Chemistry H2 P1 Prelim 2016

Section A

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct and shade your choice on the answer sheet provided.

1 For indoor air quality safety standards, the maximum safe tolerance level of carbon monoxide gas is 6×10^{-4} m^3 of carbon monoxide in 1 m^3 of air. Given that a typical room measures 4 m by 4 m by 3 m, calculate the number of molecules of carbon monoxide present in the room at this tolerance level at room temperature and pressure?

A 1.13×10^{24}

B 7.22×10^{23}

C 1.51×10^{22}

D 7.22×10^{20}

2 Soluble mercury compounds such as mercury(II) nitrate are highly toxic. One removal method involves the treatment of wastewater contaminated with mercury(II) nitrate with sodium sulfide to produce solid mercury(II) sulfide and sodium nitrate solutions.

Calculate the mass of mercury(II) sulfide formed when 0.020 dm^3 of 0.100 mol dm^{-3} sodium sulfide reacts with 0.050 dm^3 of 0.010 mol dm^{-3} mercury(II) nitrate?

A 0.117 g **B** 0.133 g **C** 0.280 g **D** 0.466 g

3 Gaseous particle **X** has a proton number n, and a charge of +1.
Gaseous particle **Y** has a proton number (n+1), and is isoelectronic with **X**.

Which statement about **X** and **Y** is correct?

A When placed in an electric field, the angle of deflection for **X** is the same as that of **Y**.

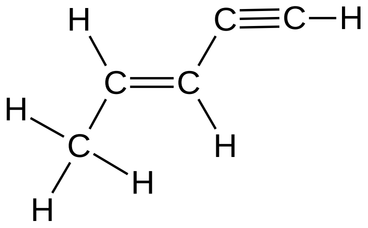
B **X** requires more energy than **Y** when a further electron is removed from each particle.

C **X** releases more energy than **Y** when an electron is added to particle.

D **X** has a larger radius than **Y**.

4 Covalent bonds are formed by orbital overlap. The shape of unsaturated hydrocarbon molecules can be explained in terms of hybridisation of orbitals.

Which bond is not present in the molecule shown below?



A σ bond formed by $2sp^3 – 2sp^2$ overlap.

B σ bond formed by $2sp^3$-2sp overlap.

C σ bond formed by 1s-2sp overlap.

D π bond formed by 2p-2p overlap.

5 Which statement about graphite is **not** correct?

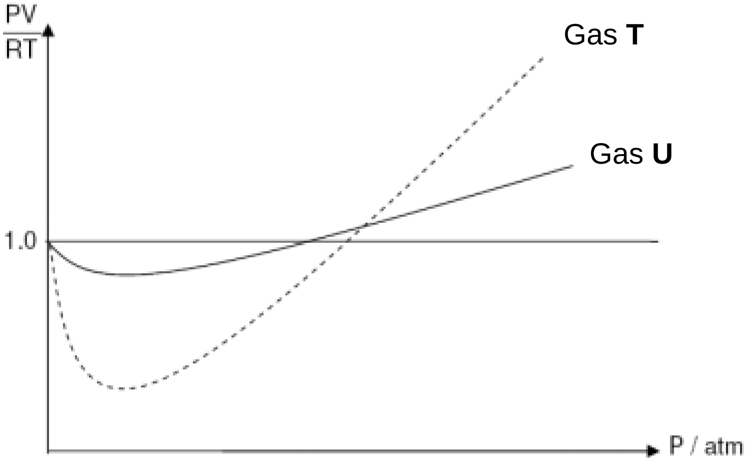
A The carbon-carbon bonds in graphite are shorter than those in diamond.

B It can act as a good lubricant due to the weak forces of attraction between the layers of atoms.

C Carbon to carbon distances between the planes of hexagonal rings are smaller than those within the planes.

D It acts as a good conductor of electricity in the direction parallel to the planes containing hexagonal rings of carbon.

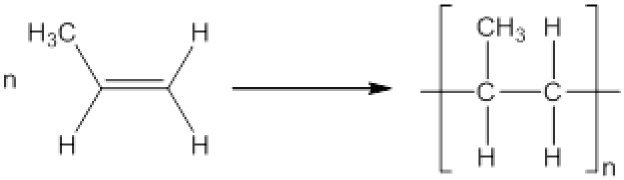
6



Which of the following could be the identities of the gases?

	Gas **T**	Gas **U**
A	H_2(g) at 298 K	CO_2(g) at 298 K
B	CH_4(g) at 298 K	NH_3(g) at 298 K
C	O_2(g) at 500 K	O_2(g) at 298 K
D	N_2(g) at 298 K	N_2(g) at 500 K

7 The polymerisation of propene to form polypropene occurs readily at room temperatures.



What will be the signs of ΔG, ΔH and ΔS for the polymerisation reaction at room temperature?

	ΔG	ΔH	ΔS
A	+	–	–
B	+	+	–
C	–	+	–
D	–	–	–

8 The rate of the redox reaction between hydrochloric acid and Mg

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$

can be followed by measuring the time taken for the same volume of hydrogen to be produced from a range of hydrochloric acid concentrations.

To find the order with respect to hydrochloric acid, which would be the most suitable graph to plot using the data?

A [HC*l*] against time

B [HC*l*] against $\frac{1}{\text{time}}$

C Volume H_2 against time

D Volume H_2 against $\frac{1}{\text{time}}$

9 The numerical value of the solubility product of nickel(II) carbonate is 6.6×10^{-9} while that of silver carbonate is 2.1×10^{-11} at 25 °C.

Which of the following statements is true?

A Addition of silver nitrate increases the solubility of silver carbonate.

B The solubility of silver carbonate is higher than the solubility of nickel(II) carbonate.

C Addition of nitric acid to a solution containing nickel(II) carbonate increases the solubility product of nickel(II) carbonate.

D Nickel(II) carbonate precipitates first when sodium carbonate is added to a solution containing equal concentrations of nickel(II) and silver ions.

10 What is the pH of 10 cm^3 of 0.05 mol dm^{-3} sodium benzoate?

[K_a of benzoic acid = 6×10^{-5} mol dm^{-3}]

A 6.46

B 7.46

C 8.46

D 9.46

11 A sample of 20.0 cm^3 of 0.20 mol dm^{-3} iron(II) sulfate is titrated against 0.05 mol dm^{-3} potassium manganate(VII) in the presence of excess fluoride ions. It is found that 20.0 cm^3 of the manganate(VII) solution is required to reach the end-point.

What is the oxidation number of manganese at end-point?

A +3

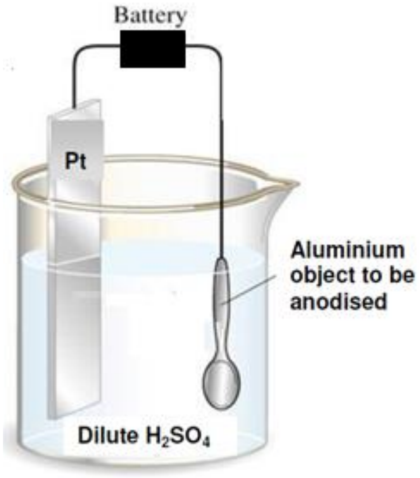
B +4

C +5

D +6

12 Anodisation is a process to increase corrosion resistance and surface hardness in aluminium objects.

A possible set up for the process is shown as below:



Which of the following statements about the anodisation of aluminium is true?

A Aluminium dissolves at the anode.

B Hydrogen gas is liberated at the anode.

C Water is oxidised at the anode to form oxygen gas.

D Replacing the electrolyte with NaOH(aq) will cause the reaction to cease.

13 Which of the following elements forms an oxide with a giant structure and a chloride which is readily hydrolysed?

A Silicon

B Barium

C Sodium

D Phosphorus

14 An element in Period 3 has the following properties:

- Its first ionisation energy is larger than both the elements before and after it across the period.
- It conducts electricity.
- It reacts slowly with cold water but react readily with steam to give a gas.

Which statement about this element is **not** correct?

A It has a high melting and boiling point.

B It forms an oxide that produces a solution that is acidic when added to water.

C It forms a chloride that produces a solution that is slightly acidic when added to water.

D Its oxidation state in compounds usually follows the group number it belongs to in the Periodic Table.

15 The following report appeared in a newspaper article.

Drums of bromine broke open after a vehicle crash on the motorway. Traffic was diverted as purple gaseous bromine drifted over the road (it is denser than air), causing irritation to drivers' eyes. Firemen sprayed water over the scene of the accident, dissolving the bromine and washing it away.

What is wrong with the report?

A Bromine does not dissolve in water.

B Bromine does not vapourise readily.

C Bromine is less dense than air.

D Bromine is not purple.

16 When crystalline potassium chromate(VI) was dissolved in water, a yellow solution **Q** was formed. Addition of dilute sulfuric acid to **Q** gave an orange solution **R**. When hydrogen sulfide was bubbled through solution **R**, there was a color change in the solution and yellow sulfur was produced.

Which process **did not** occur in the above experiment?

A Ligand exchange

B Redox reaction

C Precipitation

D Acid-base

17 Chlorine compounds show oxidation states ranging from –1 to +7.

What are the reagents and conditions necessary for the oxidation of chlorine gas into a compound containing chlorine in the +5 oxidation state?

A Cold dilute NaOH

B Hot concentrated NaOH

C Concentrated H_2SO_4 at room temperature

D $AgNO_3$(aq) followed by NH_3(aq) at room temperature

18 Which statement correctly **defines** a transition element?

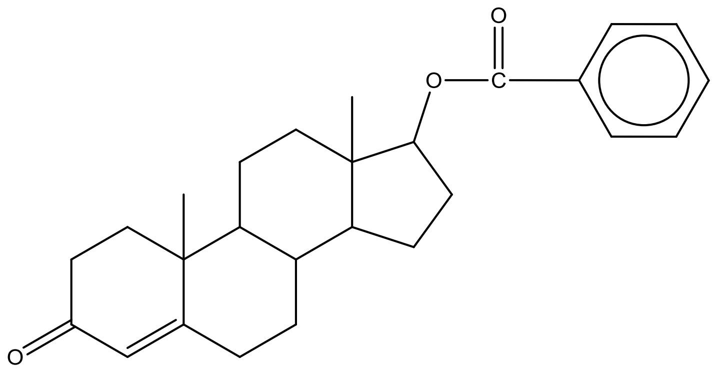
A Transition elements form many coloured compounds.

B Transition elements or their compounds are widely used as catalysts.

C Transition elements form one or more stable ions with partially filled d-orbitals.

D Transition elements exhibit more than one oxidation state in their compounds.

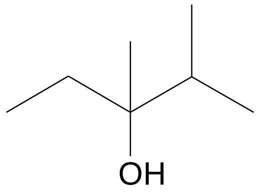
19 How many stereoisomers does a molecule of Nandrolone has?



Nandrolone

A 8 **B** 16 **C** 32 **D** 64

20 The structure of compound **Z** is as seen below:



Compound **Z**

It is completely reacted with hot concentrated H_2SO_4 to form compound **Y**. What is the total number of isomers of **Y**?

A 2 **B** 3 **C** 4 **D** 5

21 2–methylpropanoic acid can be synthesised from 1–chloropropane through a series of reactions.

Which set of reagents, used in sequential order, would be the most suitable for this synthesis?

A PCl_5, acidified $KMnO_4$

B ethanolic KCN, dilute HC*l*

C aqueous KOH, HC*l*, ethanolic KCN, dilute HC*l*

D ethanolic KOH, HBr, ethanolic KCN, dilute H_2SO_4

22 Which statement about ethanal and propanone is **not** correct?

A Both give a positive tri-iodomethane test.

B Both react with 2,4-dinitrophenylhydrazine reagent.

C Both may be prepared by the oxidation of an alcohol.

D Both react with hot acidified sodium dichromate(VI).

23 When sodium iodide in propanone is added to an optically active sample of 2-bromobutane, a sodium bromide precipitate is formed after 13 minutes upon heating.

$$\text{NaI} + CH_3CHBrCH_2CH_3 \longrightarrow CH_3CHICH_2CH_3 + \text{NaBr(s)}$$

The experiment was repeated several times and the rate equation was found to be

$$\text{Rate} = k[CH_3CHBrCH_2CH_3][\text{NaI}]$$

Which of the following statements is **not** correct?

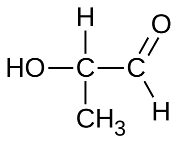
A The mechanism involves a reactive intermediate.

B The organic product sample obtained rotates the plane of polarised light.

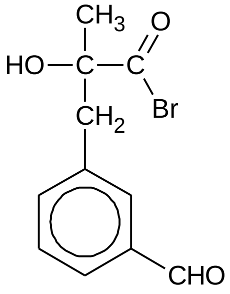
C A similar experiment, using 1-bromobutane, will produce a precipitate in less than 13 minutes.

D A similar experiment, using 2-chlorobutane, will take more than 13 minutes to produce a precipitate.

24 Which reagent can be used to distinguish between compounds **R** and **S** under suitable conditions?



R



S

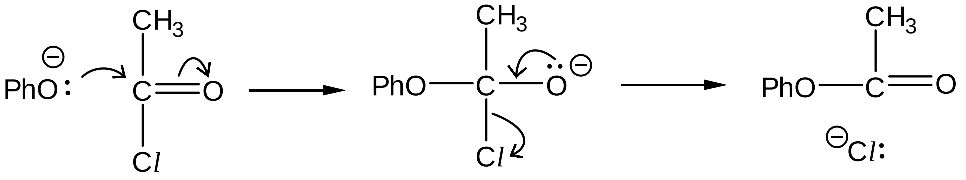
A Acidified potassium dichromate (VI)

B Alkaline copper(II) solution

C Sodium metal

D Phosphorus pentachloride

25 The two-stage reaction sequence given shows a possible mechanism for the reaction between phenoxide ion and ethanoyl chloride.



where Ph = phenyl

How should the *overall* reaction be classified?

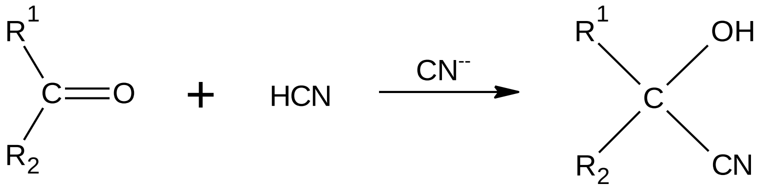
A Electrophilic addition

B Nucleophilic addition

C Electrophilic substitution

D Nucleophilic substitution

26 Cyanohydrins can be made from carbonyl compounds by generating CN^- ions from HCN in the presence of a weak base.



In a similar reaction, $^-CH_2COOCH_3$ ions are generated from CH_3COOCH_3 by strong bases.

Which compound can be made from an aldehyde and CH_3COOCH_3?

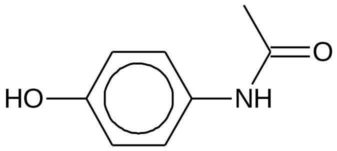
A $CH_3CH(OH)COOCH_3$

B $CH_3COOCH_2CH(OH)\ CH_3$

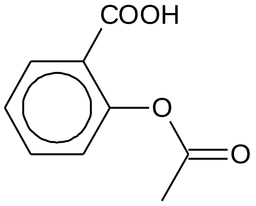
C $CH_3CH_2CH(OH)CH_2COOCH_3$

D $(CH_3)_2C(OH)CH_2COOCH_3$

27 Two common drugs administered when a patient experiences headache or fever are paracetamol and aspirin.



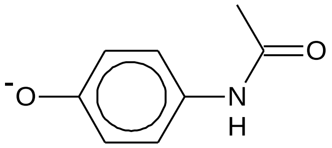
paracetamol



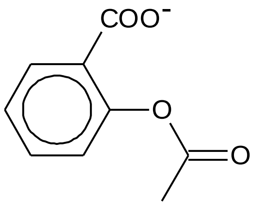
aspirin

A solution of the two drugs was hydrolysed using hot aqueous sodium hydroxide. Which organic product would be produced?

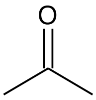
A



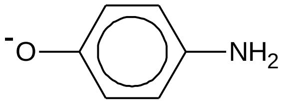
B



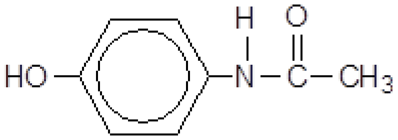
C



D



28 Acetaminophen is a drug used in headache remedies. It has the following structure:



Acetaminophen

Which of the following reagents reacts with Acetaminophen?

A Sodium carbonate

B Cold sodium hydroxide

C Alkaline aqueous iodine

D 2,4-dinitrophenylhydrazine

29 Which sequence shows the correct order of increasing pK_b in an aqueous solution of equal concentration?

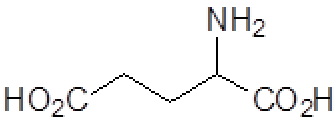
A $C_2H_5CONH_2 < C_6H_5NH_2 < C_2H_5NH_2 < C_2H_5NH_3^+$

B $C_2H_5NH_2 < C_6H_5NH_2 < C_2H_5NH_3^+ < C_2H_5CONH_2$

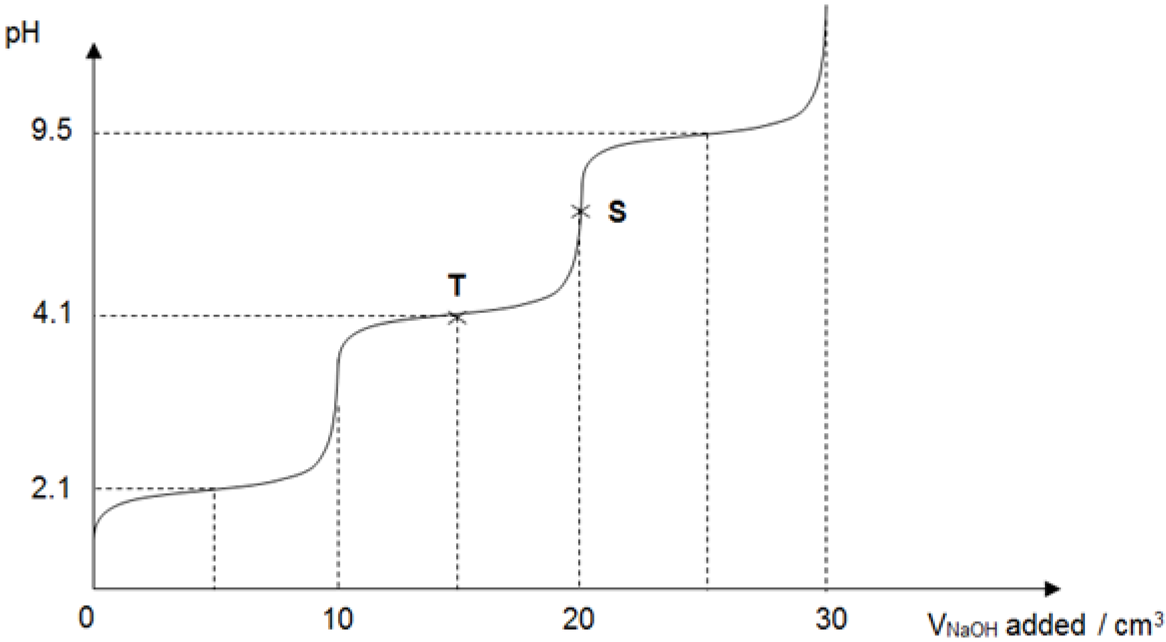
C $C_2H_5NH_2 < C_6H_5NH_2 < C_2H_5CONH_2 < C_2H_5NH_3^+$

D $C_2H_5NH_3^+ < C_2H_5CONH_2 < C_2H_5NH_2 < C_6H_5NH_2$

30 There are three pK_a values associated with glutamic acid: 2.1, 4.1 and 9.5.

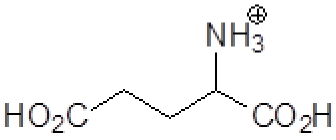


The pH-volume curve obtained when 30 cm^3 of NaOH is added to 10 cm^3 of the protonated form of glutamic acid of the same concentration is given below.

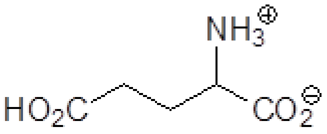


Which of the following is the major species present at point **S**?

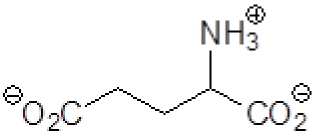
A



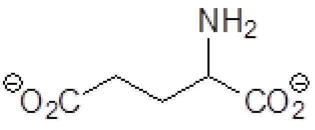
B



C



D



Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to pick a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	**B**	**C**	**D**
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

31 The radius and charge of each of the six ions are shown below.

ion	J^+	L^+	M^{2+}	X^-	Y^-	Z^{2-}
radius / nm	0.14	0.18	0.15	0.14	0.18	0.15

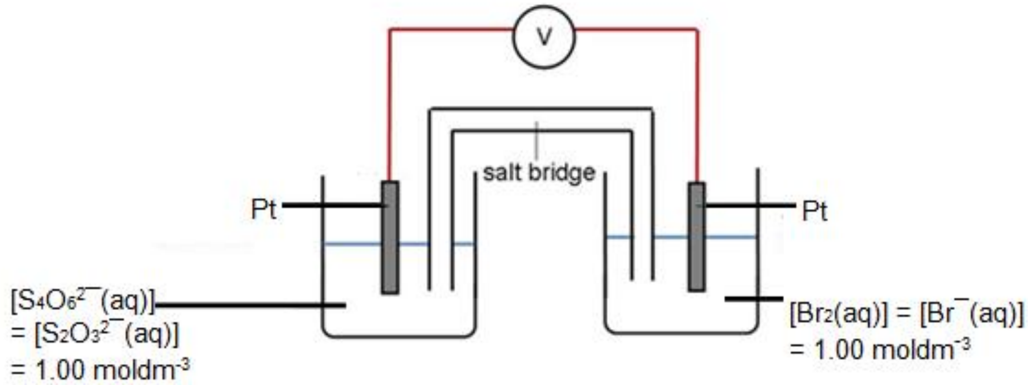
The ionic solids JX, LY and MZ are of the same lattice type. Which of the following statements are correct?

1 The melting point increases in the order LY < JX < MZ.

2 The numerical value of hydration energy of X^- is smaller than that of Z^{2-}.

3 The solution containing M^{2+} ions is more acidic than the solution containing J^+ ions.

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



Which of the following will increase the cell potential?

1 Adding iodine crystals into the anodic half cell.

2 Adding solid silver nitrate into the cathodic half cell.

3 Increasing the concentration of Br_2(aq) in the Br_2(aq)/Br^-(aq) half cell.

33 From the position of the elements present in the Periodic Table and the physical properties of the compounds, which compounds are covalent?

1	$(CH_3)_2SiCl_2$	b.p. 70°C
2	$GeCl_4$	b.p. 86°C
3	$AlBr_3$	b.p. 265°C

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

The oxides of titanium, iron and nickel are used as catalysts in the industries.

Which properties are titanium, iron and nickel likely to have in common?

1 similar ionic radii

2 high melting points

3 variable oxidation states

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

With reference to the two half equations below, which statements are correct?

$$[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-}$$

$$Fe^{3+} + e \rightleftharpoons Fe^{2+}$$

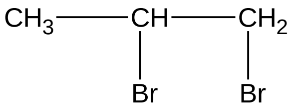
1 $[Fe(CN)_6]^{3-}$ is more stable than Fe^{3+}

2 $[Fe(CN)_6]^{4-}$ is a stronger reducing agent than Fe^{2+}

3 Both $[Fe(CN)_6]^{3-}$ and Fe^{3+} can oxidize MnO_4^{2-} to MnO_4^{-}

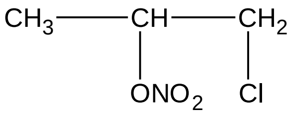
36 Propene is found to react with chlorine in the presence of aqueous sodium bromide and sodium nitrate. Which of the following are not possible products of the reaction?

1



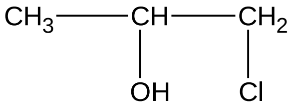
$CH_3-\underset{Br}{CH}-\underset{Br}{CH_2}$

2



$CH_3-\underset{ONO_2}{CH}-\underset{Cl}{CH_2}$

3



$CH_3-\underset{OH}{CH}-\underset{Cl}{CH_2}$

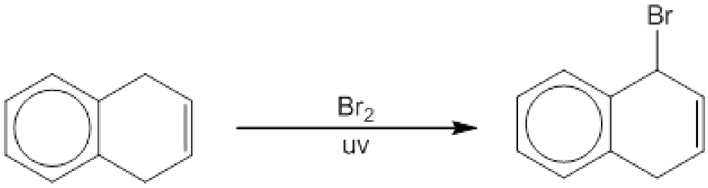
The responses **A** to **D** should be selected on the basis of

A	**B**	**C**	**D**
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

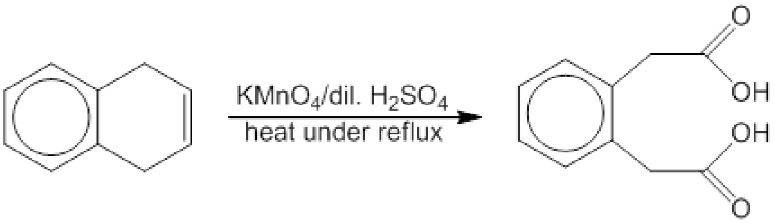
No other combination of statements is used as a correct response.

37 Which of the following reactions will not give a good yield of the desired product?

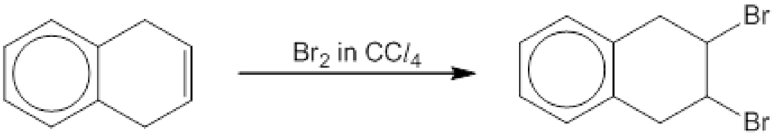
1



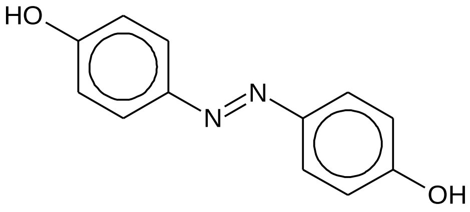
2



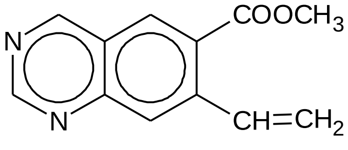
3



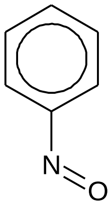
38 The three compounds **E**, **F** and **G** have the following structures?



E



F



G

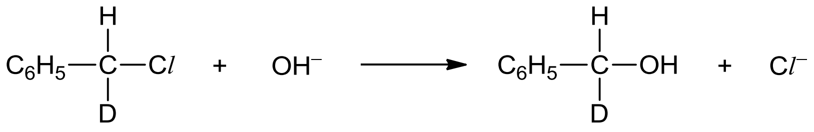
Which statements about **E**, **F** and **G** are correct?

1 **E** and **G** have the same empirical formula.

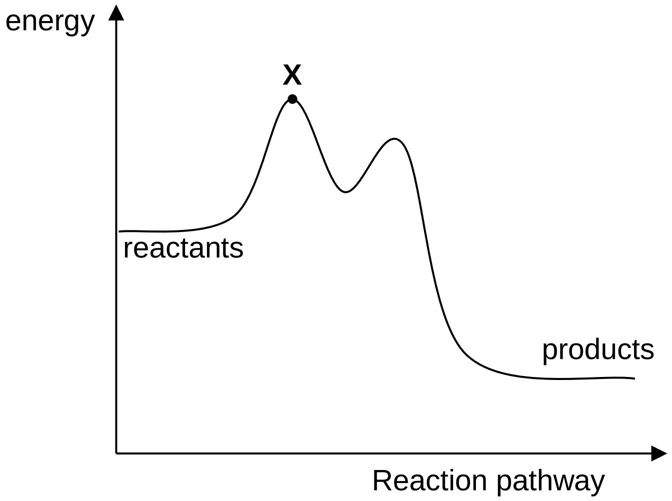
2 **E** and **F** are isomers

3 The Mr of **F** is exactly twice that of **G**

39 The energy profile for the following reaction is shown below. [D = ^2H]



$$C_6H_5CHDCl + OH^- \longrightarrow C_6H_5CHDOH + Cl^-$$

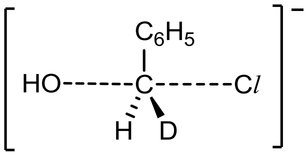


Which conclusions can be drawn?

1 The product has no effect on the rotation of plane polarised light.

2 The rate of reaction can be increased by increasing concentration of OH^-.

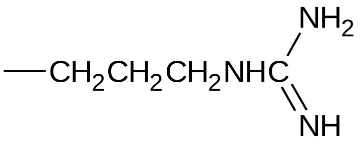
3 The structure of the transition state at point **X** is



40 Which groups within an amino acid are able to form a cross-chain link to stabilise the tertiary structure of a protein?

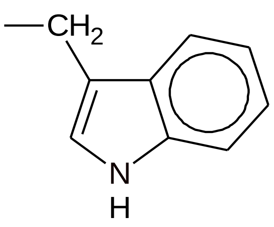
1 $—CH_2CONH_2$

2



$—CH_2CH_2CH_2NHC(=NH)NH_2$

3



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YJC Chemistry H2 prelim 2016

Section A

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct and shade your choice on the answer sheet provided.

1 For indoor air quality safety standards, the maximum safe tolerance level of carbon monoxide gas is 6×10^{-4} m^3 of carbon monoxide in 1 m^3 of air. Given that a typical room measures
4 m by 4 m by 3 m, calculate the number of molecules of carbon monoxide present in the room at this tolerance level at room temperature and pressure?

A 1.13×10^{24}

B 7.22×10^{23}

C 1.51×10^{22}

D 7.22×10^{20}

Answer: B

For 1 m^3 of air, 6×10^{-4} of CO is allowed
For $4 \times 4 \times 3 = 48$ m^3 of air, volume of CO = $48 \times 6 \times 10^{-4} = 0.0288$ m^3 = 28.8 dm^3
Number of moles of CO = 28.8 / 24 = 1.20 mol
Number of molecules
= $1.20 \times (6.02 \times 10^{23})$
= 7.22×10^{23}

2 Soluble mercury compounds such as mercury(II) nitrate are highly toxic. One removal method involves the treatment of wastewater contaminated with mercury(II) nitrate with sodium sulfide to produce solid mercury(II) sulfide and sodium nitrate solutions.

Calculate the mass of mercury(II) sulfide formed when 0.020 dm^3 of 0.100 mol dm^{-3} sodium sulfide reacts with 0.050 dm^3 of 0.010 mol dm^{-3} mercury(II) nitrate?

A 0.117 g **B** 0.133 g **C** 0.280 g **D** 0.466 g

Answer: A

Balanced equation:
$Hg(NO_3)_2(aq) + Na_2S(aq) \rightarrow HgS(s) + 2NaNO_3(aq)$

No. of moles of Na_2S
= $0.020 \times 0.100 = 2.00 \times 10^{-3}$ mol
No. of moles of $Hg(NO_3)_2$
= $0.050 \times 0.010 = 5.00 \times 10^{-4}$ mol

2.00×10^{-3} mol of Na_2S will require 2.00×10^{-3} mol of $Hg(NO_3)_2$ for complete reaction.
Since 5.00×10^{-4} mol of $Hg(NO_3)_2$ is used (lesser than 2.00×10^{-3} needed), thus $Hg(NO_3)_2$ is limiting.
No. of moles of HgS = 5.00×10^{-4} mol
Mass of HgS
= $(5.00 \times 10^{-4}) \times (201 + 32.1) = 0.11655$ g

= 0.117 g

3 Gaseous particle **X** has a proton number n, and a charge of +1.
Gaseous particle **Y** has a proton number (n+1), and is isoelectronic with **X**.

Which statement about **X** and **Y** is correct?

A When placed in an electric field, the angle of deflection for **X** is the same as that of **Y**.

B **X** requires more energy than **Y** when a further electron is removed from each particle.

C **X** releases more energy than **Y** when an electron is added to particle.

D **X** has a larger radius than **Y**.

Answer: D

Particle **X**

Number of protons	n
Number of electrons	n-1

Thus **X** has a charge of +1

Particle **Y**

Number of protons	n+1
Number of electrons	n-1

Thus **Y** has a charge of -2

A is incorrect.
Angle of deflection $\propto \frac{charge}{mass}$

Y has double the charge of **X** (−2 as compared to +1), however, the atomic mass of **Y** is not double that of **X** (**X** and **Y** are consecutive elements as deduced from their proton numbers). Thus their charge/mass ratios will not be the same.

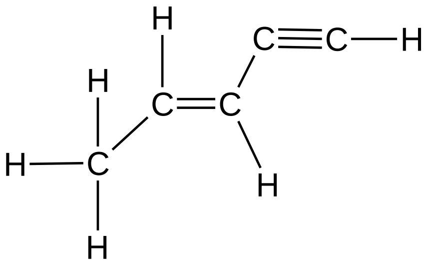
B is incorrect. As **X** has one less proton than **Y**, it has a smaller nuclear charge. As both particles are isoelectronic (same number of inner shell electrons), shielding effect will be the similar. Effective nuclear of **X** will be smaller. The valence electrons of **X** will be less strongly attracted to the nucleus. Thus less energy is needed to remove the outermost electron.

C is incorrect. **X** releases lesser energy than **Y** when an electron is added. The attractive force between the incoming electron and the nucleus is weaker than that for **Y** as **X** has smaller effective nuclear charge.

D is correct. Same explanation as Option **B**. **X** has a smaller nuclear charge (fewer protons than **Y**) and the same shielding effect as **Y** (same number of inner shell electrons). Effective nuclear of **X** will be smaller. The valence electrons of **X** will be less strongly attracted to the nucleus. Thus the radius of **X** is larger than that of **Y**.

4 Covalent bonds are formed by orbital overlap. The shape of unsaturated hydrocarbon molecules can be explained in terms of hybridisation of orbitals.

Which bond is not present in the molecule shown below?



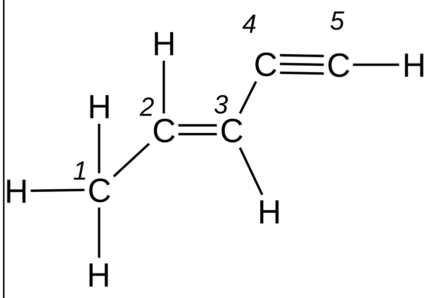
A σ bond formed by $2sp^3 – 2sp^2$ overlap.

B σ bond formed by $2sp^3$-2sp overlap.

C σ bond formed by 1s-2sp overlap.

D π bond formed by 2p-2p overlap.

Answer: B



A is correct. There is a σ bond formed by $2sp^3 – 2sp^2$ overlap present between C1-C2.

B is incorrect. There isn't any σ bond formed by $2sp^3$-2sp overlap present.

C is correct. There is a σ bond formed by 1s-2sp overlap present between hydrogen atom and C5.

D is correct. There is a π bond formed by 2p-2p overlap present between C2-C3 and C4-C5.

5 Which statement about graphite is **not** correct?

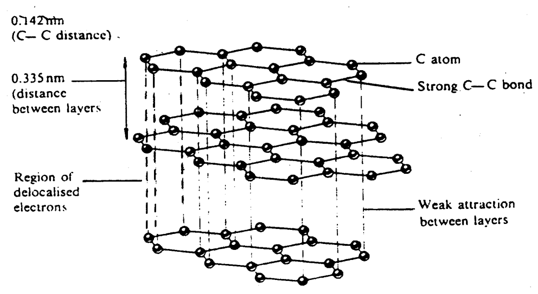
A The carbon-carbon bonds in graphite are shorter than those in diamond.

B It can act as a good lubricant due to the weak forces of attraction between the layers of atoms.

C Carbon to carbon distances between the planes of hexagonal rings are smaller than those within the planes.

D It acts as a good conductor of electricity in the direction parallel to the planes containing hexagonal rings of carbon.

Answer: C



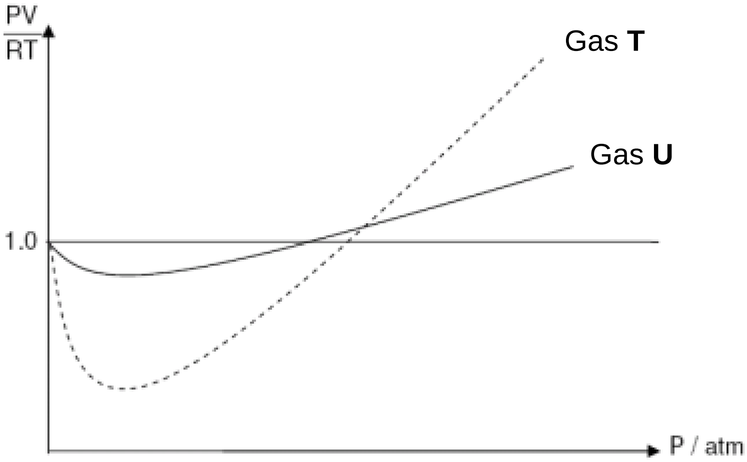
A is true. The carbon-carbon bonds in graphite are formed by sp^2-sp^2 overlap whereas carbon-carbon bonds in diamond are formed by sp^3-sp^3 overlap. sp^2-sp^2 overlap is more effective than sp^3-sp^3 overlap due to the greater s-character, thus the C-C bond length in graphite is shorter.

B is true. The weak id-id forces between the layers allow the layers to slide past one another, thus graphite is a good lubricant.

C is false. Carbon to carbon distances between the planes of hexagonal rings (weak id-id interactions) are longer than those within the planes (strong C-C covalent bonds).

D is true. Within each layer, each carbon atom is covalently bonded to three other carbon atoms using 3 of the 4 valence electrons. The presence of delocalised electrons between the layers accounts for graphite being a good conductor when a potential difference is applied along the layer. It does not conduct across the layer.

6



Which of the following could be the identities of the gases?

	Gas **T**	Gas **U**
A	H_2(g) at 298 K	CO_2(g) at 298 K
B	CH_4(g) at 298 K	NH_3(g) at 298 K
C	O_2(g) at 500 K	O_2(g) at 298 K
D	N_2(g) at 298 K	N_2(g) at 500 K

Answer: D

From graph, Gas **T** deviates more from ideality than Gas **U**.

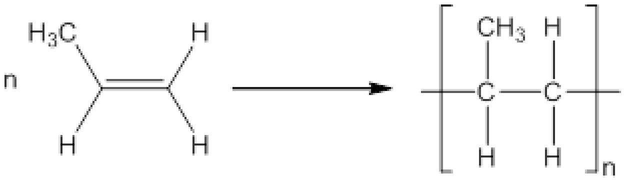
A is incorrect. Deviation of CO_2 from ideal gas behaviour is larger than that of H_2. CO_2 has a greater number of electrons than O_2, thus the electron cloud is more polarisable, resulting in stronger instantaneous dipole-induced dipole interactions between CO_2 molecules.

B is incorrect. Deviation of NH_3 from ideal gas behaviour is larger than that of CH_4. There is stronger hydrogen bonding between NH_3 molecules than instantaneous dipole-induced dipole interactions between CH_4 molecules.

C is incorrect. Deviation of O_2(g) at 298 K from ideal gas behaviour is larger than that at 500 K. At higher temperatures, particles in a gas possess large kinetic energy and are able to overcome intermolecular forces of attraction such that these attractions can be considered to be insignificant and negligible.

D is correct. Deviation of N_2(g) at 500 K from ideal gas behaviour is smaller than that at 298 K. At higher temperatures, particles in a gas possess large kinetic energy and are able to overcome intermolecular forces of attraction such that these attractions can be considered to be insignificant and negligible.

7 The polymerisation of propene to form polypropene occurs readily at room temperatures.



What will be the signs of ΔG, ΔH and ΔS for the polymerisation reaction at room temperature?

	ΔG	ΔH	ΔS
A	+	–	–
B	+	+	–
C	–	+	–
D	–	–	–

Answer: D

Question states that the reaction is spontaneous at room temperature, thus ΔG is negative.

The overall reaction involves the breaking of a C-C π bond and the formation of C-C σ bond. Since the σ bond is stronger than the π bond, the energy released from the formation of the σ bond is greater than the energy absorbed for the breaking of the π bond. Thus ΔH is negative.

The sign for ΔS is negative as there is a decrease in the number of molecules, thus there are fewer ways of arranging the molecules, level of disorderliness decreases.

8 The rate of the redox reaction between hydrochloric acid and Mg

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$

can be followed by measuring the time taken for the same volume of hydrogen to be produced from a range of hydrochloric acid concentrations.

To find the order with respect to hydrochloric acid, which would be the most suitable graph to plot using the data?

A [HC*l*] against time

B [HC*l*] against $\frac{1}{\text{time}}$

C Volume H_2 against time

D Volume H_2 against $\frac{1}{\text{time}}$

Answer: B

A is incorrect. Using graph of [HC*l*] against time, the order of reaction with respect to hydrochloric acid cannot be found but only the instantaneous rate of reaction can be found by finding drawing tangent and calculate the gradient to the tangent at different time.

B is correct. The rate equation proposed is Rate = $k[HCl]^n$. Since question has mentioned that time taken for the same volume of hydrogen to be produced, 1/time will thus be deemed as rate. If order of reaction with respect to hydrochloric acid is 1 (n=1), the appropriate graph, rate = [HC*l*] against 1/time (also deemed as rate) will be a straight line with positive gradient and the gradient = k.

C is incorrect. As the question mentioned that the data collected is time taken to produce the same volume when different concentrations of hydrochloric acid, the graph of volume of hydrogen against time will be the same even different concentrations of hydrochloric acid is used.

D is incorrect. As the question mentioned that the data collected is time taken to produce the same volume when different concentrations of hydrochloric acid, the graph of volume of hydrogen against 1/time will be the same despite that different concentrations of hydrochloric acid are used.

9 The numerical value of the solubility product of nickel(II) carbonate is 6.6×10^{-9} while that of silver carbonate is 2.1×10^{-11} at 25 °C.

Which of the following statements is true?

A Addition of silver nitrate increases the solubility of silver carbonate.

B The solubility of silver carbonate is higher than the solubility of nickel(II) carbonate.

C Addition of nitric acid to a solution containing nickel(II) carbonate increases the solubility product of nickel(II) carbonate.

D Nickel(II) carbonate precipitates first when sodium carbonate is added to a solution containing equal concentrations of nickel(II) and silver ions.

Answer: B

A is incorrect.

$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$ ---- (1)

$AgNO_3(s) \rightarrow Ag^+(aq) + NO_3^-(aq)$

Addition of silver nitrate increases $[Ag^+]$ in eqm 1, the position of eqm 1 shifts LHS, the solubility should decrease.

B is correct

$K_{sp} = [Ag^+]^2[CO_3^{2-}] = 2.1 \times 10^{-11}$

$K_{sp} = (2s)^2(s)$

$s = \sqrt[3]{\frac{2.1 \times 10^{-11}}{4}} = 1.73 \times 10^{-4}\,moldm^{-3}$

$K_{sp} = [Ni^{2+}][CO_3^{2-}] = 6.6 \times 10^{-9}$

$s = \sqrt{6.6 \times 10^{-9}} = 8.14 \times 10^{-5}\,moldm^{-3}$

From the above calculation it is seen that the solubility of silver carbonate is higher than that of nickel(II) carbonate.

C is incorrect. Solubility product is only affected by temperature. Therefore addition of nitric acid cannot change the magnitude of solubility product.

D is incorrect.

Assuming $[Ni^{2+}] = [Ag^+] = 0.100\ moldm^{-3}$

$K_{sp} = [Ni^{2+}][CO_3^{2-}] = 6.6 \times 10^{-9}$

$[CO_3^{2-}] = \frac{6.6 \times 10^{-9}}{0.100} = 6.6 \times 10^{-8}\,moldm^{-3}$

$K_{sp} = [Ag^+]^2[CO_3^{2-}] = 2.1 \times 10^{-11}$

$[CO_3^{2-}] = \frac{2.1 \times 10^{-11}}{0.100^2} = 2.1 \times 10^{-9}\ moldm^{-3}$

Since lower $[CO_3^{2-}]$ needed to see first trace of silver carbonate is lower than that of nickel (II) carbonate, silver carbonate should be precipitated out first.

10 What is the pH of 10 cm^3 of 0.05 mol dm^{-3} sodium benzoate?

[K_a of benzoic acid = 6×10^{-5} mol dm^{-3}]

A 6.46

B 7.46

C 8.46

D 9.46

Answer: C

Let the salt B^- be the benzoate salt.

$B^- + H_2O \rightleftharpoons BH + OH$

$K_b = {K_w}/{K_a}$

$= {1\times10^{-14}}/{6\times10^{-6}}$

$= 1.6667\times10^{-10}\ \text{moldm}^{-3}$

$K_b = \dfrac{[OH^-][BH]}{[B^-]} = 1.6667\times10^{-10}$

$\dfrac{[OH^-]^2}{[B^-]} = 1.6667\times10^{-10}$

$[OH^-] = \sqrt{1.6667\times10^{-10}\times0.05}$

$= 2.8868\times10^{-6}\ \text{moldm}^{-3}$

$\text{pOH} = -\log(2.8868\times10^{-6}) = 5.5395$

$\text{pH} = 14 - 5.5395 = 8.46$

11 A sample of 20.0 cm^3 of 0.20 mol dm^{-3} iron(II) sulfate is titrated against 0.05 mol dm^{-3} potassium manganate(VII) in the presence of excess fluoride ions. It is found that 20.0 cm^3 of the manganate(VII) solution is required to reach the end-point.

What is the oxidation number of manganese at end-point?

A +3

B +4

C +5

D +6

Answer: A

$MnO_4^- + 8H^+ + (7\text{-}n)e \rightarrow Mn^{n+} + 4H_2O$
$Fe^{2+} \rightarrow Fe^{3+} + e$

$\text{no of mol of electrons gained by Mn} = (7 - n)\times\dfrac{20}{1000}\times0.05 = 0.00100\text{mol}$

$\text{no of mol of electrons lost by Fe} = \dfrac{20}{1000}\times0.20 = 0.00400\ \text{mol}$

$\text{no of mol of eletctrons lost by Fe} = \text{no of mol of electrons gained by Mn}$

$(7 - n) = 4$

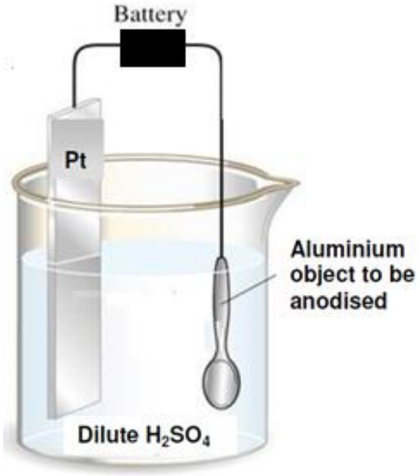
$n = 3$

Thus the new oxidation state of Mn is +3.

Alternative method:
0.00400 mol of Fe^{2+} lost 0.00400 mol of electron to Mn
0.00100 mol of MnO_4^- gained 0.00400 mol of electron from Fe^{2+}
1 mol of MnO_4^- gained 0.004/0.001 = 4 mol of electron from Fe^{2+}
The original oxidation state of Mn in MnO_4^- is +7 and the Mn gained 4 electrons, thus the new oxidation state is +3.

12 Anodisation is a process to increase corrosion resistance and surface hardness in aluminium objects.

A possible set up for the process is shown as below:



Which of the following statements about the anodisation of aluminium is true?

A Aluminium dissolves at the anode.

B Hydrogen gas is liberated at the anode.

C Water is oxidised at the anode to form oxygen gas.

D Replacing the electrolyte with NaOH(aq) will cause the reaction to cease.

Answer: C

A is not true. In this electrolytic process, water is oxidised in preference to aluminium. Therefore, aluminium is not oxidised hence it is not dissolved.

B is not true. At anode, water from electrolyte is oxidised to oxygen gas.
$2H_2O \rightarrow O_2 + 4H^+ + 4e$

C is true. The purpose of the process is to allow water from the electrolyte to be oxidised to form oxygen gas.
$2H_2O \rightarrow O_2 + 4H^+ + 4e$
Oxygen liberated then reacts with the aluminium object at the anode to form the protective layer of aluminium oxide.
$4Al + 3O_2 \rightarrow 2Al_2O_3$

D is not true. During the process, hydroxide ions from electrolyte can be oxidised to form oxygen gas at the anode. Therefore, the process does not stop.
$4OH^- \rightarrow 2H_2O + O_2 + 4e$

13 Which of the following elements forms an oxide with a giant structure and a chloride which is readily hydrolysed?

A Silicon

B Barium

C Sodium

D Phosphorus

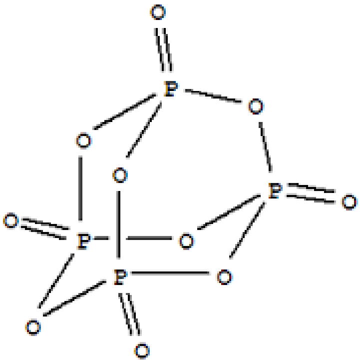
Answer: A

A is correct. The oxide of silicon, SiO_2, exists as a giant covalent structure while the chloride of silicon, $SiCl_4$, hydrolyses in water to form SiO_2 and HCl.

B is incorrect. Barium oxide has a giant ionic lattice structure and barium chloride does not undergo hydrolysis.

C is incorrect. Similar explanation to B.

D is incorrect. Phosphorus pentoxide has a simple molecular structure although phosphorus pentachloride undergoes hydrolysis readily.



Structure of P_4O_{10}

14 An element in Period 3 has the following properties:

- Its first ionisation energy is larger than both the elements before and after it across the period.
- It conducts electricity.
- It reacts slowly with cold water but react readily with steam to give a gas.

Which statement about this element is **not** correct?

A It has a high melting and boiling point.

B It forms an oxide that produces a solution that is acidic when added to water.

C It forms a chloride that produces a solution that is slightly acidic when added to water.

D Its oxidation state in compounds usually follows the group number it belongs to in the Periodic Table.

Answer: B

The element is magnesium.

A is correct. The strong metallic bonding in magnesium results in its high melting and boiling point.

B is incorrect. Magnesium oxide is basic in nature and does not produce H^+.

C is correct. When dissolved in water, hydrated Mg^{2+} is formed. Due to its relatively high charge density, Mg^{2+} partially hydrolyses in water.

$[Mg(H_2O)_6]^{2+} \rightleftharpoons [Mg(H_2O)_5(OH)]^+ + H^+$

D is correct. It has an oxidation state of +2.

15 The following report appeared in a newspaper article.

Drums of bromine broke open after a vehicle crash on the motorway. Traffic was diverted as purple gaseous bromine drifted over the road (it is denser than air), causing irritation to drivers' eyes. Firemen sprayed water over the scene of the accident, dissolving the bromine and washing it away.

What is wrong with the report?

A Bromine does not dissolve in water.

B Bromine does not vapourise readily.

C Bromine is less dense than air.

D Bromine is not purple.

Answer: D

A is correct. Bromine dissolves in water to form an orange solution.

B is correct. Bromine has a relatively high boiling point due to its big and polarisable electron cloud and hence stronger instantaneous dipole–induced dipole forces.

C is correct. Bromine has a molecular weight of 160 grams per mole, which is denser than air, which has a molecular weight of 28 grams per mole (mainly nitrogen gas).

D is incorrect. Bromine exists as a red-brown gas.

16 When crystalline potassium chromate(VI) was dissolved in water, a yellow solution **Q** was formed. Addition of dilute sulfuric acid to **Q** gave an orange solution **R**. When hydrogen sulfide was bubbled through solution **R**, there was a color change in the solution and yellow sulfur was produced.

Which process **did not** occur in the above experiment?

A Ligand exchange

B Redox reaction

C Precipitation

D Acid-base

Answer: A

K_2CrO_4 dissolves in water to give **Q**, CrO_4^{2-}.
Q undergoes acid-base reaction to give **R**, $Cr_2O_7^{2-}$. **R** undergoes redox reaction with H_2S where sulfur was precipitated.

17 Chlorine compounds show oxidation states ranging from –1 to +7.

What are the reagents and conditions necessary for the oxidation of chlorine gas into a compound containing chlorine in the +5 oxidation state?

A Cold dilute NaOH

B Hot concentrated NaOH

C Concentrated H_2SO_4 at room temperature

D $AgNO_3$(aq) followed by NH_3(aq) at room temperature

Answer: B

A is incorrect. The compound formed is NaOC*l* and the oxidation state of chlorine in the compound is +1.

B is correct. The compound formed is $NaClO_3$ and the oxidation state of chlorine in the compound is +5.

C is incorrect. No reaction occurs between chlorine gas and sulfuric acid.

D is incorrect. $Cl_2 + H_2O \rightleftharpoons HClO + HCl$
$Ag^+ + Cl^- \rightarrow AgCl$
$AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]^+Cl^-$
C*l* in product does not have oxidation state of +5.

18 Which statement correctly **defines** a transition element?

A Transition elements form many coloured compounds.

B Transition elements or their compounds are widely used as catalysts.

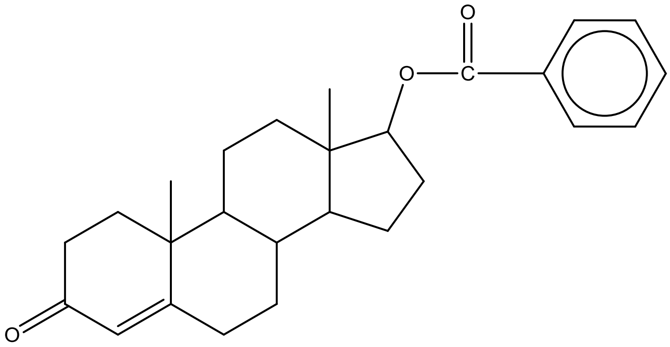
C Transition elements form one or more stable ions with partially filled d-orbitals.

D Transition elements exhibit more than one oxidation state in their compounds.

Answer: C

A transition element is defined as a d-block element which forms one or more stable ions with partially filled d-orbitals.

19 How many stereoisomers does a molecule of Nandrolone has?



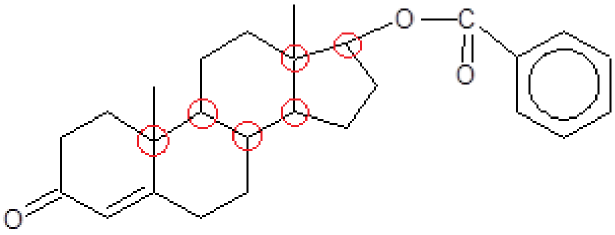
Nandrolone

A 8 **B** 16 **C** 32 **D** 64

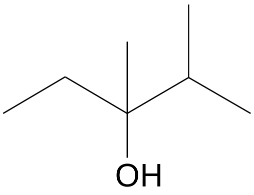
Answer: D

A chiral carbon has four different groups attached to it. Nandrolone has 6 chiral carbons. Double bond within a ring cannot exhibit cis-trans isomerism.

Total number of stereoisomers = $2^6 = 64$



20 The structure of compound **Z** is as seen below:



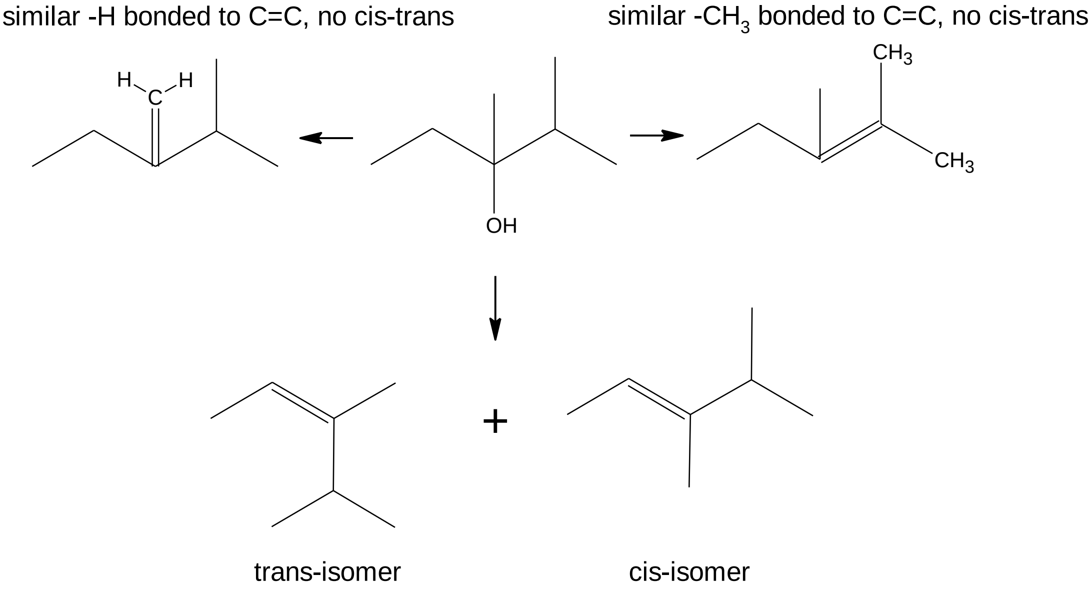
Compound **Z**

It is completely reacted with hot concentrated H_2SO_4 to form compound **Y**. What is the total number of isomers of **Y**?

A 2 **B** 3 **C** 4 **D** 5

Answer: C

This is an elimination reaction. The –OH group and a H atom on a adjacent C atom are removed to form an alkene.



21 2–methylpropanoic acid can be synthesised from 1–chloropropane through a series of reactions.

Which set of reagents, used in sequential order, would be the most suitable for this synthesis?

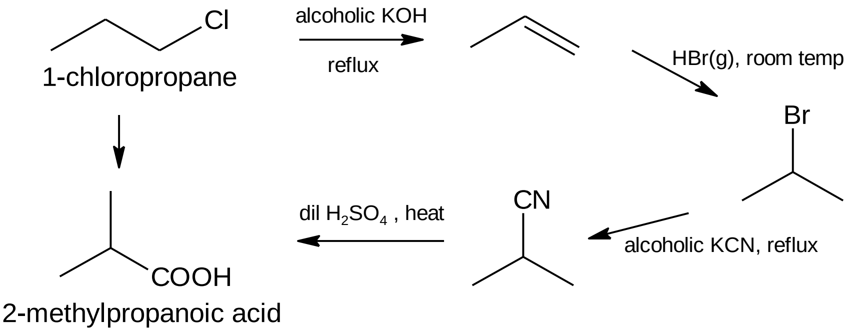
A PCl_5, acidified $KMnO_4$

B ethanolic KCN, dilute HC*l*

C aqueous KOH, HC*l*, ethanolic KCN, dilute HC*l*

D ethanolic KOH, HBr, ethanolic KCN, dilute H_2SO_4

Answer: D



22 Which statement about ethanal and propanone is **not** correct?

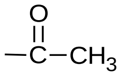
A Both give a positive tri-iodomethane test.

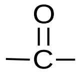
B Both react with 2,4-dinitrophenylhydrazine reagent.

C Both may be prepared by the oxidation of an alcohol.

D Both react with hot acidified sodium dichromate(VI).

Answer: D

A is correct. Both compounds contain  $-\overset{\overset{\displaystyle O}{||}}{C}-CH_3$ structure and will produce a yellow ppt, CHI_3 with aqueous alkaline iodine.

B is correct. Both compounds contain  $-\overset{\overset{\displaystyle O}{||}}{C}-$ functional group and will will produce an orange ppt with 2,4-DNPH.

C is correct. Ethanal is an aldehyde that can be prepared by the oxidation of a primary alcohol. Propanone is a ketone that can be prepared by the oxidation of a secondary alcohol.

D is incorrect. $Cr_2O_7^{2-}$ can only oxidise ethanal but not propanone. Aldehydes can be further oxidised to carboxylic acids but ketones cannot be further oxidised.

23 When sodium iodide in propanone is added to an optically active sample of 2-bromobutane, a sodium bromide precipitate is formed after 13 minutes upon heating.

$$NaI + CH_3CHBrCH_2CH_3 \longrightarrow CH_3CHICH_2CH_3 + NaBr(s)$$

The experiment was repeated several times and the rate equation was found to be

$$\text{Rate} = k[CH_3CHBrCH_2CH_3][NaI]$$

Which of the following statements is **not** correct?

A The mechanism involves a reactive intermediate.

B The organic product sample obtained rotates the plane of polarised light.

C A similar experiment, using 1-bromobutane, will produce a precipitate in less than 13 minutes.

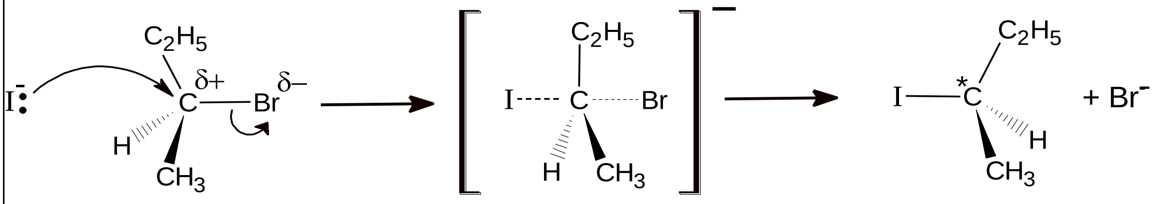
D A similar experiment, using 2-chlorobutane, will take more than 13 minutes to produce a precipitate.

Answer: A

A is incorrect. The rate equation shows that both reactants are involved in the rate-determining step. Hence, it is S_N2 mechanism where no intermediate is formed.

B is correct. The reactant is chiral and all its molecules undergo an inversion of configuration to remain as a chiral compound. The product will display optical activity.

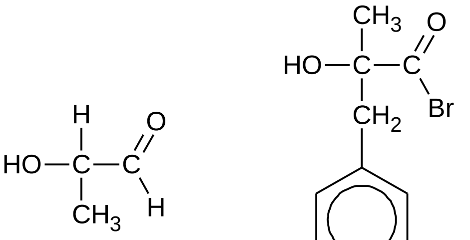
For example, the starting optically active sample contains 40% (+) and 60% (-) isomers. After S_N2 reaction, the product sample obtained will contain 60% (+) and 40% (-) isomers which is still optically active and rotate the plane of polarised light.



C is correct. 1-bromobutane is a primary halogenoalkane while 2-bromobutane is a secondary halogenoalkane. With a primary halogenoalkane, the attacking nucleophile experiences less steric hindrance when attacking the $C^{\delta+}$ and reacts more readily and the precipitate is produced faster.

D is correct. The C–C*l* bond is shorter than the C–Br bond and has higher bond energy. More energy is needed to break the bond and the rate of reaction of 2-chlorobutane will be slower than that of 2-bromobutane.

24 Which reagent can be used to distinguish between compounds **R** and **S** under suitable conditions?



R **S**

A Acidified potassium dichromate (VI)

B Alkaline copper(II) solution

C Sodium metal

D Phosphorus pentachloride

Answer: B

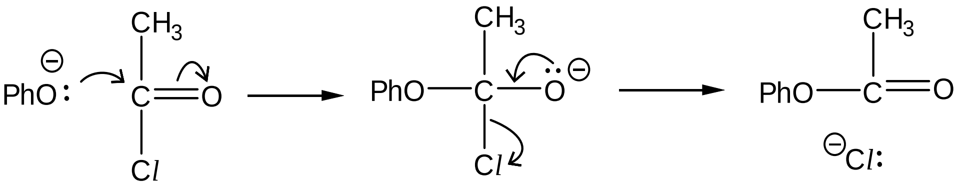
A cannot be used for the distinguishing test as it will oxidise the secondary alcohol and aldehyde in **R** as well as the aldehyde in **S**. Orange acidified $K_2Cr_2O_7$ will turn green.

B can be used for the distinguishing test. **R** is an aliphatic aldehyde and reacts to form a brick red precipitate of Cu_2O. **S** is an aromatic aldehyde and will not be able to reduce alkaline copper(II) solution.

C cannot be used for the distinguishing test. Na will react with -OH groups in both **R** and **S** and give off H_2 gas.

D cannot be used for the distinguishing test. PCl_5 will react with -OH groups in both **R** and **S** to produce white fume of HCl.

25 The two-stage reaction sequence given shows a possible mechanism for the reaction between phenoxide ion and ethanoyl chloride.



where Ph = phenyl

How should the *overall* reaction be classified?

A Electrophilic addition

B Nucleophilic addition

C Electrophilic substitution

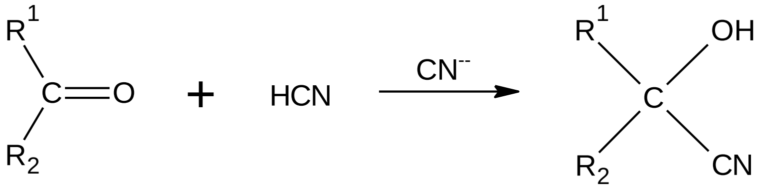
D Nucleophilic substitution

Answer: D

In the first step, PhO⁻ behaves as a nucleophile by attacking the attacking the $C^{\delta+}$ that is attached to O and C*l* atoms.

At the end of the reaction, the C*l*⁻ has left the molecule after being substituted.

26 Cyanohydrins can be made from carbonyl compounds by generating CN^- ions from HCN in the presence of a weak base.



In a similar reaction, $^-CH_2COOCH_3$ ions are generated from CH_3COOCH_3 by strong bases.

Which compound can be made from an aldehyde and CH_3COOCH_3?

A $CH_3CH(OH)COOCH_3$

B $CH_3COOCH_2CH(OH)\ CH_3$

C $CH_3CH_2CH(OH)CH_2COOCH_3$

D $(CH_3)_2C(OH)CH_2COOCH_3$

Answer: C

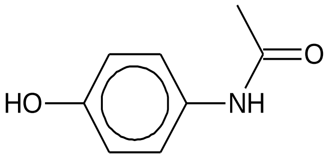
A is incorrect. The nucleophile used is $^-COOCH_3$.

B is incorrect. The nucleophile used is $CH_3COOCH_2^-$.

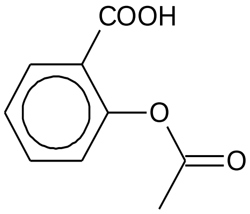
C is correct. The nucleophile used is $^-CH_2COOCH_3$ and it reacts with an aldehyde CH_3CH_2CHO.

D is incorrect. The nucleophile used is $^-CH_2COOCH_3$ but it reacts with a ketone CH_3COCH_3

27 Two common drugs administered when a patient experiences headache or fever are paracetamol and aspirin.



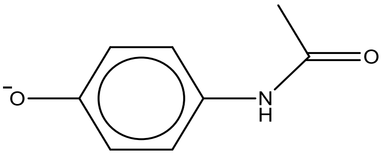
paracetamol



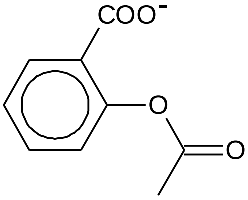
aspirin

A solution of the two drugs was hydrolysed using hot aqueous sodium hydroxide. Which organic product would be produced?

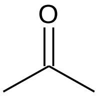
A



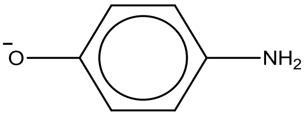
B



C

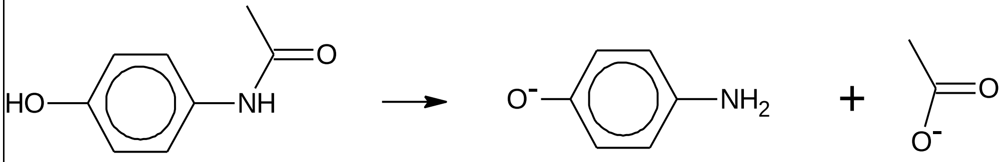


D

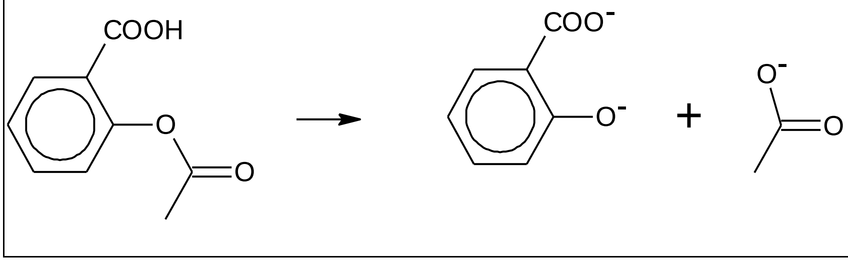


Answer: D

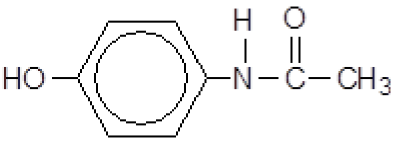
Alkaline hydrolysis of the amide bond in paracetamol produces the following:



Alkaline hydrolysis of the ester bond in aspirin produces the following:



28 Acetaminophen is a drug used in headache remedies. It has the following structure:



Acetaminophen

Which of the following reagents reacts with Acetaminophen?

A Sodium carbonate

B Cold sodium hydroxide

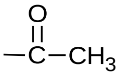
C Alkaline aqueous iodine

D 2,4-dinitrophenylhydrazine

Answer: B

A has no reaction. There is no –COOH present to react with the sodium carbonate.

B will react with the acidic phenol group in acetaminophen in a neutralisation reaction.

C has no reaction. The  $-\overset{\overset{O}{\|}}{C}-CH_3$ structure is present but no C or H is directly bonded to C=O for the reaction to occur.

D has no reaction. The aldehyde and ketone functional groups are not present.

29 Which sequence shows the correct order of increasing pK_b in an aqueous solution of equal concentration?

A $C_2H_5CONH_2 < C_6H_5NH_2 < C_2H_5NH_2 < C_2H_5NH_3^+$

B $C_2H_5NH_2 < C_6H_5NH_2 < C_2H_5NH_3^+ < C_2H_5CONH_2$

C $C_2H_5NH_2 < C_6H_5NH_2 < C_2H_5CONH_2 < C_2H_5NH_3^+$

D $C_2H_5NH_3^+ < C_2H_5CONH_2 < C_2H_5NH_2 < C_6H_5NH_2$

Answer: C

Increasing pK_b means becoming less basic.

The electron donating C_2H_5 group in $C_2H_5NH_2$ makes the lone pair of electrons on N atom most available for donation to a proton and therefore the strongest base.

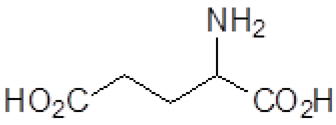
In $C_6H_5NH_2$, the lone pair of electrons on N atom is delocalised into the benzene ring, making it less available for donation to a proton. Phenylamine is therefore a weaker base than aliphatic amines.

In $C_2H_5CONH_2$, the lone pair of electrons on N atom is delocalised over the carbonyl C=O and hence not available for donation to a proton.

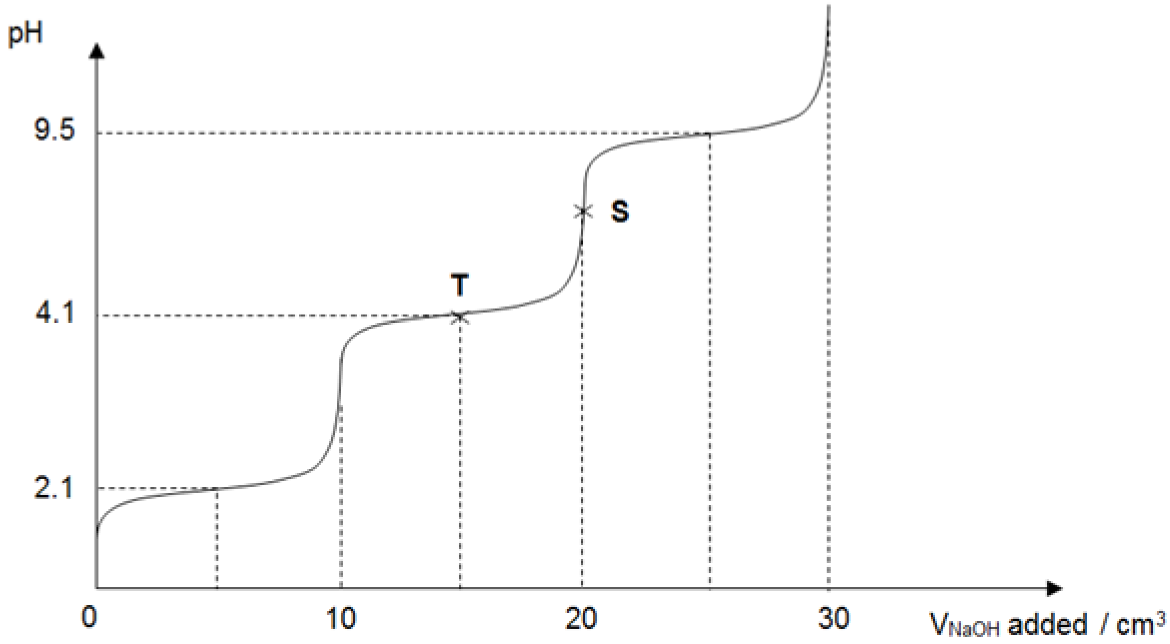
In $C_2H_5NH_3^+$, there are no lone pair of electrons on the N atom for donation to a proton.

-NH_3^+ is an acidic group with a proton for donation.

30 There are three pK_a values associated with glutamic acid: 2.1, 4.1 and 9.5.

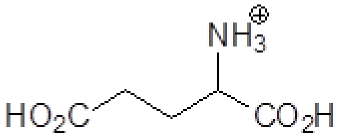


The pH-volume curve obtained when 30 cm^3 of NaOH is added to 10 cm^3 of the protonated form of glutamic acid of the same concentration is given below.

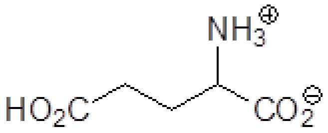


Which of the following is the major species present at point **S**?

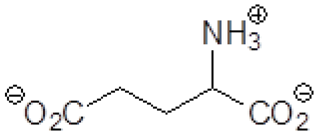
A



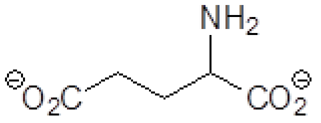
B



C

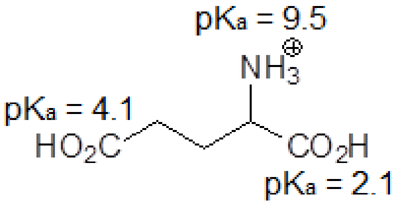


D



Answer: C

The protonated form of glutamic acid and its associated pK_a values are:

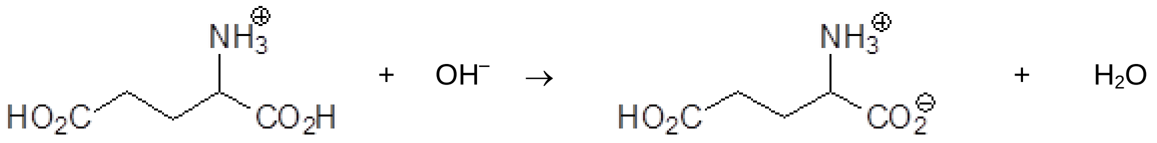


-COOH with pKa of 2.1 is the most acidic. $-NH_3^+$ is an electron withdrawing group and disperses the negative charge of $-COO^-$ of its conjugate base and stabilises it. $-NH_3^+$ is closer to -COOH with pKa of 2.1 than -COOH with pKa of 4.1. Hence, the dissociation of the carboxylic acid with pKa of 2.1 occurs to a larger extent.

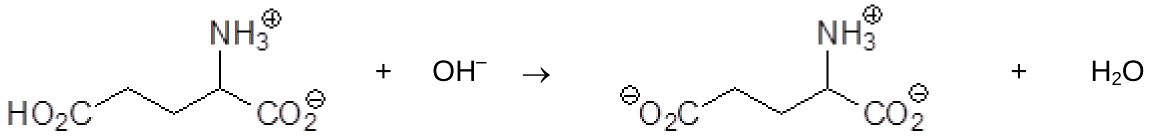
Carboxylic acid is more acidic than protonated amine ($-NH_3^+$) as the conjugate base of the carboxylic acid ($-COO^-$) is resonance stabilised. Hence, the dissociation of the carboxylic acid occurs to a larger extent than $-NH_3^+$.

Adding NaOH would result in three equivalence points being obtained as shown in the graph.

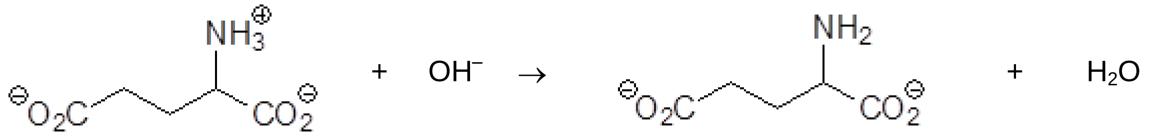
The 1st equivalence point is achieved when 10 cm^3 of NaOH was added:



At point S, the 2nd equivalence point is achieved when 20 cm^3 of NaOH was added:



The 3rd equivalence point is achieved when 30 cm^3 of NaOH was added:



Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to pick a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	**B**	**C**	**D**
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

31 The radius and charge of each of the six ions are shown below.

ion	J^+	L^+	M^{2+}	X^-	Y^-	Z^{2-}
radius / nm	0.14	0.18	0.15	0.14	0.18	0.15

The ionic solids JX, LY and MZ are of the same lattice type. Which of the following statements are correct?

1 The melting point increases in the order LY < JX < MZ.

2 The numerical value of hydration energy of X^- is smaller than that of Z^{2-}.

3 The solution containing M^{2+} ions is more acidic than the solution containing J^+ ions.

Answer: A

Option 1 is correct. JX, LY and MZ are ionic solids, thus their melting points are determined by the strength of electrostatic forces of attraction between the oppositely charged ions. The larger the magnitude of the lattice energy, the higher the melting point.

Lattice energy $\propto \left|\frac{q^+ \times q^-}{r^+ + r^-}\right|$

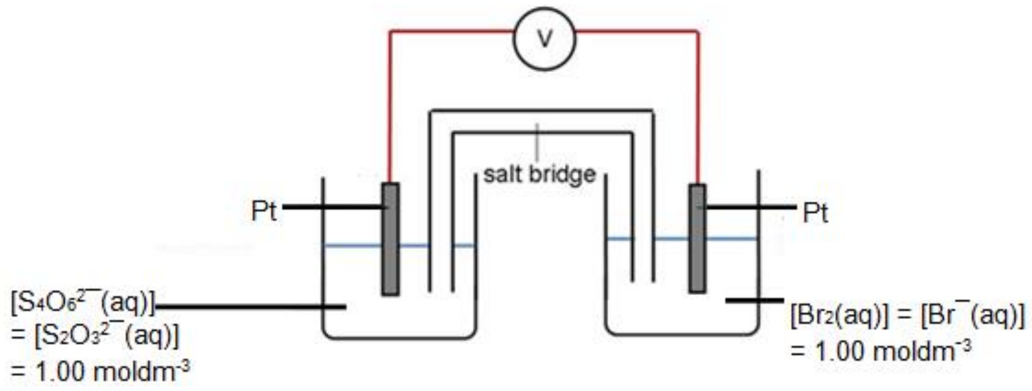
Lattice energy for JX, LY and MZ are: 3.57, 2.78 and 13.3 respectively. Thus melting point increases in the order LY < JX < MZ.

Option 2 is correct. Numerical value of hydration energy is dependent on the charge density of the ion$\left(\frac{q}{r}\right)$. Charge density of X^- is 1 / 0.14 = 7.14 while that of Z^{2-} is 2 / 0.15 = 13.3.

Thus the numerical value of hydration energy of X^- is smaller than that of Z^{2-}.

Option 3 is correct. Charge density of M^{2+} is 2 / 0.15 = 13.3 while that of J^+ is 1 / 0.14 = 7.14. Hence, M^{2+} has a higher charge density and thus a higher polarising power. M^{2+} draws electron density from the datively bonded water molecule towards itself more and weaken the O-H bond to a greater extent. This gives rise to a more acidic solution.

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



Which of the following will increase the cell potential?

1 Adding iodine crystals into the anodic half cell.

2 Adding solid silver nitrate into the cathodic half cell.

3 Increasing the concentration of $Br_2(aq)$ in the $Br_2(aq)/Br^-(aq)$ half cell.

Answer: C

Option 1 is incorrect. Adding iodine crystals remove thiosulfate ions through redox reaction. $[S_2O_3^{2-}]$ decreases while $[S_4O_6^{2-}]$ will increase at the anode.
$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$
The equilibrium at anode will be disturbed. According to Le Chatelier's principle, the position of equilibrium shift right to replenish the $S_2O_3^{2-}$ ions lost and to use up the $S_4O_6^{2-}$ ions which were added from the above redox reaction. This makes $E^{\circ}_{\text{oxd (anode)}}$ to be more positive.
$S_4O_6^{2-} + 2e \rightleftharpoons 2S_2O_3^{2-}$
E°_{cell} becomes less positive as the $E^{\circ}_{\text{red (cathode)}}$ of same magnitude subtracts a larger positive $E^{\circ}_{\text{oxd (anode)}}$.

Option 2 is correct. Solid silver nitrate removes Br^- ions in the cathode. This reduces $[Br^-]$.
$Ag+(aq) + Br^-(aq) \rightarrow AgBr(s)$
The equilibrium at cathode will be disturbed. According to Le Chatelier's principle, the position of equilibrium will shift to right to replenish bromide ions which are precipitated out. This makes $E^{\circ}_{\text{red (cathode)}}$ to be more positive.
$Br_2 + 2e \rightleftharpoons 2Br^-$
$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red (cathode)}} - E^{\circ}_{\text{oxd (anode)}}$
E°_{cell} becomes more positive as the more positive $E^{\circ}_{\text{red (cathode)}}$ subtracts positive $E^{\circ}_{\text{oxd (anode)}}$ which has the same magnitude.

Option 3 is correct. At the cathode,
$Br_2 + 2e \rightleftharpoons 2Br^-$
Increasing $[Br_2]$ shifts the equilibrium at cathode towards right. Le Chatelier's principle predicts that position of equilibrium shifts to the right to use up the bromine added. This makes $E^{\circ}_{\text{red (cathode)}}$ to be more positive.
$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red (cathode)}} - E^{\circ}_{\text{oxd (anode)}}$

E°_{cell} becomes more positive as the more positive $E^{\circ}_{red\ (cathode)}$ subtracts positive $E^{\circ}_{oxd\ (anode)}$ which has the same magnitude.

33 From the position of the elements present in the Periodic Table and the physical properties of the compounds, which compounds are covalent?

1	$(CH_3)_2SiCl_2$	b.p. 70°C
2	$GeCl_4$	b.p. 86°C
3	$AlBr_3$	b.p. 265°C

Answer: A

$(CH_3)_2SiCl_2$ is covalent. This can be inferred from its low boiling point and that it resembles $(CH_3)_2CCl_2$ since both Si and C are in the same group.

$GeCl_4$ is covalent. Similar reasoning as above since both Ge and Si are in the same group.

$AlBr_3$ is covalent as its boiling point is relatively low. Al^{3+} has a high charge density and polarises the electron cloud of Cl^- such that $AlCl_3$ is covalent. Since Br^- is more polarisable due to larger electron cloud than Cl^-, $AlBr_3$ is likely to be covalent.

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

The oxides of titanium, iron and nickel are used as catalysts in the industries.

Which properties are titanium, iron and nickel likely to have in common?

1 similar ionic radii

2 high melting points

3 variable oxidation states

Answer: A

Titanium, iron and nickel belong to the first row of the d-block transition elements.

They have similar ionic radii due to the increase in shielding effect which is largely cancelled out by the increase in nuclear charge. The effective nuclear charge remains relatively constant across the first row of the d-block elements.

They have high melting points due to the strong metallic bonding, as both their 4s and 3d electrons have similar energy and can be delocalised.

They have variable oxidation states as both the 3d and 4s orbitals are similar in energy. The 4s and some (or all) of the 3d electrons can be removed without requiring too much energy.

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

With reference to the two half equations below, which statements are correct?

$$[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-}$$

$$Fe^{3+} + e \rightleftharpoons Fe^{2+}$$

1 $[Fe(CN)_6]^{3-}$ is more stable than Fe^{3+}

2 $[Fe(CN)_6]^{4-}$ is a stronger reducing agent than Fe^{2+}

3 Both $[Fe(CN)_6]^{3-}$ and Fe^{3+} can oxidize MnO_4^{2-} to MnO_4^-

Answer: B

$$[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-} \qquad E^\theta = +0.36\ V$$

$$Fe^{3+} + e \rightleftharpoons Fe^{2+} \qquad E^\theta = +0.77\ V$$

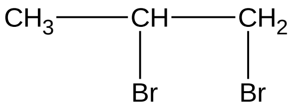
Option 1 is correct. From the reduction potential values, it can be inferred that CN^- stabilises the higher oxidation state of Fe (Fe^{3+}) to a greater extent than H_2O.

Option 2 is correct. The reduction potential of $[Fe(CN)_6]^{3-}$ is less positive than that of Fe^{3+}, hence $[Fe(CN)_6]^{3-}$ is a weaker oxidising agent than Fe^{3+}. Thus $[Fe(CN)_6]^{4-}$ is a stronger reducing agent than Fe^{2+}.

Option 3 is incorrect. Reduction potential of MnO_4^-/MnO_4^{2-} is +0.56 V, hence the cell potential for the reaction of $[Fe(CN)_6]^{3-}$ and MnO_4^- is –0.20 V. Since the cell potential is negative, the reaction is non-spontaneous.

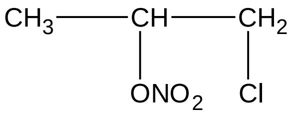
36 Propene is found to react with chlorine in the presence of aqueous sodium bromide and sodium nitrate. Which of the following are not possible products of the reaction?

1



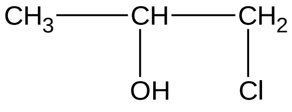
$CH_3-CH(Br)-CH_2Br$

2



$CH_3-CH(ONO_2)-CH_2Cl$

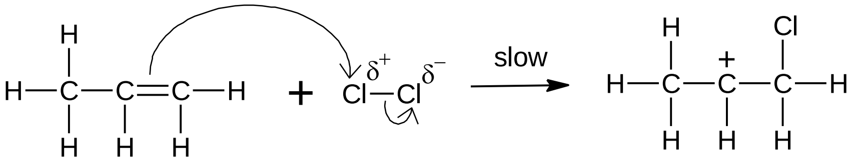
3



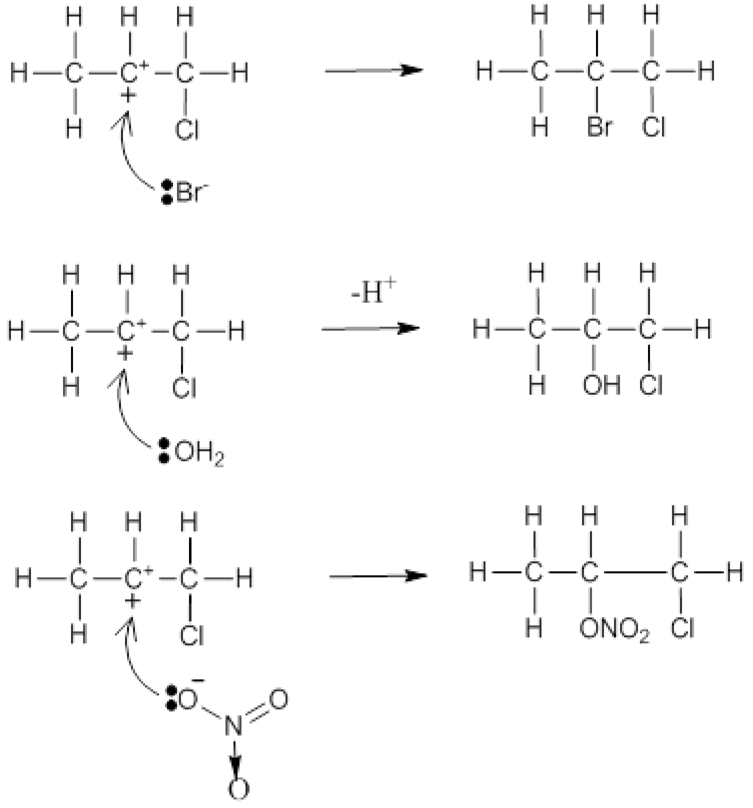
$CH_3-CH(OH)-CH_2Cl$

Answer: D

The reaction proceeds via electrophilic addition, during which a carbocation intermediate is formed.

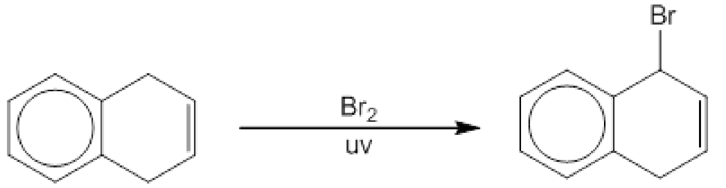


The carbocation reacts with the different nucleophiles present, giving rise to only these possible products.

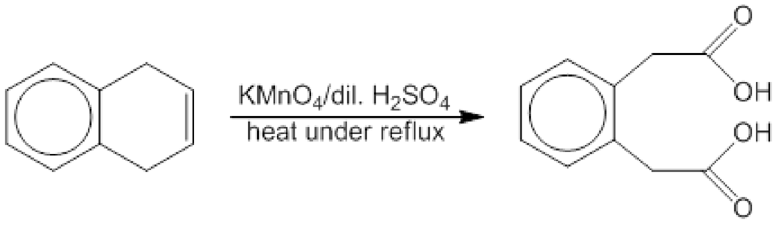


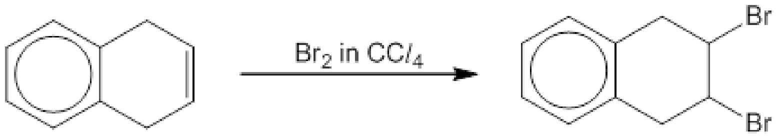
37 Which of the following reactions will not give a good yield of the desired product?

1



2

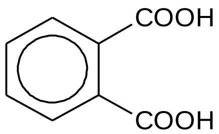


3 

Answer: B

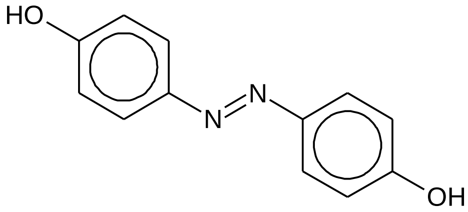
Both reactions 1 and 2 will not give a good yield of the desired product.

Reaction 1 is free radical substitution which can lead to multiple substitution due to the numerous C–H bonds present.

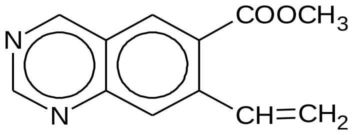
In reaction 2, 

will be formed by the oxidation of the two side chains of the benzene structure.

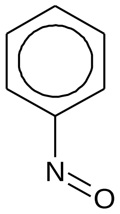
38 The three compounds **E**, **F** and **G** have the following structures?



E



F



G

Which statements about **E**, **F** and **G** are correct?

1 **E** and **G** have the same empirical formula.

2 **E** and **F** are isomers

3 The Mr of **F** is exactly twice that of **G**

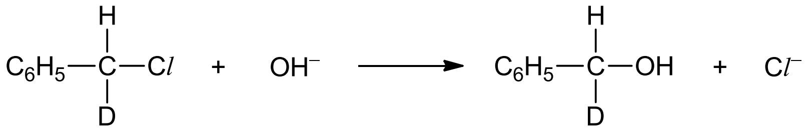
Answer: A

Option 1 is correct.
The molecular formua of **E** is $C_{12}H_{10}N_2O_2$
The molecular formua of **G** is C_6H_5NO
Therefore, the empirical formula of **E** and **G** are the same, C_6H_5NO

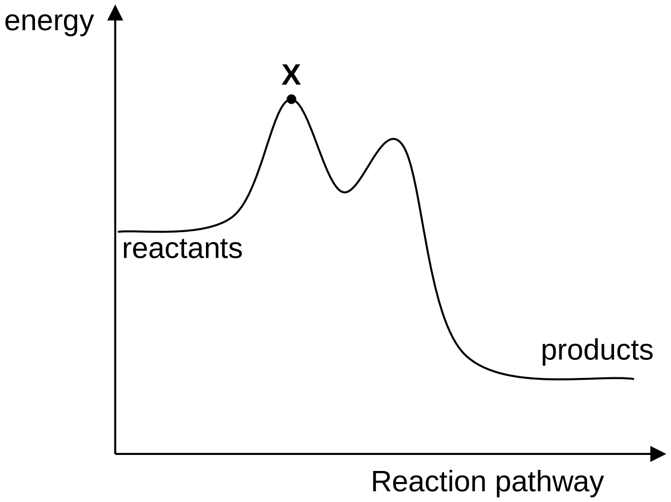
Option 2 is correct.
The molecular formua of **E** is $C_{12}H_{10}N_2O_2$
The molecular formua of **F** is $C_{12}H_{10}N_2O_2$
Therefore, **E** and **F** have the same molecular formula but different structural formula. They are isomers.

Option 3 is correct.
The molecular formua of **F** is $C_{12}H_{10}N_2O_2$
The molecular formua of **G** is C_6H_5NO
Since **F** has twice the number of atoms of each element in **G**, the M_r of **F** is exactly twice that of **G**.

39 The energy profile for the following reaction is shown below. [D = ^{2}H]



$$C_6H_5-C(H)(D)-Cl + OH^- \longrightarrow C_6H_5-C(H)(D)-OH + Cl^-$$

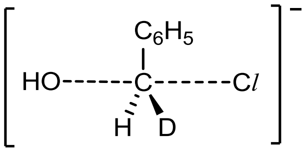


Which conclusions can be drawn?

1 The product has no effect on the rotation of plane polarised light.

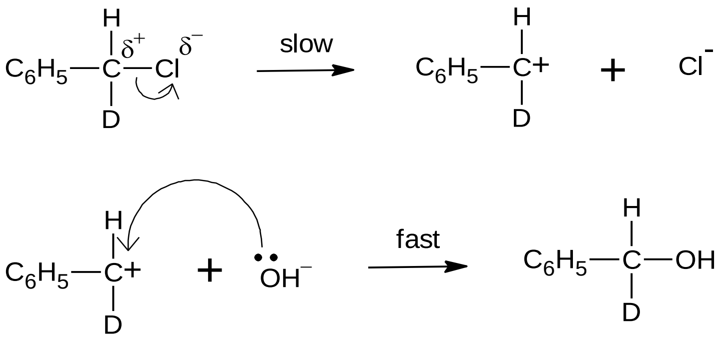
2 The rate of reaction can be increased by increasing concentration of OH^-.

3 The structure of the transition state at point **X** is



Answer: D

Option 1 is correct.
The graphs shows 2-steps in the mechanism. Hence, it is S_N1 mechanism.



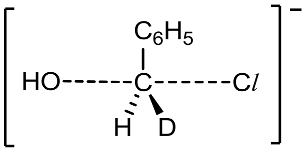
$$C_6H_5-\overset{\delta+}{C}(H)(D)-\overset{\delta-}{Cl} \xrightarrow{\text{slow}} C_6H_5-C^+(H)(D) + Cl^-$$

$$C_6H_5-C^+(H)(D) + :OH^- \xrightarrow{\text{fast}} C_6H_5-C(H)(D)-OH$$

The carbocation intermediate formed is planar, allowing OH^- to approach from either side of the plane, forming equimolar amount of both enantiomers. Therefore, the product does not display any optical activity due to the rotation of polarised light cancelling off each other due to being equal but opposite in direction of rotation.

Option 2 is not correct.
From the slow step of the mechanism, rate=k[$C_6H_5CH(Cl)D$]
Therefore, the rate of reaction is independent of [OH^-].

Option 3 is not correct.

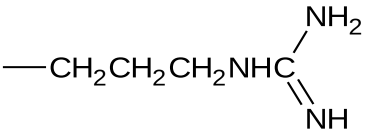


is the transition state from a S_N2 mechanism, and not S_N1.

40 Which groups within an amino acid are able to form a cross-chain link to stabilise the tertiary structure of a protein?

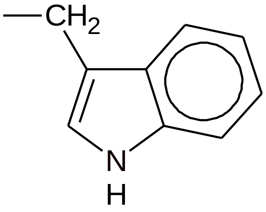
1 $—CH_2CONH_2$

2



$—CH_2CH_2CH_2NHC(=NH)NH_2$

3



Answer: A

All of the above shown are R groups of α-amino acids which are used to stabilise the tertiary structure of a protein.

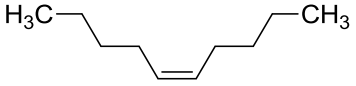
YJC Chemistry H2 P2 Prelim 2016

Answer **all** the questions.

1 Planning (P)

The selective partial hydrogenation of alkynes, which contain C≡C triple bonds, to cis-alkenes represents an importance class of chemical transformations that have found extensive uses such as in bioactive molecules, in lubricants as well as in the syntheses of organic intermediates.

The partial hydrogenation of 5-decyne forms cis-dec-5-ene and the reaction is as shown :

$CH_3CH_2CH_2CH_2C{\equiv}CCH_2CH_2CH_2CH_3 + H_2 \rightarrow$  ΔH_1

The enthalpy change for hydrogenation of 5-decyne, ΔH_1 cannot be measured directly in the laboratory. You are required to plan an experiment to find the enthalpy change for hydrogenation of 5-decyne, ΔH_1 via Hess's Law.

The enthalpy change for the combustion of hydrogen is $-$ 286 kJ mol^{-1}. 5-decyne and cis-dec-5-ene are both liquids at standard conditions.

(a) Based on the given information and the equation above, state **two** enthalpy changes that are necessary to calculate ΔH_1.

………………………………………………………………………………………………

………………………………………………………………………………………………[1]

(b) Using the information given above and your answer in **(a)**, you are required to write a plan to determine a value for the enthalpy change for hydrogenation of 5-decyne, ΔH_1.

You may assume that you are provided with

- liquid 5-decyne
- liquid cis-dec-5-ene
- copper calorimeter
- two spirit lamps with a 5 cm-wick each
- deionised water
- a lighter
- thermometer
- apparatus normally found in a school or college laboratory

Your plan should contain the following:
- a diagram of the experimental set-up

For Examiner's Use

- appropriate quantities of chemicals and solutions
- all essential experimental details

Diagram of the experimental set-up

Procedure:

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[Turn over

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………………………………………………………………………………………………[7]

(c) List the measurements that have to be tabulated and recorded to calculate the value of enthalpy change for hydrogenation of 5-decyne, ΔH_1. In your answer, you need to show how these measurements are used to obtain the value of ΔH_1.

You may assume the specific heat capacity of water is 4.18 J g^{-1} K^{-1} and density of water is 1 g cm^{-3}.

Tables used to tabulate and record experimental data:

For
Examiner's
Use

Treatment of results:

[4]

[Total: 12]

[Turn over

2 Eighty-five percent of all pharmaceutical agents and vitamins involve chlorine chemistry; many drugs require chlorine, fluorine, or bromine to be effective.

Data about the halides are given below.

Halide (X)	pK_a (HX)	Percentage of HX decomposed at 2000°C	Boiling point of HX / °C	Dipole moment of C–X / D	K_a (HOX) at 298K
F	+3	6×10^{-5}	19.5	1.82	
C*l*	–7	4×10^{-1}	–84.2	1.08	2.9×10^{-8}
Br	–9	4	–67.1	0.82	2.4×10^{-9}
I	–10	30	–35.1	0.44	

(a) Hydrogen halides decompose at high temperature according to the equation:

$$2HX(g) \rightarrow H_2(g) + X_2(g)$$

Use relevant data from the *Data Booklet*, explain the trend indicated by percentage decomposition of HX.

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(b) The boiling point of HF is higher than the rest of the hydrogen halides despite it being the smallest molecule. By means of a diagram, indicate the interaction between two molecules of HF that leads to this significant difference.

[2]

(c) When dissolved in water, the hydrogen halides show different pK_a values. Write balanced equations to represent the extent of ionisation of HF and HI in water.

HF : ……………………………………………………………………………………………

HI : ………………………………………………………………………………………………

[2]

(d) **(i)** Draw a diagram to illustrate the shape of oxoacid, HOC*l*, indicating clearly the bond angle.

[2]

(ii) Using the information from the table, state which of the two acids, HOC*l* or HOBr is stronger?

…………………………………………………………………………………………… [1]

(iii) Hypoiodous acid has the formula HOI. Predict and explain whether HOI is a stronger or weaker acid than the acid you identified in **(d)(ii)**.

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……………………………………………………………………………………………..

……………………………………………………………………………………………..

[Turn over

……………………………………………………………………………………………[2]

(iv) Some solid NaOC*l* solution is dissolved in a solution of HOC*l* at 298 K. The pH of this mixture is determined to be 6.48. Calculate the ratio of OCl^- to HOC*l* in this mixture.

[2]

(e) The halides can react with concentrated sulfuric acid.

(i) When concentrated sulfuric acid was warmed with sodium chloride, white fumes of hydrogen chloride was evolved. Write a balanced equation for the reaction.

……………………………………………………………………………………………[1]

(ii) The method described in **e(i)** cannot be used to prepare hydrogen iodide. Describe what you would observe when sodium iodide is heated with concentrated sulfuric acid. Explain the chemistry behind it, and give any relevant equations.

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[Total: 20]

3 **(a)** $AlCl_3$ is a compound of interest to scientists due to its industrial applications. For example, $AlCl_3$ can react with molten aluminium to form $AlCl$(g). This is a useful procedure as the $AlCl$ formed can be used to recover useful metalloids from their compounds.

Typically, the reaction has to be carried out in the presence of argon instead of air.

(i) The reaction has to be carried out in an atmosphere of argon. Suggest a reason for the need of argon.

…………………………………………………………………………………………….[1]

Consider the reaction between $AlCl_3$(g) and molten aluminium that was carried out at 1573 K :

$$2Al(l) + AlCl_3(g) \rightleftharpoons 3\,AlCl(g) \qquad \text{reaction } \mathbf{1}$$

In the reaction vessel, 0.200 mol of $AlCl_3$(g) was reacted with 0.400 mol of molten Al. When the reaction system achieved equilibrium with a total pressure of 1.50 atm, it was determined that 0.200 mol of molten Al remained in the vessel.

(ii) Write an expression for the equilibrium constant, K_p for reaction **1** and hence calculate its value at 1573 K.

[3]

[Turn over

The same reaction vessel was heated to 1700 K rapidly in a way such that no reaction took place during the short interval of heating. The reaction system was allowed to re-establish equilibrium. It was found that the partial pressure of $AlCl_3$(g) was 0.390 atm when the equilibrium was re-established.

(iii) Using the information from **a(ii)**, determine the partial pressures of $AlCl_3$(g) and $AlCl$(g) at the instant when the reaction was heated to 1700 K, before the equilibrium was re-established. You can assume that the gases behave ideally and the volume of vessel is unchanged.

[2]

(iv) Using the calculated values from **a(iii)**, calculate K_p of the reaction at 1700 K. Hence, explain whether reaction **1** is endothermic or exothermic.

[4]

(v) The rate equation for reaction between Al and $AlCl_3$ is shown below.

$$\text{rate} = k[AlCl_3][Al]$$

Suggest which of the two mechanisms shown is a possible mechanism for the reaction.

Mechanism **1**:

$Al + AlCl_3 \rightarrow AlCl_2 + AlCl$ (slow)

$Al + AlCl_2 \rightarrow 2\ AlCl$ (fast)

Mechanism **2**:

$AlCl_3 \rightarrow AlCl + Cl_2$ (slow)

$2\ Al + Cl_2 \rightarrow 2\ AlCl$ (fast)

………………………………………………………………………………………………..

……………………………………………………………………………………………[1]

(b) Anhydrous $AlCl_3$ is often used as a catalyst in the Friedel-Crafts alkylation of benzene.

$$C_6H_6 + CH_3CH_2CH_2Cl \xrightarrow{AlCl_3} C_6H_5CH_2CH_2CH_3 + HCl \qquad \text{reaction } \mathbf{2}$$

(i) Explain why $AlCl_3$ can act as a catalyst in Friedel-Crafts alkylation.

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…………………………………………………………………………………………… [1]

(ii) With the aid of an equation, explain the need to have anhydrous condition when $AlCl_3$ is used for reaction **2**.

………………………………………………………………………………………………..

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……………………………………………………………………………………………[2]

(iii) Use information from the *Data Booklet,* calculate the enthalpy change of reaction for reaction **2**.

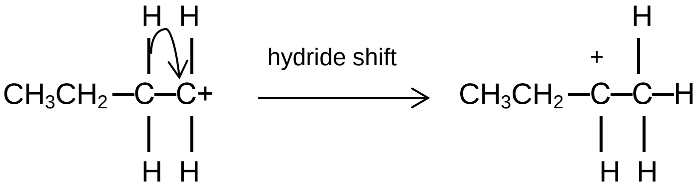
[Turn over

[2]

(iv) Describe the mechanism for the formation of $C_6H_5CH_2CH_2CH_3$ in reaction **2**, showing clearly the movement of electrons and partial charges.

[3]

One key limitation of the alkylation reaction is that a mixture of products tends to form despite using only one type of halogenoalkane. For primary halogenoalkane, this is due to the occurrence of a process known as hydride shift which results in rearrangement of primary carbocation intermediates as shown :



(v) Explain why hydride shift occurs for primary halogenoalkane.

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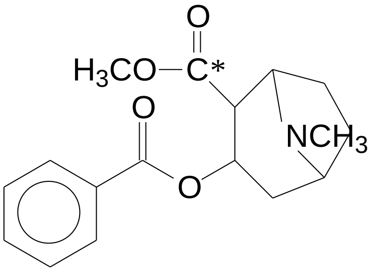
…………………………………………………………………………………………[3]

[Total: 22]

4 **(a)** Cocaine, $C_{17}H_{21}NO_4$, was first used as a local anaesthetic. It is also a powerful stimulant. Its structure is as shown:



cocaine

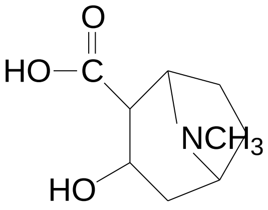
(i) State the functional groups, other than phenyl ring, present in cocaine.

………………………………………………………………………………………….[1]

(ii) State the hybridisation of the carbon atom labelled with the asterisk (*).

………………………………………………………………………………………….[1]

(b) Student **X** was asked to suggest a suitable synthetic route to prepare cocaine from methylbenzene and compound **A**.



compound **A**

Student **X** suggested the following steps:

Step **1**	Methylbenzene is oxidised with hot, acidified $KMnO_4$ to give benzoic acid.
Step **2**	Benzoic acid is converted into benzoyl chloride by reacting the resultant solution from step **1** with phosphorus pentachloride.
Step **3**	Benzoyl chloride is reacted with compound **A** at room temperature.
Step **4**	The resultant compound from step 3 is reacted with methanol in the presence of concentrated sulfuric acid at room conditions.

[Turn over

Explain why steps **2** and **4** of the synthetic route will not work.

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……………………………………………………………………………………………[2]

(c) Cocaine is sold in its protonated hydrochloride salt, known as cocaine hydrochloride. Suggest a possible reason for this.

……………………………………………………………………………………………[1]

(d) Smoking cocaine is more stimulating than inhaling the salt as it is absorbed quickly by the capillaries in the lung tissues. The salt is converted back to cocaine before smoking.

(i) Suggest a suitable reagent to convert cocaine hydrochloride back into cocaine.

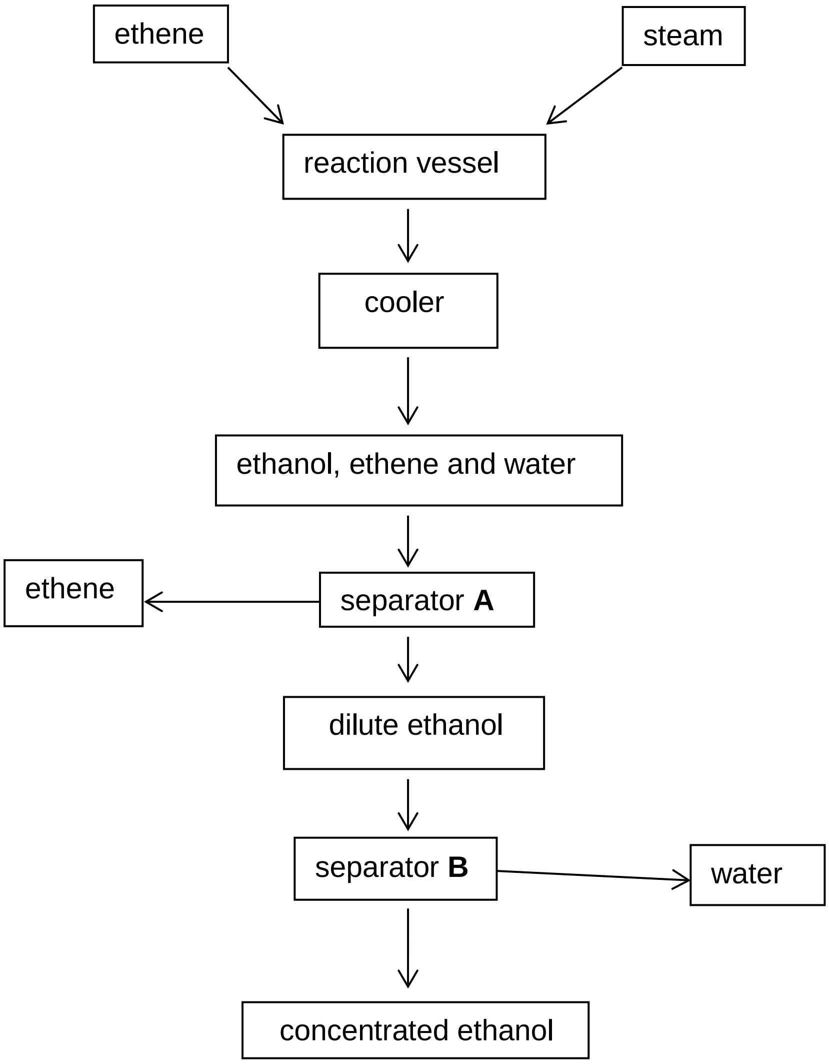
……………………………………………………………………………………[1]

(ii) Suggest a suitable solvent to extract cocaine and separate it from its salt.

……………………………………………………………………………………[1]

[Total: 7]

5 An industrial method for the production of ethanol, C_2H_5OH, is outlined in the following flow diagram.



(a) **(i)** Unreacted ethene is removed in separator **A**. Suggest how the separated ethene could be used to increase the efficiency of the overall process of the manufacture of ethanol.

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……………………………………………………………………………………………[1]

(ii) Name the process that takes place in separator **B**.

…………………………………………………………………………….……..[1]

(b) In the reaction vessel, ethanol is produced in an exothermic reaction.

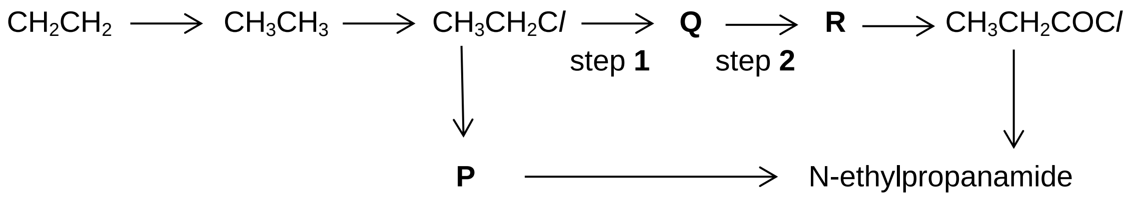
(i) State the reagents and conditions for the industrial preparation of ethanol from ethene.

……………………………………………………..……………………………… [2]

(ii) If 1.64 kg of ethanol is produced from 10.0 kg of ethene, calculate the percentage yield of ethanol.

[2]

(c) Ethene is used to synthesise N-ethylpropanamide as shown in the following reaction scheme:



(i) Give the structural formulae of compounds **P**, **Q** and **R**.

Compound **P**: ……………………………

Compound **Q**: ……………………………

Compound **R**: ……………………………

[3]

(ii) State the reagents and conditions for steps **1** and **2**.

Step **1 :** …………………………………………………..

Step **2 :** ………………………………………………….

[2]

[Total: 11]

End of Paper

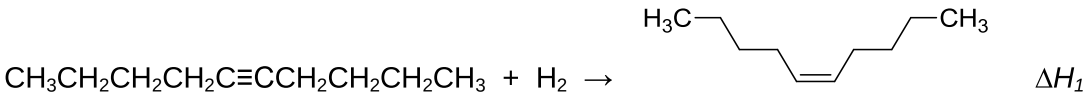
YJC Chemistry H2 P2 Prelim 2016

Answer **all** the questions.

1 Planning (P)

The selective partial hydrogenation of alkynes, which contain C≡C triple bonds, to cis-alkenes represents an importance class of chemical transformations that have found extensive uses such as in bioactive molecules, in lubricants as well as in the syntheses of organic intermediates.

The partial hydrogenation of 5-decyne forms cis-dec-5-ene and the reaction is as shown :



The enthalpy change for hydrogenation of 5-decyne, ΔH_1 cannot be measured directly in the laboratory. You are required to plan an experiment to find the enthalpy change for hydrogenation of 5-decyne, ΔH_1 via Hess's Law.

The enthalpy change for the combustion of hydrogen is $-$ 286 kJ mol^{-1}. 5-decyne and cis-dec-5-ene are both liquids at standard conditions.

(a) Based on the given information and the equation above, state **two** enthalpy changes that are necessary to calculate ΔH_1.

Enthalpy change for combustion of 5-decyne and enthalpy change for combustion of cis-dec-5-ene.

(b) Using the information given above and your answer in **(a)**, you are required to write a plan to determine a value for the enthalpy change for hydrogenation of 5-decyne, ΔH_1.

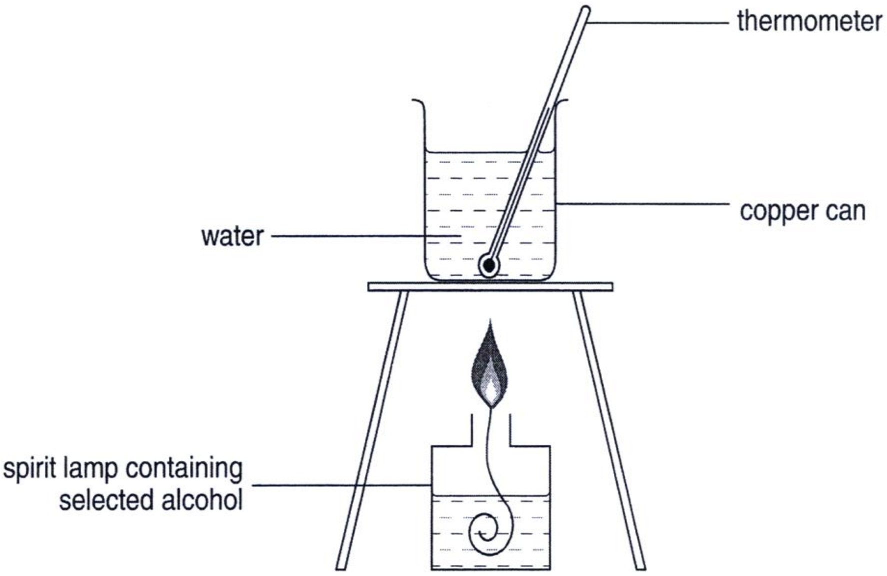
You may assume that you are provided with

- liquid 5-decyne
- liquid cis-dec-5-ene
- copper calorimeter
- two spirit lamps with a 5 cm-wick each
- deionised water
- a lighter
- thermometer
- apparatus normally found in a school or college laboratory

Your plan should contain the following:
- a diagram of the experimental set-up
- appropriate quantities of chemicals and solutions

- all essential experimental details

Diagram of the experimental set-up



5-decyne

Procedure:

1. **Using a 100 cm^3 measuring cylinder, measure 100 cm^3 of water into the copper calorimeter provided. Place the thermometer and record the initial temperature of water in the calorimeter.**
2. **Add 5-decyne to the spirit lamp until it is about half filled. Weigh using a weighing balance and record the total mass.**
3. **Place the spirit lamp under the calorimeter and light the wick of the lamp.**
4. **Stir the water with the thermometer until there is a rise of about 5°C. Extinguish the flame and record the final temperature of the water.**
5. **Reweigh the spirit lamp and content and record the final mass.**
6. **Repeat the whole procedure with cis-dec-5-ene.**

(c) List the measurements that have to be tabulated and recorded to calculate the value of enthalpy change for hydrogenation of 5-decyne, ΔH_1. In your answer, you need to show how these measurements are used to obtain the value of ΔH_1.

You may assume the specific heat capacity of water is 4.18 J g^{-1} K^{-1} and density of water is 1 g cm^{-3}.

Tables used to tabulate and record experimental data:

Mass of spirit lamp and 5-decyne before combustion / g	**A**
Mass of spirit lamp and 5-decyne after combustion / g	**B**

Mass of spirit lamp and cis-dec-5-ene before combustion / g	**C**
Mass of spirit lamp and cis-dec-5-ene after combustion / g	**D**

Temperature of water in calorimeter (for experiment involving 5-decyne) before combustion / °C	**E**
Temperature of water in calorimeter (for experiment involving 5-decyne) after combustion / °C	**F**

Temperature of water in calorimeter (for experiment involving cis-dec-5-ene) before combustion / °C	**G**
Temperature of water in calorimeter (for experiment involving cis-dec-5-ene) after combustion / °C	**H**

Treatment of results:

Mass of 5-decyne combusted = (A–B) g
Amount of 5-decyne combusted, n = (A–B)/molar mass of 5-decyne = X mol

Rise in temperature, ΔT = (F–E) K

Volume of water used = 100 cm^3

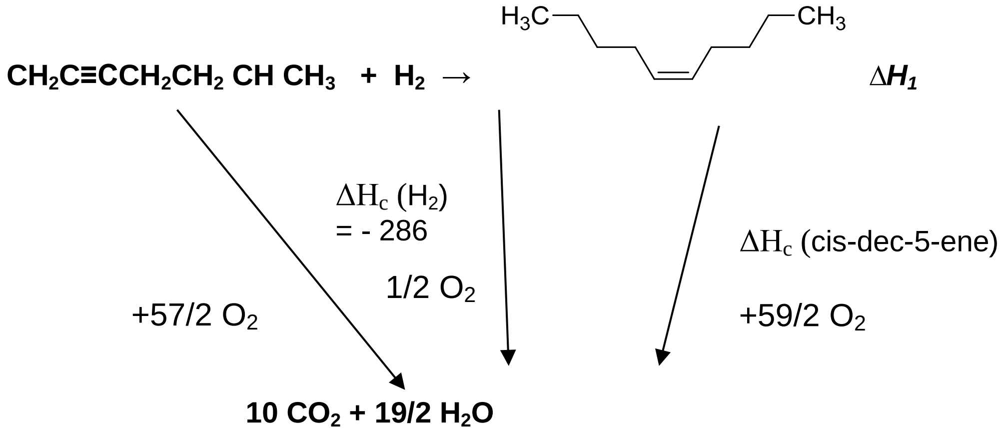
Density of water = 1 g cm^{-3}
Mass of water = 100 g

Assume no heat loss to surroundings and negligible heat capacity of copper calorimeter

Heat evolved from combustion, q = heat absorbed by water = mcΔT
= (100)(4.18)(ΔT) J

Enthalpy change for combustion of 5-decyne = –(q/n) kJ mol^{-1}

Repeat same steps for cis-dec-5-ene



By Hess's law,

$\Delta H_1 = \Delta H_c$ (5-decyne) + ΔH_c (H_2) – ΔH_c (cis-dec-5-ene)

$\Delta H_1 = \Delta H_c$ (5-decyne) – 286 – ΔH_c (cis-dec-5-ene)

[Total: 12]

[Turn over

2 Eighty-five percent of all pharmaceutical agents and vitamins involve chlorine chemistry; many drugs require chlorine, fluorine, or bromine to be effective.

Data about the halides are given below.

Halide (X)	pK_a (HX)	Percentage of HX decomposed at 2000°C	Boiling point of HX / °C	Dipole moment of C–X / D	K_a (HOX) at 298K
F	+3	6×10^{-5}	19.5	1.82	
C*l*	–7	4×10^{-1}	–84.2	1.08	2.9×10^{-8}
Br	–9	4	–67.1	0.82	2.4×10^{-9}
I	–10	30	–35.1	0.44	

(a) Hydrogen halides decompose at high temperature according to the equation:

$$2HX(g) \rightarrow H_2(g) + X_2(g)$$

Use relevant data from the *Data Booklet*, explain the trend indicated by percentage decomposition of HX.

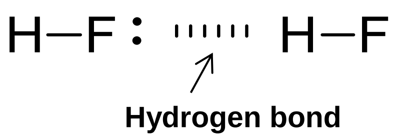
Bond energies of HX in kJ mol^{-1} in decreasing order:
HF – 562 ; HC*l* – 431; HBr – 366; HI – 299
shows decreasing bond strength from HF to HI.

Covalent bond strength decreases from HF to HI is due to increasing atomic radius of F to I, leading to less effective overlap of orbitals from F to I with H.

Hence thermal stability decreases in the order HF, HC*l*, HBr, HI and percentage decomposition increases from HF to HI as indicated in the table.

(b) The boiling point of HF is higher than the rest of the hydrogen halides despite it being the smallest molecule. By means of a diagram, indicate the interaction between two molecules of HF that leads to this significant difference.

δ^+ δ^- δ^+ δ^-

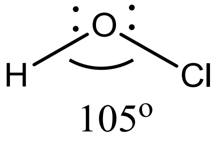


(c) When dissolved in water, the hydrogen halides show different pK_a values. Write balanced equations to represent the extent of ionisation of HF and HI in water.

HF : $HF + H_2O \rightleftharpoons F^- + H_3O^+$ must be reversible arrow

HI : $HI + H_2O \rightarrow I^- + H_3O^+$ or $HI \rightarrow I^- + H^+$

(d) **(i)** Draw a diagram to illustrate the shape of oxoacid, HOC*l*, indicating clearly the bond angle.



shape : bent **bond angle: 105°**

(ii) Using the information from the table, state which of the two acids, HOC*l* or HOBr is stronger?

HOC*l* is a stronger acid as its K_a value is larger than that of HOBr.

(iii) Hypoiodous acid has the formula HOI. Predict and explain whether HOI is a stronger or weaker acid than the acid you identified in **(d)(ii)**.

HOI is a weaker acid. The conjugate base OC*l*⁻ is more stable than OI⁻. This is due to C*l* being more electronegative hence <u>more electron withdrawing and disperses the negative charge on oxygen to a larger extent, stabilising OC*l*⁻</u>. Hence HOC*l* <u>ionises more</u> than HOI.

OR

HOI is a weaker acid. The conjugate base OI⁻ is less stable than OC*l*⁻. This is due to I being less electronegative hence <u>less electron withdrawing disperses the negative charge on oxygen to a smaller extent.</u> Hence HOI <u>ionises less</u> than HOC*l*.

(iv) Some solid NaOC*l* solution is dissolved in a solution of HOC*l* at 298 K. The pH of this mixture is determined to be 6.48. Calculate the ratio of OCl^- to $HOCl$ in this mixture.

Using pH = pKa + lg ([OCl^-] / [$HOCl$]

6.48 = –lg (2.9 x 10^{-8}) + lg ([OCl^-] / [$HOCl$]

[OCl^-] / [$HOCl$] = 0.0876

(e) The halides can react with concentrated sulfuric acid.

(i) When concentrated sulfuric acid was warmed with sodium chloride, white fumes of hydrogen chloride was evolved. Write a balanced equation for the reaction.

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

(ii) The method described in **e(i)** cannot be used to prepare hydrogen iodide. Describe what you would observe when sodium iodide is heated with concentrated sulfuric acid. Explain the chemistry behind it, and give any relevant equations.

$NaI + H_2SO_4 \rightarrow NaHSO_4 + HI$

$8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O$

<u>Black solid and violet fumes of I_2</u> seen and pungent (or rotten egg smell) H_2S evolved.

HI is a <u>stronger reducing agent</u> than HC*l*.

HI is oxidized to iodine, hence pure HI cannot be obtained.

[Total: 20]

3 (a) $AlCl_3$ is a compound of interest to scientists due to its industrial applications. For example, $AlCl_3$ can react with molten aluminium to form $AlCl$(g). This is a useful procedure as the $AlCl$ formed can be used to recover useful metalloids from their compounds.

Typically, the reaction has to be carried out in the presence of argon instead of air.

(i) The reaction has to be carried out in an atmosphere of argon. Suggest a reason for the need of argon.

To prevent oxygen in air from reacting with molten aluminium.

Consider the reaction between $AlCl_3$(g) and molten aluminium that was carried out at 1573 K :

$$2Al(l) + AlCl_3(g) \rightleftharpoons 3\,AlCl(g) \qquad \text{reaction } \mathbf{1}$$

In the reaction vessel, 0.200 mol of $AlCl_3$(g) was reacted with 0.400 mol of molten A*l*. When the reaction system achieved equilibrium with a total pressure of 1.50 atm, it was determined that 0.200 mol of molten A*l* remained in the vessel.

(ii) Write an expression for the equilibrium constant, K_p for reaction **1** and hence calculate its value at 1573 K.

	$2Al(l)$ +	$AlCl_3(g)$ $\rightleftharpoons$	$3\,AlCl(g)$
n_i/mol	**0.400**	**0.200**	**0**
n_c/mol	**–0.200**	**–0.100**	**+ 3/2 x 0.200**
n_e/mol	**0.200**	**0.100**	**0.300**

Total number of moles of gases at equilibrium = 0.100 + 0.300 = 0.400 mol

$$K_p = (P_{AlCl})^3 / (P_{AlCl3}) = (0.3/0.4 \times 1.5)^3/(0.1/0.4 \times 1.5) = 3.80\ \text{atm}^2$$

The same reaction vessel was heated to 1700 K rapidly in a way such that no reaction took place during the short interval of heating. The reaction system was allowed to re-establish equilibrium. It was found that the partial pressure of $AlCl_3$(g) was 0.390 atm when the equilibrium was re-established.

(iii) Using the information from **a(ii)**, determine the partial pressures of $AlCl_3$(g) and $AlCl$(g) at the instant when the reaction was heated to 1700 K, before the equilibrium was re-established. You can assume that the gases behave ideally and the volume of vessel is unchanged.

PV = nRT, since V, R and n are constant, P α 1/T

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

Thus,

[Turn over

$$\frac{P_{AlCl}}{1700} = \frac{\frac{0.300}{0.400} \times 1.5}{1573}$$

P_{AlCl} = 1.22 atm

$$\frac{P_{AlCl3}}{1700} = \frac{\frac{0.100}{0.400} \times 1.5}{1573}$$

P_{AlCl3} = 0.405 atm

(iv) Using the calculated values from **a(iii)**, calculate K_p of the reaction at 1700 K. Hence, explain whether reaction **1** is endothermic or exothermic.

$2Al(l) + AlCl_3(g) \rightleftharpoons 3\,AlCl(g)$

P_i/atm	–	**0.405**	**1.22**
P_c/atm	–	**-0.015**	**+0.045**
P_e/atm	–	**0.390**	**1.265**

$K_p = (1.265)^3/0.390 = 5.19$ atm^2

<u>K_p value is larger at 1700K compared to 1573K</u> showing forward reaction is favoured. By Le Chatelier's Principle, reaction 1 equilibrium position has <u>shifted to the right</u> to remove <u>excess heat.</u>

Hence reaction 1 is endothermic.

(v) The rate equation for reaction between Al and $AlCl_3$ is shown below.

rate = k[$AlCl_3$][Al]

Suggest which of the two mechanisms shown is a possible mechanism for the reaction.

Mechanism **1**:
$Al + AlCl_3 \rightarrow AlCl_2 + AlCl$ (slow)
$Al + AlCl_2 \rightarrow 2\,AlCl$ (fast)

Mechanism **2**:
$AlCl_3 \rightarrow AlCl + Cl_2$ (slow)
$2\,Al + Cl_2 \rightarrow 2\,AlCl$ (fast)

Mechanism 1 is the possible mechanism. It tallies with the rate equation where one mole of Al reacts with 1 mole of $AlCl_3$ in the slow step.

(b) Anhydrous $AlCl_3$ is often used as a catalyst in the Friedel-Crafts alkylation of benzene.

$$C_6H_6 + CH_3CH_2CH_2Cl \xrightarrow{AlCl_3} C_6H_5CH_2CH_2CH_3 + HCl \qquad \text{reaction } \mathbf{2}$$

(i) Explain why $AlCl_3$ can act as a catalyst in Friedel-Crafts alkylation.

Al has empty 3p orbital (or empty p orbital) to accept a lone pair of electrons when generating electrophile.

(ii) With the aid of an equation, explain the need to have anhydrous condition when $AlCl_3$ is used for reaction **2**.

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

$AlCl_3$ will dissolve (or undergoes hydration) in water to form $[Al(H_2O)_6]^{3+}$ which then <u>undergoes hydrolysis in water</u>.

(iii) Use information from the *Data Booklet,* calculate the enthalpy change of reaction for reaction **2**.

$$\Delta H = [BE(C–H) + BE(C–Cl)] – [BE(H–Cl) + BE(C–C)]$$
$$= (410 + 340) – (431 + 350) = –31 \text{ kJ mol}^{–1}$$

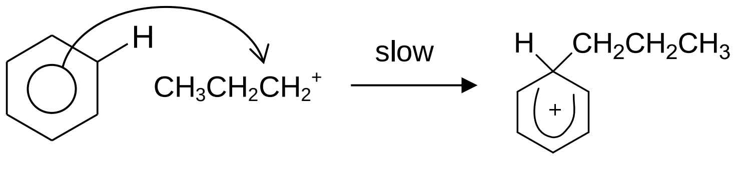
(iv) Describe the mechanism for the formation of $C_6H_5CH_2CH_2CH_3$ in reaction **2**, showing clearly the movement of electrons and partial charges.

Electrophilic substitution

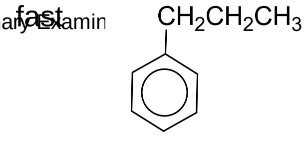
<u>Step 1: Generation of strong electrophile</u>

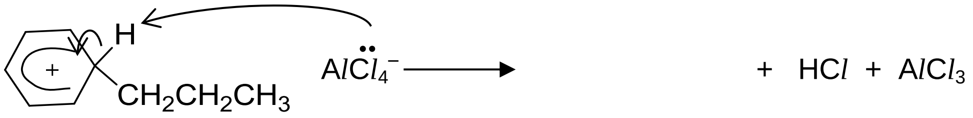
$$CH_3CH_2CH_2Cl + AlCl_3 \xrightarrow{\text{fast}} CH_3CH_2CH_2^+ + AlCl_4^–$$

<u>Step 2: Electrophilic attack on ring to form a carbocation intermediate</u>

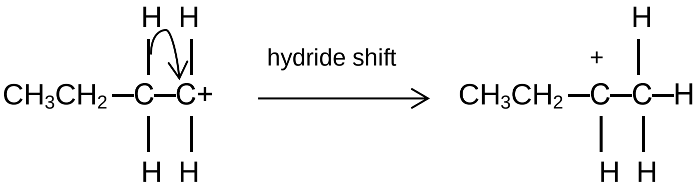


<u>Step 3: Restoring the benzene ring and regeneration of catalyst</u>





One key limitation of the alkylation reaction is that a mixture of products tends to form despite using only one type of halogenoalkane. For primary halogenoalkane, this is due to the occurrence of a process known as hydride shift which results in rearrangement of primary carbocation intermediates as shown :

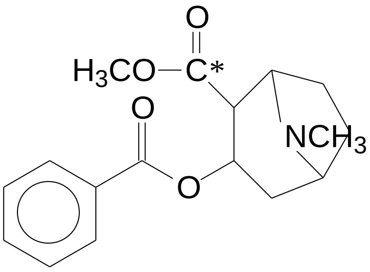


(v) Explain why hydride shift occurs for primary halogenoalkane.

Hydride shift leads to a <u>more stable secondary carbocation</u> as there are <u>more electron donating alkyl groups directly bonded to positively charged carbon</u>. Hence the <u>positive charge in the carbocation is dispersed</u>.

[Total: 22]

4 **(a)** Cocaine, $C_{17}H_{21}NO_4$, was first used as a local anaesthetic. It is also a powerful stimulant. Its structure is as shown:



cocaine

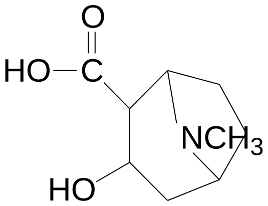
(i) State the functional groups, other than phenyl ring, present in cocaine.

Ester and tertiary amine

(ii) State the hybridisation of the carbon atom labelled with the asterisk (*).

sp^2

(b) Student **X** was asked to suggest a suitable synthetic route to prepare cocaine from methylbenzene and compound **A**.



compound **A**

Student **X** suggested the following steps:

Step **1**	Methylbenzene is oxidised with hot, acidified $KMnO_4$ to give benzoic acid.
Step **2**	Benzoic acid is converted into benzoyl chloride by reacting the resultant solution from step **1** with phosphorus pentachloride.
Step **3**	Benzoyl chloride is reacted with compound **A** at room temperature.
Step **4**	The resultant compound from step 3 is reacted with methanol in the presence of concentrated sulfuric acid at room conditions.

Explain why steps **2** and **4** of the synthetic route will not work.

In step 2, phosphorus pentachloride will be hydrolysed in the presence of aqueous solution. (or phosphorus pentachloride will react with water)

Heat is required for step 4.

(c) Cocaine is sold in its protonated hydrochloride salt, known as cocaine hydrochloride. Suggest a possible reason for this.

It has a higher melting point and is more stable.

[Turn over

(d) Smoking cocaine is more stimulating than inhaling the salt as it is absorbed quickly by the capillaries in the lung tissues. The salt is converted back to cocaine before smoking.

(i) Suggest a suitable reagent to convert cocaine hydrochloride back into cocaine.

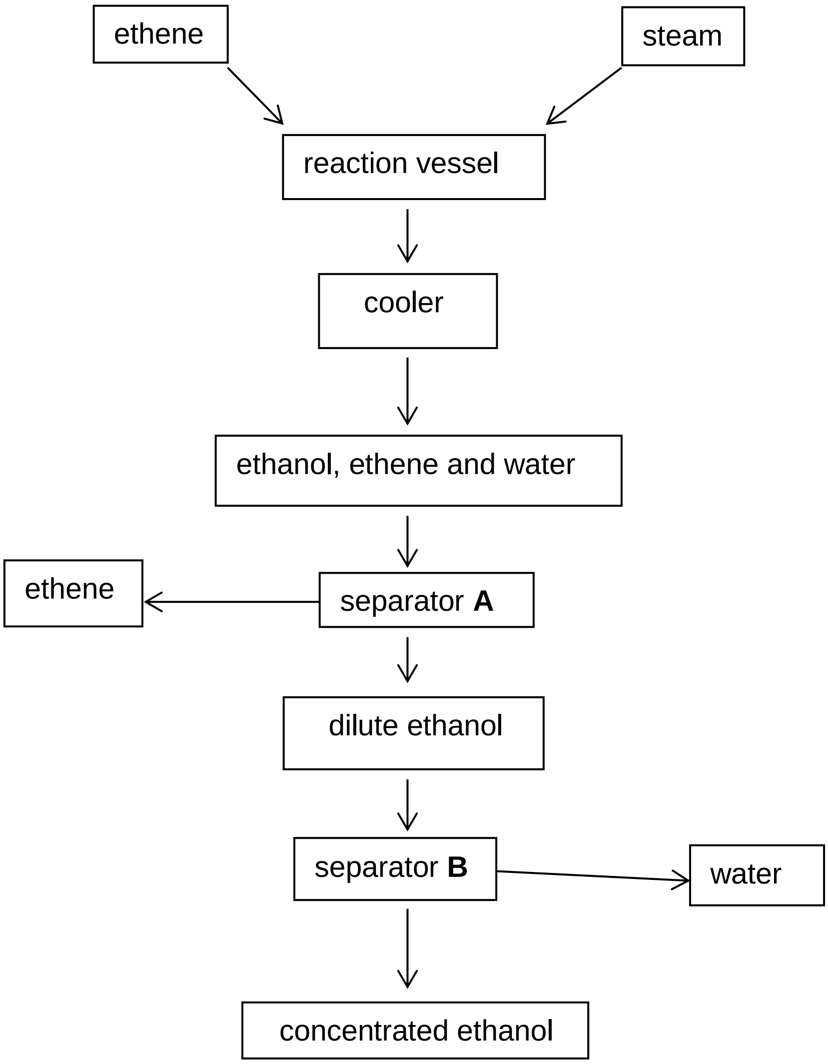
NaOH(aq)

(ii) Suggest a suitable solvent to extract cocaine and separate it from its salt.

Ether (or any other organic solvent less polar than water)

[Total: 7]

5 An industrial method for the production of ethanol, C_2H_5OH, is outlined in the following flow diagram.



(a) **(i)** Unreacted ethene is removed in separator **A**. Suggest how the separated ethene could be used to increase the efficiency of the overall process of the manufacture of ethanol.

The separated ethene can be returned back to the reaction vessel to produce more ethanol.

(ii) Name the process that takes place in separator **B**.

Fractional distillation (or distillation)

(b) In the reaction vessel, ethanol is produced in an exothermic reaction.

(i) State the reagents and conditions for the industrial preparation of ethanol from ethene.

H_2O and concentrated H_3PO_4
300°C, 60 atm

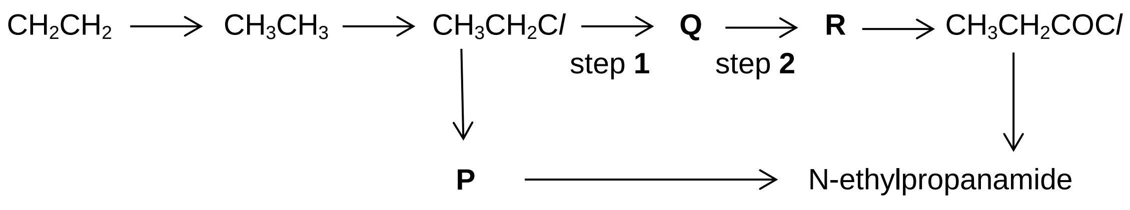
(ii) If 1.64 kg of ethanol is produced from 10.0 kg of ethene, calculate the percentage yield of ethanol.

$CH_2{=}CH_2\,(g) + H_2O\,(g) \rightleftharpoons CH_3CH_2OH(l)$

Theoretical yield of $= \frac{10 \times 1000}{12 \times 2 + 4} \times (12 \times 2 + 6 + 16) = 1.6429 \times 10^4$ **g**
$= 16.429$ **kg**
$= 16.4$ **kg**

Percentage yield $= \frac{1.64}{16.4} \times 100 = 10.0\ \%$

(c) Ethene is used to synthesise N-ethylpropanamide as shown in the following reaction scheme:



(i) Give the structural formulae of compounds **P**, **Q** and **R**.

P : $CH_3CH_2NH_2$
Q : CH_3CH_2CN

R : CH_3CH_2COOH

(ii) State the reagents and conditions for steps **1** and **2**.

step 1 : ethanolic KCN, heat
step 2 : dilute sulfuric acid, heat

[Total: 11]

End of Paper

YJC Chemistry H2 P3 Prelim 2016

Answer any **four** questions

1 Phosphorus was first discovered by the German alchemist, Hennig Brandt's experiment with human waste, urine. Phosphorus occurs in different alloptropic forms with the two common ones being white phosphorus and red phosphorus.

(a) Depending if oxygen is in excess, phosphorus reacts with oxygen to form two different oxides, phosphorus(III) oxide and phosphorus(V) oxide.

(i) Write the equations for the reactions of phosphorus(III) oxide and phosphorus(V) oxide with water separately, including state symbols. [2]

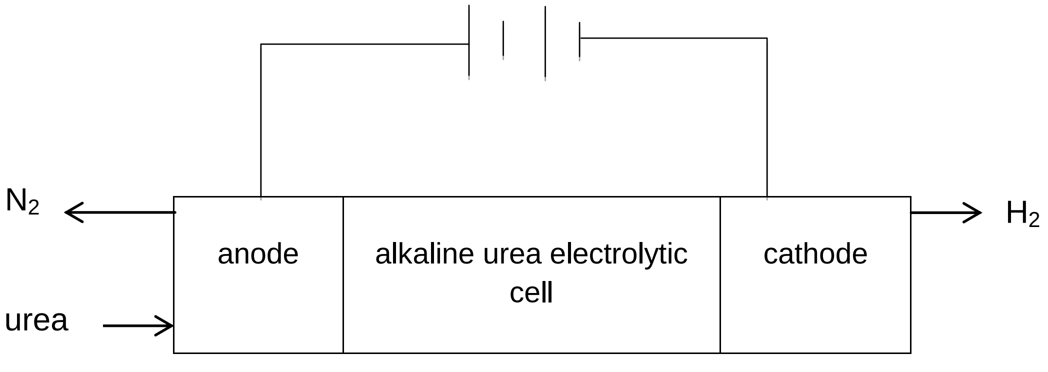
(ii) Describe the observation when the resulting solutions from **(i)** are added to solid aluminium oxide. [1]

(b) Nitrogen, which is in the same group as phosphorus, forms an important molecule ammonia, NH_3. NH_3 is used to make fertilisers as well as explosives.

(i) When aqueous ammonia is gradually added to an aqueous solution containing $Cu^{2+}(aq)$, several observations are seen. Describe and explain these observations and write equations where appropriate. [3]

(ii) When black copper(II) oxide is stirred with liquid ammonia, it dissolves to give a coloured solution. During this reaction the oxide ion is acting as a Bronsted-Lowry base. Suggest an equation for this reaction, and suggest the colour of the solution. [1]

(c) A group of researchers have recently developed an efficient way of producing hydrogen from urine, a nitrogen containing compound as shown in the diagram below.



Urea, $CO(NH_2)_2$, in aqueous KOH, which acts as the electrolyte, is oxidized at the anode to form nitrogen and carbon dioxide. At the cathode, water is reduced to hydrogen gas.

The overall equation for the urea electrolyte cell is :

$$CO(NH_2)_2(aq) + H_2O(l) \rightarrow N_2(g) + 3H_2(g) + CO_2(g)$$

(i) Write the half equation, with state symbols, occurring at each electrode in this urea electrolytic cell. [2]

(ii) By considering why CO_2 is not liberated at the anode, deduce the by-product produced at the anode. [1]

(d) Nitrogen is also commonly found in organic compounds. **D**, $C_{12}H_{16}O_3N_2$, is a neutral compound with a benzene ring. Upon reaction with hot sodium hydroxide, **E** and **F** are formed. On acidification, **E** forms $C_2H_4O_2$ which gives effervescence with sodium carbonate.

One mole of **F**, $C_8H_{12}N_2O$, reacts with one mole of aqueous sulfuric acid at room temperature. One mole of **F** is also able to decolourise three moles of aqueous bromine and gives a white ppt, **G**.

When acidified orange potassium dichromate(VI) is added to **F**, compound **H**, $C_8H_{10}N_2O$ is formed and the solution turns green. A yellow ppt is also formed when **F** and **H** is reacted with alkaline aqueous iodine separately.

Suggest the structures for compounds **D**, **E**, **F**, **G** and **H** and explain the observations described above. You do not need to consider the positions of the substituents on the benzene ring. [10]

[Total :20]

2 **(a)** With the aid of an equation, define the term *standard enthalpy change of formation* of calcium carbonate, $CaCO_3$. [2]

(b) The enthalpy change of the reaction, ∆H for the reaction shown below is determined to be – 622 kJ mol^{-1}**.**

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

In a similar experiment, solid calcium carbonate reacted with an excess of hydrochloric acid and the enthalpy change of reaction was found to be – 95.0 kJ per mole of calcium carbonate.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l) \quad \Delta H = -95.0 \text{ kJ mol}^{-1}$$

The values of enthalpy change of formation of water and enthalpy change of combustion of carbon are provided.

$$\Delta H_f^{\ominus}(H_2O) = -286 \text{ kJ mol}^{-1}$$
$$\Delta H_c^{\ominus}(C) = -394 \text{ kJ mol}^{-1}$$

Using the information given, calculate the standard enthalpy change of formation of calcium carbonate. [3]

(c) Magnesium carbonate decomposes on heating according to the equation shown below. The values of the standard enthalpy change and standard entropy change of the decomposition are provided.

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$$

$$\Delta H^{\ominus} = +117 \text{ kJ mol}^{-1} \ ; \ \Delta S^{\ominus} = +175 \text{ J mol}^{-1} \text{ K}^{-1}$$

(i) Why does the entropy increase when magnesium carbonate decomposes? [1]

(ii) Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for the decomposition of magnesium carbonate. Hence, comment on the spontaneity of the decomposition of magnesium carbonate at room temperature. [2]

(iii) Compare the ease of thermal decomposition of magnesium carbonate with barium carbonate. [3]

(d) Describe the reaction of Mg and Ca with water, giving appropriate equations with state symbols. [2]

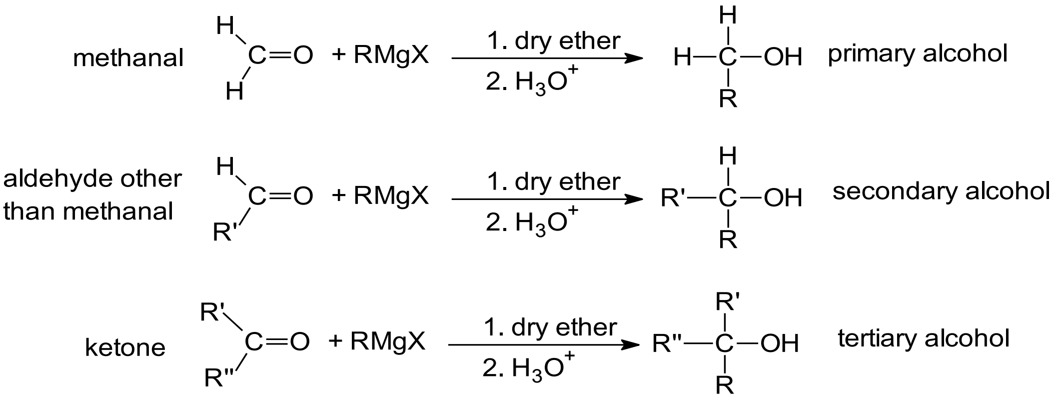
(e) Mg reacts with halogenoalkanes, RX in dry ether, forming Grignard reagents which are important intermediates used to produce many organic compounds.

$$RX + Mg \xrightarrow{\text{dry ether}} \underset{\delta-}{R}—\underset{2\delta+}{Mg}—\underset{\delta-}{X}$$

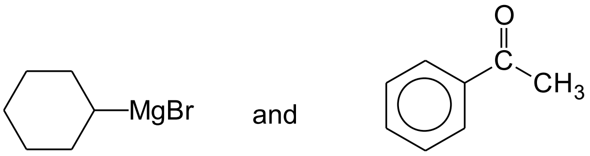
Grignard reagent

RMgX is called an organometallic compound, where R is an alkyl group and X is chlorine, bromine or iodine. R in RMgX behaves like an anion R^-, and is strongly basic and nucleophilic.

On reaction with carbonyl compounds, RMgX forms various classes of alcohols:



(i) Draw the structure of the organic products formed when the following compounds are reacted:

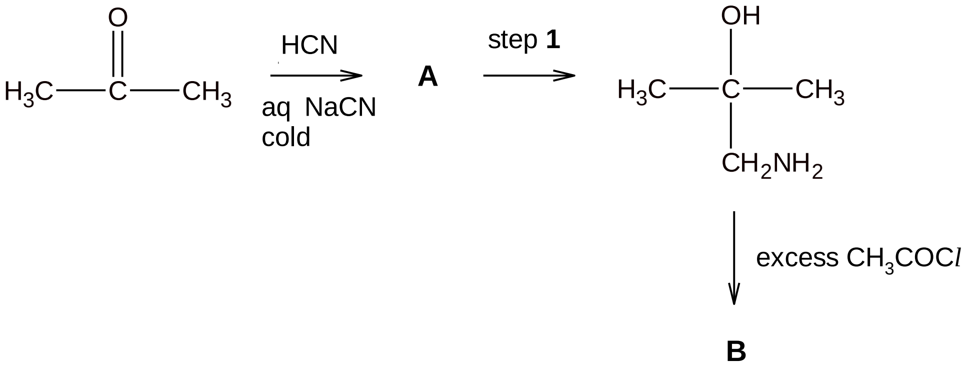


[1]

(ii) Give the displayed formula of the bromoalkane which can be used to form a Grignard reagent that would react with butanal to give 2–methylhexan–3–ol. [1]

(iii) When RMgBr is reacted with ethanoyl bromide, 2 moles of RMgBr are required per mole of ethanoyl bromide and the product formed is CH_3CR_2OH. Explain why one mole of ethanoyl bromide reacts with two moles of RMgBr while one mole of aldehyde or ketone reacts with one mole of RMgBr. [2]

(f) Ketones and aldehydes react with HCN via nucleophilic addition mechanism similar to the reaction with Grignard reagents. The reaction scheme below is one such example.



(i) Draw the structures of compounds **A and** **B**. [2]

(ii) State the reagent and condition for step **1**. [1]

[Total :20]

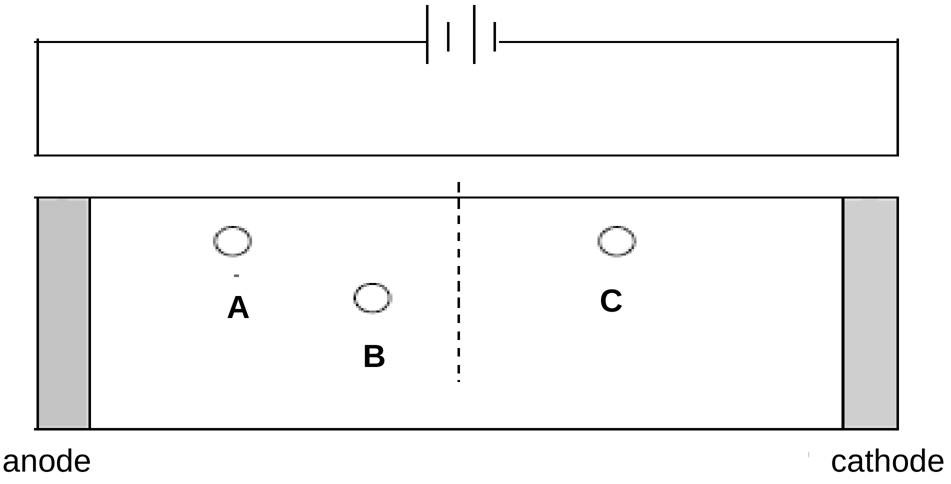
3 Transport proteins serve the function of moving other materials within an organism. They are vital to the growth and life of all living things. Haemoglobin is an iron-containing oxygen-transport protein found in the red blood cells of all vertebrates.

(a) State the type of bonding or interactions involved in the *primary*, *secondary*, *tertiary* and *quaternary* structures of proteins like haemoglobin. [2]

(b) The following amino acids are some of the amino acids present in the primary sequence of haemoglobin.

Amino Acids	**Formula of side chain (R' in R'CH(NH$_2$)CO$_2$H)**	**Isoelectric Point**
Lysine	$-(CH_2)_4NH_2$	9.74
Glutamic acid	$-CH_2CH_2COOH$	3.15
Aspartic acid	$-CH_2COOH$	2.77

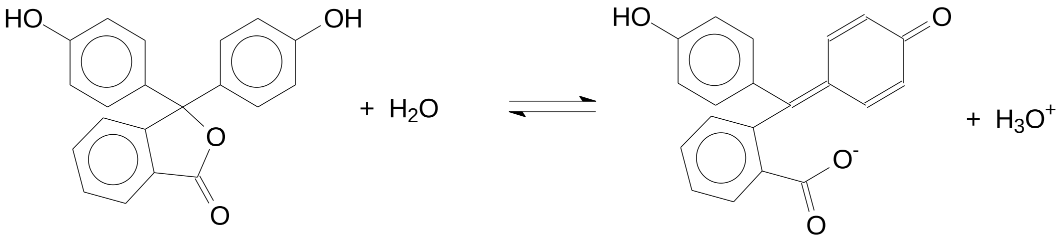
An electrophoresis experiment is ran on a solution containing the above three amino acids at pH 5.00. The relative positions of the amino acids are shown in the diagram below.



Suggest the identities of amino acids **A**, **B** and **C**. [1]

(c) Haemoglobin is able to exhibit peroxidase-like activity to catalyse the oxidation of colourless phenolphthalein into its bright pink conjugate base. This reaction is often used to test for the presence of blood at a crime scene.

Phenolphthalein is a *weak acid* which dissociates in water according to the following equation:



Phenolphthalein
colourless

Conjugate base of phenolphthalein
pink

The K_a of phenolphthalein is 3.00 x 10^{-10} mol dm^{-3}.

Distinct colour change for phenolphthalein occurs when half of the indicator is phenolphthalein and the other half is its conjugate base.

(i) Calculate the pH at which phenolphthalein shows distinct colour change. [1]

(ii) The change of colour for phenolphthalein occurs over a limited range of pH and falls within ± 1.00 of the pK_a value.

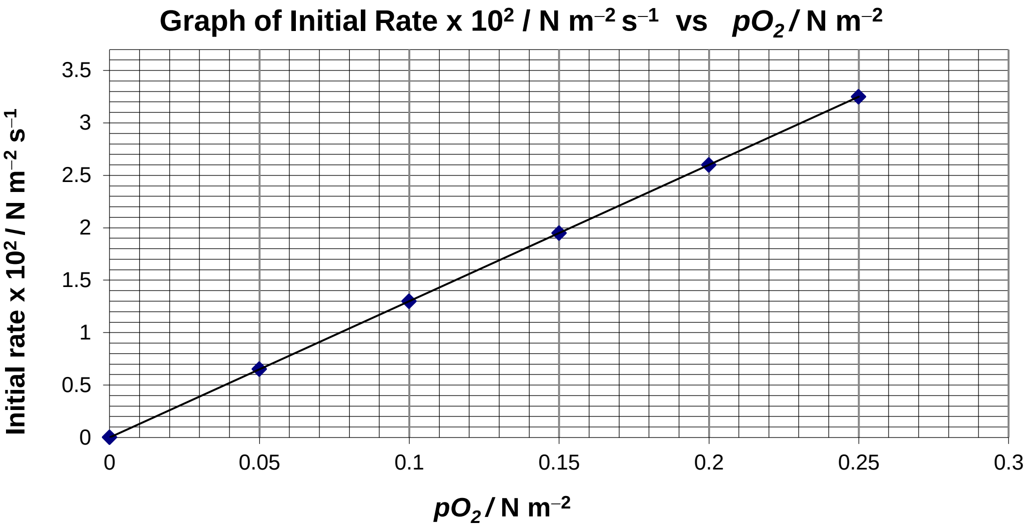
In an experiment, a solution of a weak acid hydroxylammonium chloride, $NH_3OH^+Cl^-$, was titrated against a solution of sodium hydroxide as shown by the equation below:

$$NH_3OH^+Cl^- + NaOH \rightarrow NH_2OH + NaCl + H_2O$$

With the aid of an equation and your answer in **(i)**, explain if phenolphthalein is a suitable indicator for this titration. [2]

(d) The reaction kinetics of oxygen binding to haemoglobin in human red blood cell suspension is studied. This is done by measuring the rates of uptake of oxygen by haemoglobin at different partial pressures of oxygen.

The graph of initial rate against partial pressure of oxygen was plotted below.



(i) Using the graph above, state the order of reaction with respect to oxygen. [1]

(ii) The concentration of haemoglobin was halved and a new series of experiments was conducted at the same temperature. When a similar graph was plotted, the gradient at each point was half that obtained from the above graph.

Deduce the order of reaction with respect to haemoglobin? Explain your answer. [2]

(iii) Using your answers to **(i)** and **(ii)**, construct the rate equation for the reaction between haemoglobin and oxygen. [1]

(iv) Oxygen dissolves in blood in the lungs and its concentration under common conditions is kept at 1.6×10^{-6} mol dm^{-3} by breathing. The concentration of haemoglobin in the blood of lung capillaries is also constant and is equal to 8.0×10^{-6} mol dm^{-3}.

Calculate the rate constant, including the unit, given that the rate of oxyhaemoglobin formation is 2.68×10^{-5} mol dm^{-3} s^{-1} at 37 °C. [1]

(e) Another type of protein that transports oxygen throughout the bodies of invertebrates is *haemocyanin*, which contains two copper atoms that reversibly bind a single oxygen molecule.

(i) *Haemocyanin* exhibits catalytic activity to catalyse the hydroxylation of monophenols to diphenols.

Using an appropriate sketch of the Maxwell-Boltzmann distribution curve, explain how the presence of *haemocyanin* increases the rate of hydroxylation of monophenols. [3]

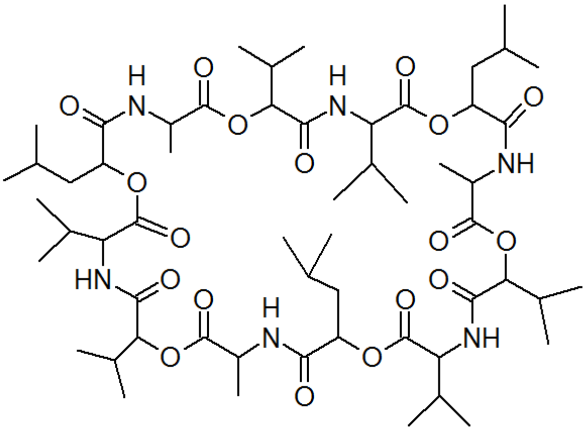
(ii) Partial *denaturation* actually improves *haemocyanin*'s catalytic ability by providing greater access to the active site.

1 What is meant by the term *denaturation*?

2 Suggest how a weak acid might interact with *haemocyanin* to bring about denaturation.

[3]

(f) *Cereulide* is another example of a transport protein. As a natural dodecadepsipeptide ionophore, *cereulide* acts as potassium transporters, where potassium, K^+, plays a vital role in bacterial physiology.



Cereulide

(i) Apart from the peptide group, name another functional group that is present in the molecule? [1]

When treated with a peptidase enzyme, the peptide bonds in the ring are hydrolysed. Only two different products are formed.

(ii) Out of the products formed, two of the amino acid residues are present **more than once** in the protein. Draw the structural formula of these two amino acid residues. [2]

[Total :20]

4 **(a)** Manganese is a transition element that can exist in several oxidation states.

Manganese species	Mn^{2+}	MnO_4^{2-}	MnO_4^-
Colour (in aqueous medium)	pale pink	green	purple

(i) Write the full electronic configurations of Mn in Mn^{2+} and MnO_4^-, and explain why Mn can exhibit variable oxidation states. [2]

(ii) Explain why transition elements form compounds that are coloured. [3]

(b) A student wanted to investigate the rate of reaction between MnO_4^- and $C_2O_4^{2-}$ ions in an acidic medium. The reaction is shown in the equation below.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + + 8H_2O$$

The rate of reaction was followed by mixing the following two solutions, and measuring the concentration of remaining MnO_4^- ions at fixed time intervals.

Solution **A**: 100 cm^3 of 0.20 mol dm^{-3} ethanedioic acid, 5 cm^3 of 2 mol dm^{-3} sulfuric acid, 15 cm^3 of 0.20 mol dm^{-3} copper(II) sulfate and 80 cm^3 of water

Solution **B**: 50 cm^3 of 0.020 mol dm^{-3} potassium manganate(VII)

The following results were obtained.

Time/s	$[MnO_4^-]$ / mol dm^{-3}
0	0.0040
10	0.0026
20	0.0016
30	0.00096
50	0.00040
75	0.00016

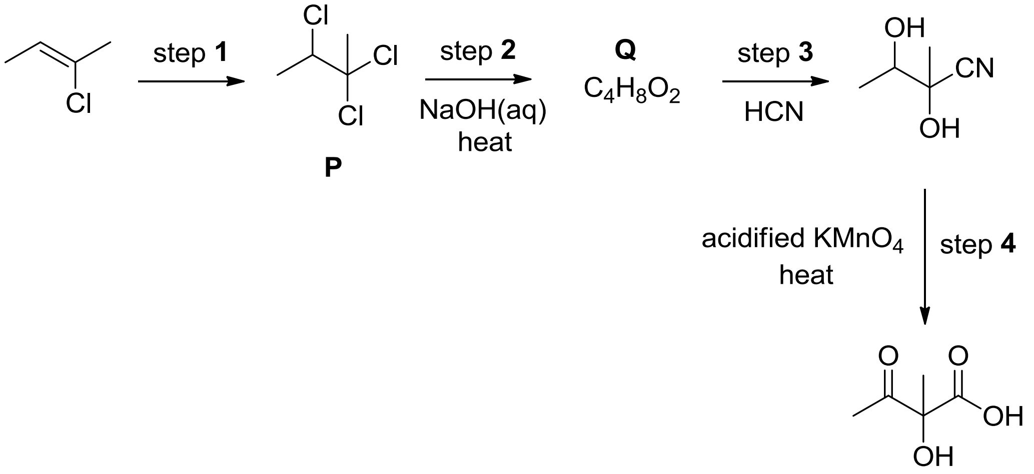
(i) By means of a graphical method, determine the rate equation under the conditions whereby the reaction was conducted. [3]

(ii) The rate of consumption of MnO_4^-(aq) at a particular time is 1.2×10^{-4} mol dm^{-3} s^{-1}. Using the equation for the reaction between MnO_4^- and $C_2O_4^{2-}$, calculate the rate of consumption of ethanedioate ions at that particular time? [1]

(iii) What is the role of copper(II) sulfate in the reaction? [1]

(c) Potassium manganate(VII) is commonly used as an oxidising agent in organic chemistry.

Acetolactic acid, $C_5H_8O_4$, is a precursor in the biosynthesis of the branched chain amino acids, valine and leucine. Acetolactic acid can be synthesised from 2-chlorobut-2-ene by the following reactions.



Acetolactic acid

(i) State the reagent and conditions used in step **1** and outline the mechanism for this reaction. In your answer, you should include curly arrows showing the movement of electrons and any relevant charges and dipoles. [4]

(ii) Compound **P** obtained from step **1** does not rotate the plane of polarised light despite it containing a chiral carbon. Use the mechanism which you have proposed in **(i)**, to explain this observation. [3]

(iii) Suggest the structure of compound **Q.** [1]

(iv) Draw the organic products formed when acetolactic acid is warmed with iodine in the presence of aqueous potassium hydroxide. [2]

[Total :20]

5 **(a)** New applications such as hybrid electric vehicles and power backup require rechargeable batteries that combine high energy density with high charge and discharge rate capability. One such current battery electrode material in used is $LiCoO_{2.}$

The following cell diagram notation is a simplified illustration of the electrochemical cell.

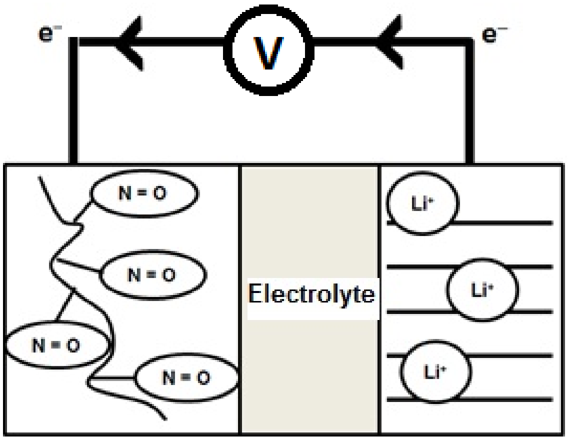
$$Li \mid Li^+ \parallel Li^+, CoO_2 \mid LiCoO_2 \mid Pt$$

In this cell, Li is oxidised to Li^+ while CoO_2 is reduced to $LiCoO_2$. State the oxidation state of Co in $LiCoO_2$ and hence write the electronic configuration of Co in $LiCoO_2$. [2]

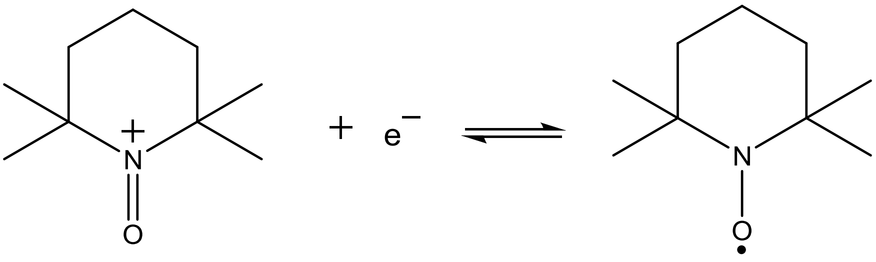
(b) In recent years, organic radical polymers have been developed as alternatives to inorganic materials because of their light weight, flexibility and their environmentally-friendly features. With the increase in demand for thinner mobile phones and tablet computers, there is a surge to invent film-like organic-derived electrode-active battery materials to power such devices.

One such material is **TEMPO-NO radical** which is capable of repeated stable oxidation-reduction between **N=O** radicals and **N=O** cations. Its voltage when paired with a Li/Li^+ half-cell is able to reach +3.60 V which is comparable to a common lithium-ion battery.

The following is a simplified illustration of the electrochemical cell set-up.



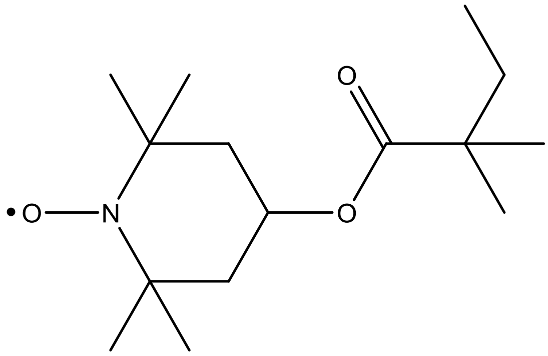
(i) The following half-equation represents the reaction which occurs at the organic derived electrode.



TEMPO-NO radical

With the use of the *Data Booklet* and the information above, write the overall balanced equation for the electrochemical reaction and calculate the standard electrode potential for **TEMPO-NO** radical half cell. [3]

(ii) In order for the radical polymer to be used as an electrode, it must not be soluble in the electrolyte. To improve the usability of **TEMPO-NO** radical, the material can be converted to **PTMA** which has the following structure:

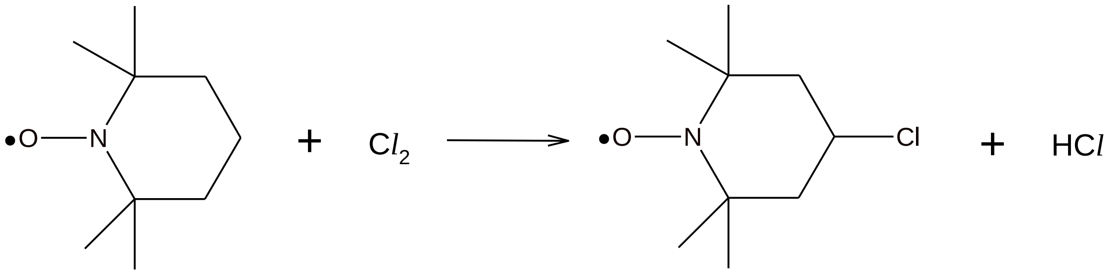


PTMA

Explain how the structure of **PTMA** will help to reduce its solubility in polar solvents like water. [3]

(iii) Water cannot be used as the solvent for Li^+ | Li half cell. Write an equation to illustrate the reaction when an aqueous medium is used at the Li^+ | Li half cell which hinders the working of the battery. [1]

(iv) The synthesis of **PTMA** required the mono-substitution of the **TEMPO-NO** radical with chlorine as shown in the reaction below.



TEMPO-NO radical

Outline the mechanism for this reaction. [4]

(v) Suggest the synthesis route for the formation of **PTMA** from **TEMPO-NO** radical. [4]

(c) When the organic radical battery is recharged, lithium ion is being converted back to lithium metal. Given that the charging process is 87% efficient, how many hours does it take to restore 1.25 g of lithium metal using a current of 3 A? [3]

[Total :20]

End of Paper

YJC Chemistry H2 P3 Prelim 2016

Answer any **four** questions

1 Phosphorus was first discovered by the German alchemist, Hennig Brandt's experiment with human waste, urine. Phosphorus occurs in different alloptropic forms with the two common ones being white phosphorus and red phosphorus.

(a) Depending if oxygen is in excess, phosphorus reacts with oxygen to form two different oxides, phosphorus(III) oxide and phosphorus(V) oxide.

(i) Write the equations for the reactions of phosphorus(III) oxide and phosphorus(V) oxide with water separately, including state symbols. [2]

$P_4O_6(s) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$
$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

(ii) Describe the observation when the resulting solutions from **(i)** are added to solid aluminium oxide. [1]

Aluminium oxide dissolves in the acidic solution to form a colourless solution.

(b) Nitrogen, which is in the same group as phosphorus, forms an important molecule ammonia, NH_3. NH_3 is used to make fertilisers as well as explosives.

(i) When aqueous ammonia is gradually added to an aqueous solution containing $Cu^{2+}(aq)$, several observations are seen. Describe and explain these observations and write equations where appropriate. [3]

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s)$ -------- (1)

$NH_3(aq)$ undergoes hydrolysis in water to form OH^-. When a small amount of NH_3 is added, a blue precipitate of $Cu(OH)_2$ is formed.

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

Addition of excess ammonia causes the formation of the more stable deep blue $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion through a ligand-exchange reaction.

The reaction lowers the concentration of $Cu^{2+}(aq)$ causing $Cu(OH)_2$ to dissolve.

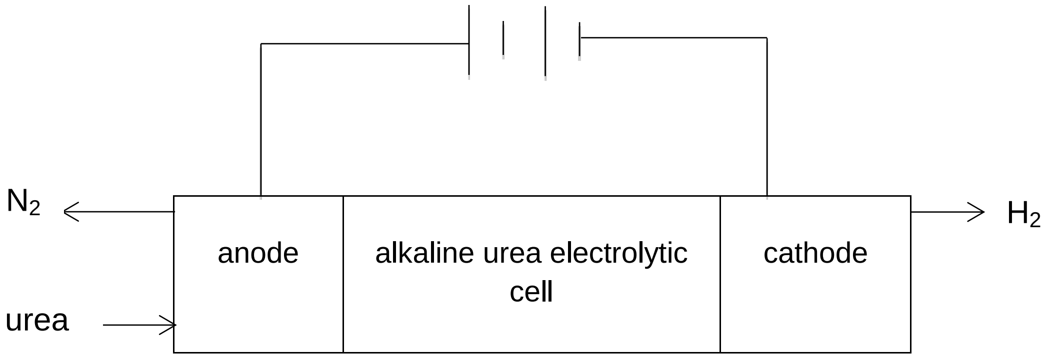
Equilibrium position (1) shifts to the left and the ionic product < K_{sp}.

(ii) When black copper(II) oxide is stirred with liquid ammonia, it dissolves to give a coloured solution. During this reaction the oxide ion is acting as a Bronsted-Lowry base. Suggest an equation for this reaction, and suggest the colour of the solution. [1]

On addition of $NH_3(l)$, a dark blue solution is observed as a complex $[Cu(NH_3)_4]^{2+}$ is formed.

$CuO + 5NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + OH^- + NH_2^-$

(c) A group of researchers have recently developed an efficient way of producing hydrogen from urine, a nitrogen containing compound as shown in the diagram below.



Urea, $CO(NH_2)_2$, in aqueous KOH, which acts as the electrolyte, is oxidized at the anode to form nitrogen and carbon dioxide. At the cathode, water is reduced to hydrogen gas.

The overall equation for the urea electrolyte cell is :

$$CO(NH_2)_2(aq) + H_2O(l) \rightarrow N_2(g) + 3H_2(g) + CO_2(g)$$

(i) Write the half equation, with state symbols, occurring at each electrode in this urea electrolytic cell. [2]

Anode : $CO(NH_2)_2(aq) + 6OH^-(aq) \rightarrow N_2(g) + 5H_2O(l) + CO_2(g) + 6e^-$

Cathode : $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

(ii) By considering why CO_2 is not liberated at the anode, deduce the by-product produced at the anode. [1]

K_2CO_3 (or $KHCO_3$) is produced as acidic CO_2 reacts with alkaline KOH.

(d) Nitrogen is also commonly found in organic compounds. **D**, $C_{12}H_{16}O_3N_2$, is a neutral compound with a benzene ring. Upon reaction with hot sodium hydroxide, **E** and **F** are formed. On acidification, **E** forms $C_2H_4O_2$ which gives effervescence with sodium carbonate.

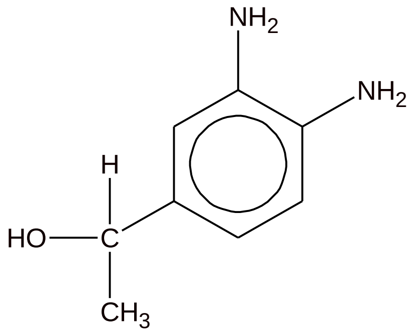
One mole of **F**, $C_8H_{12}N_2O$, reacts with one mole of aqueous sulfuric acid at room temperature. One mole of **F** is also able to decolourise three moles of aqueous bromine and gives a white ppt, **G**.

When acidified orange potassium dichromate(VI) is added to **F**, compound **H**, $C_8H_{10}N_2O$ is formed and the solution turns green. A yellow ppt is also formed when **F** and **H** is reacted with alkaline aqueous iodine separately.

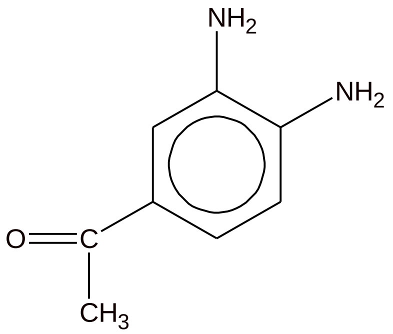
Suggest the structures for compounds **D**, **E**, **F**, **G** and **H** and explain the observations described above. You do not need to consider the positions of the substituents on the benzene ring. [10]

Statement	**Type of reaction**	**Deduction**
D reacts with hot sodium hydroxide to form E and F	**√ hydrolysis**	**√ D could be ester or amide**
On acidification, E forms $C_2H_4O_2$ which gives effervescence with sodium carbonate.	**√ neutralisation**	**√ E is acid salt forming CH_3COOH**
One mole of F, $C_8H_{12}N_2O$, reacts with one mole of sulfuric acid at room temperature	**√ neutralisation**	**√ F is basic as it reacts with aq H_2SO_4. F could be phenylamine.** **√ Since F : H_2SO_4 = 1 : 1, F has 2 $–NH_2$.**
One mole of F is able to decolourise three moles of aqueous bromine and give a white ppt, G.	**√ electrophilic substitution**	**√ F contains ring activating/electron donating NH_2 groups attached to benzene ring** **√ This shows that 2,4,6 positions in the benzene are substituted.**
Acidified orange potassium dichromate(VI) is added to F, compound H, $C_8H_{10}N_2O$ is formed and the solution turns green.	**√ oxidation**	**√ F contains a secondary alcohol group which is oxidised to a ketone in H.**
A yellow ppt is also formed when F and H is reacted with alkaline aqueous iodine separately.	**√ oxidation**	**H has √ CH_3CO and F has √ $CH_3CH(OH)$.** **√ Yellow ppt is CHI_3.**

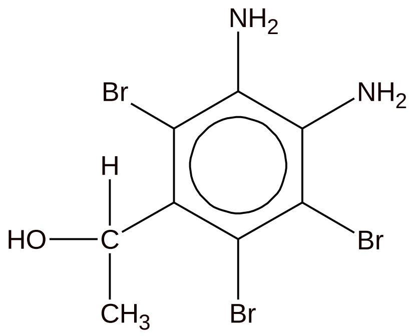
E **CH_3COONa**



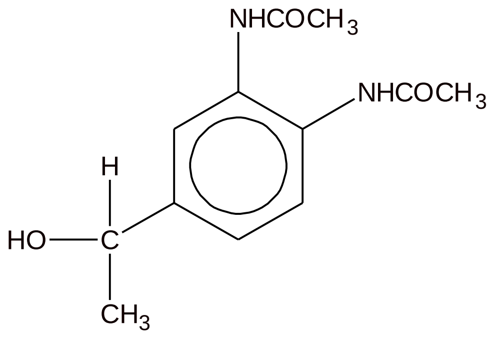
F



H



G



D

[Total :20]

2 **(a)** With the aid of an equation, define the term *standard enthalpy change of formation* of calcium carbonate, $CaCO_3$. [2]

Standard enthalpy of formation of $CaCO_3$ is the energy released or required when 1 mole of $CaCO_3$ is formed from its constituent elements under standard conditions of 298 K and 1 atm.

$Ca(s) + C(s) + 3/2\ O_2(g) \rightarrow CaCO_3(s)$

(b) The enthalpy change of the reaction, ΔH for the reaction shown below is determined to be – 622 kJ mol^{-1}**.**

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

In a similar experiment, solid calcium carbonate reacted with an excess of hydrochloric acid and the enthalpy change of reaction was found to be – 95.0 kJ per mole of calcium carbonate.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l) \quad \Delta H = -95.0\ kJ\ mol^{-1}$$

The values of enthalpy change of formation of water and enthalpy change of combustion of carbon are provided.

$$\Delta H_f^{\ominus}(H_2O) = -286\ kJ\ mol^{-1}$$
$$\Delta H_c^{\ominus}(C) = -394\ kJ\ mol^{-1}$$

Using the information given, calculate the standard enthalpy change of formation of calcium carbonate. [3]

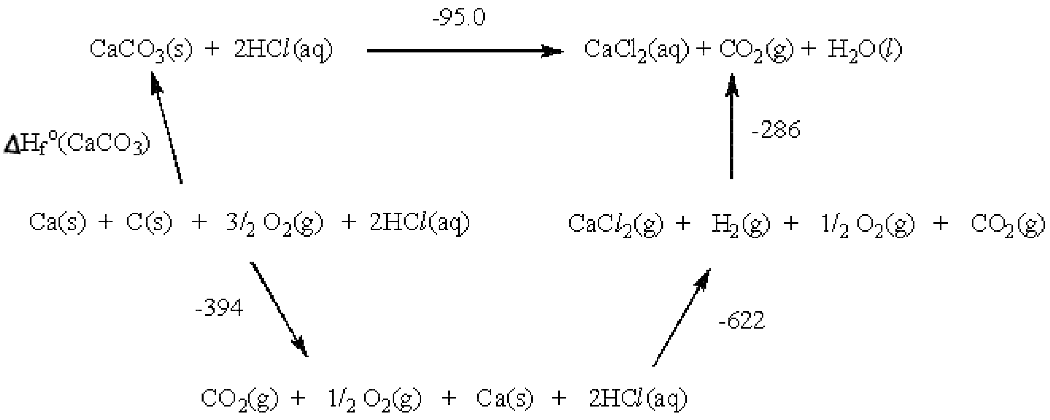
$Ca(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2(g)$ ------- (1) $-622\ kJ\ mol^{-1}$

$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$ ------ (2) $-95.0\ kJ\ mol^{-1}$

(1) + reverse (2):
$Ca(s) + CO_2(g) + H_2O(l) \rightarrow CaCO_3(s) + H_2(g)$
$\Delta H_r = -622 + 95.0 = -527\ kJ\ mol^{-1}$

$-527 = [\Delta H_f^{\ominus}(CaCO_3) + 0] - [0 + \Delta H_f^{\ominus}(CO_2) + (\Delta H_f^{\ominus}(H_2O)]$
$-527 = \Delta H_f^{\ominus}(CaCO_3) - [(-394) + (-286)]$
$\Delta H_f^{\ominus}(CaCO_3) = -1207\ kJ\ mol^{-1}$

OR



Cycle

$\Delta H_f^{\ominus}(CaCO_3)$ = – 394 – 622 – 286 + 95.0
= –1207 kJ mol^{-1}

(c) Magnesium carbonate decomposes on heating according to the equation shown below. The values of the standard enthalpy change and standard entropy change of the decomposition are provided.

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$$

$$\Delta H^{\ominus} = +\,117 \text{ kJ mol}^{-1} \;;\; \Delta S^{\ominus} = +\,175 \text{ J mol}^{-1}\text{ K}^{-1}$$

(i) Why does the entropy increase when magnesium carbonate decomposes? [1]

The entropy increases due to increase in the number of gaseous particles, resulting in more disorderliness in the system and more ways of distributing the energy/arranging the particles.

(ii) Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for the decomposition of magnesium carbonate. Hence, comment on the spontaneity of the decomposition of magnesium carbonate at room temperature. [2]

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$$= +117 - \left(298 \times \frac{+175}{1000}\right)$$

= +117 – 52.15

= + 64.9 kJ mol^{-1}

Since $\Delta G^{\ominus}$ is positive, the decomposition is not spontaneous at room temperature.

(iii) Compare the ease of thermal decomposition of magnesium carbonate with barium carbonate. [3]

$MgCO_3$ decomposes at a lower temperature (or more easily) than $BaCO_3$. This is because Mg^{2+} ion, being smaller and has higher charge density and polarising power than Ba^{2+}.

Mg^{2+} is able to polarise the large electron cloud of the carbonate ion to a larger extent and weakening C-O bond more, resulting in lower thermal stability in $MgCO_3$.

(d) Describe the reaction of Mg and Ca with water, giving appropriate equations with state symbols. [2]

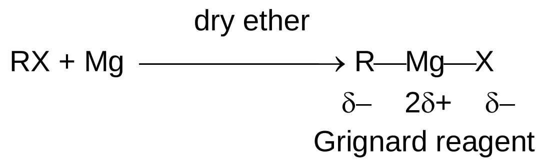
Mg reacts with slowly with hot water, effervescence observed and a white ppt is formed.

$$Mg(s) + H_2O(l) \rightarrow MgO(s) + H_2(g)$$

Ca reacts rapidly with cold water, effervescence observed and a colourless solution is formed.

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$$

(e) Mg reacts with halogenoalkanes, RX in dry ether, forming Grignard reagents which are important intermediates used to produce many organic compounds.

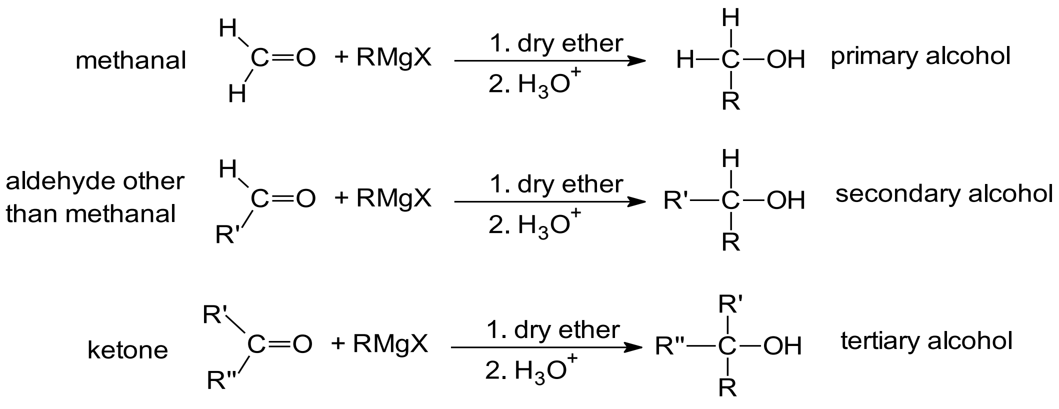


$$RX + Mg \xrightarrow{\text{dry ether}} \underset{\delta-}{R}—\underset{2\delta+}{Mg}—\underset{\delta-}{X}$$

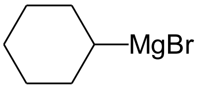
Grignard reagent

RMgX is called an organometallic compound, where R is an alkyl group and X is chlorine, bromine or iodine. R in RMgX behaves like an anion R^-, and is strongly basic and nucleophilic.

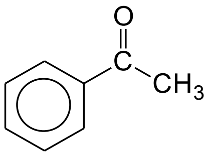
On reaction with carbonyl compounds, RMgX forms various classes of alcohols:



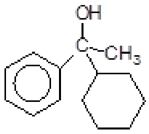
(i) Draw the structure of the organic products formed when the following compounds are reacted:



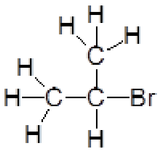
and



[1]



(ii) Give the displayed formula of the bromoalkane which can be used to form a Grignard reagent that would react with butanal to give 2–methylhexan–3–ol. [1]



(iii) When RMgBr is reacted with ethanoyl bromide, 2 moles of RMgBr are required per mole of ethanoyl bromide and the product formed is CH_3CR_2OH. Explain why one mole of ethanoyl bromide reacts with two moles of RMgBr while one mole of aldehyde or ketone reacts with one mole of RMgBr. [2]

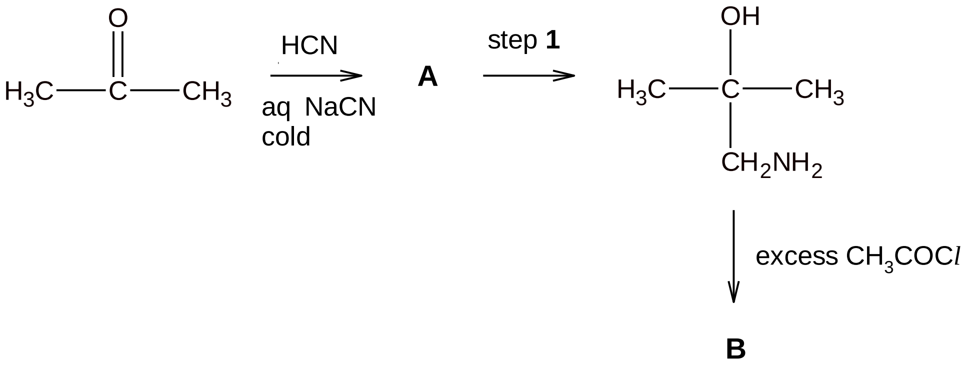
One mole of RMgBr reacts with one mole of CH_3COBr via nucleophilic substitution mechanism to form one mole of the ketone CH_3COR.
The one mole of CH_3COR formed then reacts with another mole of RMgBr to form CH_3CR_2OH.

$$CH_3COBr + RMgBr \rightarrow CH_3COR$$

$$CH_3COR + RMgBr \rightarrow CH_3COHR_2$$

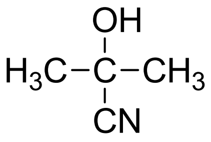
Explanation by writing the 2 equations are acceptable.

(f) Ketones and aldehydes react with HCN via nucleophilic addition mechanism similar to the reaction with Grignard reagents. The reaction scheme below is one such example.



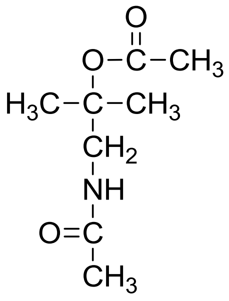
(i) Draw the structures of compounds **A and B**. [2]

A:



$H_3C-\overset{OH}{\underset{CN}{C}}-CH_3$

B:



$H_3C-\overset{O-\overset{O}{\overset{\|}{C}}-CH_3}{\underset{CH_2-NH-C(=O)-CH_3}{C}}-CH_3$

(ii) State the reagent and condition for step **1**. [1]

H_2, Pt or
H_2, Ni, heat or
$LiAlH_4$ in dry ether

[Total :20]

3 Transport proteins serve the function of moving other materials within an organism. They are vital to the growth and life of all living things. Haemoglobin is an iron-containing oxygen-transport protein found in the red blood cells of all vertebrates.

(a) State the type of bonding or interactions involved in the *primary*, *secondary*, *tertiary* and *quaternary* structures of proteins like haemoglobin. [2]

Primary Structure – covalent bonds (or amide or peptide linkage)

Secondary Structure – hydrogen bonding

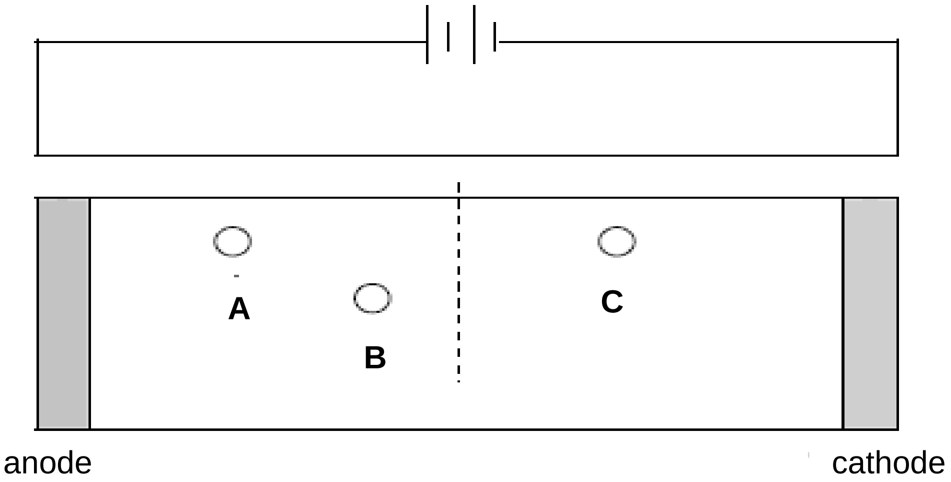
Tertiary Structure – Van der Waal's forces, ionic bond, hydrogen bonding and disulfide linkage

Quaternary Structure – Van der Waal's forces, ionic bond, hydrogen bonding and disulfide linkage

(b) The following amino acids are some of the amino acids present in the primary sequence of haemoglobin.

Amino Acids	**Formula of side chain (R' in R'CH(NH_2)CO_2H)**	**Isoelectric Point**
Lysine	-$(CH_2)_4NH_2$	9.74
Glutamic acid	-CH_2CH_2COOH	3.15
Aspartic acid	-CH_2COOH	2.77

An electrophoresis experiment is ran on a solution containing the above three amino acids at pH 5.00. The relative positions of the amino acids are shown in the diagram below.

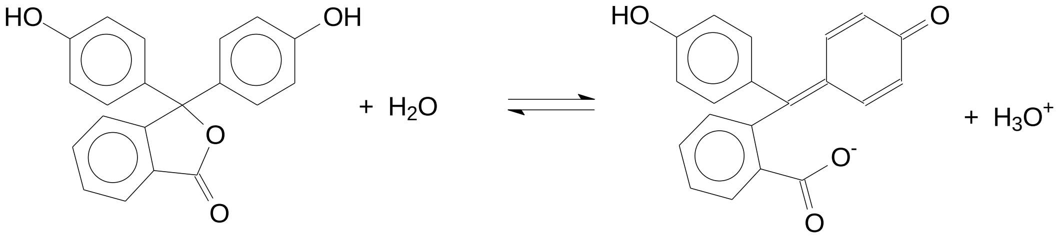


Suggest the identities of amino acids **A**, **B** and **C**. [1]

A: Aspartic acid ; B: Glutamic acid ; C : Lysine

(c) Haemoglobin is able to exhibit peroxidase-like activity to catalyse the oxidation of colourless phenolphthalein into its bright pink conjugate base. This reaction is often used to test for the presence of blood at a crime scene.

Phenolphthalein is a *weak acid* which dissociates in water according to the following equation:



Phenolphthalein **colourless**

Conjugate base of phenolphthalein **pink**

The K_a of phenolphthalein is 3.00 x 10^{-10} mol dm^{-3}.

Distinct colour change for phenolphthalein occurs when half of the indicator is phenolphthalein and the other half is its conjugate base.

(i) Calculate the pH at which phenolphthalein shows distinct colour change. [1]

pH = –lg (3 x 10^{-10}) = 9.52

(ii) The change of colour for phenolphthalein occurs over a limited range of pH and falls within ±1.00 of the pK_a value.

In an experiment, a solution of a weak acid hydroxylammonium chloride, $NH_3OH^+Cl^-$, was titrated against a solution of sodium hydroxide as shown by the equation below:

$$NH_3OH^+Cl^- + NaOH \rightarrow NH_2OH + NaCl + H_2O$$

With the aid of an equation and your answer in **(i)**, explain if phenolphthalein is a suitable indicator for this titration. [2]

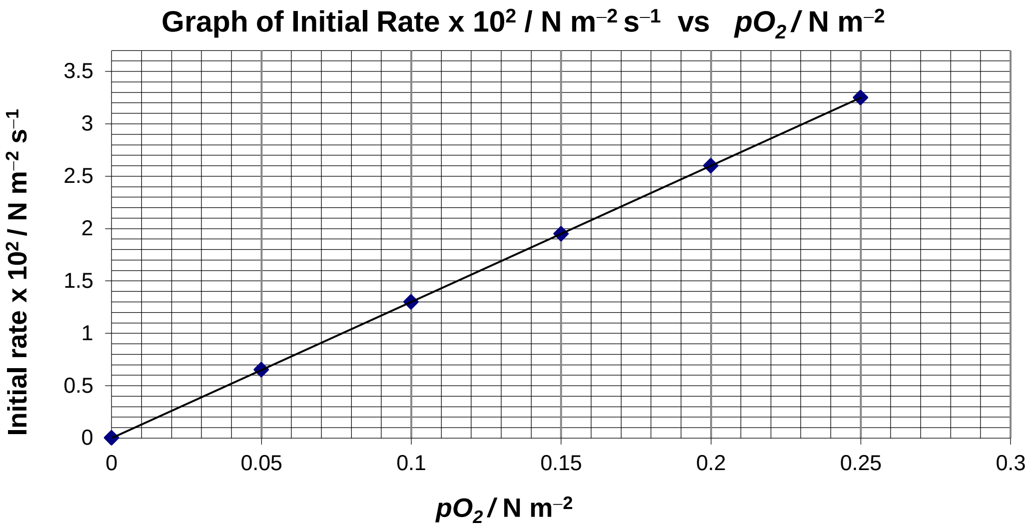
$NH_2OH + H_2O \rightleftharpoons NH_3OH^+ + OH^-$

NH_2OH undergoes hydrolysis to produce OH^- hence its pH > 7

Phenolphthalein is suitable as the pH transition range of the indicator (8.52 – 10.52) lies within the rapid pH change over the equivalence point (pH > 7).

(d) The reaction kinetics of oxygen binding to haemoglobin in human red blood cell suspension is studied. This is done by measuring the rates of uptake of oxygen by haemoglobin at different partial pressures of oxygen.

The graph of initial rate against partial pressure of oxygen was plotted below.



(i) Using the graph above, state the order of reaction with respect to oxygen. [1]

Order of reaction with respect to O_2 is 1.

(ii) The concentration of haemoglobin was halved and a new series of experiments was conducted at the same temperature. When a similar graph was plotted, the gradient at each point was half that obtained from the above graph.

Deduce the order of reaction with respect to haemoglobin? Explain your answer. [2]

Order of reaction with respect to haemoglobin is 1.

When concentration of haemoglobin was halved, change in the gradient of the graph is halved and rate of reaction was also halved.

(iii) Using your answers to **(i)** and **(ii)**, construct the rate equation for the reaction between haemoglobin and oxygen. [1]

Rate = k [haemoglobin] [O_2]

(iv) Oxygen dissolves in blood in the lungs and its concentration under common conditions is kept at 1.6×10^{-6} mol dm^{-3} by breathing. The concentration of haemoglobin in the blood of lung capillaries is also constant and is equal to 8.0×10^{-6} mol dm^{-3}.

Calculate the rate constant, including the unit, given that the rate of oxyhaemoglobin formation is 2.68×10^{-5} mol dm^{-3} s^{-1} at 37 °C. [1]

Rate = k [haemoglobin] [O_2]

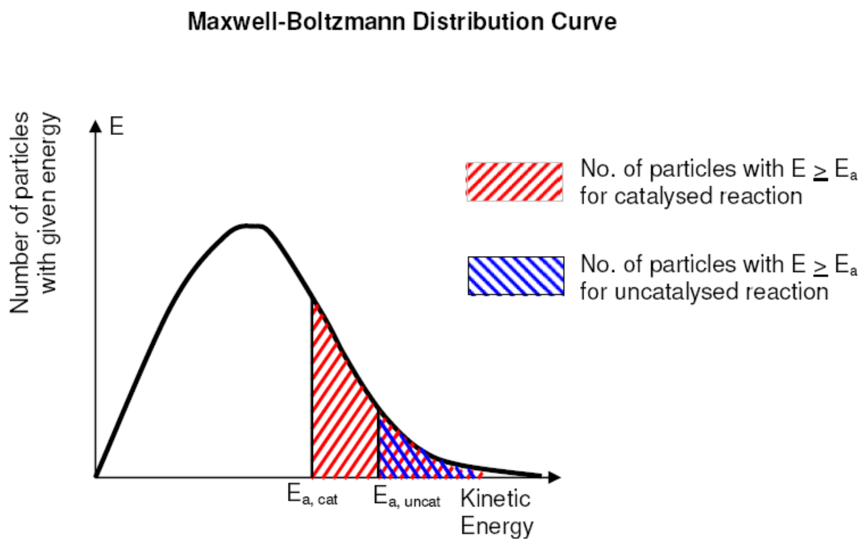
$2.68 \times 10^{-5} = k\,(8.0 \times 10^{-6})\,(1.6 \times 10^{-6})$

$k = 2.09 \times 10^{6}\ \mathrm{dm^{3}\ mol^{-1}\ s^{-1}}$

(e) Another type of protein that transports oxygen throughout the bodies of invertebrates is *haemocyanin*, which contains two copper atoms that reversibly bind a single oxygen molecule.

(i) *Haemocyanin* exhibits catalytic activity to catalyse the hydroxylation of monophenols to diphenols.

Using an appropriate sketch of the Maxwell-Boltzmann distribution curve, explain how the presence of *haemocyanin* increases the rate of hydroxylation of monophenols. [3]



[1]

E_a is lowered due to an alternative reaction pathway. The proportion of reactants with energy greater than or equals the activation energy increases.

Frequency of effective collisions increases, rate constant value increases and hence rate of reaction increases.

(ii) Partial *denaturation* actually improves *haemocyanin*'s catalytic ability by providing greater access to the active site.

1 What is meant by the term *denaturation*?

2 Suggest how a weak acid might interact with *haemocyanin* to bring about denaturation.

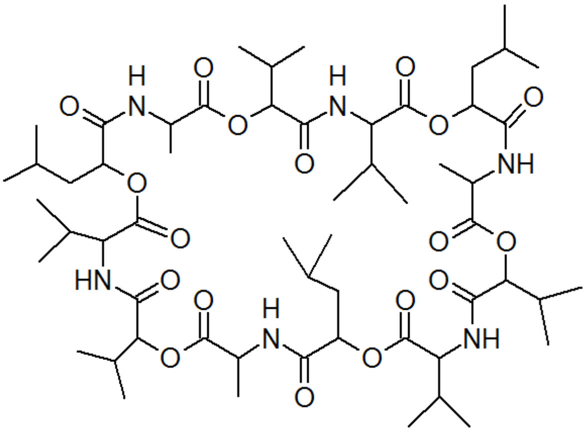
[3]

1 **Denaturation refers to the breaking of weak bonds holding the secondary, tertiary and quaternary structure but not the covalent bonds within the primary**

structure.

2 **Protonates the anionic group, -COO^- found in side chain for example glutamic acid, [1] and disrupts ionic bond between the charged R groups of –COO^- and –NH_3^+ .**

(f) *Cereulide* is another example of a transport protein. As a natural dodecadepsipeptide ionophore, *cereulide* acts as potassium transporters, where potassium, K^+, plays a vital role in bacterial physiology.



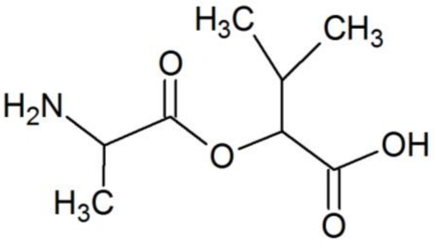
Cereulide

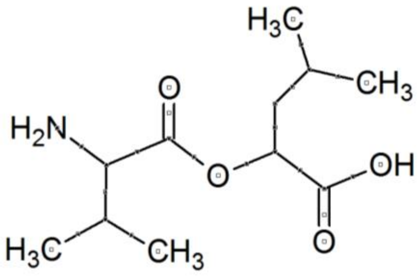
(i) Apart from the peptide group, name another functional group that is present in the molecule? [1]

Ester

When treated with a peptidase enzyme, the peptide bonds in the ring are hydrolysed. Only two different products are formed.

(ii) Out of the products formed, two of the amino acid residues are present **more than once** in the protein. Draw the structural formula of these two amino acid residues. [2]





[Total :20]

4 **(a)** Manganese is a transition element that can exist in several oxidation states.

Manganese species	Mn^{2+}	MnO_4^{2-}	MnO_4^-
Colour (in aqueous medium)	pale pink	green	purple

(i) Write the full electronic configurations of Mn in Mn^{2+} and MnO_4^-, and explain why Mn can exhibit variable oxidation states. [2]

The electronic configuration of Mn in Mn^{2+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$.
The electronic configuration of Mn in MnO_4^- is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$.

The energy difference between the 3d and 4s subshells is relatively small. Hence, a variable number of electrons can be removed. (or a variable number of electrons can be used for bond formation)

(ii) Explain why transition elements form compounds that are coloured. [3]

In the presence of ligands, the degenerate 3d orbitals are split into two different energy levels. Since the 3d subshell is partially filled, the electrons in the lower energy 3d orbitals can absorb a photon of energy from the visible light range to promote to the higher energy 3d orbitals. The observed colour is complementary to the wavelength absorbed.

(b) A student wanted to investigate the rate of reaction between MnO_4^- and $C_2O_4^{2-}$ ions in an acidic medium. The reaction is shown in the equation below.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + + 8H_2O$$

The rate of reaction was followed by mixing the following two solutions, and measuring the concentration of remaining MnO_4^- ions at fixed time intervals.

Solution **A**: 100 cm^3 of 0.20 mol dm^{-3} ethanedioic acid, 5 cm^3 of 2 mol dm^{-3} sulfuric acid, 15 cm^3 of 0.20 mol dm^{-3} copper(II) sulfate and 80 cm^3 of water

Solution **B**: 50 cm^3 of 0.020 mol dm^{-3} potassium manganate(VII)

The following results were obtained.

Time/s	$[MnO_4^-]$ / mol dm^{-3}
0	0.0040
10	0.0026
20	0.0016
30	0.00096
50	0.00040
75	0.00016

(i) By means of a graphical method, determine the rate equation under the conditions whereby the reaction was conducted. [3]

Plot a graph of $[MnO_4^-]$ against time.

Determine 2 half-life from the graph and show that they have the same value or approximately the same ($t_{1/2} \approx 15$s). Refer to graph at the last page.

Rate = k$[MnO_4^-]$

(ii) The rate of consumption of MnO_4^-(aq) at a particular time is 1.2×10^{-4} mol dm^{-3} s^{-1}. Using the equation for the reaction between MnO_4^- and $C_2O_4^{2-}$, calculate the rate of consumption of ethanedioate ions at that particular time? [1]

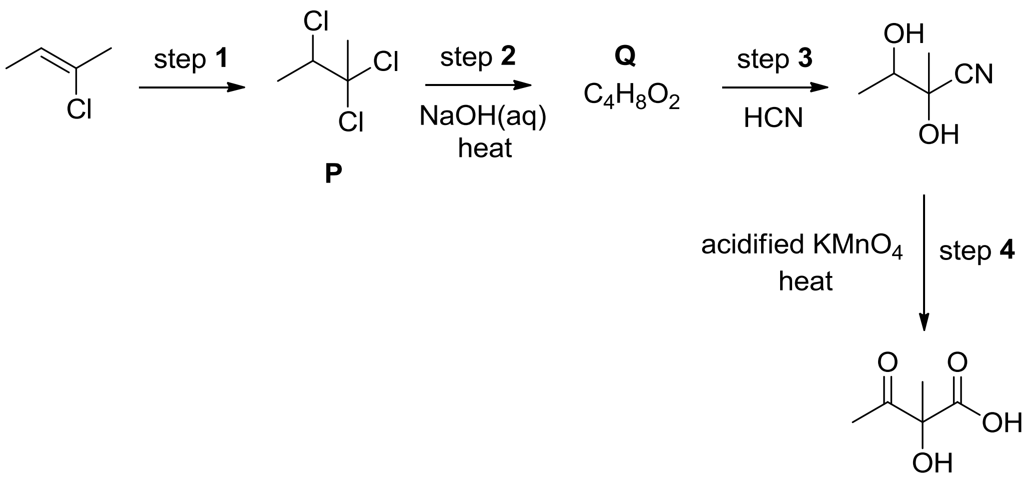
Rate of consumption of $C_2O_4^{2-}$ = 5/2 x Rate of consumption of MnO_4^-
= 3.0×10^{-4} mol dm^{-3} s^{-1}

(iii) What is the role of copper(II) sulfate in the reaction? [1]

Homogenous catalyst

(c) Potassium manganate(VII) is commonly used as an oxidising agent in organic chemistry.

Acetolactic acid, $C_5H_8O_4$, is a precursor in the biosynthesis of the branched chain amino acids, valine and leucine. Acetolactic acid can be synthesised from 2-chlorobut-2-ene by the following reactions.

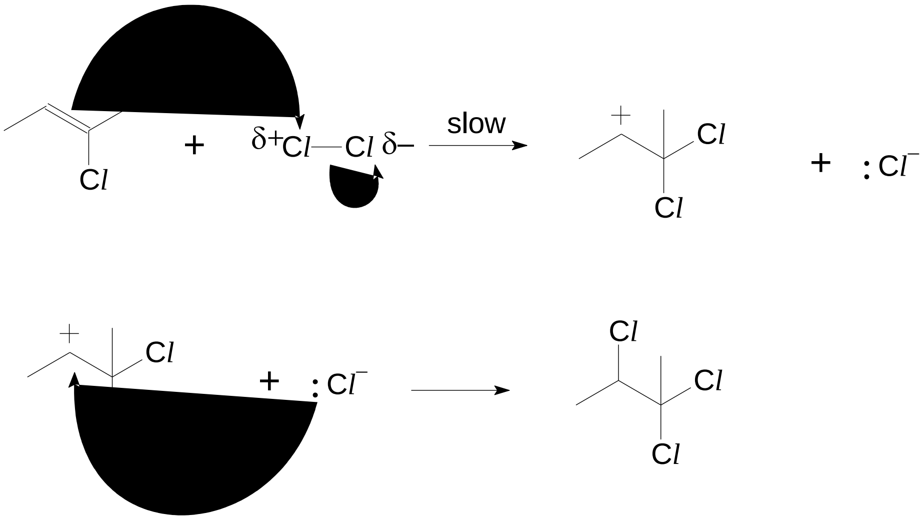


Acetolactic acid

(i) State the reagent and conditions used in step **1** and outline the mechanism for this reaction. In your answer, you should include curly arrows showing the movement of electrons and any relevant charges and dipoles. [4]

Cl_2(g), or Cl_2 in CCl_4, room temperature

Electrophilic addition

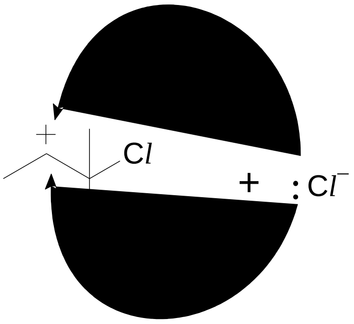


Note:

- **The type of mechanism reaction must be stated.**
- **The mechanism arrows must be shown in the equation to illustrate the movement of electrons.**
- **Lone pair on the chloride ion must be clearly shown.**
- **Slow step and the partial charges on chlorine must be indicated in the mechanism**

(ii) Compound **P** obtained from step **1** does not rotate the plane of polarised light despite it containing a chiral carbon. Use the mechanism which you have proposed in **(i)**, to explain this observation. [3]

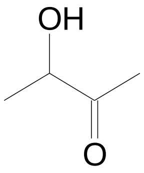
The geometry about the positively charged carbon atom of the carbocation is trigonal planar (or planar).



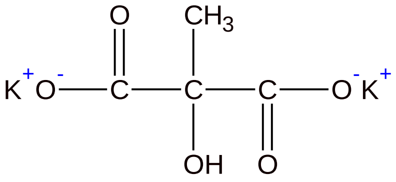
Hence, the nucleophile has equal chances of attacking the positively charged carbon atom from both above and below the plane, to produce equal amount of the 2 enantiomers, resulting an racemic mixture.

The optical activity of the two enantiomers cancel out each other completely. Thus, it is not optically active.

(iii) Suggest the structure of compound **Q.** [1]



(iv) Draw the organic products formed when acetolactic acid is warmed with iodine in the presence of aqueous potassium hydroxide. [2]



$$K^+\,{}^-O-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\underset{OH}{C}}-\underset{O}{\underset{\|}{C}}-O^-\,K^+$$

+ CHI_3

[Total :20]

5 **(a)** New applications such as hybrid electric vehicles and power backup require rechargeable batteries that combine high energy density with high charge and discharge rate capability. One such current battery electrode material in used is $LiCoO_2$.

The following cell diagram notation is a simplified illustration of the electrochemical cell.

$$Li \mid Li^+ \parallel Li^+, CoO_2 \mid LiCoO_2 \mid Pt$$

In this cell, Li is oxidised to Li^+ while CoO_2 is reduced to $LiCoO_2$. State the oxidation state of Co in $LiCoO_2$ and hence write the electronic configuration of Co in $LiCoO_2$. [2]

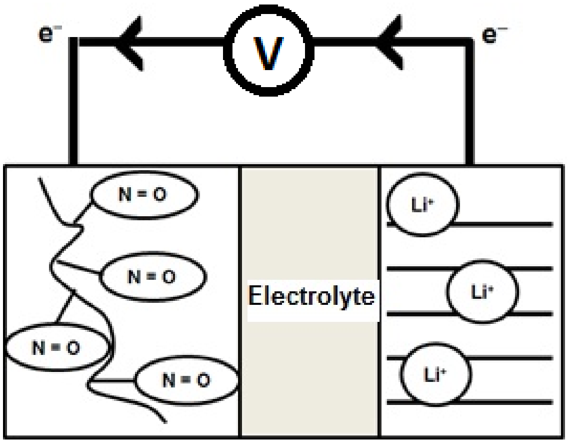
Oxidation state of Co is +3

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$

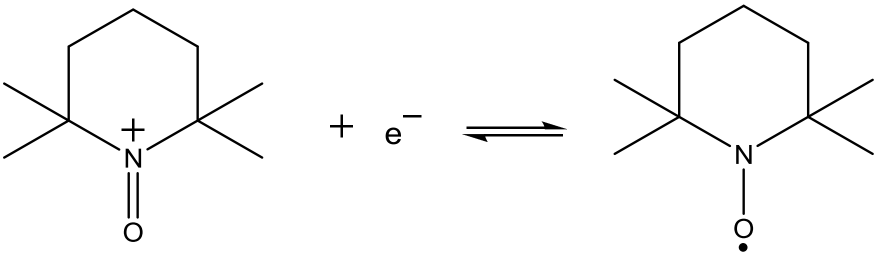
(b) In recent years, organic radical polymers have been developed as alternatives to inorganic materials because of their light weight, flexibility and their environmentally-friendly features. With the increase in demand for thinner mobile phones and tablet computers, there is a surge to invent film-like organic-derived electrode-active battery materials to power such devices.

One such material is **TEMPO-NO radical** which is capable of repeated stable oxidation-reduction between **N=O** radicals and **N=O** cations. Its voltage when paired with a Li/Li^+ half-cell is able to reach +3.60 V which is comparable to a common lithium-ion battery.

The following is a simplified illustration of the electrochemical cell set-up.



(i) The following half-equation represents the reaction which occurs at the organic derived electrode.



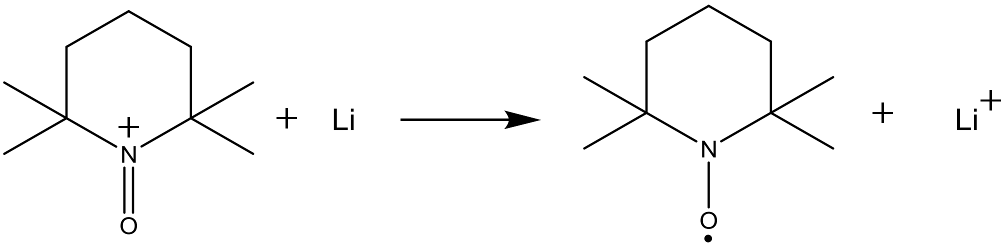
TEMPO-NO radical

With the use of the *Data Booklet* and the information above, write the overall balanced equation for the electrochemical reaction and calculate the standard electrode potential for **TEMPO-NO** radical half cell. [3]

From Data Booklet

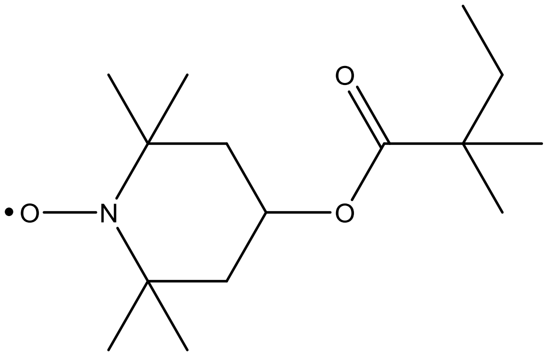
$Li^+ + e \rightleftharpoons Li$ **$E^\ominus = -3.04$ V**

Overall equation:



$E^\ominus$ cell = $E^\ominus$ reduction – $E^\ominus$ oxidation
+3.60 = $E^\ominus$ reduction – (–3.04)
$E^\ominus$ reduction = +0.56 V

(ii) In order for the radical polymer to be used as an electrode, it must not be soluble in the electrolyte. To improve the usability of **TEMPO-NO** radical, the material can be converted to **PTMA** which has the following structure:



PTMA

Explain how the structure of **PTMA** will help to reduce its solubility in polar solvents like water. [3]

With the increase in carbon side chains, the electron cloud size increases and becomes more polarisable, resulting in an increase in instantaneous dipole-induced dipole (id-id) interactions in PTMA compared to TEMPO-NO radical.

Hence, the formation of hydrogen bonding between water and PTMA will not be exothermic enough to overcome the stronger id-id interaction between PTMA as well as hydrogen bonding between water molecules to dissolve it. Hence, solubility is reduced.

Alternative answer:

With the increase in carbon side chains, the induced dipole-permanent dipole interaction (or instantaneous dipole-induced dipole interaction) between the carbon side chain and water becomes the predominant interaction.

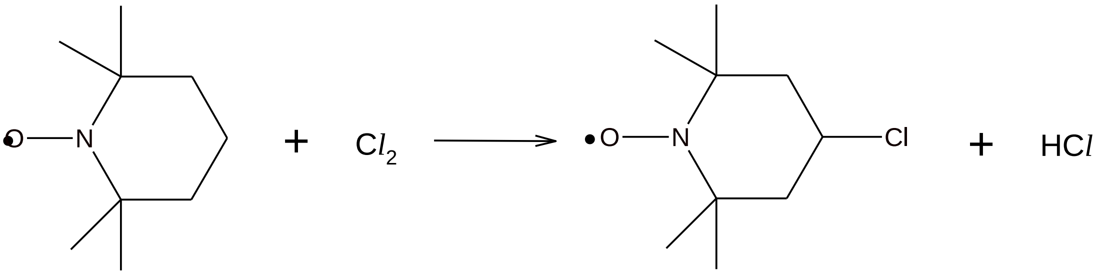
Insufficient energy is released to overcome the hydrogen bonding between water molecules as well as the stronger id-id interaction between PTMA.

(iii) Water cannot be used as the solvent for Li^+ | Li half cell. Write an equation to illustrate the reaction when an aqueous medium is used at the Li^+ | Li half cell which hinders the working of the battery. [1]

Li will react with water to form LiOH

$$2Li + 2H_2O \rightarrow 2LiOH + H_2$$

(iv) The synthesis of **PTMA** required the mono-substitution of the **TEMPO-NO** radical with chlorine as shown in the reaction below.

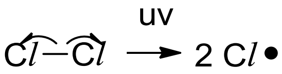


TEMPO-NO radical

Outline the mechanism for this reaction. [4]

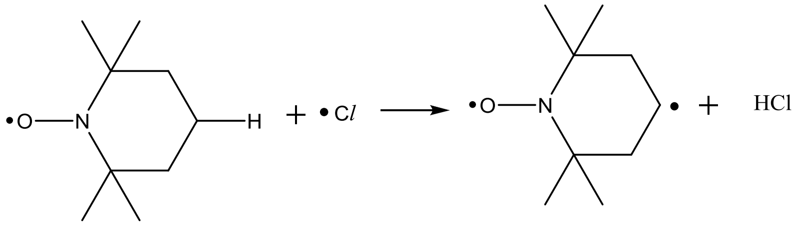
Free radical substitution

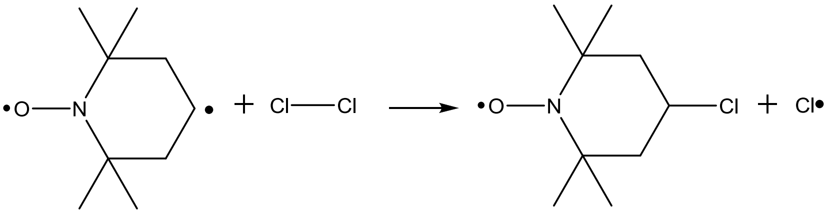
Initiation



$$Cl\text{—}Cl \xrightarrow{uv} 2\,Cl\bullet$$

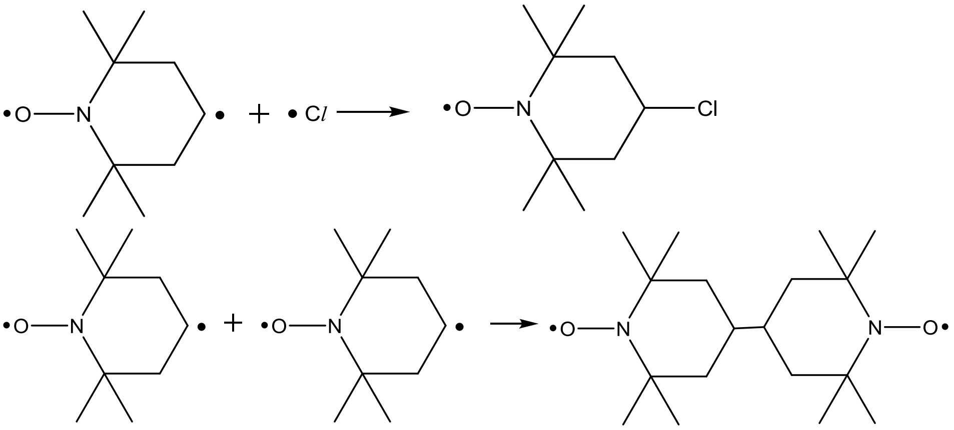
Propagation





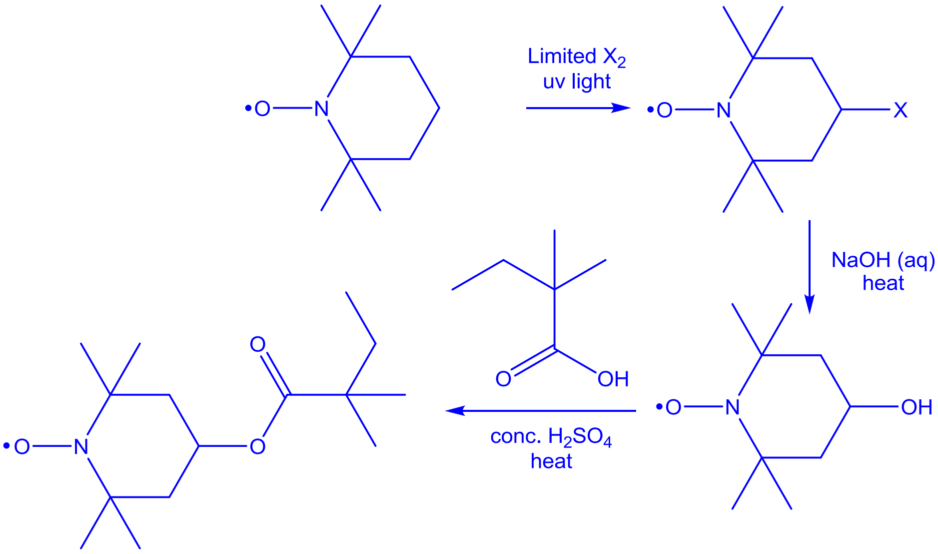
Termination (Any 2)

$2\,Cl\bullet \longrightarrow Cl-Cl$



[1]

(v) Suggest the synthesis route for the formation of **PTMA** from **TEMPO-NO** radical. [4]



(c) When the organic radical battery is recharged, lithium ion is being converted back to lithium metal. Given that the charging process is 87% efficient, how many hours does it take to restore 1.25 g of lithium metal using a current of 3 A? [3]

Mass of Li to be restored = 100/87 x 1.25 = 1.4368 g

No. of mole of Li = 1.4367/ 6.9 = 0.20823 mol

Q = 0.20823 x 96500 = 20094 C

Time = 20094/ 3 = 6698 s = 1.86 h

Or

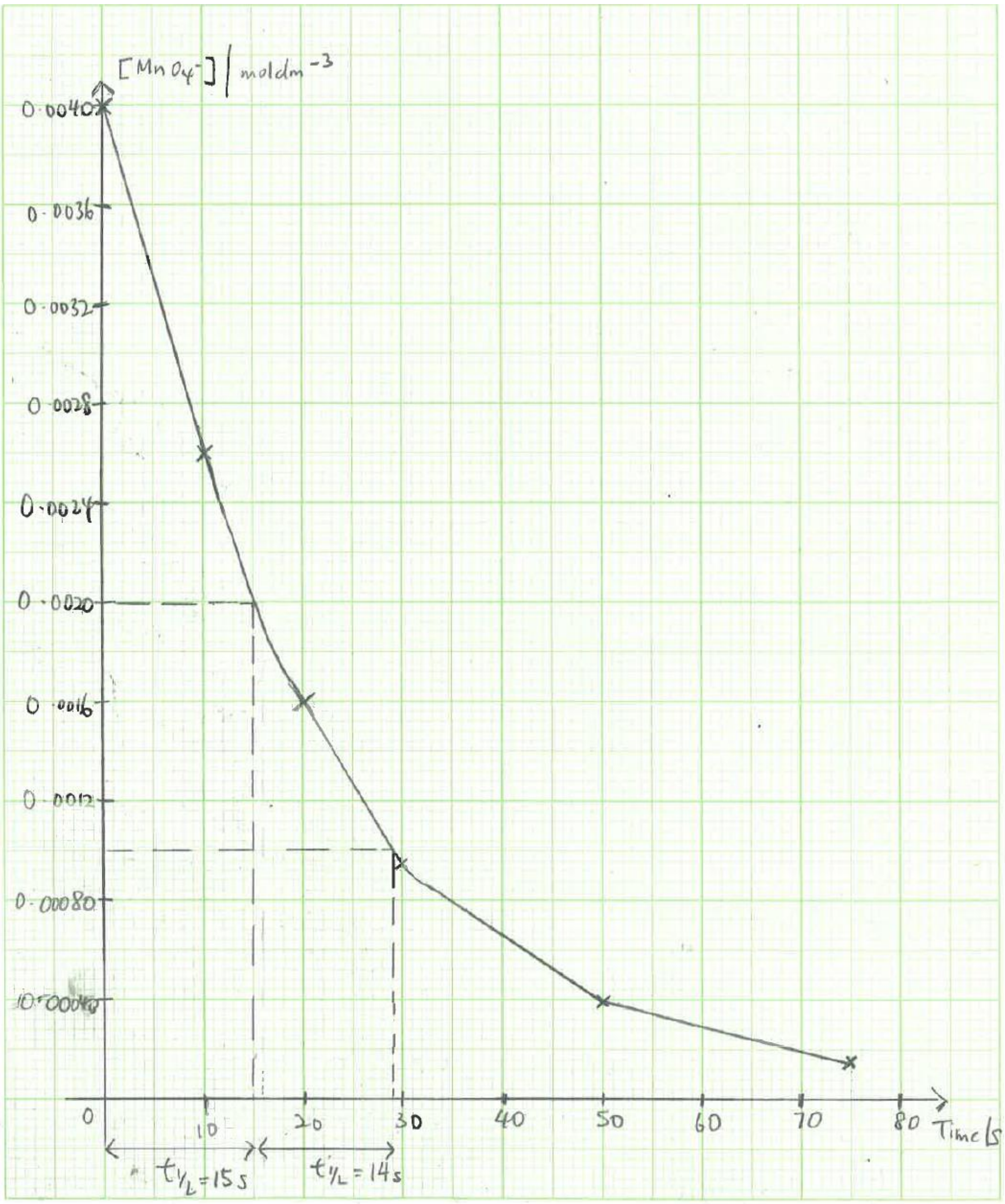
Mass of Li to be restored = 100/87 x 1.25 = 1.4367 g

$$\frac{96500}{3t} = \frac{6.9}{1.4367}$$

$$\mathrm{t} = 6697.6s$$

$$= 1.86\mathrm{h}$$

[Total :20]


[MnO4-] / mol dm-3
0.0040
0.0036
0.0032
0.0028
0.0024
0.0020
0.0016
0.0012
0.00080
0.00040
0
10
20
30
40
50
60
70
80
Time / s
t1/2 = 15 s
t1/2 = 14 s

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