dicarboxylic acids of similar mass and structure as shown in Table 5.1 below.

Table 5.1

compound type	example	molar mass /g mol^{-1}	melting point /^{o}C
diamine	 hexane-1,1-diamine	116.2	39
dicarboxylic acid	 methylpropanedioic acid	118.1	184
amino acid	 2-amino-3-methylbutanoic acid (valine)	117.2	298

Explain why the melting points show an increasing trend from diamine to amino acid in terms of structure and bonding.

……

……

……

……

……

……[4]

(b) When 50.0 cm^3 of hexane was shaken with 20.0 cm^3 of an aqueous solution containing 1.10 g of 2-amino-3-methylbutanoic acid (valine), it was found that 0.050 g of valine was extracted into the hexane. At equilibrium, the ratio of the concentration of valine in the two immiscible solvents is a constant called partition coefficient where

$$K_{partition} = \frac{[valine]_{hexane}}{[valine]_{aq}}$$

(i) Calculate the partition coefficient, $K_{partition}$, of valine between hexane and water.

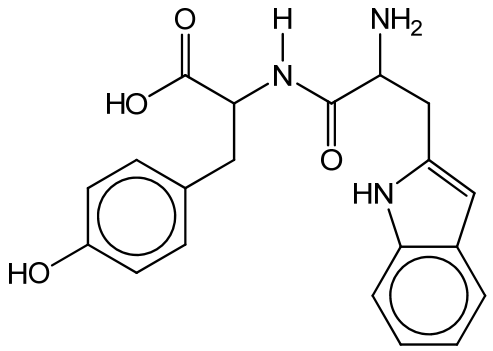
[1]

(ii) State which is a better solvent for valine and explain the reason for its solubility in that solvent.

……

…….. [2]

(c) Tryptophan is an essential amino acid found in foods such as chicken, eggs, cheese and milk. It is needed to create the neurotransmitter serotonin which promotes sleep. Two amino acids, tyrosine (tyr) and tryptophan (trp), form a dipeptide, tyr-trp, as shown by the following structure.



tyr–trp

Draw the structures of the products of the reactions of tyr-trp with an excess of each of the following reagents.

(i) NaOH(aq) at room temperature

[1]

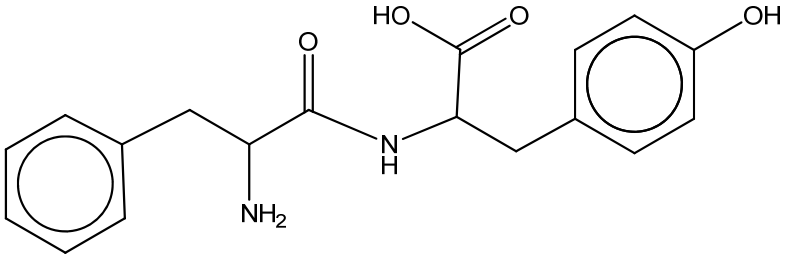
(ii) HC*l*(aq) and heat under reflux

product 1

product 2

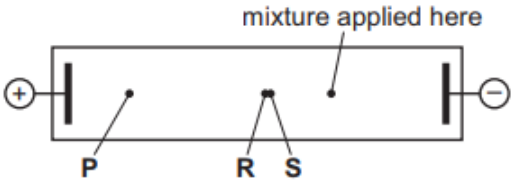
[2]

(d) Phenylalanine and tyrosine form another dipeptide (phe-tyr) as shown below



phe-tyr

A mixture of the dipeptide (phe-tyr) and its two constituent amino acids (phenylalanine and tyrosine) was subjected to electrophoresis in a buffer at pH 12. At the end of the experiment the following results were seen. Spots **R** and **S** remained very close together.



The three spots are due to the three species phenylalanine, tyrosine and the dipeptide, phe-tyr.

(i) Draw the structural formula of the species responsible for spot **P.**

[1]

(ii) Suggest why the other two species give spots **R** and **S** that are so close together.

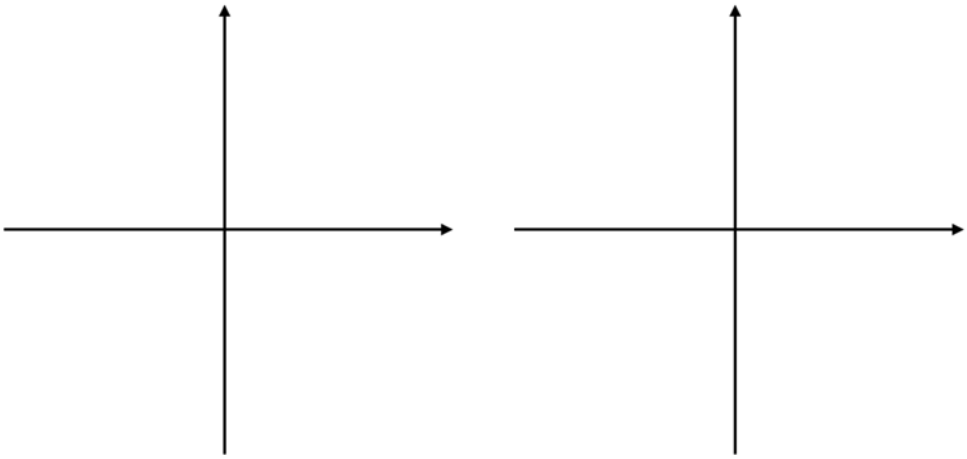
……

…….. [1]

[Total: 12]

6 In an isolated transition metal atom, the five 3d-orbitals are degenerate. However, in an octahedral complex ion, the presence of ligands splits the five orbitals into a group of three and a group of two. These two groups have slightly different energies.

(a) Using the axes provided below, draw and label the shape of **one** d-orbital in **each** of the two groups mentioned above.



[2]

(b) Explain how the presence of the six ligands, **L**, in $[Ni\mathbf{L}_6]^{2+}$ splits the five 3d orbitals into two groups of different energy, and explain whether the two-orbital group or the three-orbital group has the higher energy.

…….....

……..

……..

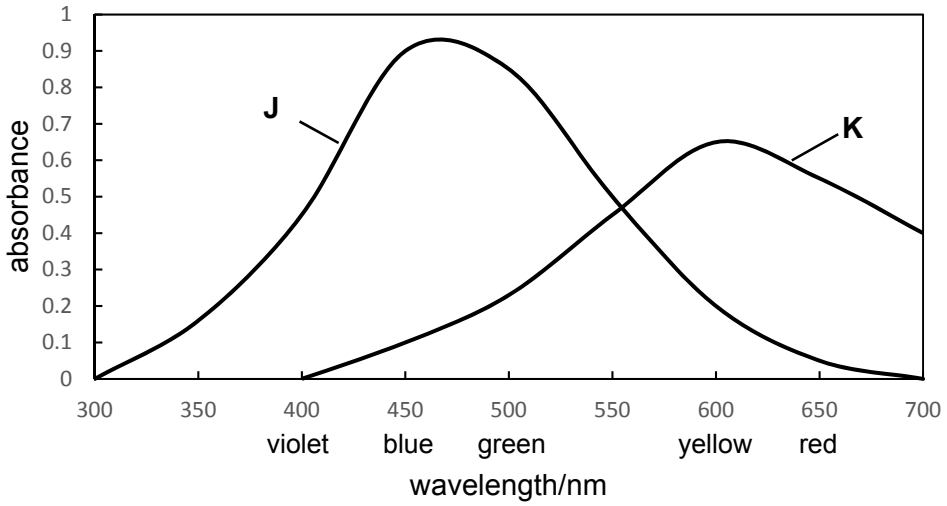
……..

……..

……..

……. [3]

(c) The absorbance spectra of solutions of two transition metal complexes **J** and **K** are shown in the diagram below.



A list of possible colours for these complexes is as follows.

yellow red green blue

Choose one of the colours above to describe the observed colour of each solution.

Solution **J** …….. Solution **K** ……..

[2]

(d) Ligands are classified based on their ability to split the five 3d orbitals into two groups with an energy difference (ΔE). Strong field ligands produce a large ΔE while weak field ligands produce a small ΔE.

The energy of a photon can be obtained by Planck's equation:

$$E = \frac{hc}{\lambda}$$

where: E is the energy of the photon (in J)
λ is the wavelength of the photon (in m)
h is Planck's constant
c is the speed of light in vacuum

Use the data below as well as data from the *Data Booklet*, complete the table and arrange the ligands in order of increasing field strength.

species	$[M(CN)_6]^{2-}$	$[M(F)_6]^{4-}$	$[M(H_2O)_6]^{2+}$
λ / nm	430	650	600
ΔE / J			

Increasing field strength: ……<……<……. [2]

[Total: 9]

7 The oxidising power of our atmosphere has been well-studied and is of importance as many environmental trace gases, such as methane, are removed.

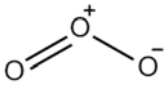
The most abundant oxidants in the atmosphere are oxygen and ozone molecules. These molecules have strong bonds and are hence relatively unreactive except towards radicals. Research in the 1950s suggested that the hydroxyl radical, •OH, is a strong oxidant.

In the stratosphere, UV light from the sun heterolytically breaks ozone molecules into oxygen molecules and oxygen atoms. The oxygen atoms react homolytically with water vapour to produce hydroxyl radicals, •OH.

$$O_3 \xrightarrow{UV} O_2 + O \qquad \text{----------(1)}$$

$$O + H_2O \longrightarrow 2\bullet OH \qquad \text{----------(2)}$$

(a) Use equations (1) and (2) to draw the mechanism for the formation of the hydroxyl radical, •OH. Include in your mechanism the necessary curly arrows and electrons.

Use  as the structure of ozone.

[2]

(b) Hydroxyl radicals are particularly reactive towards H-containing molecules due to H-abstraction converting •OH back to H_2O.

$$\bullet OH + CH_4 \longrightarrow H_2O + \bullet CH_3 \qquad \text{----------(3)}$$

Some information about an elementary reaction (3) was obtained.

[•OH] / molecules cm^{-3}	1.0×10^{6}
$[CH_4]$ / molecules cm^{-3}	4.4×10^{13}
rate constant, k / cm^3 $molecule^{-1}$ s^{-1}	1.4×10^{-5}

Source: Jacob, D. J. Introduction to Atmospheric Chemistry; Princeton University Press: 1999

(i) Use information in the table to write an equation to represent the rate equation for the pseudo-first-order reaction with respect to the concentration of the hydroxyl radical, •OH.

…….. [1]

(ii) Calculate the half-life of the hydroxyl radical, •OH to the nearest **2 significant figures**.

[2]

(c) The relative rates of disappearance in air at 305 K for a series of hydrocarbons were measured in an environmental chamber under simulated atmospheric conditions. Absolute rate constants obtained from the reaction are as follows.

hydrocarbon	k / × 10^9 mol^{-1} dm^3 s^{-1}
butane	1.8
hexane	3.8
cis-but-2-ene	39.2

Source: J. Phys. Chem. 80, 8, 789-794

(i) Use the information given in **(b)** and refer to the bonding within butane and hexane to suggest a reason for the difference in their reactivity.

……..

…….. [1]

(ii) The reaction between hydroxyl radicals and alkenes proceed via a different mechanism and this increases the rate of reaction.

Account for this difference referring to the terms 'sigma' and 'pi'.

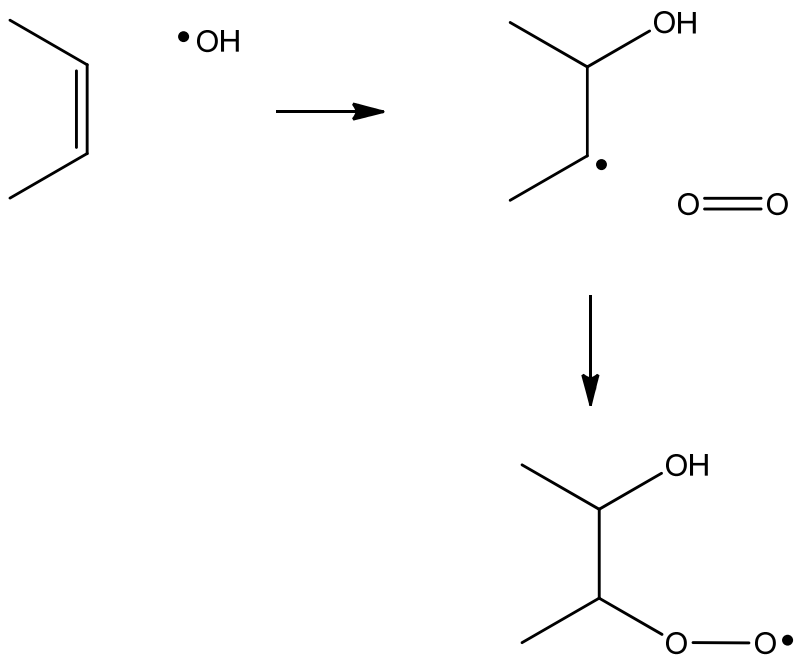
……..

……..

…….. [1]

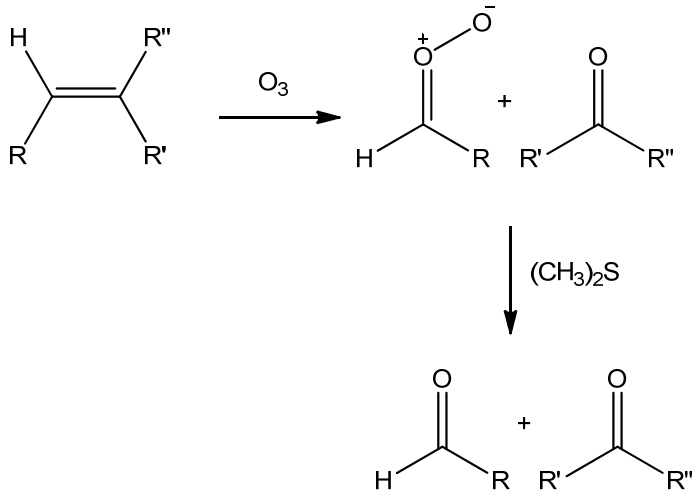
After the attack of the hydroxyl radical on cis-but-2-ene, the intermediate is now reactive enough to react with molecular oxygen.

(iii) Complete the diagram to suggest a mechanism to show how the hydroxyperoxyl radical is formed. Show the movement of electrons by using curly arrows.

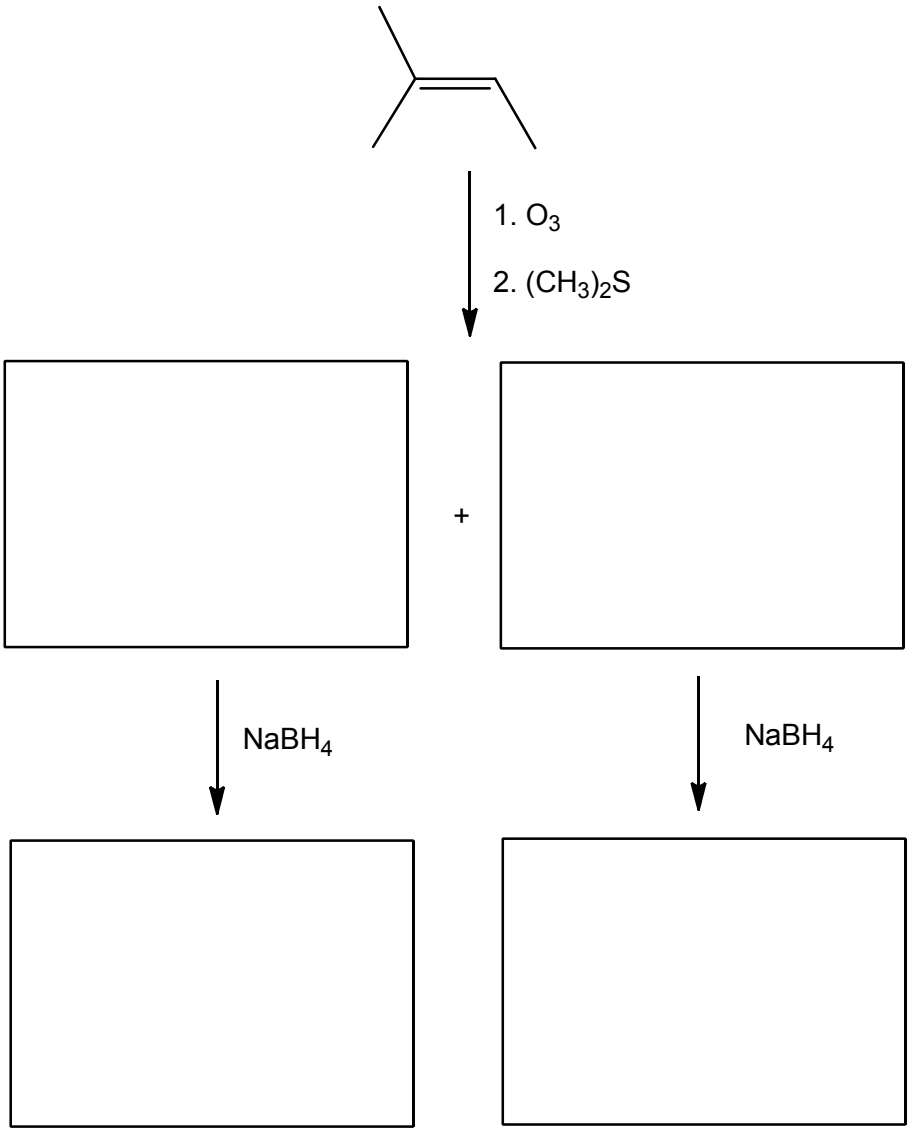


[2]

(d) Alkenes can also react with ozone directly via a process known as ozonolysis and the first step produces a carbonyl oxide and a carbonyl compound. Quenching with dimethyl sulfide produces two carbonyl compounds.



Complete the reaction scheme below.



[3]

[Total: 12]

Answer **all** the questions in the spaces provided.

1 A mixture contains two white solids **X**CO_3 and **Y**SO_4 where **X** and **Y** could be either magnesium, zinc or barium. The following investigations were carried out to determine the identity of **X** and **Y**.

(a) When the mixture of solids was treated with excess dilute hydrochloric acid, a colourless gas was evolved and some, but not all, of the mixture dissolved.

The resulting mixture was filtered. To the filtrate, dilute aqueous ammonia was added dropwise till in excess. The white precipitate formed was insoluble in excess aqueous ammonia.

Deduce the identity of elements **X** and **Y**, showing your reasoning clearly. [3]

- **X- Mg Y- Ba**
- **<u>$BaSO_4$ insoluble</u> in dil HCl ,**
- **filtrate contains Mg^{2+} which ppt to form <u>$Mg(OH)_2$ white ppt insol in excess aq ammonia</u>**
  OR
- **White ppt contains Mg^{2+} as Zn^{2+} forms ppt but it is soluble in excess NH_3**

(b) Group 2 carbonates decompose according to the following equation:

$$ZCO_3\ (s) \longrightarrow ZO\ (s) + CO_2\ (g)$$

element	magnesium	calcium	barium
enthalpy change for the reaction, ΔH_r/ kJ mol^{-1}	+101	+178	+269

(i) Use the data above to state and explain the trend in the thermal stability of the Group 2 carbonates. [3]

- **ΔH_r become more endo, thermal stability increases**
- **increasing ionic radii leading to decreasing charge density/ polarising power and**
- **less distortion of electron cloud of large anion**

(ii) Lithium carbonate, a Group 1 carbonate, decomposes on heating.

Use relevant data from the Data booklet to calculate relative charge densities of the above cations and hence deduce which of the above ΔH_r values in the table is likely to be the nearest to that of lithium carbonate. [2]

	Mg^{2+}	Ca^{2+}	Ba^{2+}	Li^{+}
Relative charge density	**2/0.065 =30.8**	**2/0.099 =20.2**	**2/0.135 =14.8**	**1/0.06 =16.7**

ΔH_r of Li_2CO_3 resembles that of $BaCO_3$

(c) Patients with digestive tract problems are sometimes asked to take an x-ray after they have swallowed a "barium meal", consisting of a suspension of $BaSO_4$ in water.

(i) Write an expression for the solubility product, K_{sp}, for $BaSO_4$, including its units.

$K_{sp} = [Ba^{2+}][SO_4^{2-}]$ units: $mol^2\ dm^{-6}$

(ii) The numerical value of K_{sp} is 1.30×10^{-10}. Calculate $[Ba^{2+}(aq)]$ in a saturated solution of $BaSO_4$.

In saturated solution, IP = K_{sp}
$[Ba^{2+}] = \sqrt{1.30 \times 10^{-10}} = 1.14 \times 10^{-5}$ mol dm^{-3}

(iii) Although Ba^{2+} ions are toxic, the $[Ba^{2+}(aq)]$ in a saturated solution of $BaSO_4$ is too low to cause any problems of toxicity.

The numerical value of K_{sp} for $BaCO_3$ (5×10^{-10}) is not significantly higher than that of $BaSO_4$, but $BaCO_3$ is **very** poisonous if ingested. Suggest a reason why this might be so.

$BaCO_3$ reacts with the acid in the stomach to release Ba^{2+} ions.

(iv) $BaSO_4$ is commonly prepared in the laboratory by combining solutions containing Ba^{2+} and SO_4^{2-}.

Determine if $BaSO_4$ will form when equal volumes of 2.00×10^{-2} mol dm^{-3} $Ba(NO_3)_2$ and 4.00×10^{-2} mol dm^{-3} Na_2SO_4 are mixed.

$[Ba^{2+}]$ after mixing = 1.00×10^{-2} mol dm^{-3}
$[SO_4^{2-}]$ after mixing = 2.00×10^{-2} mol dm^{-3}

IP on mixing = $2.00 \times 10^{-4} > K_{sp}$ (1.14×10^{-10})
Hence precipitation will take place.

[2]

[Total: 14]

2 A student conducted two separate electrolysis using inert electrodes under room temperature and pressure.

electrolysis reaction	electrolyte	volume of gas collected at anode / cm^3	duration
1	concentrated hydrochloric acid	150	10 minutes
2	aqueous sodium sulfate	37.5	

(a) **(i)** Write the half-equation with state symbols for the reaction occurring at the anode for electrolysis reaction **1**. [1]

$2Cl^-$ (aq) → Cl_2 (g)+ $2e^-$

(ii) Calculate the current that was used in electrolysis reaction **1**. [2]

Amt of Cl_2 collected = 150/24000 = 6.25 x 10^{-3} mol

Amt of electrons passed through = 6.25 x 10^{-3} x 2 = 0.0125 mol

Quantity of charge passed through = 0.0125 x 96500 = 1206.25 C

Current used = 1206.25 / (10 x 60) = 2.01 A

(b) **(i)** Write the half-equation with state symbols for the reaction occurring at the anode for electrolysis reaction **2**. [1]

$2H_2O$ (l) → O_2 (g) + $4H^+$ (aq) + $4e^-$

(ii) Determine the current used in electrolysis reaction **2**. [2]

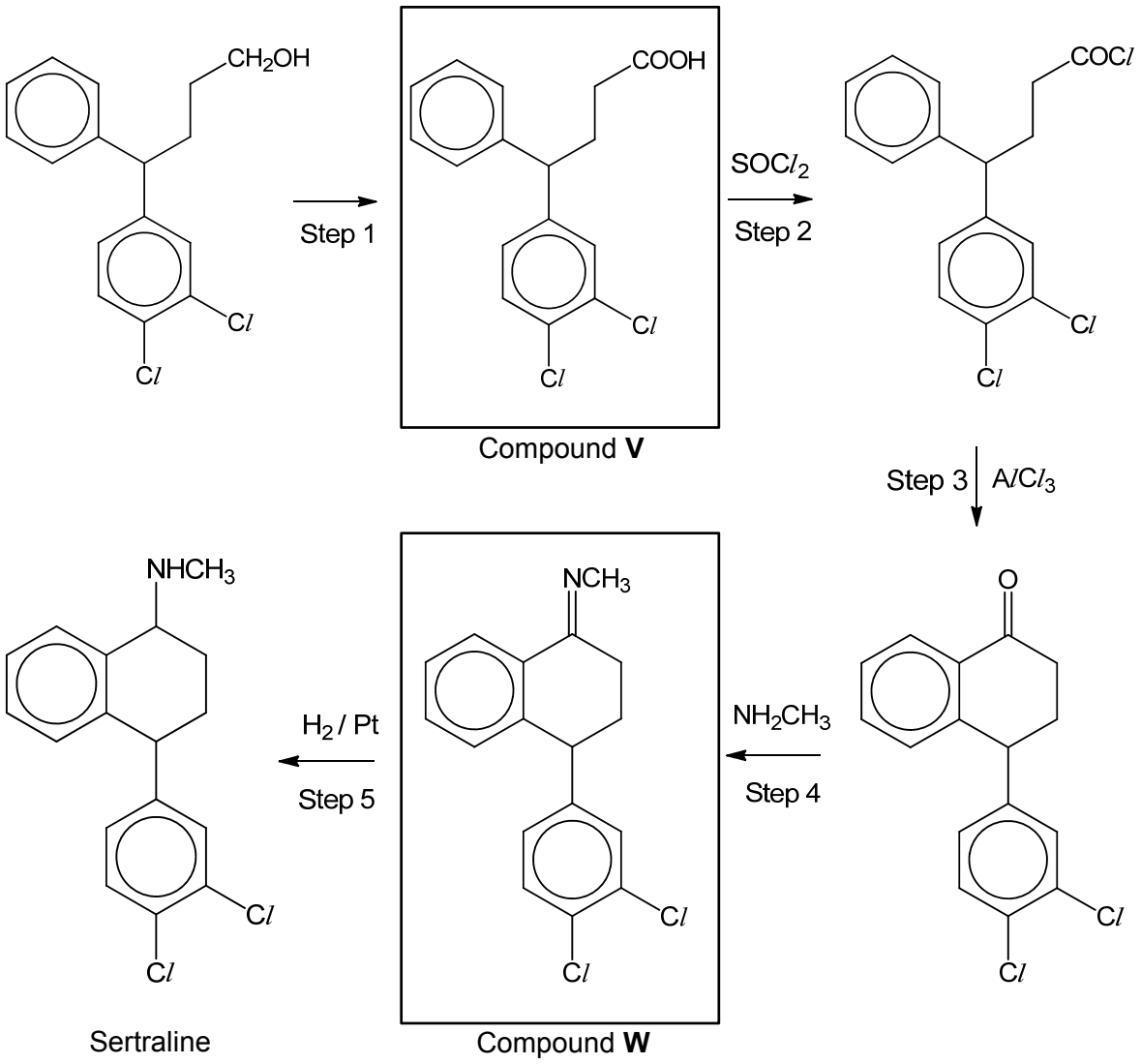
If the current used was the same, the volume of gas obtained in reaction should be halved based on the number of e- required. Since the volume of gas is four times less than that in reaction 1, the current used must be halved.

Current used = ½ x 2.01 =1.005 = 1.01A

[Total: 6]

3 Sertraline is an antidepressant used to treat depression, obsessive compulsive disorder, post-traumatic stress disorder and related conditions. This medication can help to improve mood, mental alertness, energy level and sleep pattern for the patients. Sertraline works by helping to restore the balance of serotonin, a neurotransmitter in the brain which regulates anxiety, mood and happiness.

A proposed synthesis route of sertraline is shown below.

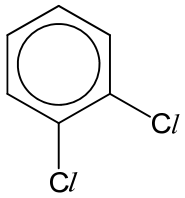


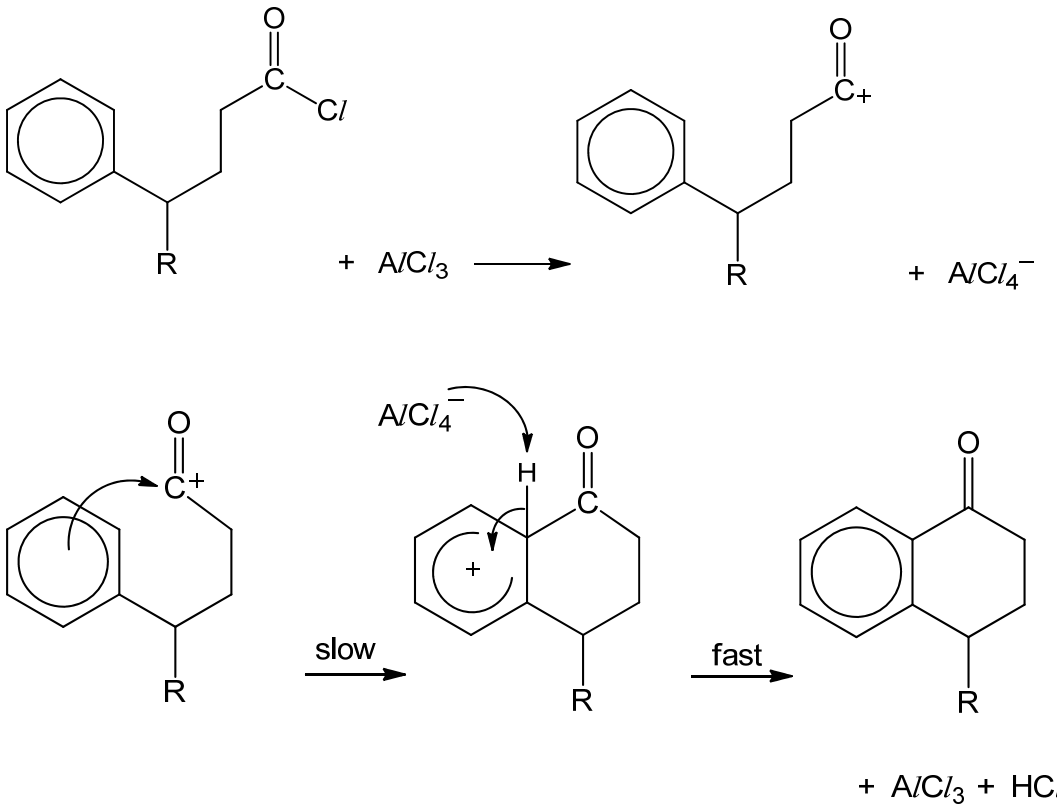
(a) State the reagents and conditions needed for step 1 and draw the structure of compound **V** in the box above.

$K_2Cr_2O_7$, dilute H_2SO_4, heat under reflux

(b) Electrophilic substitution takes place in step 3 where $AlCl_3$ acts as a Lewis acid catalyst and reacts with the acyl chloride functional group to generate the electrophile.

Write an equation to show the generation of the electrophile and hence draw the mechanism for the reaction that occurs in step 3.

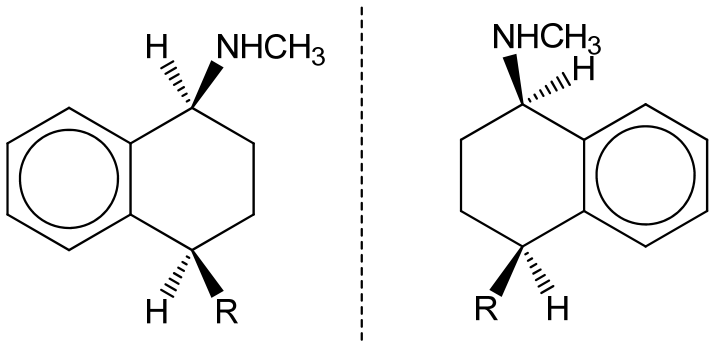
You may use R to represent  in Sertraline for part **(b)** and part **(d)**.

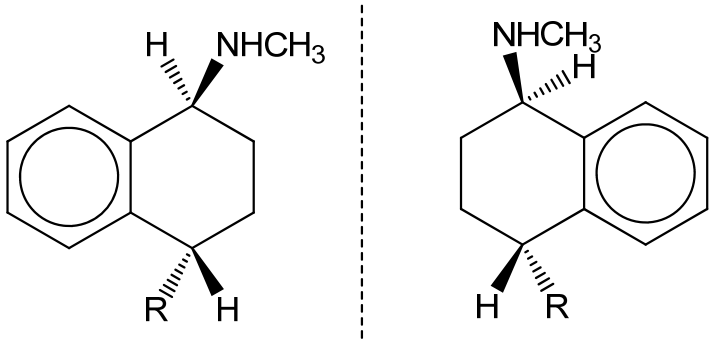


(c) State the type of reaction taking place in step 4 and draw the structure of compound **W** in the box above.

Condensation

(d) Sertraline exists as a mixture of stereoisomers. Draw the structures of the stereoisomers of Sertraline.





[Total: 9]

4 **(a)** The change in colour from blue to pink of the cobalt complexes has been the basis of cobalt chloride indicator papers for the detection of the presence of water.

The two differently coloured cobalt(II) complex ions, $Co(H_2O)_6^{2+}$ and $CoCl_4^{2-}$, exist together in equilibrium in solution in the presence of chloride ions. This is represented by the equation below.

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

An experiment is conducted to investigate the effects on the equilibrium position by imposing a series of changes on the system. The shift in equilibrium position can be indicated by any colour change of the solution.

species	colour
$Co(H_2O)_6^{2+}$ (aq)	pink
$CoCl_4^{2-}$ (aq)	blue
initial equilibrium mixture containing $Co(H_2O)_6^{2+}$ and $CoCl_4^{2-}$	purple

After a 3.00 cm^3 sample of an initial equilibrium mixture was placed in three separate boiling tubes, a different substance was added to each tube, as indicated in Table 4.1.

(i) Complete Table 4.1 by predicting:
- the change in concentration, if any, of each ions in solution compared to the initial solution, after a new equilibrium position is reached.
- the colour change, if any, that takes place from the initial purple-coloured solution.

Table 4.1

Substance added	Change in concentration from initial solution to new equilibrium (increase, decrease, unchanged)			Colour change (pink, blue or unchanged)
	$[Co(H_2O)_6]^{2+}$	Cl^-	$[CoCl_4]^{2-}$	
$H_2O(l)$				
Concentrated HCl				

$AgNO_3(aq)$				

[3]

Substance added	Change in concentration from initial equilibrium to final equilibrium (increase, decrease, unchanged)			Colour favoured (pink, blue or unchanged)
	$[Co(H_2O)_6]^{2+}$	Cl^-	$[CoCl_4]^{2-}$	
$H_2O(l)$	**decrease**	**decrease**	**decrease**	**pink**
Concentrated HCl	**decrease**	**increase**	**increase**	**blue**
$AgNO_3(aq)$	**increase**	**decrease**	**decrease**	**pink**

[3]

(ii) Another experiment was conducted to investigate the effect of temperature on the same equilibrium mixture. When 3.00 cm^3 of the original equilibrium mixture in a test tube was placed in an ice bath, the solution became pink.

Determine whether the forward reaction, as illustrated by the equation above, is exothermic or endothermic. Use Le Châtelier's Principle to justify your answer.

A decrease in temperature shifts position of equilibrium to the left (pink colour) and a decrease in temperature favours exothermic reaction to release heat.

Hence the reverse reaction is exothermic and the forward reaction is endothermic.

(b) At room temperature, a solution of sodium tartrate, $Na_2C_4H_4O_6$, does not react with hydrogen peroxide. When heated in a water bath, the reaction mixture reacts giving a very slow stream of carbon dioxide.

When a few drops of an aqueous pink cobalt(II) salt are added, the colour of the solution soon turns green and a vigorous effervescence of carbon dioxide takes place.

When the reaction stops, the pink colour is restored.

The half equation for the oxidation of tartrate ions is given as shown:

$$C_4H_4O_6^{2-}(aq) + 8OH^-(aq) \longrightarrow 4CO_2(g) + 6H_2O(l) + 10e^-$$

(i) In alkaline medium, H_2O_2 exists as hydroperoxide ions, HO_2^-. Construct a balanced half equation for the reduction of HO_2^- to OH^-.

$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$

(ii) Write a balanced ionic equation for the reaction between tartrate ions and hydroperoxide ions.

Oxidation half-equation
$C_4H_4O_6^{2-} + 8OH^- \rightarrow 4CO_2 + 6H_2O + 10e^-$

Reduction half-equation

$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$

Balanced eqn:
$C_4H_4O_6^{2-} + 5\ HO_2^- \rightarrow 4CO_2 + H_2O + 7OH^-$

(iii) Suggest why there is no reaction observed when tartrate ions and hydroperoxide ions are mixed at room temperature even though the reaction is energetically feasible.

The activation energy is high due to electrostatic repulsion between the two negatively charged ions.

(iv) Explain why a slow stream of carbon dioxide is observed when reaction mixture is heated in a water bath.

As temperature increases, more particles have energy more than or equal to the activation energy and
hence frequency of effective collision increases and rate increases.

(v) State the identity of the aqueous ions responsible for the green colour.

Aqueous cobalt (III) ions

(vi) Use your answer in **(b)(v)** to describe the catalysed two-step reactions involving aqueous cobalt ions with the tartrate ions and hydroperoxide ions.

New mechanism:

Step 1- pink cobalt(II) ions is oxidised by hydroperoxide ions to green cobalt(III) ions

Step 2-green cobalt(III) ions are reduced by tartrate ions back to pink cobalt(II) ions, thus regenerating the catalyst.

Or
Step 1
$2Co^{2+} + HO_2^- + H_2O \rightarrow 2Co^{3+} + 3OH^-$

Step 2
$C_4H_4O_6^{2-} + 8OH^- + 10Co^{3+} \rightarrow 4CO_2 + 6H_2O + 10Co^{2+}$

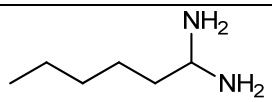
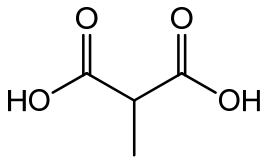
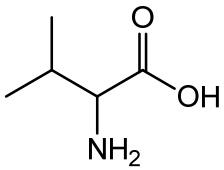
[Total: 13]

5 **(a)** Amino acids are biologically-important organic compounds containing both amine ($-NH_2$) and carboxylic acid (-COOH) functional groups.

To consider the effect of having both an amine and a carboxylic acid functional group on the same molecule, amino acids can be compared with other organic compounds such as diamines and dicarboxylic acids.

Amino acids have significantly higher melting points than diamines and dicarboxylic acids of similar mass and structure as shown in Table 5.1 below.

Table 5.1

compound type	example	molar mass / g mol^{-1}	melting point / ^{o}C
diamine	 hexane-1,1-diamine	116.2	39
dicarboxylic acid	 methylpropanedioic acid	118.1	184
amino acid	 2-amino-3-methylbutanoic acid (valine)	117.2	298

Explain why the melting points show an increasing trend from diamine to amino acid in terms of structure and bonding.

Diamine and dicarboxylic acid have simple molecular structures with hydrogen bonds between polar molecules.

Dicarboxylic acid has stronger hydrogen bonds than diamine as O-H bond is more polarised and has more extensive hydrogen bonds than diamines.

Hence more energy is needed to break hydrogen bonds in dicarboxylic acid than in diamine, hence it has higher m.p.

Valine has a giant ionic lattice with strong electrostatic forces of attraction(or ionic-bonds) between the zwitterions.

More energy is needed to break stronger ionic bonds compared to hydrogen bonds, hence it has the highest m.p.

(b) When 50.0 cm^3 of hexane was shaken with 20.0 cm^3 of an aqueous solution containing 1.10 g of 2-amino-3-methylbutanoic acid (valine), it was found that 0.050 g of valine was extracted into the hexane. At equilibrium, the ratio of the concentration of valine in the two immiscible solvents is a constant called partition coefficient where

$$K_{\text{partition}} = \frac{[\text{valine}]_{\text{hexane}}}{[\text{valine}]_{\text{aq}}}$$

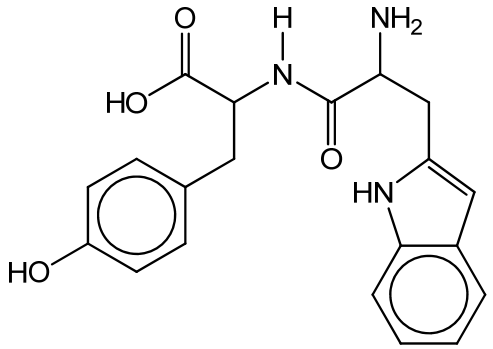
(i) Calculate the partition coefficient, $K_{\text{partition}}$, of valine between hexane and water.

$K_{\text{partition}}$ = $[\text{valine}]_{\text{hexane}}/[\text{valine}]_{\text{aq}}$
= (0.05/50)/(1.05/20) = 0.0190

(ii) State which is a better solvent for valine and explain the reason for its solubility in that solvent.

Water is a better solvent as valine exists as zwitterion and forms ion-dipole interactions with water.

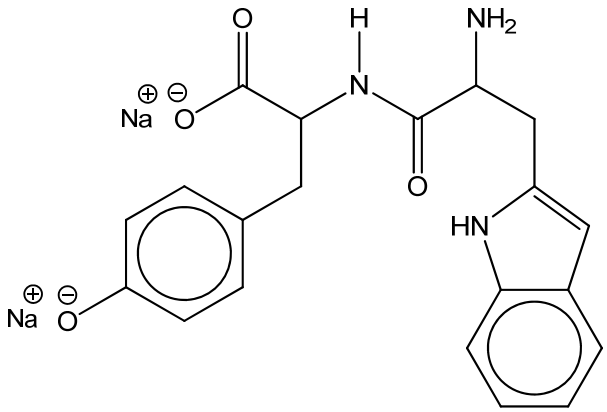
(c) Tryptophan is an essential amino acid found in foods such as chicken, eggs, cheese and milk. It is needed to create the neurotransmitter serotonin which promotes sleep. Two amino acids, tyrosine (tyr) and tryptophan (trp), form a dipeptide, tyr-trp, as shown by the following structure.



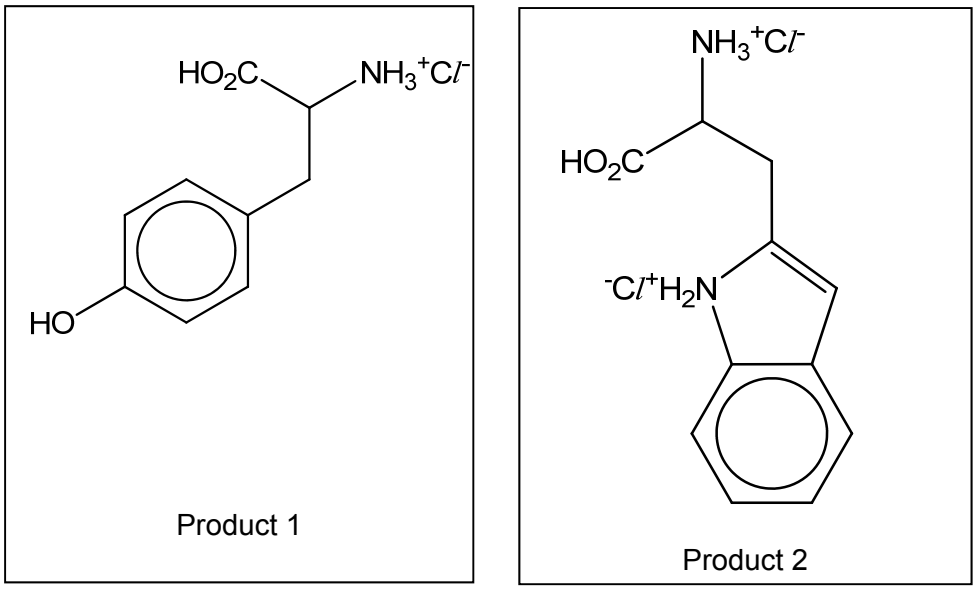
tyr–trp

Draw the structures of the products of the reactions of tyr-trp with an excess of each of the following reagents.

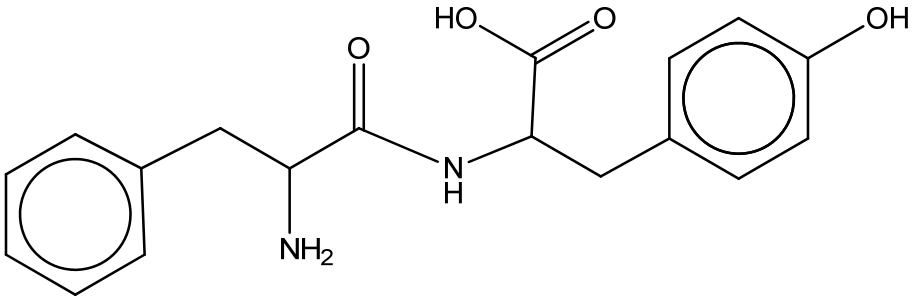
(i) NaOH(aq) at room temperature



(ii) HC*l*(aq) and heat under reflux

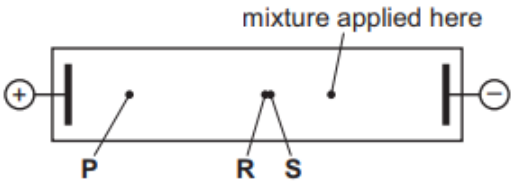


(d) Phenylalanine and tyrosine form another dipeptide (phe-tyr) as shown below.



phe-tyr

A mixture of the dipeptide (phe-tyr) and its two constituent amino acids (phenylalanine and tyrosine) was subjected to electrophoresis in a buffer at pH 12. At the end of the experiment the following results were seen. Spots **R** and **S** remained very close together.



The three spots are due to the three species phenylalanine, tyrosine and the dipeptide, phe-tyr.

(i) Draw the structural formula of the species responsible for spot **P.**

[1]

(ii) Suggest why the other two species give spots **R** and **S** that are so close together.

dipeptide / phe-tyr) has 2– and its M_r is about double that of phe with 1

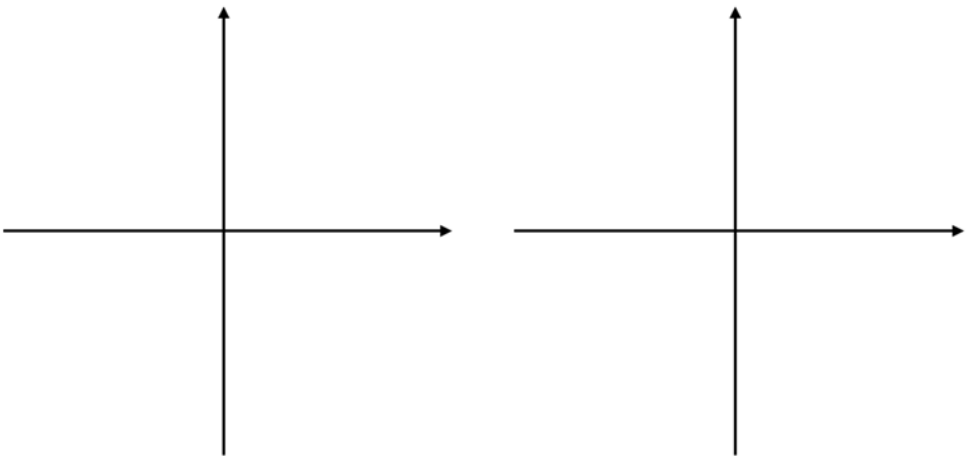
OR

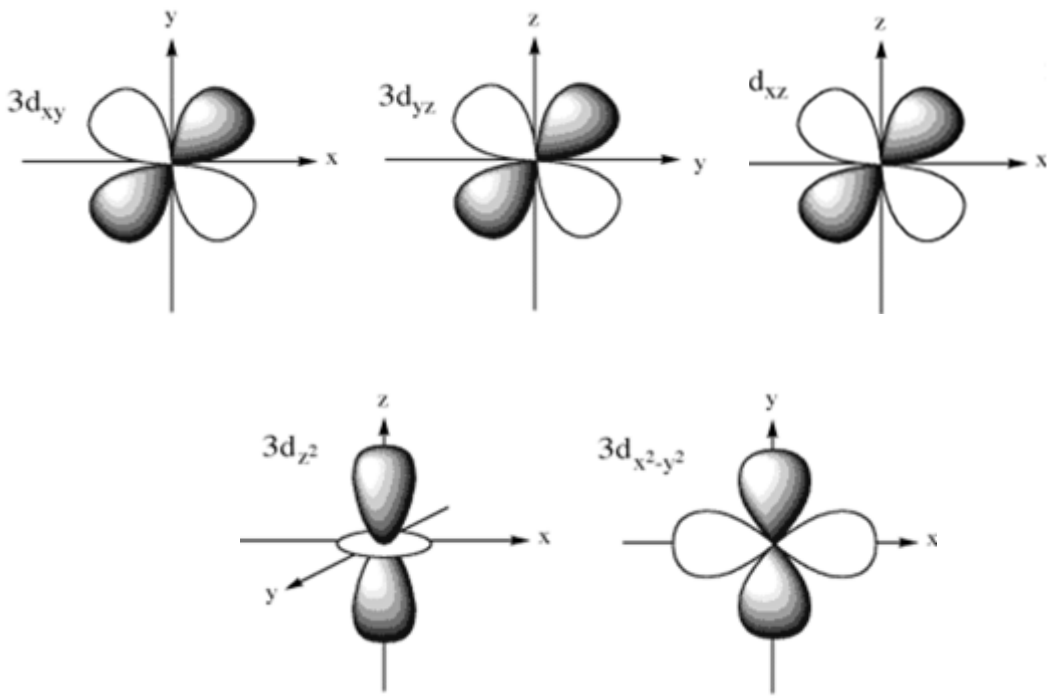
charge / mass ratios are about the same for the dipeptide (phe-tyr) and phe

[Total: 12]

6 In an isolated transition metal atom, the five 3d-orbitals are degenerate. However, in an octahedral complex ion, the presence of ligands splits the five orbitals into a group of three and a group of two. These two groups have slightly different energies.

(a) Using the axes provided below, draw and label the shape of **one** d-orbital in **each** of the two groups mentioned above.





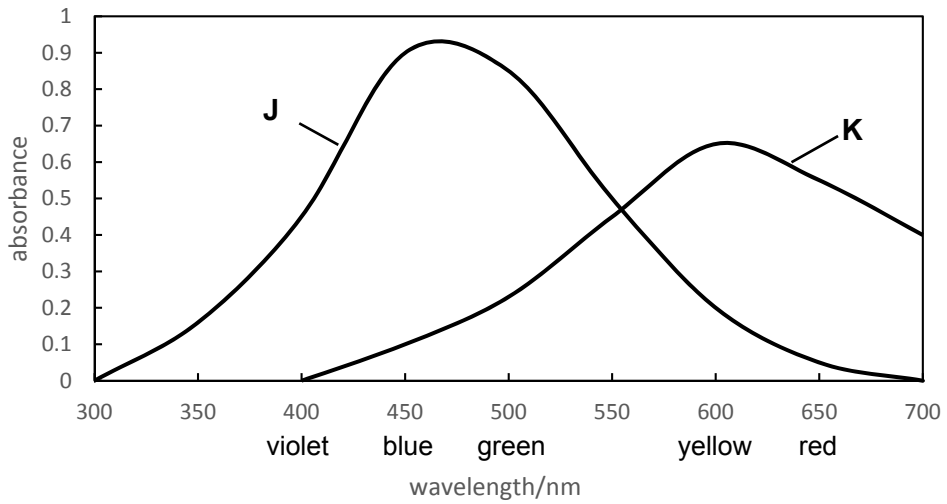
(b) Explain how the presence of the six ligands, L, in $[NiL_6]^{2+}$ splits the five 3d orbitals into two groups of different energy, and explain whether the two-orbital group or the three-orbital group has the higher energy.

Ligands have lone pairs of electrons and they approach the metal ion along the primary axes.

The d electrons in the orbitals pointing towards the ligands experience repulsion and hence of a higher energy level.

Since the $d(x^2-y^2)$ and dz^2 orbitals point towards the ligands, the two-orbital group is higher in energy.

(c) The absorbance spectra of solutions of two transition metal complexes **J** and **K** are shown in the diagram below.



A list of possible colours for these complexes is as follows.

yellow red green blue

Choose one of the colours above to describe the observed colour of each solution.
Solution **J** …….. Solution **K** ……..

Solution J red **Solution K blue**

(d) Ligands are classified based on their ability to split the five 3d orbitals into two groups with an energy difference (ΔE). Strong field ligands produce a large ΔE while weak field ligands produce a small ΔE.

The energy of a photon can be obtained by Planck's equation:

$$E = \frac{hc}{\lambda}$$

where:

E is the energy of the photon
λ is the wavelength of the photon
h is Planck's constant
c is the speed of light in vacuum

Use the data below as well as data from the *Data Booklet*, complete the table and arrange the ligands in order of increasing field strength.

species	$[M(CN)_6]^{2-}$	$[M(F)_6]^{4-}$	$[M(H_2O)_6]^{2+}$
λ / nm	430	650	600
ΔE / J			

Increasing field strength: ……<……<…… [2]

species	**$[M(CN)_6]^{2-}$**	**$[M(F)_6]^{4-}$**	**$[M(H_2O)_6]^{2+}$**
λ/nm	**430**	**650**	**600**
ΔE/ J	**4.63×10^{-19}**	**3.06×10^{-19}**	**3.32×10^{-19}**

Increasing field strength: $F^- < H_2O < CN^-$

[Total: 9]

7 The oxidising power of our atmosphere has been well-studied and is of importance as many environmental trace gases, such as methane, are removed.

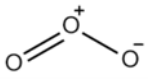
The most abundant oxidants in the atmosphere are oxygen and ozone molecules. These molecules have strong bonds and are hence relatively unreactive except towards radicals. Research in the 1950s suggested that the hydroxyl radical, •OH, is a strong oxidant.

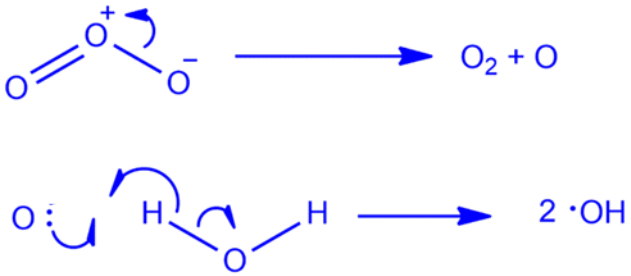
In the stratosphere, UV light from the sun heterolytically breaks ozone molecules into oxygen molecules and oxygen atoms. The oxygen atoms react homolytically with water vapour to produce hydroxyl radicals, •OH.

$$O_3 \xrightarrow{UV} O_2 + O \qquad \text{----------(1)}$$

$$O + H_2O \longrightarrow 2{\bullet}OH \qquad \text{----------(2)}$$

(a) Use equations (1) and (2) to draw the mechanism for the formation of the hydroxyl radical, •OH. Include in your mechanism the necessary curly arrows and electrons. [2]

Use  as the structure of ozone.



(b) Hydroxyl radicals are particularly reactive towards H-containing molecules due to H-abstraction converting •OH back to H_2O.

$$\bullet OH + CH_4 \longrightarrow H_2O + \bullet CH_3 \qquad \text{----------(3)}$$

Some information about an elementary reaction (3) was obtained.

[•OH] / molecules cm^{-3}	1.0×10^{6}
$[CH_4]$ / molecules cm^{-3}	4.4×10^{13}
rate constant, k / cm^3 $molecule^{-1}$ s^{-1}	1.4×10^{-5}

Source: Jacob, D. J. Introduction to Atmospheric Chemistry; Princeton University Press: 1999

(i) Use information in the table to write an equation to represent the rate equation for the pseudo-first-order reaction with respect to the concentration of the hydroxyl radical, •OH.

rate = k' [•OH]

(ii) Calculate the half-life of the hydroxyl radical, •OH to the nearest **2 significant figures**.

rate = k' [•OH], k' = k [CH_4]

k' = $1.4 \times 10^{-5} \times 4.4 \times 10^{13} = 6.16 \times 10^{8}$ s^{-1}

$t_{1/2} = \frac{ln2}{k'} = \frac{ln2}{6.16\times10^{8}} = 1.1 \times 10^{-9}$ s

(c) The relative rates of disappearance in air at 305 K for a series of hydrocarbons were measured in an environmental chamber under simulated atmospheric conditions. Absolute rate constants obtained from the reaction are as follows.

hydrocarbon	k / × 10^9 mol^{-1} dm^3 s^{-1}
butane	1.8
hexane	3.8
cis-but-2-ene	39.2

Source: J. Phys. Chem. 80, 8, 789-794

(i) Use the information given in **(b)** and refer to the bonding within butane and hexane to suggest a reason for the difference in their reactivity.

There are more C–H bonds in hexane than butane, leading to a faster rate of H-abstraction.

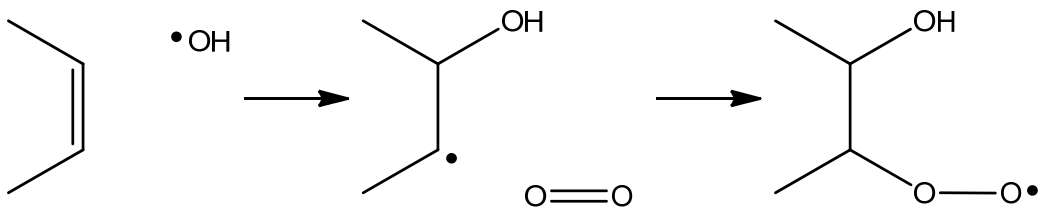
(ii) The reaction between hydroxyl radicals and alkenes proceed via a different mechanism and this increases the rate of reaction.

Account for this difference referring to the terms 'sigma' and 'pi'.

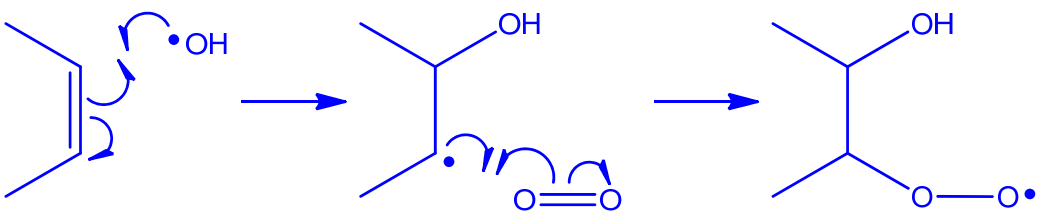
The pi electrons in the alkene C=C bond are less tightly bound to the nucleus
OR
weaker as compared to the sigma electrons in the C–H bond and hence reaction with alkenes proceed faster.

After the attack of the hydroxyl radical on cis-but-2-ene, the intermediate is now reactive enough to react with molecular oxygen.

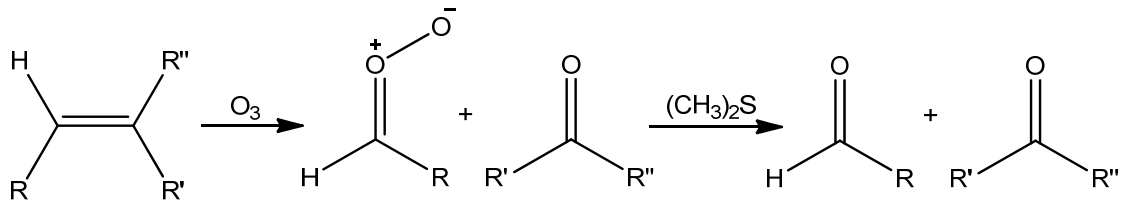
(iii) Complete the diagram to suggest a mechanism to show how the hydroxyperoxyl radical is formed. Show the movement of electrons by using curly arrows.



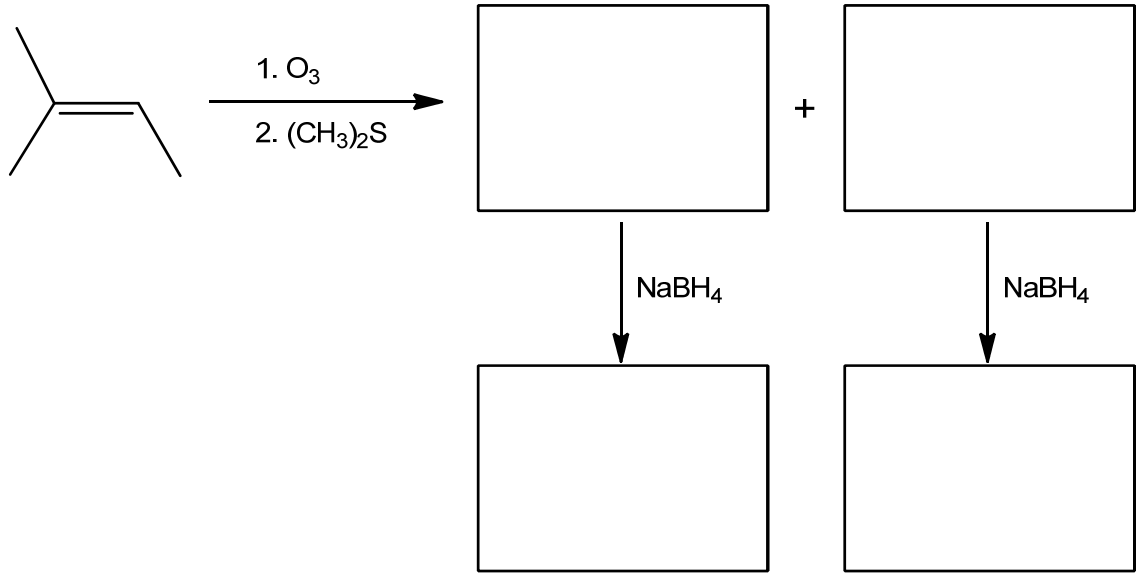
[2]



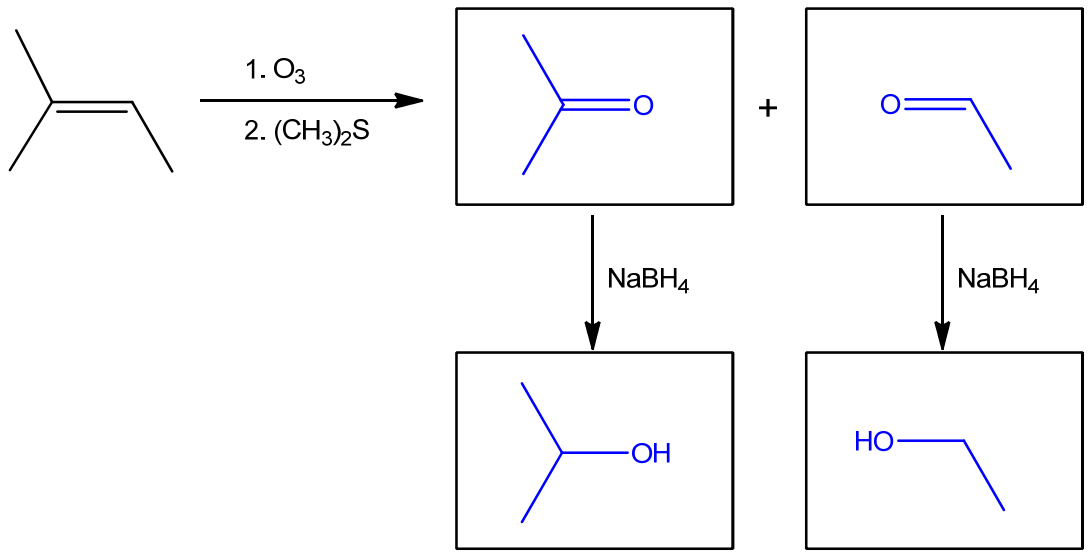
(d) Alkenes can also react with ozone directly via a process known as ozonolysis and the first step produces a carbonyl oxide and a carbonyl compound. Quenching with dimethyl sulfide produces two carbonyl compounds.



Complete the reaction scheme below.



[3]



[Total: 12]

~ End of Paper~

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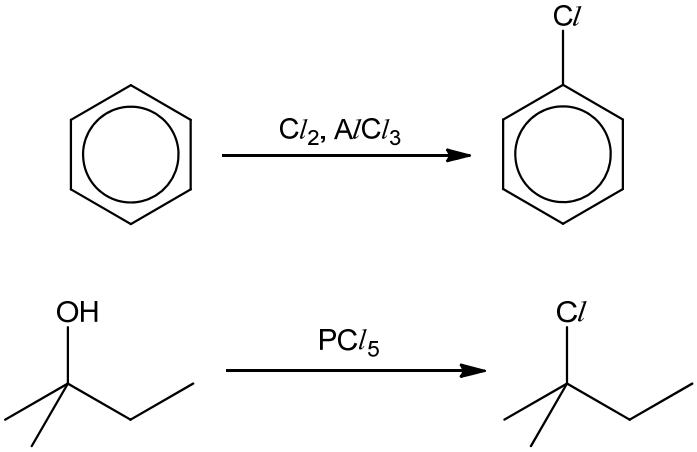
Section A

Answer **all** questions in this section.

1 (a) (i) Due to reactivity of $AlCl_3$ and PCl_5 in water, the following reactions are carried out under anhydrous conditions.



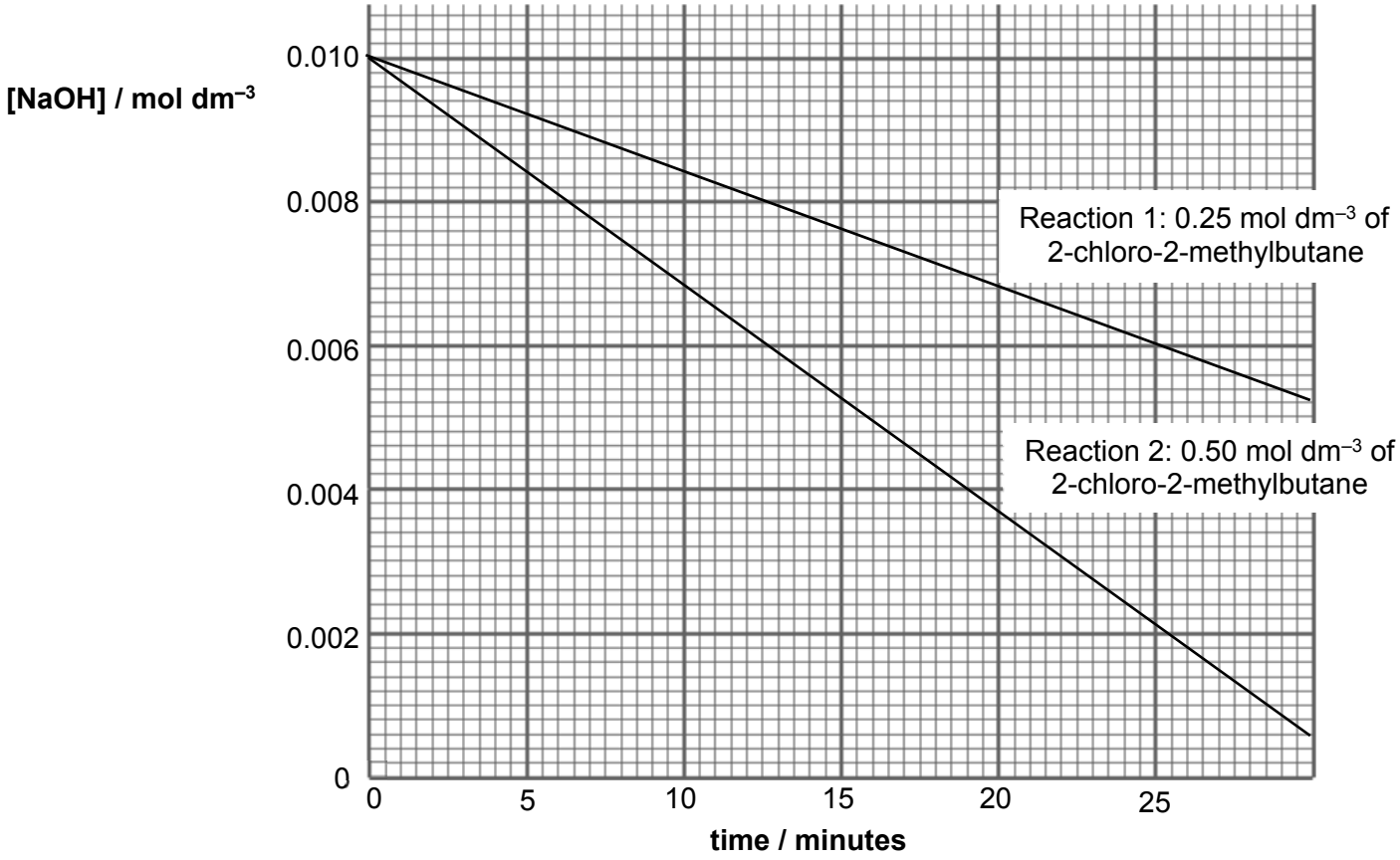
Write equations showing the reactions of aluminium chloride and phosphorus pentachloride in water. State the pH of resulting solutions. [3]

(ii) Chlorobenzene and 2-chloro-2-methylbutane are separately boiled with aqueous sodium hydroxide and acidified with nitric acid before aqueous silver nitrate is added.

State and explain the difference in observations. Write equations for the reactions that occur. [3]

(b) To study the kinetics of the reaction between 2-chloro-2-methylbutane and sodium hydroxide in alcoholic medium, two experiments with different initial concentrations of 2-chloro-2-methylbutane were carried out at constant temperature.

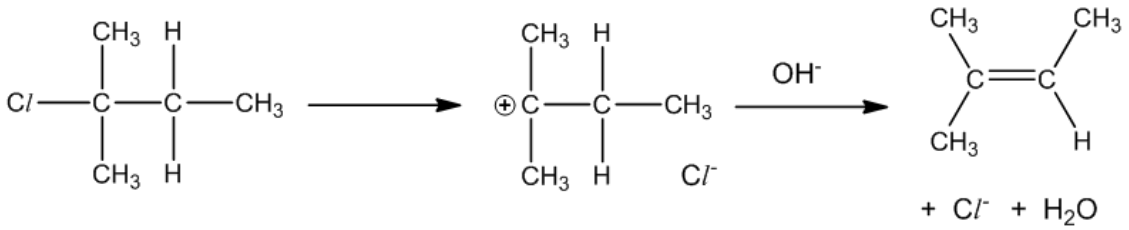
A [NaOH]–time graph was plotted using the results obtained from the experiments.



(i) Deduce the orders of reaction with respect to 2-chloro-2-methylbutane and NaOH. [2]

(ii) Hence state the rate equation of this reaction. [1]

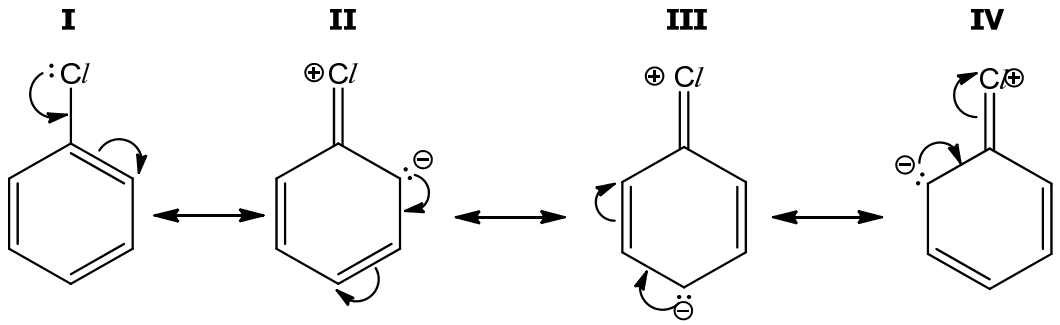
(iii) The proposed mechanism of 2-chloro-2-methylbutane with alcoholic sodium hydroxide is given below.



Using your answer in **(b)(ii)** and the above steps, suggest the complete mechanism by

- drawing curly arrows,
- showing lone pair(s) of electrons and
- identifying the slow step. [3]

(c) Chlorobenzene has the following resonance structures which represent the alternative distribution of electrons on the molecule. Using these structures, suggest why the electrophilic substitution of chlorobenzene is 2,4-directing. [2]



(d) When butane is reacted with chlorine gas under strong UV rays, a mixture of compounds is formed.

(i) Assuming that primary and secondary hydrogen atoms have similar reactivity, draw the structures of alkyl radicals formed during the reaction and state their likely ratio of formation. [2]

(ii) During the termination stage, the alkyl radicals in **(d)(i)** form three structures with the molecular formula C_8H_{18}. Suggest their structures and the ratio of these structures. [4]

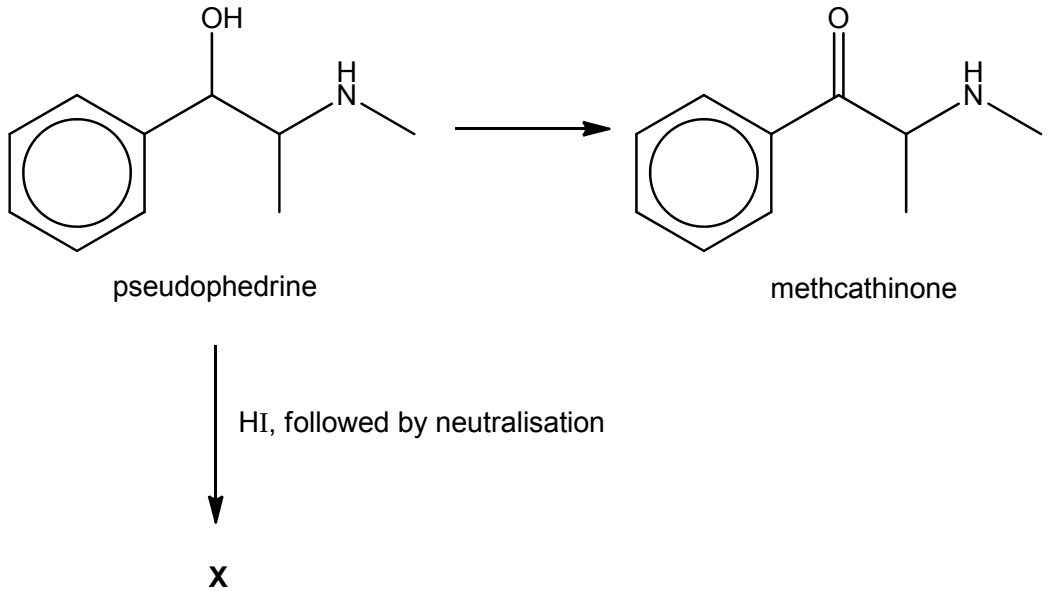
(e) Chlorofluoroalkanes, CFCs, were once used as refrigerant fluids and aerosol propellants. In many applications, they have now been replaced by alkanes. This is because CFCs contribute to the destruction of the ozone layer.

(i) Suggest one reason why CFCs were originally used for this purpose. [1]

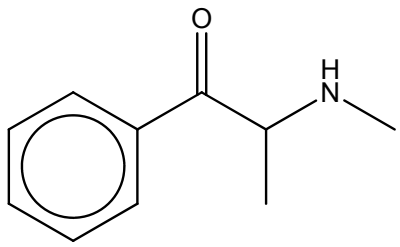
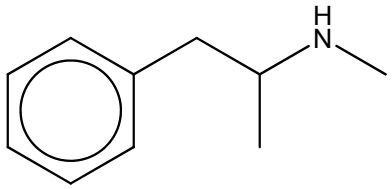
(ii) Suggest one potential hazard of using alkanes instead of CFCs. [1]

[Total: 22]

2 Recreational drugs like methamphetamine and methcathinone can be synthesised easily from pseudoephedrine, a common nasal decongestant found in cough medicine.



(a) **(i)** The structures of methcathinone and methamphetamine, with pK_b values at 298 K, are shown in the table below.

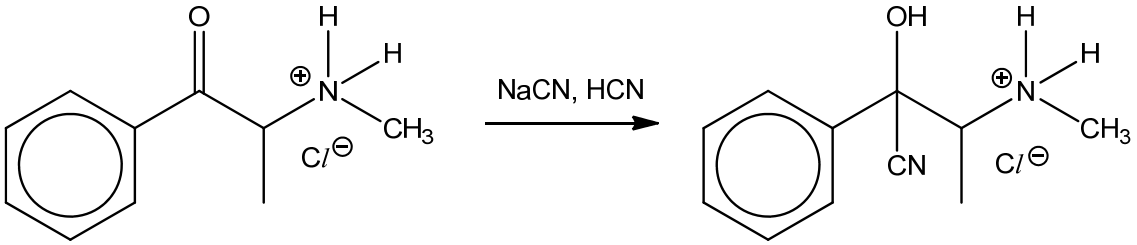
compound	pK_b
 methcathinone	5.98
 methamphetamine	3.79

Explain why methcathinone has a higher pK_b value than methamphetamine. [2]

(ii) Suggest the structure of intermediate **X**. [1]

(b) Commercially, methcathinone is sold in its salt form as solid methcathinone hydrochloride.

Methcathinone hydrochloride undergoes the following reaction to form a possible analogue, **Y**, with hallucinogenic properties.



methcathinone hydrochloride

Y

Name the type of reaction and describe its mechanism, showing curly arrows, charges and any relevant lone pairs. [3]

(c) Hydrogen iodide, HI, is listed as a controlled substance as it is often used illegally to produce popular recreational drugs like methamphetamine.

The commercial preparation of hydrogen iodide, HI, involves the reaction of iodine I_2, with hydrazine, N_2H_4, which has ammonia-like properties.

$$N_2H_4(l) + 2I_2(aq) \longrightarrow N_2(g) + 4HI(g)$$

(i) During the preparation, gaseous hydrogen iodide produced must be removed immediately. Suggest a reason why this is done. [1]

(ii) Hydrogen halides can be unstable to heat. Write an equation for the reaction undergone on heating hydrogen iodide, HI. [1]

(iii) Using your knowledge of the chemistry of Group 17, deduce with reason how the thermal stability of hydrogen astatide, HAt, differ from that of hydrogen iodide, HI. [2]

(d) A 40.0 g sample of solid ammonium carbonate is placed in a closed evacuated 3.0 dm^3 flask and heated to 400°C. It decomposes to produce ammonia, water and carbon dioxide according to the equation :

$$(NH_4)_2CO_3(s) \rightleftharpoons 2NH_3(g) + H_2O(g) + CO_2(g)$$

The value of the equilibrium constant, K_p, for the reaction is 0.295 at 400 °C.

In a gaseous reaction, the reactants and products can be expressed in partial pressures in atmospheres (atm). The relationship between K_c and K_p is given :

$$K_p = K_c(RT)^4$$

Assume that the gases are under ideal conditions.

(i) Write down the expression of K_p for the above equilibrium system. Hence show that $K_p = K_c(RT)^4$. [2]

(ii) Calculate the partial pressure of $NH_3(g)$ at equilibrium at 400°C. [2]

(iii) Calculate the total pressure inside the flask at equilibrium. [1]

(iv) Calculate the mass of solid ammonium carbonate in the flask at equilibrium. [3]

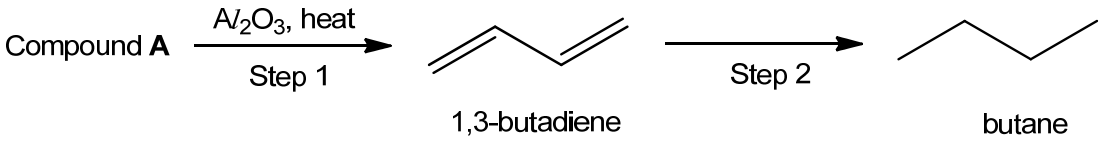
[Total: 18]

3 In chemistry, a conjugated system refers to a system of overlapping p orbitals which allows the delocalisation of π electrons in a molecule. It is represented by having alternating single and multiple bonds in the molecule.

1,3-butadiene is the simplest conjugated diene which has double bonds that is separated by a single bond. It is a colourless gas which is industrially important as a monomer in the production of synthetic rubber.

In general, conjugated dienes have similar chemical properties as the usual alkenes. However, they are associated with extra stability as the delocalisation of π electrons lowers the overall energy of the molecule.

(a) The 2-step synthesis of butane shown in the figure below makes use of 1,3-butadiene as the intermediate.



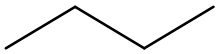
(i) Given that compound **A** does not rotate plane polarised light, suggest a structure for it and state the type of reaction that takes place in step 1. [2]

(ii) Write an equation to show the standard enthalpy change of hydrogenation, $\Delta H^{\ominus}_{hydrogenation}$ of 1,3-butadiene in step 2. [1]

(iii) A student calculated the expected $\Delta H^{\ominus}_{hydrogenation}$ of 1,3-butadiene in step 2 to be –252 kJ mol^{-1}. However, 1,3-butadiene is 16 kJ mol^{-1} more stable than expected.

Calculate the actual $\Delta H^{\ominus}_{hydrogenation}$ of 1,3-butadiene. [1]

(iv) Hence, using the value calculated in **(iii)** and the information given below, construct a fully labelled energy level diagram to determine the standard enthalpy change of combustion, $\Delta H^{\ominus}_c$ of 1,3-butadiene. [3]

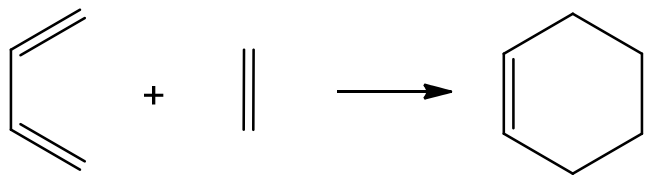
substance	$\Delta H^{\ominus}_c$ / kJ mol^{-1}
	–2877
H_2	–286

(v) According to valence bond theory, the stability of conjugated diene could also be explained by orbital hybridisation.

By making reference to the C–C single bond formed in 1,3-butadiene and butane, and the hybridisation of the orbitals in the two molecules, explain the extra stability of 1,3-butadiene. [2]

(b) Conjugate dienes can undergo addition with alkenes in a process called Diels-Alder reaction to form cyclic products. It is an important synthetic method which is widely used in organic chemistry to form unsaturated cyclic products.

An example of the Diels-Alder reaction is shown below where 1,3-butadiene reacts with ethene to form cyclohexene.:



In the process, the two reactants react in a single step through a cyclic redistribution of bonding electrons and two new carbon-carbon bonds are formed at the same time.

(i) By using full-headed curly arrows, suggest the mechanism that takes place in the above reaction to form cyclohexene. [1]

(ii) Compound **B** has the molecular formula of $C_8H_{12}O$ and it can be synthesised when 1,3-butadiene reacts with compound **C**, C_4H_6O, in the **Diels-Alder** reaction. It is known that compound **C** is able to react with 2 moles of hydrogen gas in the presence of Pt and produce a yellow precipitate with alkaline aqueous I_2. Compound **C** also gives a positive test with 2,4-dinitrophenylhydrazine and negative test with Tollens' reagent.

Suggest structures for compounds **B** and **C**, and explain the reactions described. [5]

(c) Compounds of aluminium such as aluminium oxide, Al_2O_3 and aluminium chloride, $AlCl_3$ are often used in organic reactions as catalysts.

(i) Aluminium oxide has unique chemical properties as it is able to react with both acid and base.

Write balanced chemical equations for the reactions between aluminium oxide and the following respectively.

- HBr
- KOH [2]

(ii) Account for the acid-base behaviour of aluminium oxide by making reference to its structure and bonding and state the nature of the oxide. [3]

[Total: 20]

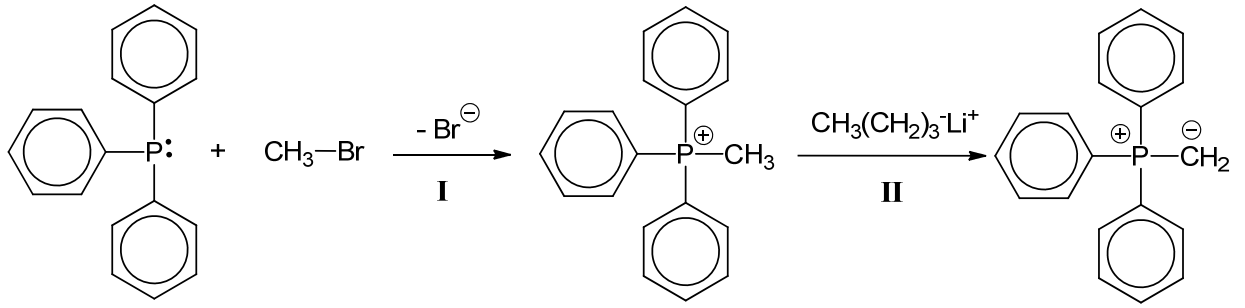
TURN OVER FOR SECTION B

Section B

Answer **one** question from this section.

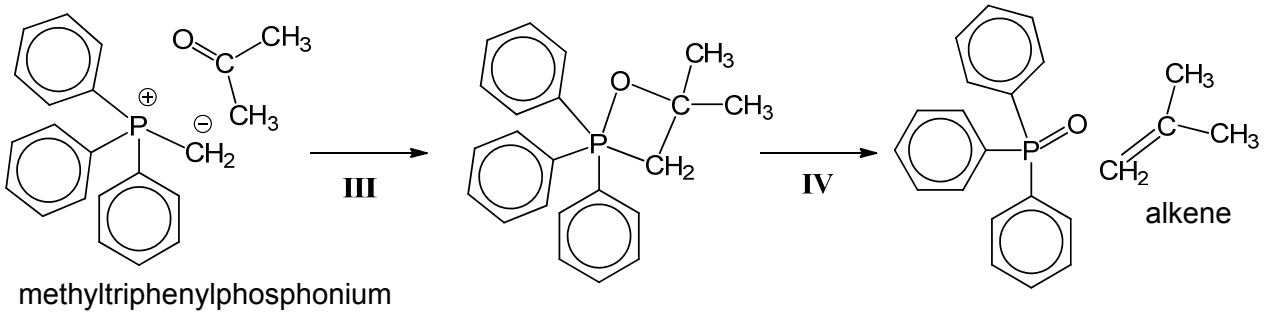
4 (a) The Wittig reaction converts carbonyl compounds into alkenes by reacting aldehydes or ketones with alkyltriphenylphosphonium, such as methyltriphenylphosphonium.

Stage 1 – Preparation of methyltriphenylphosphonium



triphenylphosphine methyltriphenylphosphonium

Stage 2 – Formation of alkene



methyltriphenylphosphonium

Different alkenes can be formed by using different carbonyl compounds and R-groups on the alkyltriphenylphosphonium.

(i) The melting points of four compounds, including triphenylphosphine and methyltriphenylphosphonium bromide are given below.

compound	formula	melting point / °C
triphenylphosphine	$P(C_6H_5)_3$	80
water	H_2O	0
methyltriphenylphosphonium bromide	$(C_6H_5)_3P{=}CH_2^+Br^-$	232
sodium chloride	NaC*l*	801

With reference to their structure and bonding, suggest why the melting point of

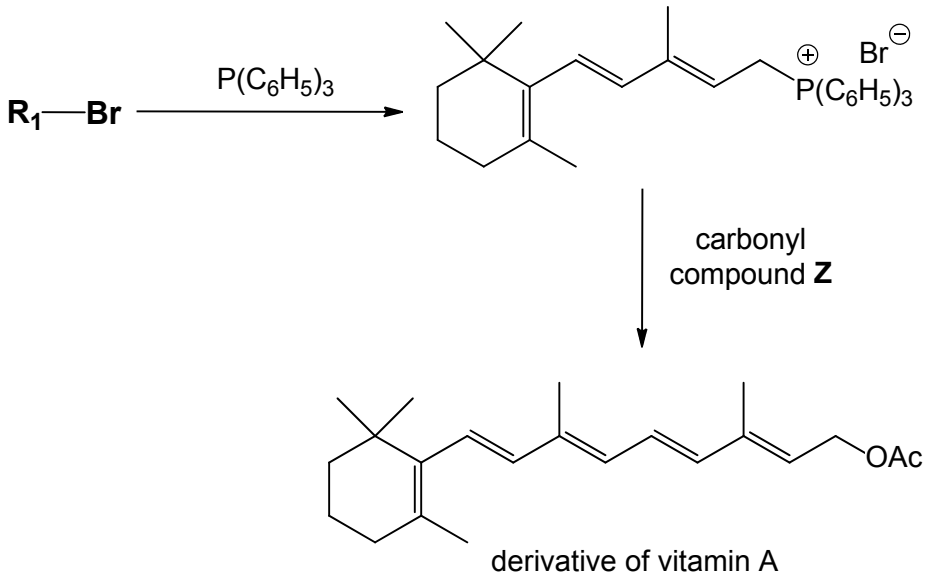
1. triphenylphosphine is higher than water; and
2. methyltriphenylphosphonium bromide is lower than sodium chloride

[4]

(ii) State the type of reaction in step **I**. [1]

(iii) State the role of $CH_3(CH_2)_3^-Li^+$ in step **II**. [1]

(iv) The advantage of Wittig reaction is the predictability of its alkene product. It is used in industrial processes such as the formation on vitamin A.



Suggest the structures of alkylbromide **R_1–Br** and carbonyl compound **Z** for forming the derivative of vitamin A. You may assume that the OAc group remains unchanged during the reaction. [2]

(b) Triphenylphosphine, $P(C_6H_5)_3$, is prepared by reacting phosphorus trichloride, chlorobenzene and sodium. Sodium chloride is precipitated during the reaction due to its insolubility in the organic mixture.

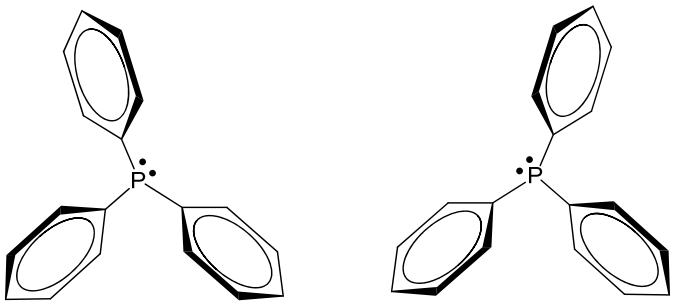
(i) Write the balanced equation for the preparation of triphenylphosphine. [1]

(ii) Triphenylphosphine does not form in the above reaction when water is present. Given that phosphorus trichloride reacts with water according to this equation

$$PCl_3 + H_2O \longrightarrow H_3PO_3 + HCl$$

describe, with the aid of equation(s), any other reactions that will take place when water is used as a solvent. Hence or otherwise, suggest the colour of universal indicator in the resulting mixture. [3]

(iii) It has been suggested that triphenylphosphine is a chiral compound. Two structures of triphenylphosphine are shown below.



State the relationship of the two structures and suggest why triphenylphosphine is a chiral compound. [2]

(c) **(i)** The aqueous solutions of two acids were prepared and their pH measured.

acid	concentration / mol dm^{-3}	pH
M	0.75	1.11
N	0.25	0.60

Given that **M** and **N** are monobasic acids, show calculations to explain whether each acid is a strong or weak acid. [3]

(ii) It is known that the electronegativity of the central atom in the acid affects its acidity.

With reference to the increasing trend of electronegativity across the period, suggest the correct identities of the acids **M** and **N**, given that they could be H_3PO_2 or $HClO_3$. [3]

[Total: 20]

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

Osmium is a bluish-white metal found as a trace element in alloys, mostly in platinum ores. Not surprisingly, osmium was discovered in 1803 by Smithson Tennant when he noticed a residue remaining after dissolving crude platinum in aqua regia – a mixture of concentrated nitric acid and concentrated hydrochloric acid.

Platinum reacts with concentrated nitric acid to produce aqueous platinum(IV) cations, nitrogen dioxide and water. The platinum(IV) cations are then complexed with chloride *ligands* to produce hexachloroplatinate(IV) anions which are recovered through the reaction with ammonium chloride to produce yellow crystals.

(a) **(i)** Define the term *ligand*. [1]

(ii) Write a balanced ionic equation to represent the reaction of platinum with concentrated nitric acid. [1]

(iii) Suggest the identity of the yellow crystals obtained. [1]

(iv) The solubility of the yellow crystals in water at room temperature is 5.0 g dm^{-3} but decreases to 0.028 g dm^{-3} in 1 mol dm^{-3} ammonium chloride at the same temperature.

Write an equation to represent the dissolution of the yellow crystals in **(a)(iii)** and use the equation to account for the decreased solubility in 1 mol dm^{-3} ammonium chloride. [2]

(v) Explain why hexachloroplatinate(IV) is coloured. [3]

When powdered osmium is exposed to air, it forms the toxic compound osmium tetroxide, OsO_4 with a strong odour like that of chlorine.

$$Os + 2O_2 \longrightarrow OsO_4$$

(b) **(i)** Use the standard electrode potential given and choose another appropriate equation from the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for the reaction between osmium and air. [1]

$$OsO_4 + 8H^+ + 8e^- \rightleftharpoons Os + 4H_2O \qquad E^{\ominus} = +0.84\ V$$

(ii) Hence calculate $\Delta G^{\ominus}_{cell}$ for the reaction in **(b)(i)**, leaving your answer in kJ mol^{-1}. [1]

(iii) Suggest, with reasoning, the sign for the standard enthalpy change of reaction for the reaction between osmium and air, making reference to the terms in the Gibbs free energy equation and your answer in **(b)(ii)**. [2]

The figure below shows part of a label on a bottle of osmium tetroxide.

<u>Osmium Tetroxide, OsO_4</u>

Molar mass: 254.2 g mol^{-1}
Density: 4.9 g cm^{-3}
Vapour pressure: 933 Pa
Max. permissible exposure limit: 200 µg m^{-3}

Net weight: 1000 g
Volume of container: 250 cm^3

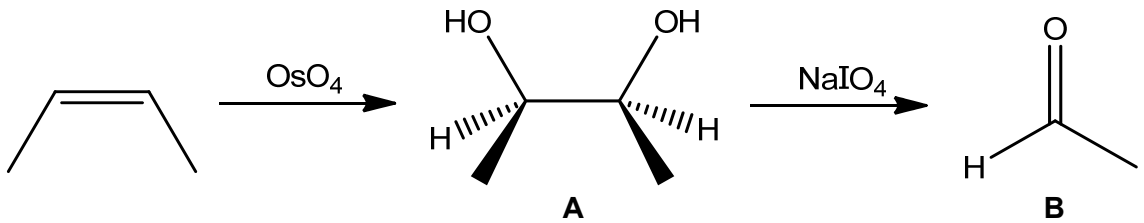
Note:
Vapour pressure – the pressure of vapour in equilibrium with its solid/liquid form.
1 µg = 1 x 10^{-6} g

(c) **(i)** Use the information above to calculate the amount of OsO_4 in the vapour phase within an unopened container of OsO_4 at room temperature. Assume ideal gas behaviour. [2]

(ii) Hence determine the concentration of OsO_4, in µg m^{-3}, in the air of a 100 m^3 laboratory where a new container is opened. Assume that the air has evenly mixed. [2]

(iii) Discuss whether it is safe for researchers to open the container in this laboratory without a proper fume cupboard, considering your answer in **(c)(ii)** and the approach used to calculate it. [1]

Osmium tetroxide, OsO_4 can oxidise alkenes to give diols. $NaIO_4$ will react further with the diol to produce carbonyl compounds.

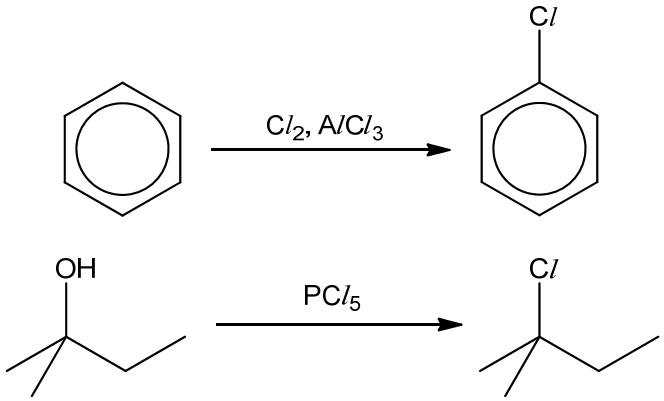


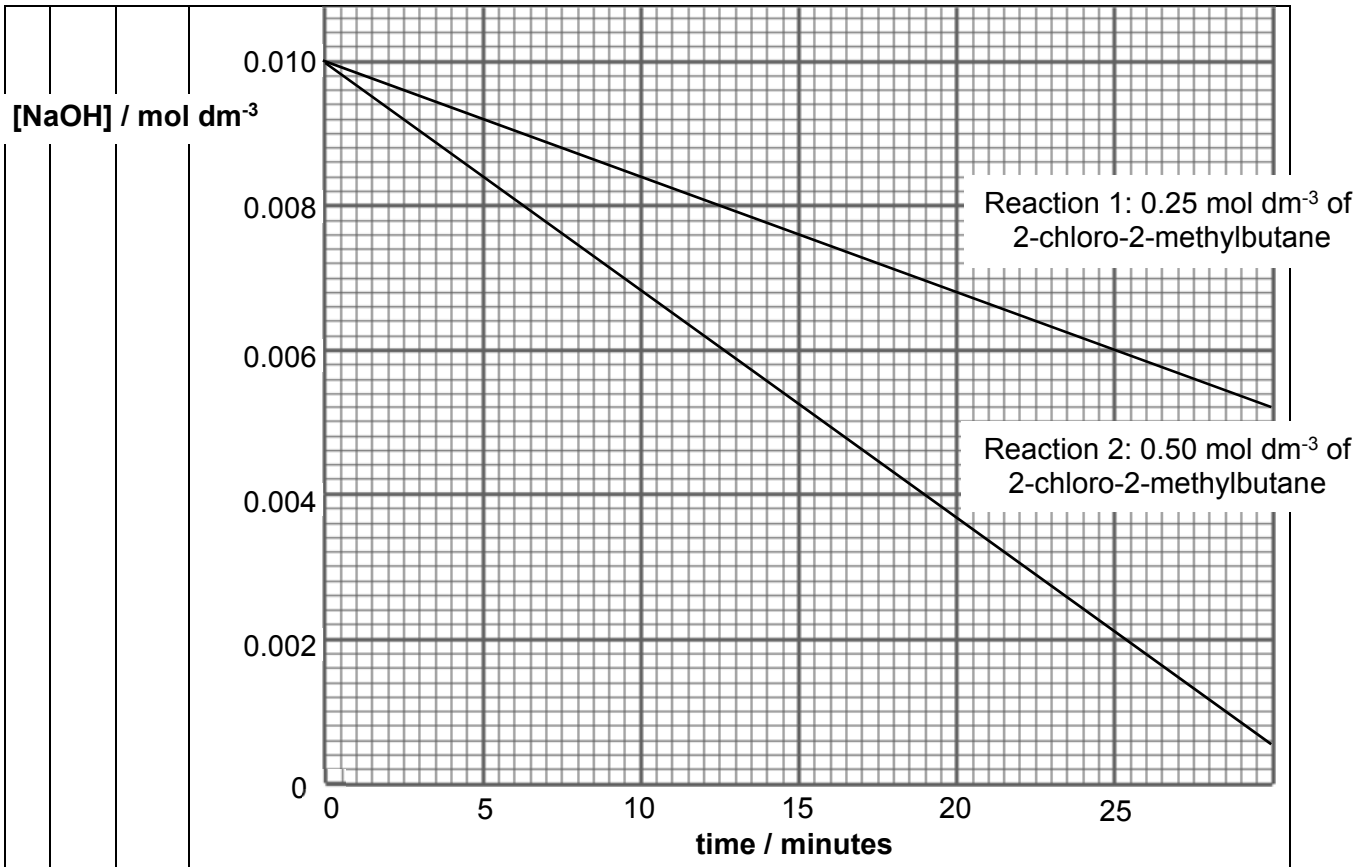
(d) Suggest a simple chemical test to distinguish between compounds **A** and **B** and write a balanced equation for the positive test. [3]

[Total: 20]

Section A

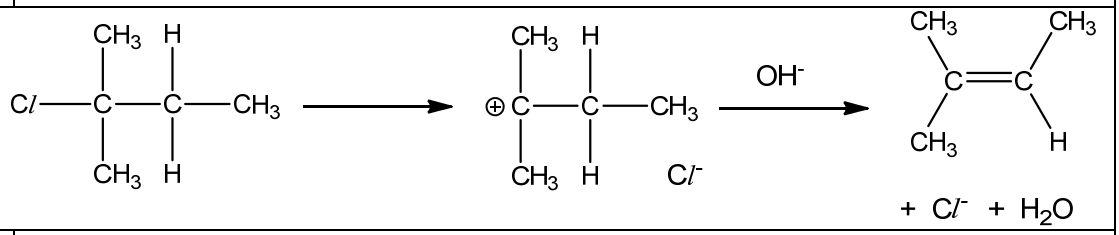
Answer **all** questions in this section.

1	**(a)**	**(i)**	Due to reactivity of $AlCl_3$ and PCl_5 in water, the following reactions are carried out under anhydrous conditions.  Write equations showing the reactions of aluminium chloride and phosphorus pentachloride in water. State the pH of resulting solutions. [3]
			$AlCl_3 + 6H_2O \longrightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$ **$[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H^+$** **pH 3** **$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$ $POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$** **OR $PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$** **pH 2**
		(ii)	Chlorobenzene and 2-chloro-2-methylbutane are separately boiled with aqueous sodium hydroxide and acidified with nitric acid before aqueous silver nitrate is added. State and explain the difference in observations. Write equations for the reactions that occur. [3]
			2-chloro-2-methylbutane forms a white ppt while chlorobenzene does not. **The C–C*l* bond in chlorobenzene is strengthened by partial double bond character due to the overlap of p-orbital on C*l* atom and π-orbital of benzene. Hence chlorobenzene is resistant to hydrolysis.** **$CH_3C(CH_3)ClCH_2CH_3 + OH^- \longrightarrow CH_3C(CH_3)OHCH_2CH_3 + Cl^-$** **$Ag^+ + Cl^- \longrightarrow AgCl$**
	(b)	**(i)**	To study the kinetics of the reaction between 2-chloro-2-methylbutane and sodium hydroxide in alcoholic medium, two experiments with different initial concentrations of 2-chloro-2-methylbutane were carried out at constant temperature. A [NaOH]–time graph was plotted using the results obtained from the experiments.



		(i)	Deduce the order of reaction with respect to 2-chloro-2-methylbutane and NaOH. [2]
			Using Reaction 1 (or 2), when [NaOH] decreases, gradient remains constant, hence rate of reaction is constant. Rate of reaction is independent of [NaOH], hence the reaction is zero order wrt [NaOH]. **Comparing reactions 1 and 2, when [2-chloro-2-methylbutane] doubles from 0.25 to 0.50 mol dm^{-3}, the gradient doubles, showing that the rate of reaction doubles from 1.60 × 10^{-4} to 3.15 × 10^{-4} mol dm^{-3} min^{-1}. Rate of reaction ∝ [2-chloro-2-methylbutane], hence the reaction is first order wrt [2-chloro-2-methylbutane].**
		(ii)	Hence, state the rate equation of this reaction. [1]
			Rate = k[2-chloro-2-methylbutane]

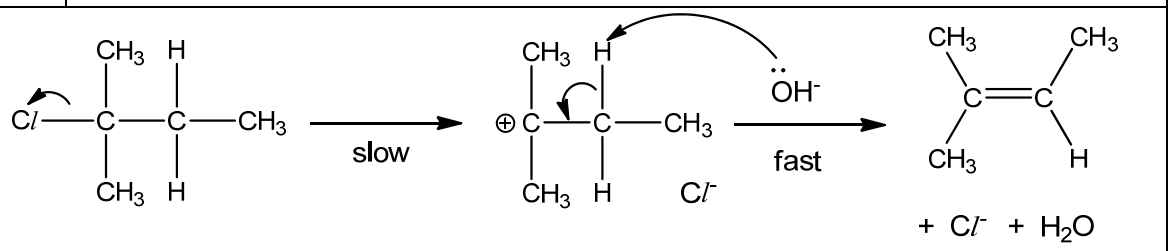
(iii) The proposed mechanism of 2-chloro-2-methylbutane with alcoholic sodium hydroxide is given below.



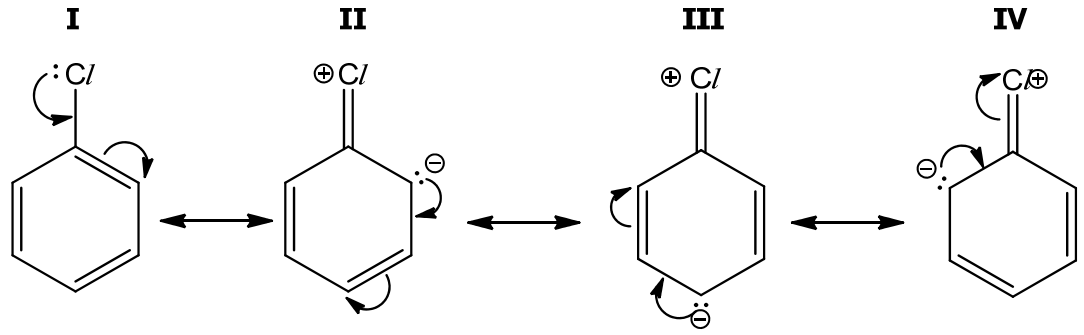
Using your answer in **(b)(ii)** and the above steps, suggest the complete mechanism by

- drawing curly arrows,
- showing lone pair(s) of electrons and
- identifying the slow step.

[3]



(c) Chlorobenzene has the following resonance structures which represent the alternative distribution of electrons on the molecule. Using these structures, suggest why the electrophilic substitution of chlorobenzene is 2,4-directing. [2]



The negative charges are located on positions 2 and 4 with respect to the chloro-group, hence the electrophilic attack is more likely to occur at these positions OR electrophile is more likely to react at these positions.

(d) When butane is reacted with chlorine gas under strong UV rays, a mixture of compounds is formed.

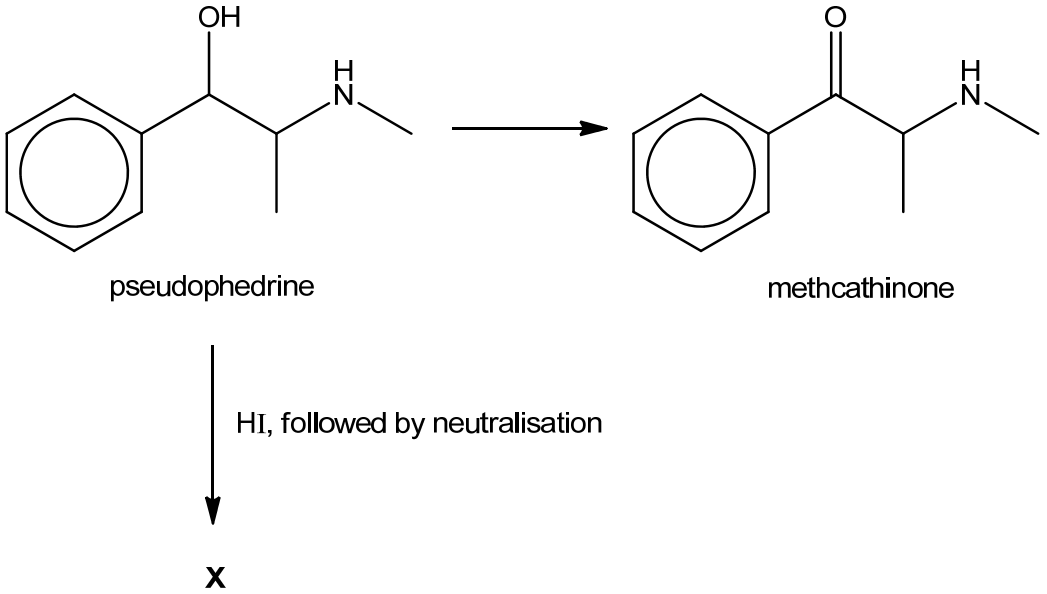
(i) Assuming that primary and secondary hydrogen atoms have similar reactivity, draw the structures of alkyl radicals formed during the reaction and state their likely ratio of formation. [2]

$CH_3CH_2CH_2\dot{C}H_2$ and $CH_3CH_2\dot{C}HCH_3$

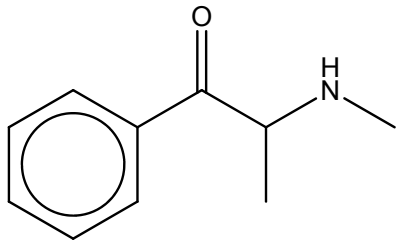
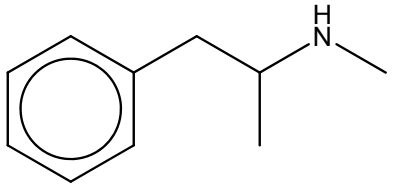
3 : 2

		(ii)	During the termination stage, the alkyl radicals in **(d)(i)** form three structures with the molecular formula C_8H_{18}. Suggest their structures and the ratio of these structures. [4]
			• **$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ 3/5 x 3/5 = 9/25** • **$CH_3CH_2CH(CH_3)CH(CH_3)CH_2CH_3$ 2/5 x 2/5 = 4/25** • **$CH_3CH_2CH_2CH_2CH(CH_3)CH_2CH_3$ 2 (3/5 x 2/5) = 12/25** • **Ratio = 9 : 4 : 12**
	(e)	Chlorofluoroalkanes, CFCs, were once used as refrigerant fluids and aerosol propellants. In many applications, they have now been replaced by alkanes. This is because CFCs contribute to the destruction of the ozone layer.	
		(i)	Suggest one reason why CFCs were originally used for this purpose. [1]
			CFCs have high heat capacity OR They are not easily flammable.
		(ii)	Suggest one potential hazard of using alkanes instead of CFCs. [1]
			Alkanes are flammable.
			[Total: 22]

2 Recreational drugs like methamphetamine and methcathinone can be synthesised easily from pseudoephedrine, a common nasal decongestant found in cough medicine.



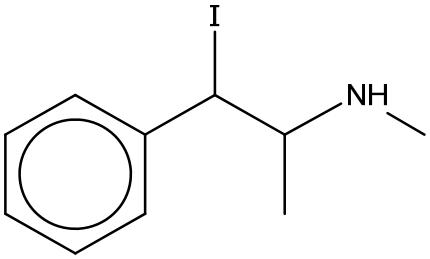
(a) **(i)** The structure of methcathinone and methamphetamine with pK_b values at 298 K, are shown in the table below.

compound	pK_b
 methcathinone	5.98
 methamphetamine	3.79

Explain why methcathinone has a higher pK_b value than methamphetamine. [2]

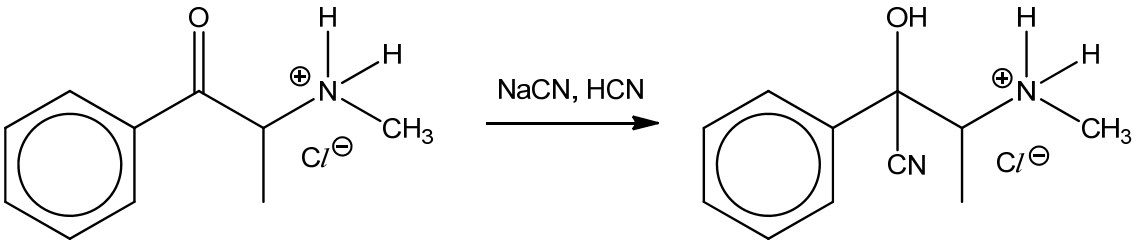
Methcathinone is a weaker base (higher pK_b) as it has a carbonyl (C=O) functional group two carbons away from secondary amine functional group, which is electron withdrawing. Hence the lone pair of electrons on N for methcathinone is less available for coordination with H^+ ion. (dative bonding with H^+ ion)

(ii) Suggest the structure of intermediate **X**. [1]



(b) Commercially, methcathinone is sold in its salt form as solid methcathinone hydrochloride.

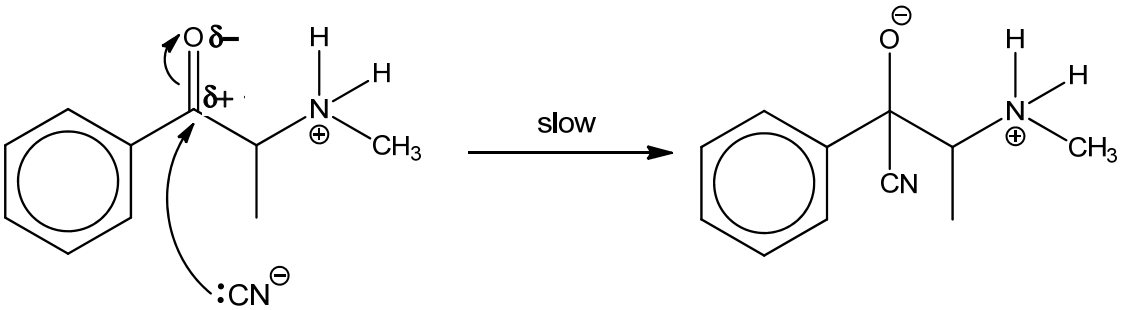
Methcathinone hydrochloride undergoes the following reaction to form a possible analogue, **Y**, with hallucinogenic properties.

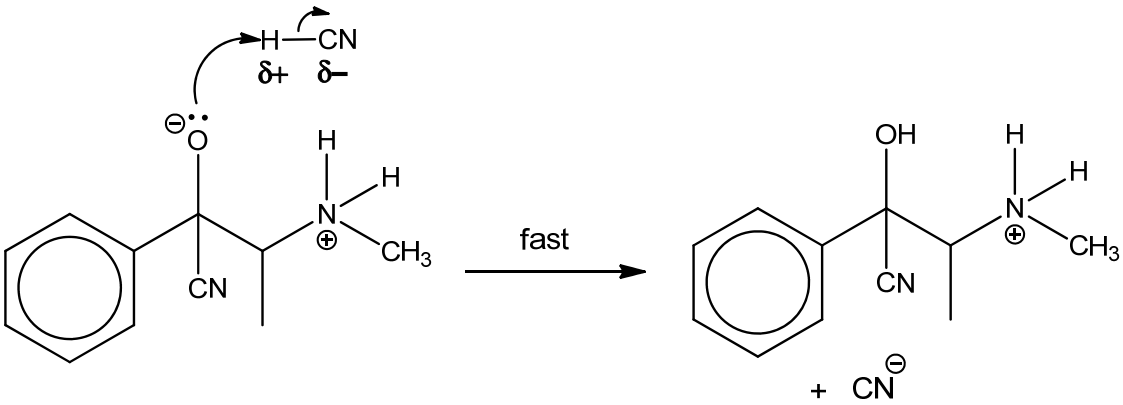


methcathinone hydrochloride **Y**

Name the type of reaction and describe its mechanism, showing curly arrows, charges and any relevant lone pairs. [3]

Nucleophilic addition





(c) Hydrogen iodide, HI, is listed as a controlled substance as it is often used illegally to produce popular recreational drugs like methamphetamine.

The commercial preparation of hydrogen iodide, HI, involves the reaction of iodine I_2, with hydrazine, N_2H_4, which has ammonia-like properties.

$$N_2H_4(l) + 2I_2(aq) \longrightarrow N_2(g) + 4HI(g)$$

(i) During the preparation, gaseous hydrogen iodide produced must be removed immediately. Suggest a reason why this is done. [1]

Hydrazine N_2H_4 is basic and it can react with HI (acidic) to form a salt $N_2H_5^+I^-$

(ii) Hydrogen halides can be unstable to heat. Write an equation for the reaction undergone on heating hydrogen iodide, HI. [1]

$$2HI \longrightarrow H_2 + I_2$$

(iii) Using your knowledge of the chemistry of Group 17, deduce with reason how the thermal stability of hydrogen astatide, HAt, differ from that of hydrogen iodide, HI. [2]

At is below I in Group 17 so it forms weaker covalent bond with hydrogen. As a result, HAt has lower thermal stability than HI.

(d) A 40.0 g sample of solid ammonium carbonate is placed in a closed evacuated 3.0 dm^3 flask and heated to 400°C. It decomposes to produce ammonia, water and carbon dioxide according to the equation :

$$(NH_4)_2CO_3(s) \rightleftharpoons 2NH_3(g) + H_2O(g) + CO_2(g)$$

The value of the equilibrium constant, K_p, for the reaction is 0.295 at 400 °C.

In a gaseous reaction, the reactants and products can be expressed in partial pressures in atmospheres (atm). The relationship between K_c and K_p is given :

$$K_p = K_c(RT)^4$$

Assume that the gases are under ideal conditions.

(i) Write down the expression of K_p for the above equilibrium system. Hence show that $K_p = K_c(RT)^4$. [2]

$K_p = (P_{NH_3})^2(P_{H_2O})(P_{CO_2})$

Using pV = nRT

P = (n/V)RT = CRT

$K_p = ([NH_3]RT)^2 ([H_2O]RT) ([CO_2]RT)$
$= [NH_3]^2 [H_2O][CO_2] (RT)^4$
$= K_c(RT)^4$

(ii) Calculate the partial pressure of $NH_3(g)$ at equilibrium at 400°C. [2]

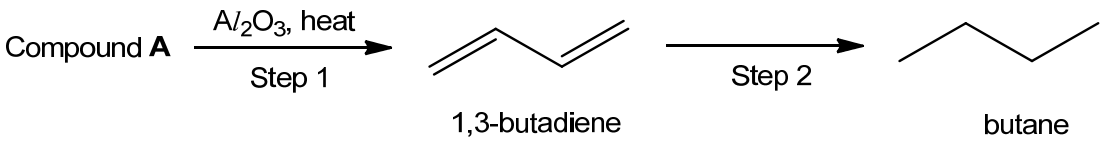
			$(NH_4)_2CO_3(s) \rightleftharpoons 2NH_3(g) + H_2O(g) + CO_2(g)$ I / atm 0 0 0 C / atm +2x +x +x E / atm 2x x x $K_p = (P_{NH_3})^2(P_{H_2O})(P_{CO_2})$ $0.295 = (2x)^2(x)\ x)$ $x = 0.521$ $P_{NH_3} = 2x = 1.04$ atm
		(iii)	Calculate the total pressure inside the flask at equilibrium. [1]
			$P_{total} = (P_{NH_3}) + (P_{H_2O}) + (P_{CO_2})$ $= 2(0.521) + (0.521) + (0.521)$ $= 2.08$ atm
		(iv)	Calculate the mass of solid ammonium carbonate in the flask at equilibrium. [3]
			PV = nRT $(0.521 \times 101325\ Pa)(0.003\ m^3) = n\ (8.31)(673\ K)$ n = 0.02832 mol Mass of $(NH_4)_2CO_3 = (40.0 - 0.02832)x(2(14.0) + 8(1.0) + 12.0 + 3(16.0))$ = 37.3 g
			[Total: 18]

3 In chemistry, a conjugated system refers to a system of overlapping p orbitals which allows the delocalisation of π electrons in a molecule. It is represented by having alternating single and multiple bonds in the molecule.

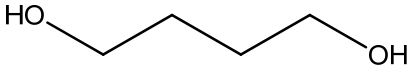
1,3-butadiene is the simplest conjugated diene which has double bonds that is separated by a single bond. It is a colourless gas which is industrially important as a monomer in the production of synthetic rubber.

In general, conjugated dienes have similar chemical properties as the usual alkenes. However, they are associated with extra stability as the delocalisation of π electrons lowers the overall energy of the molecule.

(a) The 2-step synthesis of butane shown in the figure below makes use of 1,3-butadiene as the intermediate.

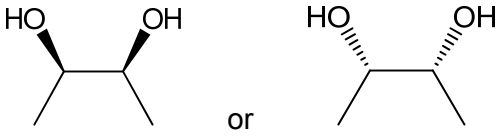


(i) Given that compound **A** does not rotate plane polarised light, suggest a structure for it and state the type of reaction that takes place in step 1. [2]

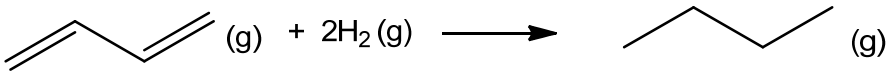


Elimination

Alternative answer:



(ii) Write an equation to show the standard enthalpy change of hydrogenation, $\Delta H^{\ominus}_{hydrogenation}$ of 1,3-butadiene in step 2. [1]

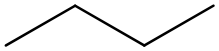


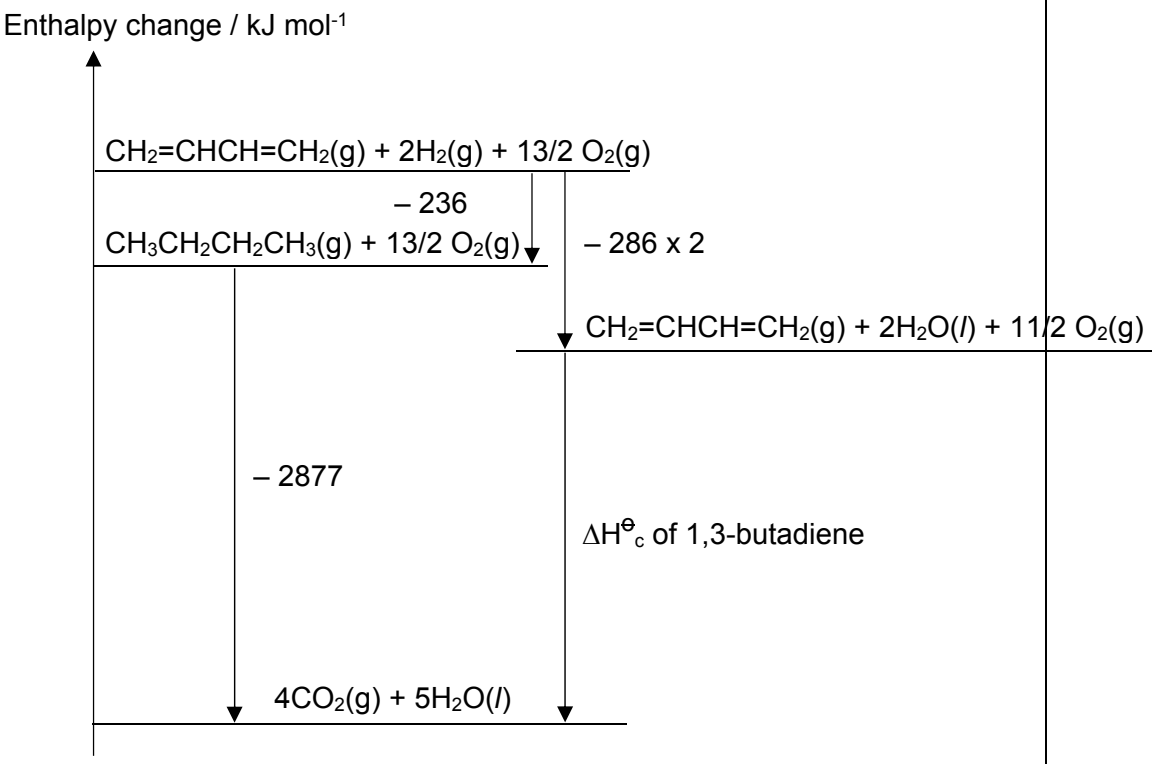
(iii) A student calculated the expected $\Delta H^{\ominus}_{hydrogenation}$ of 1,3-butadiene in step 2 to be –252 kJ mol^{-1}. However, 1,3-butadiene is 16 kJ mol^{-1} more stable than expected.

Calculate the actual $\Delta H^{\ominus}_{hydrogenation}$ of 1,3-butadiene. [1]

Actual $\Delta H^{\ominus}_{hydrogenation}$ of 1,3-butadiene = – 252 + 16 = –236 kJ mol^{-1}

(iv) Hence, using the value calculated in **(iii)** and the information given below, construct a fully labelled energy level diagram to determine the standard enthalpy change of combustion, $\Delta H^{\ominus}_c$ of 1,3-butadiene. [3]

substance	$\Delta H^{\ominus}_c$ / kJ mol^{-1}
	**–**2877
H_2	**–**286



$\Delta H^{\ominus}_c$ of 1,3-butadiene = – 2(–286) – 236 – 2877 = –2540 kJ mol^{-1}

(v) According to valence bond theory, the stability of conjugated diene could also be explained by orbital hybridisation.

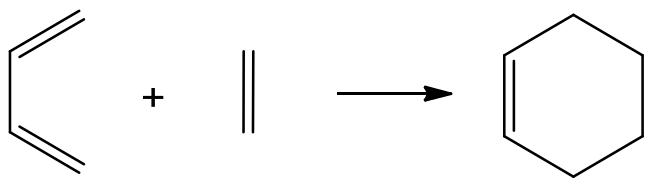
By making reference to the C–C single bond formed in 1,3-butadiene and butane, and the hybridisation of the orbitals in the two molecules, explain the extra stability of 1,3-butadiene. [2]

The C–C single bond in 1,3-butadiene are formed from the sigma overlap of sp^2 orbitals while the C–C single bond in butane are formed from the sigma overlap of sp^3 orbitals.

Since sp^2 orbital has more s character than sp^3 orbital, the electrons are sp^2 orbitals are closer to the nucleus, resulting in a stronger bond formed. Hence the extra stability of 1,3-butadiene results from the greater amount of s character in the orbital forming the stronger C–C single bond.

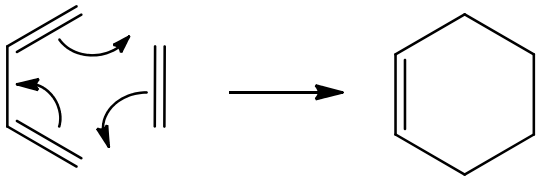
(b) Conjugate dienes can undergo addition with alkenes in a process called Diels-Alder reaction to form cyclic products. It is an important synthetic method which is widely used in organic chemistry to form unsaturated cyclic products.

An example of the Diels-Alder reaction is shown below where 1,3-butadiene reacts with ethene to form cyclohexene.:



In the process, the two reactants react in a single step through a cyclic redistribution of bonding electrons and two new carbon-carbon bonds are formed at the same time.

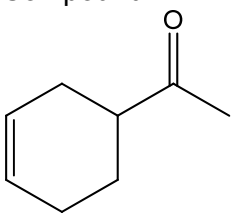
(i) By using full-headed curly arrows, suggest the mechanism that takes place in the above reaction to form cyclohexene. [1]



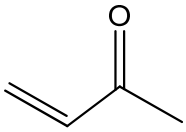
(ii) Compound **B** has the molecular formula of $C_8H_{12}O$ and it can be synthesised when 1,3-butadiene reacts with compound **C**, C_4H_6O, in the **Diels-Alder** reaction. It is known that compound **C** is able to react with 2 moles of hydrogen gas in the presence of Pt and produce a yellow precipitate with alkaline aqueous I_2. Compound **C** also gives a positive test with 2,4-dinitrophenylhydrazine and negative test with Tollens' reagent.

Suggest structures for compounds **B** and **C**, and explain the reactions described. [5]

Compound **B**:

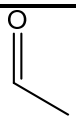


Compound **C**:



[

	Deductions
Compound **B** can be synthesised when 1,3-butadiene reacts with compound **C**, C_4H_6O, in the **Diels-Alder** reaction.	• Compound **B** is a cyclic compound which contains an alkene functional group. • Compound **C** contains an alkene functional group which allows it to react with 1,3-butadiene.
Compound **C** is able to react with 2 moles of hydrogen gas in the presence of Pt and produce a yellow precipitate with alkaline aqueous I_2.	• Compound **C** undergoes reduction with 2 moles of hydrogen gas as it has two unsaturated bonds / alkene and ketone functional group.

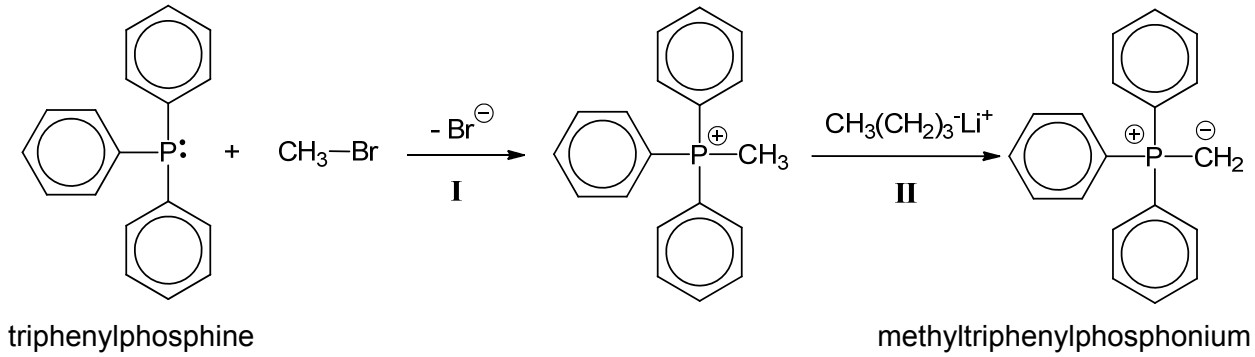
				• Compound **C** contains  group.
			Compound **C** also gives a positive test with 2,4-dinitrophenylhydrazine and negative test for Tollens' reagent.	• Compound **C** undergoes <u>condensation</u> with 2,4-DNPH and it contains a <u>ketone</u> functional group.
	(c)	Compounds of aluminium such as aluminium oxide, Al_2O_3 and aluminium chloride, $AlCl_3$ are often used in organic reactions as catalysts.		
		(i)	Aluminium oxide has unique chemical properties as it is able to react with both acid and base. Write balanced chemical equations for the reactions between aluminium oxide and the following respectively. • HBr • KOH [2] **$Al_2O_3(s) + 6HBr(aq) \longrightarrow 2AlBr_3(aq) + 3H_2O(l)$** **$Al_2O_3(s) + 2KOH(aq) + 3H_2O(l) \longrightarrow 2K[Al(OH)_4](aq)$**	
		(ii)	Account for the acid-base behaviour of aluminium oxide by making reference to its structure and bonding and state the nature of the oxide. [3] **Aluminium oxide has a giant ionic lattice structure with strong electrostatic forces of attraction between Al^{3+} and O^{2-} ions. However, due to the high charge density of the Al^{3+} ion, there is considerable covalent character in the compound, hence resulting it being an amphoteric oxide which can react with both acids and alkalis.**	

Section B

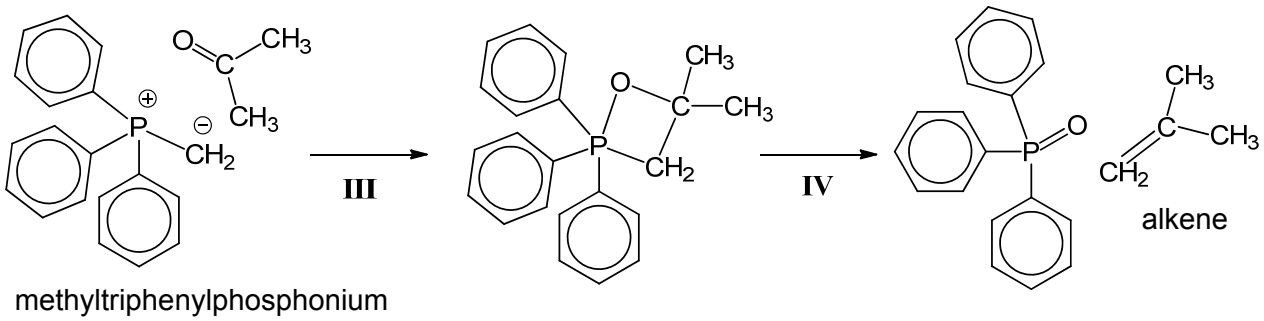
Answer **one** question from this section.

4 **(a)** The Wittig reaction converts carbonyl compounds into alkenes by reacting aldehydes or ketones with alkyltriphenylphosphonium, such as methyltriphenylphosphonium. During the reaction, the number of carbon atoms also increases.

Stage 1 – Preparation of methyltriphenylphosphonium



Stage 2 – Formation of alkene



Different alkenes can be formed by using different carbonyl compounds and R-groups on the alkyltriphenylphosphonium.

(i) The melting points of four compounds are given below.

compound	*formula*	*melting point / °C*
triphenylphosphine	$P(C_6H_5)_3$	80
water	H_2O	0
methyltriphenylphosphonium bromide	$(C_6H_5)_3P{=}CH_2^+Br^-$	232
sodium chloride	NaC*l*	801

With reference to their structure and bonding, suggest why the melting point of

1. triphenylphosphine is higher than water; and
2. methyltriphenylphosphonium bromide is lower than sodium chloride [4]

1. Both compounds have simple molecular structures with weak intermolecular forces of attraction between their molecules. Triphenylphosphine has larger and more polarizable electron cloud than water. Thus is has stronger instantaneous dipole-induced dipole interaction than (the hydrogen bonding of) water.
2. Both compounds have giant ionic lattice structures. Methyltriphenylphosphonium bromide has ions with larger radii than NaC*l*, hence lattice energy is less exothermic and melting point is lower.

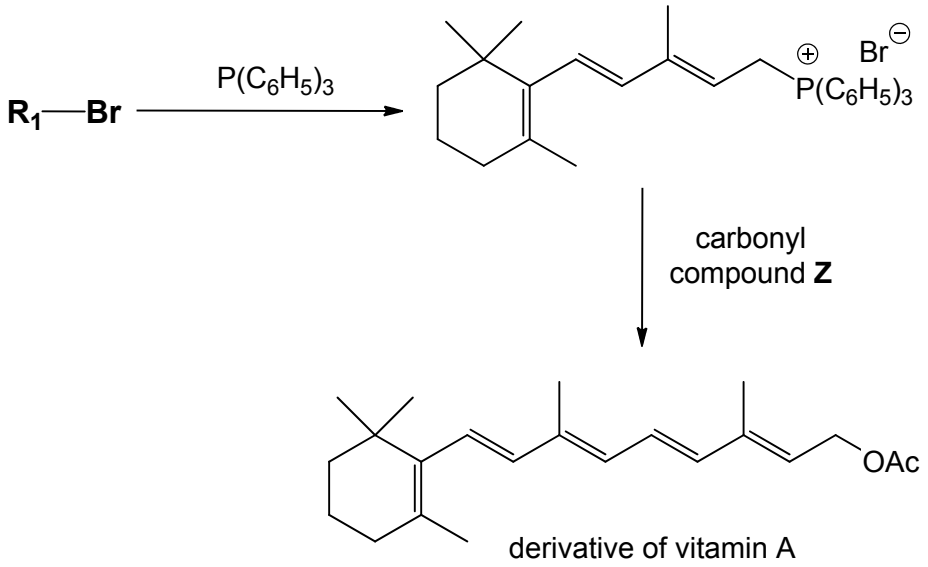
(ii) State the type of reaction in step **I**. [1]

Nucleophilic substitution or S_N2

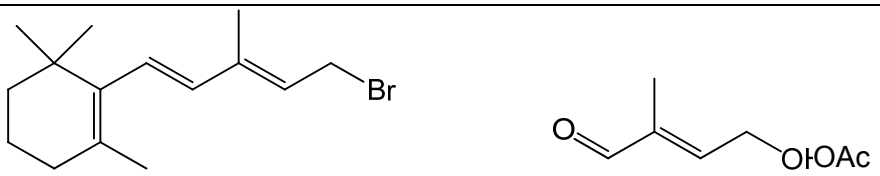
(iii) State the role of $CH_3(CH_2)_3^-Li^+$ in Step **II**. [1]

Base

(iv) The advantage of Wittig reaction is the predictability of its alkene product. It is used in industrial processes such as the formation on vitamin A.



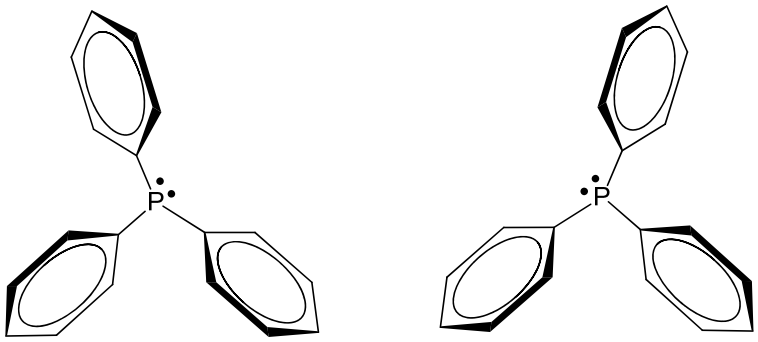
Suggest the structures of alkylbromide **R_1–Br** and carbonyl compound **Z** for forming the derivative of vitamin A. You may assume that the OAc group remains unchanged during the reaction. [2]

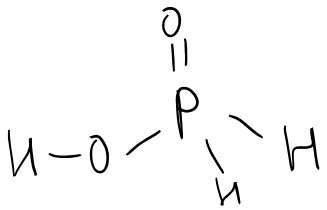
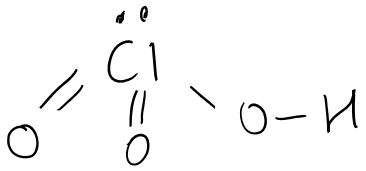


(b) Triphenylphosphine, $P(C_6H_5)_3$, is prepared by reacting phosphorus trichloride, chlorobenzene and sodium. Sodium chloride is precipitated during the reaction due to its insolubility in the organic mixture.

(i) Write the balanced equation for the preparation of triphenylphosphine. [1]

$$PCl_3 + 3C_6H_5Cl + 6Na \longrightarrow P(C_6H_5)_3 + 6NaCl$$

		(ii)	Triphenylphosphine does not form in the above reaction when water is present. Given that phosphorus trichloride reacts with water according to the equation $PCl_3 + H_2O \longrightarrow H_3PO_3 + HCl$ describe, with the aid of equation(s), any other reactions that will take place when water is used as a solvent. Hence or otherwise, suggest the colour of universal indicator in the resulting mixture. [3]
			Using the mole ratio of PCl_3 and Na in the previous equation in (b)(i), **$6Na + 6H_2O \longrightarrow 6NaOH + 3H_2$** **$H_3PO_3 + 2NaOH \longrightarrow Na_2HPO_4 + H_2O$** **$HCl + NaOH \longrightarrow NaCl + H_2O$** **OR** **3 mol of NaOH is needed to completely react with 1 mol of H_3PO_3 and 1 mol of HC*l*.** **Due to the excess of NaOH, universal indicator shows a blue / violet colour.**
		(iii)	It has been suggested that triphenylphosphine is a chiral compound. Two structures of triphenylphosphine are shown below.  State the relationship of the two structures and suggest why triphenylphosphine is a chiral compound. [2]
			The two structures are enantiomers. **Triphenylphosphine has non-superimposable mirror images / no internal plane of symmetry.**
	(c)	**(i)**	The aqueous solutions of two acids were prepared and their pH measured. *acid* | *concentration / mol dm^{-3}* | *pH* **M** | 0.75 | 1.11 **N** | 0.25 | 0.60 Given that **M** and **N** are monobasic acids, show calculations to explain whether each acid is a strong or weak acid. [3]
			To determine if acid M dissociates fully: **–log(0.75) = 0.125** **Since pH is higher than 0.125, M did not dissociate fully. M is a weak acid.** **To determine if acid N dissociates fully:** **–log(0.25) = 0.60**

			Since pH is 0.60, N dissociated fully. N is a strong acid.
		(ii)	It is known that the electronegativity of the central atom in the acid affects its acidity. With reference to the increasing trend of electronegativity across the period, suggest the correct identities of the acids **M** and **N**, given that they could be H_3PO_2 or $HClO_3$. [3]
			M is H_3PO_2 and N is $HClO_3$.   **C*l* atom is more electronegative than P , so it polarizes the O–H bond in $HClO_3$ to a greater extent, causing H^+ ion to be given off more readily, hence $HClO_3$ is a stronger acid, and must be N.** **OR** **C*l* atom is more electronegative than P , so it disperses the negative charge on the conjugate base, ClO_3^-, to a greater extent. As the conjugate base is more stabilized, the acid is a stronger one.**
			[Total: 20]

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

Osmium is a bluish-white metal found as a trace element in alloys, mostly in platinum ores. Not surprisingly, osmium was discovered in 1803 by Smithson Tennant when he noticed a residue remaining after dissolving crude platinum in aqua regia – a mixture of concentrated nitric acid and concentrated hydrochloric acid.

Platinum reacts with concentrated nitric acid to produce aqueous platinum(IV) cations, nitrogen dioxide and water. The platinum(IV) cations are then complexed with chloride *ligands* to produce hexachloroplatinate(IV) anions which are recovered through the reaction with ammonium chloride to produce yellow crystals.

(a) (i) Define the term *ligand*. [1]

A ligand is a neutral molecule or anion with at least one atom bearing a lone pair of electrons capable of dative bonding/coordinating to the central metal atom or ion.

(ii) Write a balanced ionic equation to represent the reaction of platinum with concentrated nitric acid. [1]

$$\mathbf{Pt + 8HNO_3 \longrightarrow Pt^{4+} + 4NO_2 + 4NO_3^- + 4H_2O}$$

(iii) Suggest the identity of the yellow crystals obtained. [1]

$\mathbf{(NH_4)_2PtCl_6}$

(iv) The solubility of the yellow crystals in water at room temperature is 5.0 g dm^{-3} but decreases to 0.028 g dm^{-3} in 1 mol dm^{-3} ammonium chloride at the same temperature.

Write an equation to represent the dissolution of the yellow crystals in in **(a)(iii)** and use the equation to account for the decreased solubility in 1 mol dm^{-3} ammonium chloride. [2]

$$\mathbf{(NH_4)_2PtCl_6\ (s) \rightleftharpoons 2NH_4^+\ (aq) + PtCl_6^{2-}\ (aq)}$$

The solubility of the yellow crystals will be reduced as the position of equilibrium in the solubility equilibria is pushed back to the left due to the common ion effect brought about by NH_4^+.

(v) Explain why hexachloroplatinate(IV) is coloured. [3]

When chloride ligands approach the Pt^{4+} central cation, the degenerate d-orbitals/d-subshell split into two groups of different energy levels. An electron in the lower level can absorb energy equivalent to the energy gap which corresponds to a certain wavelength of light from the visible region of the electromagnetic spectrum and be promoted to the higher energy level. The colour seen is complementary to the colour absorbed.

When powdered osmium is exposed to air, it forms the toxic compound osmium tetroxide, OsO_4 with a strong odour like that of chlorine.

$$Os + 2O_2 \longrightarrow OsO_4$$

(b) (i) Use the standard electrode potential given and choose another appropriate equation from the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for the reaction between osmium and air. [1]

$$OsO_4 + 8H^+ + 8e^- \rightleftharpoons Os + 4H_2O \qquad E^{\ominus} = +0.84\ V$$

Choose $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $\quad E^{\ominus} = +1.23$ V

$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$
$= +1.23 - (+0.84)$
$= +0.39$ V

(ii) Hence calculate $\Delta G^{\ominus}_{cell}$ for the reaction in **(b)(i)**, leaving your answer in kJ mol^{-1}. [1]

$\Delta G^{\ominus}_{cell} = -nFE^{\ominus}_{cell}$
$= -(8)(96500)(+0.39)$
$= -301\ 080$ J mol^{-1}
$= -301$ kJ mol^{-1}

(iii) Suggest, with reasoning, the sign for the standard enthalpy change of reaction for the reaction between osmium and air, making reference to the terms in the Gibbs free energy equation and your answer in **(b)(ii)**. [2]

Since the standard entropy change is negative due to the decrease in number of moles of gaseous oxygen/loss of oxygen, the standard enthalpy change of reaction must be negative too for $\Delta G^{\ominus}_{cell}$ to be overall negative.

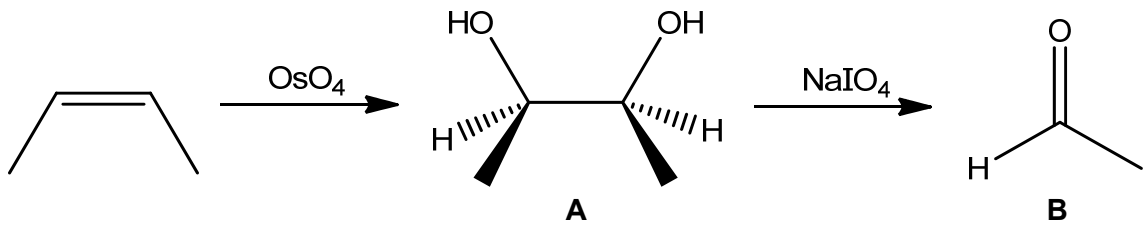
The figure below shows part of a label on a bottle of osmium tetroxide.

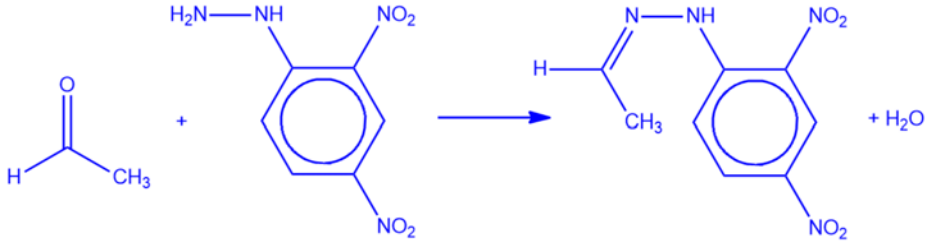
<u>Osmium Tetroxide, OsO_4</u>

Molar mass: 254.2 g mol^{-1}
Density: 4.9 g cm^{-3}
Vapour pressure: 933 Pa
Max. permissible exposure limit: 200 µg m^{-3}

Net weight: 1000 g
Volume of container: 250 cm^3

Note:
Vapour pressure – the pressure of vapour in equilibrium with its solid/liquid form.
1 µg = 1 x 10^{-6} g

	(c)	**(i)**	Use the information above to calculate the amount of OsO_4 in the vapour phase within an unopened container of OsO_4 at room temperature. Assume ideal gas behaviour. [2] **Gas volume = 250 – $\frac{1000}{4.9}$ = 45.9 cm^3** **n(OsO_4 vapour) = $\frac{pV}{RT}$ = $\frac{933 \times \frac{45.9}{1\,000\,000}}{8.31 \times 293}$ = 1.76 x 10^{-5} mol**
		(ii)	Hence determine the concentration of OsO_4, in μg m^{-3}, in the air of a 100 m^3 laboratory where a new container is opened. Assume that the air has evenly mixed. [2] **m(OsO_4 vapour) = 1.76 x 10^{-5} x 254.2 = 4.47 x 10^{-3} g** **[OsO_4] = $\frac{4.47\times10^{-3}}{100}$ = 4.47 x 10^{-5} g m^{-3} = 44.7 μg m^{-3}**
		(iii)	Discuss whether it is safe for researchers to open the container in this laboratory without a proper fume cupboard, considering your answer in **(c)(ii)** and the approach used to calculate it. [1] **Yes, since the effective concentration of 44.7 μg m^{-3} is less than the maximum permissible exposure limit of 200 μg m^{-3}.** **OR** **No, it is not safe as the vapour takes time to diffuse evenly throughout the room. The immediate air around the researchers will have a concentration of OsO_4 exceeding the maximum permissible limit**.
	Osmium tetroxide, OsO_4 can oxidise alkenes to give diols. $NaIO_4$ will react further with the diol to produce carbonyl compounds.  		
	(d)	Suggest a simple chemical test to distinguish between compounds **A** and **B** and write a balanced equation for the positive test. [3] 2,4-DNPH, room conditions Yellow crystals formed with **B** but no yellow crystals formed with **A**.	



OR

Tollens' reagent, warm
Silver mirror formed with **B** but no silver mirror formed with **A**.
$CH_3CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow 2Ag + 4NH_3 + CH_3CO_2^- + 2H_2O$

OR

Fehling's reagent, warm
Red-brown ppt formed with **B** but no red-brown ppt formed with **A**.
$CH_3CHO + 2Cu^{2+} + 5OH^- \longrightarrow CH_3CO_2^- + Cu_2O + 3H_2O$

OR

Sodium, room conditions
Effervescence observed with **A**. Gas evolved extinguishes lighted splint with a pop sound. No effervescence observed with **B**.

OR

PCl_5, room conditions
Steamy/White fumes observed with **A** but no white fumes observed with **B**.
$CH_2(OH)CH_2OH + 2PCl_5 \longrightarrow CH_2ClCH_2Cl + 2POCl_3 + 2HCl$

OR

$SOCl_2$ (pyridine), heat
Steamy/White fumes observed with **A** but no white fumes observed with **B**.
$CH_2(OH)CH_2OH + 2SOCl_2 \longrightarrow CH_2ClCH_2Cl + 2HCl + 2SO_2$

[Total: 20]

– End of Paper –