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CLASS 20S

JURONG PIONEER JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2021

CHEMISTRY**9729/01****Higher 2****24 September 2021**

Paper 1 Multiple Choice

1 hour

Candidates answer on separate paper.

Additional Materials: Multiple Choice Answer Sheet
Data Booklet**READ THESE INSTRUCTIONS FIRST**

Write in soft pencil.

Do not use staples, paper clips, glue or correction fluid.

Write your name, class and exam index number on the Answer Sheet in the spaces provided unless this has been done for you.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C** or **D**.Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.**Read the instructions on the Answer Sheet very carefully.**

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

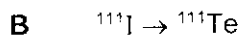
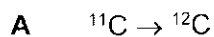
Any rough working should be done in this booklet.

The use of an approved scientific calculator is expected, where appropriate.

This document consists of **16** printed pages.

- 1 Some isotopes are unstable and undergo nuclear (radioactive) reactions. In one type of reaction, an unstable nucleus assimilates an electron from an inner orbital of its electron cloud. The net effect is the conversion of a proton and an electron into a neutron.

Which of the following describes this type of reaction?



- 2 **Figure 1** shows the first six ionisation energies of an element **P**. **Figure 2** shows the second ionisation energies of eight consecutive elements (including **P**).

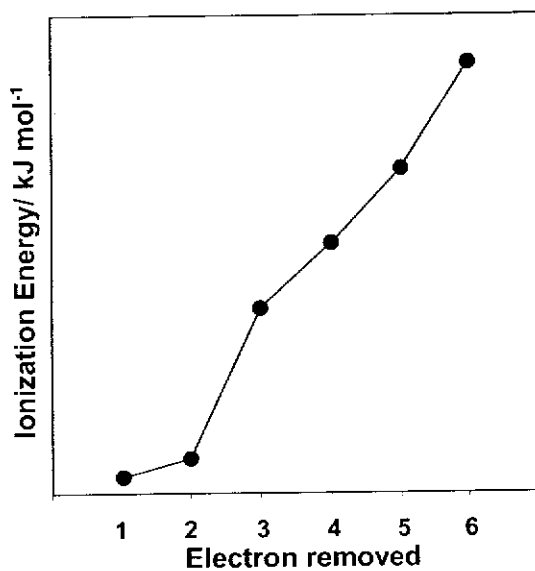


Figure 1

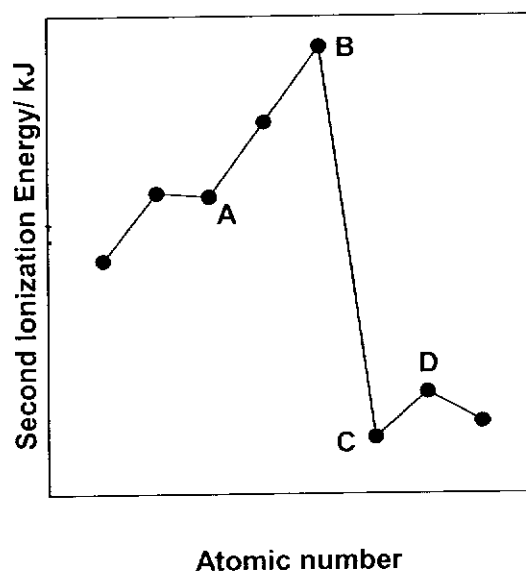


Figure 2

With reference to **Figure 2**, which of the options, **A**, **B**, **C** or **D**, corresponds to the second ionisation energy of element **P**?

- 3 Which of the following has the largest bond angle?



- 4 Molecular dimerisation can be described as the process in which two identical molecules combine to give a single product.

Examples of dimers are N_2O_4 and $(\text{CH}_3\text{CO}_2\text{H})_2$.

Which of the following descriptions about the above dimers is **incorrect**?

- A Hydrogen bonds hold the $\text{CH}_3\text{CO}_2\text{H}$ molecules together in the dimer.
- B There is one nitrogen-nitrogen single bond in N_2O_4 .
- C $(\text{CH}_3\text{CO}_2\text{H})_2$ is a non-planar molecule.
- D The nitrogen-oxygen bonds in N_2O_4 are of different length.

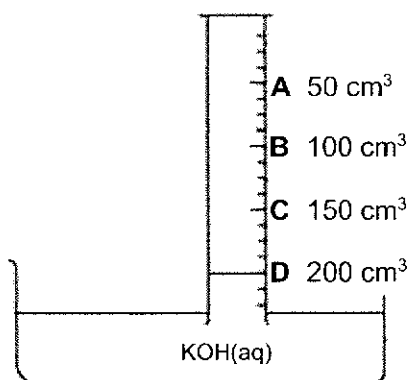
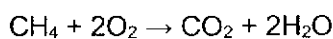
- 5 Naturally-occurring silicon is a mixture of three isotopes, ^{28}Si , ^{29}Si and ^{30}Si . The relative atomic mass of silicon is 28.109.

What could be the relative abundance of each of the three isotopes?

- A 91.1% ^{28}Si , 7.9% ^{29}Si and 1.0% ^{30}Si
- B 92.2% ^{28}Si , 4.7% ^{29}Si and 3.1% ^{30}Si
- C 95.0% ^{28}Si , 3.2% ^{29}Si and 1.8% ^{30}Si
- D 96.3% ^{28}Si , 0.3% ^{29}Si and 3.4% ^{30}Si

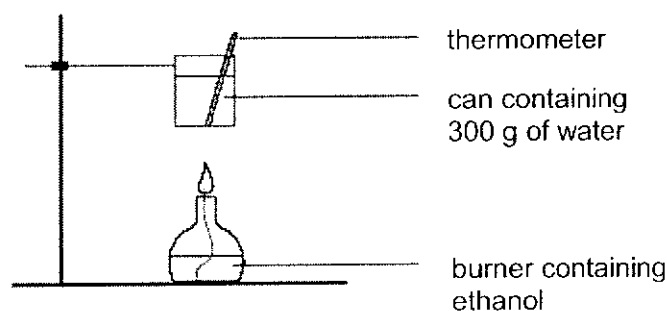
- 6 A tube filled with 50 cm^3 of methane and 150 cm^3 of oxygen at room temperature was inverted over a vessel containing $\text{KOH}(\text{aq})$ as shown in the diagram.

The hydrocarbon was ignited for the following reaction to take place.



When the setup is cooled to room temperature, at which level will the liquid be?

- 7 An experiment was conducted to determine the efficiency of the heating of a can of water using a spirit burner.



The following data were recorded:

Mass of ethanol burnt	= m g
Change in temperature of water	= ΔT °C

You are also given that:

Relative molecular mass of ethanol	= 46.0
Enthalpy change of combustion of ethanol	= -1371 kJ mol ⁻¹
Specific heat capacity of water	= c J g ⁻¹ K ⁻¹

Which expression below gives the efficiency of this heating process?

A $\frac{300 \times c \times \Delta T \times 46.0}{m \times 1371 \times 1000} \times 100\%$

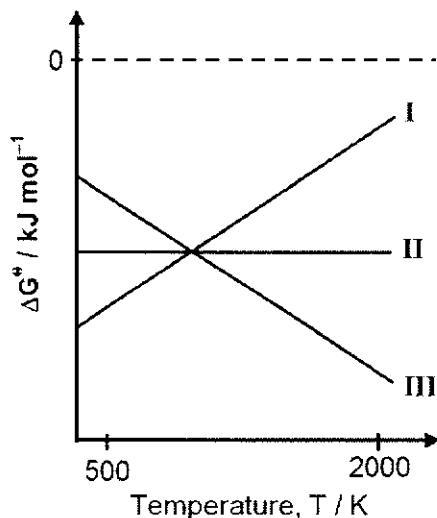
B $\frac{m \times c \times \Delta T \times 46.0}{300 \times 1371 \times 1000} \times 100\%$

C $\frac{300 \times c \times \Delta T \times 46.0}{m \times 1371} \times 100\%$

D $\frac{m \times 1371 \times 1000}{300 \times c \times \Delta T \times 46.0} \times 100\%$

- 8 In 1944, T. Ellingham published plots of ΔG° against temperature T for a number of reactions. Today, such plots are called Ellingham diagrams.

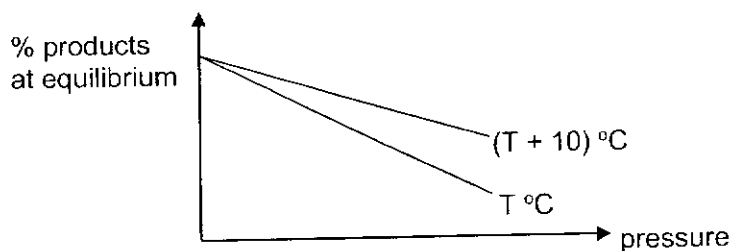
An Ellingham diagram for three reactions involving the oxidation of C and CO is shown below.



Which of the following shows correctly the three reactions corresponding to I, II and III in the above Ellingham diagram?

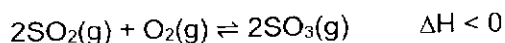
	I	II	III
A	$2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	$2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$
B	$2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$	$2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$
C	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	$2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$	$2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$
D	$2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	$2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$

- 9 The graphs below show how the percentage of gaseous products present at equilibrium vary with temperature and pressure.

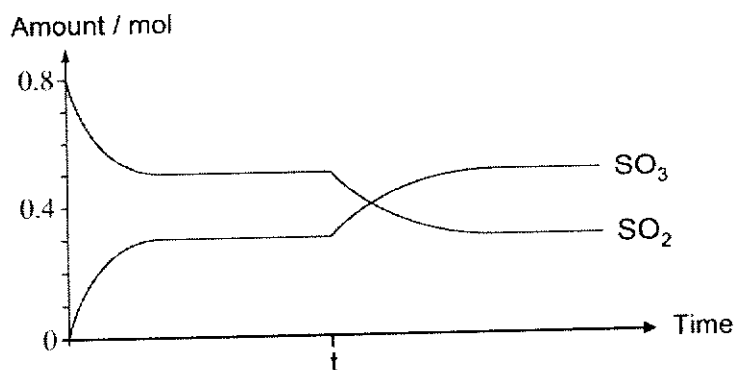


Which one of the following reactions could the graph represent?

- A $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ $\Delta H = +57 \text{ kJ mol}^{-1}$
- B $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ $\Delta H = +53 \text{ kJ mol}^{-1}$
- C $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ $\Delta H = -92 \text{ kJ mol}^{-1}$
- D $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g})$ $\Delta H = -99 \text{ kJ mol}^{-1}$
- 10 At a temperature $T \text{ K}$, 0.80 mol of SO_2 and 0.40 mol of O_2 were introduced into a 10 dm^3 vessel and allowed to come to equilibrium.



The graph below shows the variations in the amounts of SO_2 and SO_3 in the system with time. A change was made to the system at time t .



Which of the following statements are correct?

- 1 A catalyst was added at time t
- 2 Temperature was decreased at time t
- 3 An inert gas was added at constant volume at time t
- 4 The value of K_c before time t is 14.4

- A 1 and 2 B 1 and 3 C 2 and 3 D 2 and 4

- 11 At body temperature of 37 °C, K_w has a value of 2.4×10^{-14} .
What is the concentration of OH^- if the pH of blood is 7.4 under these conditions?

- A 7.00×10^{-7} B 2.51×10^{-7}
C 6.03×10^{-7} D 3.98×10^{-8}

- 12 A $0.100 \text{ mol dm}^{-3}$ solution of lead(II) nitrate is added, with stirring, into an equal volume of a solution containing a mixture of Cl^- , Br^- , and I^- ions, each with the same concentration of $1.0 \times 10^{-2} \text{ mol dm}^{-3}$.

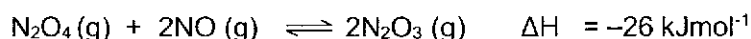
Given the following data:

Compound	Numerical value of K_{sp} (at 25 °C)
Lead(II) chloride	1.7×10^{-5}
Lead(II) bromide	6.6×10^{-6}
Lead(II) iodide	9.8×10^{-9}

Which one of the following statements is correct?

- A No precipitate will form.
B Only PbI_2 precipitate will form.
C A mixture of PbI_2 and PbBr_2 precipitates will form.
D All three precipitates, PbI_2 , PbBr_2 , and PbCl_2 , will form.

- 13 When the gases dinitrogen tetroxide and nitrogen monoxide are mixed in a 1:2 ratio, the two gases slowly react to form the blue compound dinitrogen trioxide according to the following equilibrium.



The forward and backward rate constants are given as k_1 and k_{-1} respectively.

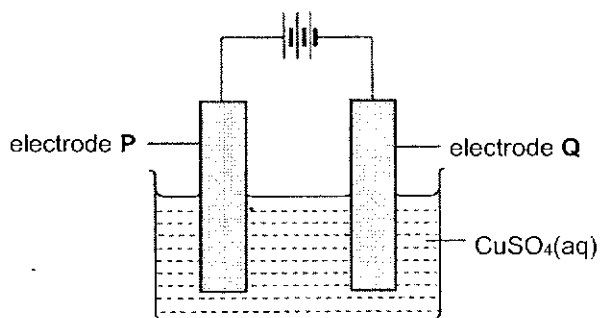
What happens to the equilibrium constant K_p , k_1 , and k_{-1} if at equilibrium, the temperature of the reaction mixture is increased?

	k_1	k_{-1}	K_p
A	Increases	Decreases	Increases
B	Unchanged	Increases	Unchanged

C	Increases	Increases	Decreases
D	Decreases	Increases	Decreases

- 14 Consider one mole of ideal gas at a given pressure.
Which processes will increase the number of molecules which have an energy greater than a particular value?
- 1 increasing the temperature
 - 2 introducing more of the same gas into the same volume at the same temperature
 - 3 compressing the gas at constant temperature
- A 1, 2 and 3 B 1 and 2 C 2 and 3 D 1 only
- 15 Which statements about the properties of a catalyst are correct?
- 1 A catalyst increases the average kinetic energy of the reacting particles.
 - 2 A catalyst increases the rate of the reverse reaction.
 - 3 A catalyst has no effect on the enthalpy change ΔH .
- A 1, 2 and 3 B 1 and 2 C 2 and 3 D 1 only
- 16 *The use of Data Booklet is relevant to this question.*
In many areas, tap water becomes slightly acidic due to dissolved carbon dioxide.
By considering the relevant E values, which of the following metals will not be dissolved by tap water containing carbon dioxide?
- A Chromium B Copper C Iron D Lead

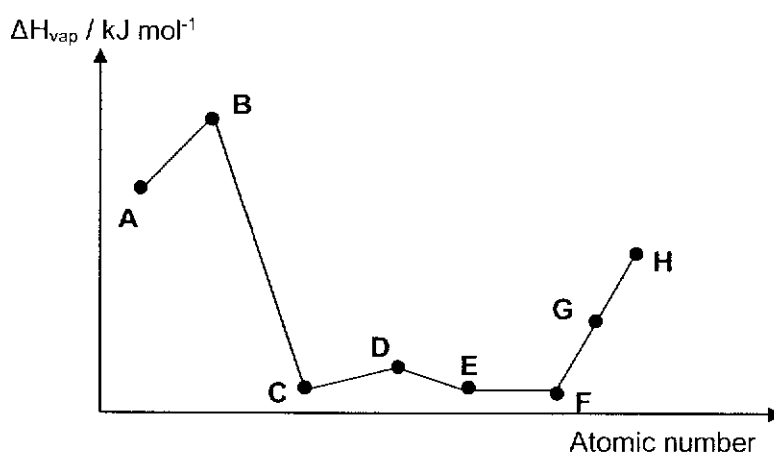
- 17 In an experiment, a cell was set up to obtain pure copper from a copper-silver alloy as shown below.



When a current of 40.0 A flows through the electrolyte for 26.8 minutes, the mass of the anode changes by 26.47 g.

Which of the following statements is correct?

- A Electrode **P** is pure copper and electrode **Q** is the copper-silver alloy.
 B The concentration of $\text{CuSO}_4(\text{aq})$ decreases during the experiment.
 C The mass of the cathode changes by 26.47 g during the experiment.
 D The copper-silver alloy contains 20% silver by mass.
- 18 The graph below shows the variation in the enthalpy change of vaporisation, ΔH_{vap} for eight consecutive elements in the Periodic Table, all with atomic number ≤ 20 .



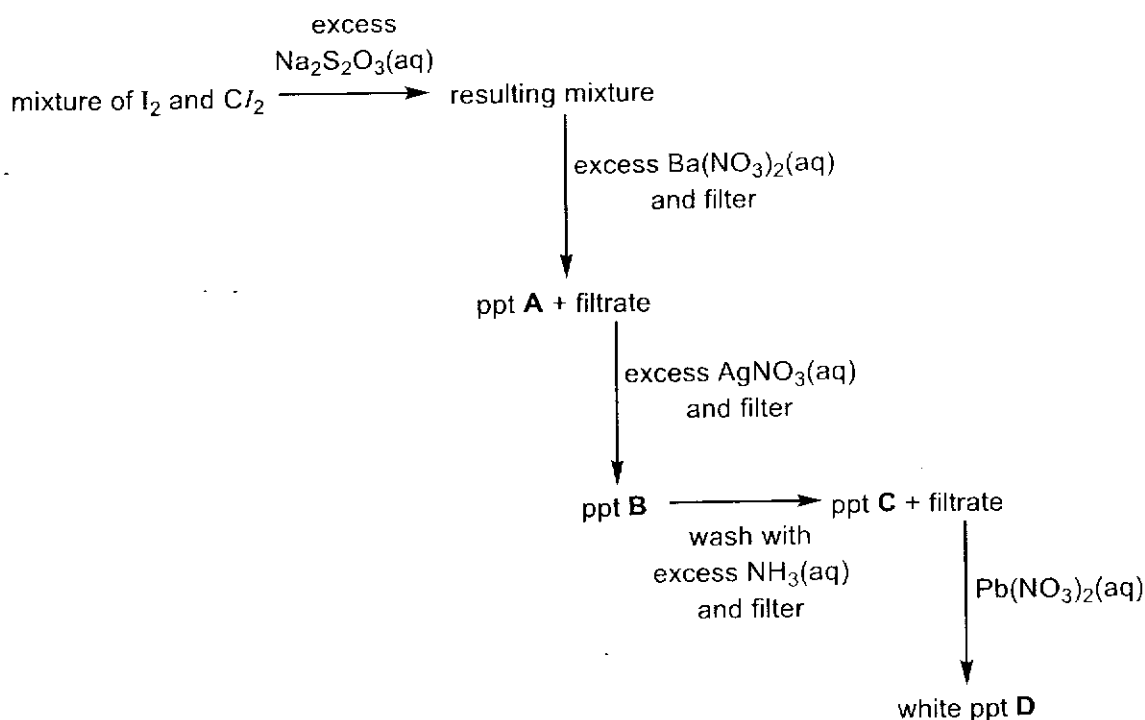
What can be deduced from the above graph?

- A **E** is soluble in warm benzene whereas **F** is not.
 B The chlorides become less acidic from **A** to **C**.
 C The pH of the solution containing a mixture of oxide of **G** and oxide of **D** is greater

than 7.

- D The oxide of **A** reacts with excess aqueous sodium hydroxide to form a soluble complex.

- 19 Consider the following reaction route:



Which anion was present in each of the precipitates respectively?

	ppt A	ppt C	ppt D
A	I ⁻	SO ₄ ²⁻	NO ₃ ⁻
B	Cl ⁻	I ⁻	NO ₃ ⁻
C	SO ₄ ²⁻	I ⁻	Cl ⁻
D	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻

- 20 In the preparation of ethene, ethanol was added to a drop of heated reagent **L**. The impure ethene was washed by being bubbled through a solution of **M** before collection.

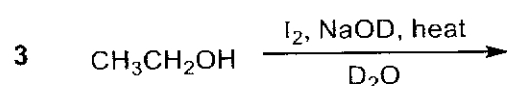
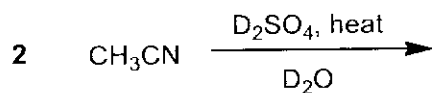
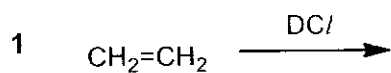
What are the reagents **L** and **M** likely to be?

	Reagent L	Reagent M
A	ethanolic NaOH	concentrated H ₂ SO ₄
B	dilute NaOH	concentrated H ₂ SO ₄
C	concentrated H ₂ SO ₄	ethanolic NaOH

D	concentrated H ₂ SO ₄	dilute NaOH
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21 Deuterium, D, is the ²₁H isotope of hydrogen.

Which of the following reactions yield a carbon compound containing deuterium?



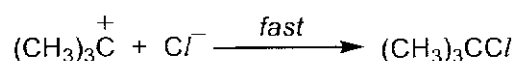
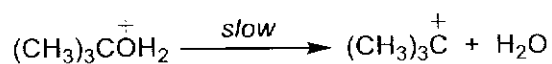
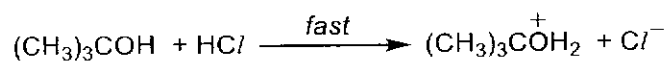
A 1, 2 and 3

B 1 and 2

C 2 and 3

D 1 only

22 The mechanism for a certain reaction is given below.



Which of the following statements is not true?

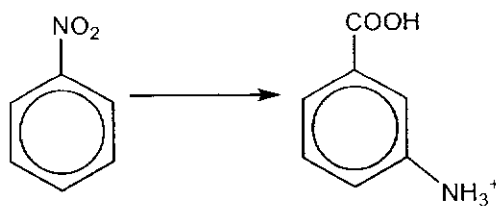
A $(\text{CH}_3)_3\text{COH}_2^+$ and $(\text{CH}_3)_3\text{COH}$ are conjugate acid-base pair.

B The nucleophile in the reaction is HCl.

C The overall reaction is $(\text{CH}_3)_3\text{COH} + \text{HCl} \rightarrow (\text{CH}_3)_3\text{CCl} + \text{H}_2\text{O}$

D The above mechanism is a nucleophilic substitution reaction.

- 25 The following synthesis can be carried out in three steps.



Which is the best method for this synthesis?

	Step 1	Step 2	Step 3
1	CH ₃ Cl anhydrous AlCl ₃ heat	Concentrated HCl, Sn, heat	Dilute H ₂ SO ₄ , KMnO ₄ , heat
2	Concentrated HCl, Sn, heat	CH ₃ Cl anhydrous AlCl ₃ heat	Dilute H ₂ SO ₄ , KMnO ₄ , heat
3	CH ₃ Cl anhydrous AlCl ₃ heat	Dilute H ₂ SO ₄ , KMnO ₄ , heat	Concentrated HCl, Sn, heat followed by dilute NaOH
4	Concentrated HCl, Sn, heat followed by dilute NaOH	CH ₃ Cl anhydrous AlCl ₃ heat	Dilute H ₂ SO ₄ , KMnO ₄ , heat

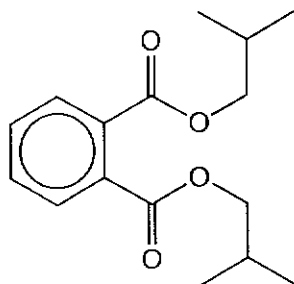
A 1 and 2

B 1 and 3

C 2 and 3

D 2 and 4

- 26 In June 2011, a variety of Taiwanese food products were found to contain diisobutyl phthalate (DIBP), a plasticiser.



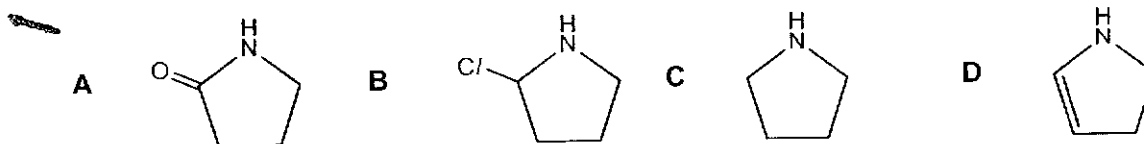
diisobutyl phthalate (DIBP)

Which of the following statements about DIBP are **incorrect**?

- 1 DIBP produces a pale yellow precipitate when heated with alkaline aqueous iodine.
- 2 When DIBP is heated with acidified potassium manganate(VII), the purple solution decolourises.
- 3 When DIBP is heated with dilute sulfuric acid, one of the products requires two molar equivalents of aqueous sodium hydroxide for complete neutralisation.

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

- 27 Which of the following compound has the lowest pK_b value?



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

- 30 In the study of a polypeptide structure of **Z**, it was digested using two different enzymes. The fragments obtained were then separated using electrophoresis. Analysis of the fragments from each digestion gave the following results:

Fragments using first enzyme: tyr-leu-leu
 tyr-ala
 gly-asp-pro
 asp-pro

Fragments using second enzyme: leu-tyr
 asp-pro-gly
 ala
 asp-pro-tyr-leu

Deduce the possible sequence of **Z**.

- A asp-pro-tyr-leu-ala-leu-tyr-asp-pro-gly
 B asp-pro-gly-asp-pro-tyr-leu-leu-tyr-ala
 C gly-asp-pro-asp-pro-tyr-ala-tyr-leu-leu
 D ala-asp-pro-gly-asp-pro-tyr-leu-leu-tyr



JURONG PIONEER JUNIOR COLLEGE
2021 JC2 H2 Chemistry (9729)
Preliminary Exam Paper 1 (Worked Solutions)

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

1 Answer: B

The reaction causes the original particle to lose 1 proton, 1 electron and gain 1 neutron.

Options A and C both have the same number of electrons and protons before and after the reaction.

Option D shows a decrease in number of electrons and protons (36 in Kr to 35 in Br) but the number of neutrons remain unchanged (both particles have 40 neutrons).

2 Answer: C

From Figure 1, large increase between the 2nd and 3rd electron removed indicates that there are two valence electrons in element P. Hence element P is in group 2.

P⁺: ns¹

From the electronic configuration of P⁺, the point corresponding to the second IE of element P is C.

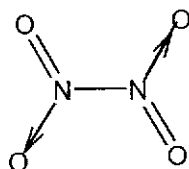
3 Answer: C

- ×A SiCl₄ has 4 bond pairs and no lone pairs around Si → bond angle is 109.5 °.
- ×B SO₂ has 2 bond pairs and 1 lone pair around S → bond angle is < 120 °.
- ✓C IF₂⁻ has 2 bond pairs and 3 lone pairs around I → bond angle is 180 °.
- ×D CH₃⁺ has 3 bond pairs and no lone pairs around C → bond angle is 120 °.

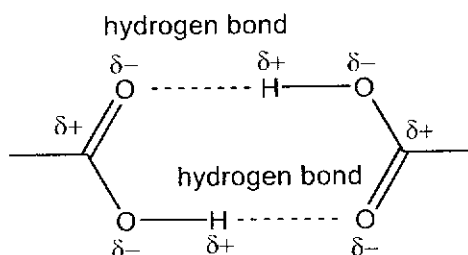
4 Answer: D

✓A and B

The structures of N₂O₄ and (CH₃CO₂H)₂ dimers are shown below.



N₂O₄



(CH₃CO₂H)₂

- ✓C The CH₃ groups in (CH₃CO₂H)₂ is still tetrahedral around the C, thus the dimer is non-planar.
- ×D Due to p-p orbital overlap, the electrons are delocalised across the O=N-O bond, making all the nitrogen-oxygen bonds to be of the same strength and thus of the same length.

5 **Answer: B**

$$A_r \text{ of Si} = \left(\frac{92.2}{100} \times 28\right) + \left(\frac{4.7}{100} \times 29\right) + \left(\frac{3.1}{100} \times 30\right) = 28.109$$

*A A_r of Si = 28.099

*C A_r of Si = 28.668

*D A_r of Si = 28.854

6 **Answer: A**

Since $1 \text{ CH}_4 \equiv 2 \text{ O}_2$

50 cm^3 of CH_4 requires 100 cm^3 of O_2 for complete reaction.

Since CO_2 will be absorbed by the alkaline KOH, it will not be collected.

Volume of gas collected = volume of O_2 left = $150 - 100 = 50 \text{ cm}^3$

7 **Answer: A**

$$\text{Total amount of heat evolved} = \frac{m}{46.0} \times 1371 \text{ kJ}$$

$$\text{Total amount of heat transferred} = 300 \times c \times \Delta T \text{ J} = \frac{300 \times c \times \Delta T}{1000} \text{ kJ}$$

$$\therefore \text{efficiency} = \frac{300 \times c \times \Delta T}{1000} \div \frac{m \times 1371}{46.0} \times 100\% = \frac{300 \times c \times \Delta T \times 46.0}{1000 \times m \times 1371} \times 100\%$$

8 **Answer: A**

Using $\Delta G = \Delta H - T\Delta S$, the negative gradient of the graph in the Ellingham diagram corresponds to ΔS of the reaction.

Reaction II has a gradient of zero, that means $\Delta S = 0$ (**reject options B and C**)

Reaction I has a positive gradient, that means $\Delta S < 0$ → decrease in disorderedness

Reaction III has a negative gradient, that means $\Delta S > 0$ → increase in disorderedness

9 **Answer: A**

The graph shows that when pressure increases, % products at equilibrium decreases.

→ POE shifts left to form less gas molecules (**reject options B and C**)

The graph also shows that when temperature increases, % products at equilibrium increases

→ POE shifts right to favour endothermic reaction (**reject option D**)

10 Answer: D (2 and 4 only)

At time t, the change caused POE to shift right to form more SO₃.

- ×1 Adding a catalyst will not cause a shift in POE.
- ✓2 When temperature decreases, POE shift right to favour exothermic reaction.
- ×3 The addition of inert gas at constant volume results in the partial pressures of all gases to remain unchanged. POE will not shift.
- ✓4 At equilibrium before time t:

From graph: $n_{\text{SO}_2} = 0.5 \text{ mol}$ and $n_{\text{SO}_3} = 0.3 \text{ mol}$

$$n_{\text{O}_2} = 0.4 - \frac{0.80 - 0.50}{2} = 0.25 \text{ mol}$$

$$\therefore K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = \frac{\left(\frac{0.3}{10}\right)^2}{\left(\frac{0.5}{10}\right)^2 \left(\frac{0.25}{10}\right)} = 14.4 \text{ mol}^{-1} \text{ dm}^3$$

11 Answer: C

$$p\text{OH} = pK_w - p\text{H} = -\lg(2.4 \times 10^{-14}) - 7.4 = 6.22$$

$$\therefore [\text{OH}^-] = 10^{-6.22} = 6.03 \times 10^{-7}$$

12 Answer: B

Since equal volumes of the solutions are used:

$$\text{ionic product of PbX}_2 = \left(\frac{0.100}{2}\right) \left(\frac{1.0 \times 10^{-2}}{2}\right)^2 = 1.25 \times 10^{-6} \text{ mol}^3 \text{ dm}^{-9}$$

Since ionic product is less than the K_{sp} of PbCl₂ and PbBr₂ but larger than the K_{sp} of PbI₂, only PbI₂ will precipitate out.

13 Answer: C

When temperature increases, POE shifts left to favour endothermic reaction

→ K_p will decrease (**reject options A and B**)

When temperature increases, **both** forward and backward rate increases. Since POE is shifting left, the backward rate increases more. (**reject option D**)

14 Answer: B (1 and 2 only)

Using the Boltzmann Distribution:

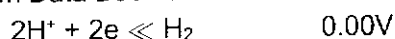
- ✓1 increasing temperature increases the number of molecules with energy $\geq E_a$
- ✓2 When more gas is added at the same temperature and volume, the number of molecules with a particular energy all increases.
- ×3 Compressing the gas increases pressure, but will not change the energy distribution of the molecules.

15 Answer: C (2 and 3 only)

- ×1 A catalyst reduces the activation energy of the reaction by providing an alternative pathway/mechanism of lower activation energy. The KE of the reacting particles are not affected.
- ✓2 A catalyst increases both the forward and backward rate of a reversible reaction by the same extent.
- ✓3 See definition of the catalyst in option 1.

16 Answer: B

From Data Booklet:

For the metal not to dissolve, E_{cell} for the reaction must be negative.

$$\times\text{A } \text{Cr}^{2+} + 2\text{e} \ll \text{Cr} \quad -0.91 \text{ V} \quad \rightarrow E_{\text{cell}} = 0.00 - (-0.91) = +0.91 \text{ V}$$

$$\checkmark\text{B } \text{Cu}^{2+} + 2\text{e} \ll \text{Cu} \quad +0.34 \text{ V} \quad \rightarrow E_{\text{cell}} = 0.00 - (+0.34) = -0.34 \text{ V}$$

$$\times\text{C } \text{Fe}^{2+} + 2\text{e} \ll \text{Fe} \quad -0.44 \text{ V} \quad \rightarrow E_{\text{cell}} = 0.00 - (-0.44) = +0.44 \text{ V}$$

$$\times\text{D } \text{Pb}^{2+} + 2\text{e} \ll \text{Pb} \quad -0.13 \text{ V} \quad \rightarrow E_{\text{cell}} = 0.00 - (-0.13) = +0.13 \text{ V}$$

17 Answer: D

×A To obtain pure copper, the pure copper electrode should be the anode (negative electrode) which is electrode **Q**.

×B $[\text{CuSO}_4]$ remains unchanged as the amount of Cu^{2+} that is oxidised at the anode is replenished by the amount of Cu that is reduced at the cathode.

$$Q = (40.0)(26.8 \times 60) = n(96500)$$

$$n_e = 0.666 \text{ mol}$$

Since $1 \text{ Cu} \equiv 2\text{e}$

$$\text{Mass of Cu} = \frac{0.666}{2} \times 63.5 = 21.2 \text{ g} \quad (\text{option C is wrong})$$

$$\% \text{ by mass of Ag} = \frac{26.47 - 21.2}{26.47} \times 100 = 20 \%$$

18 Answer: D

From graph, the sharp drop in ΔH (and hence the boiling point) from **B** to **C** signifies the change from giant structure to simple covalent molecules (group 14 to group 15 element).

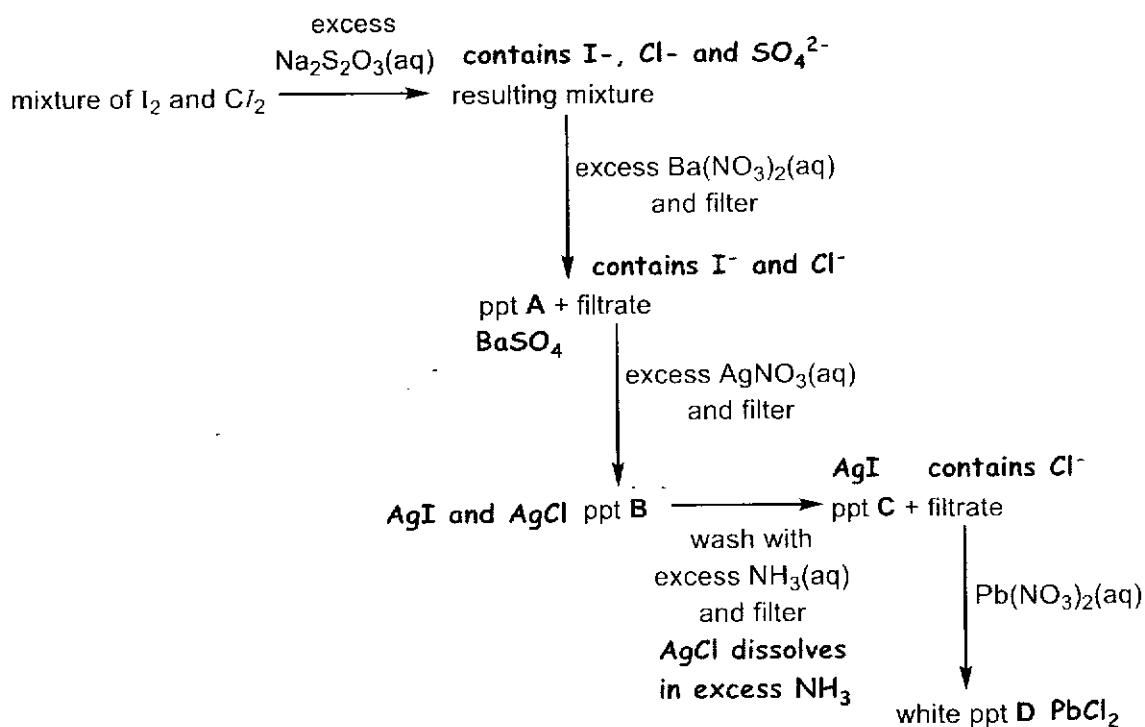
×A Element **E** is in group 17 and Element **F** is in group 18. Both are non-polar molecules thus will both be soluble in warm benzene (non-polar solvent).

×B Elements **A**, **B** and **C** are in groups 13, 14 and 15 respectively. The chlorides of these elements are acidic since the structure of the chlorides are becoming increasingly covalent in nature.

×C Element **G** is in group 1 and Element **D** is in group 16. The oxide of **G** (basic oxide) and the oxide of **D** (acidic oxide) will form a neutral salt.

✓D Oxide of **A** could be Al_2O_3 which will react with excess NaOH to form $\text{Al}(\text{OH})_4^-$ complex.

19 Answer: C

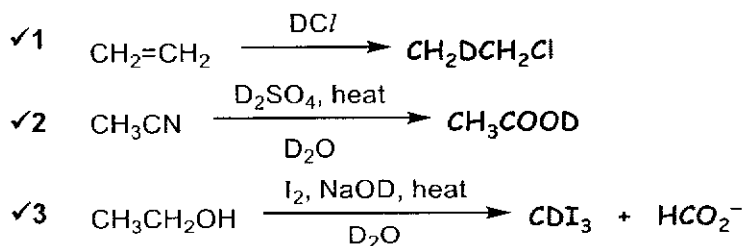


20 Answer: D

Reagent and conditions to convert alcohol to alkene: conc. H_2SO_4 , heat
 \rightarrow reagent L is conc. H_2SO_4 (reject options A and B)

Reagent M cannot be ethanolic as the alkene will dissolve in the organic solvent, making collection difficult. (reject option C)

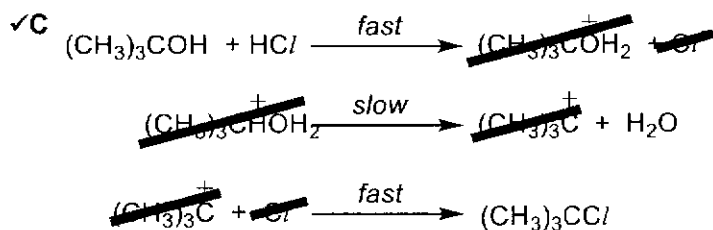
21 Answer: A (1, 2 and 3)



22 Answer: B

$\checkmark A$ $(CH_3)_3COH$ acts as a base to accept H^+ from the conjugate acid $(CH_3)_3COH_2^+$

$\times B$ HCl acts as an acid to protonate the $-OH$ group in $(CH_3)_3COH$ to make it a better leaving group so as to form the carbocation in step 2.



$\checkmark D$ Steps 2 and 3 are representative of the S_N1 mechanism.

23 Answer: C

If the reaction is an elimination reaction or an S_N1 reaction, the resulting mixture will be a racemic mixture with no optical activity. (**reject options A and D**)

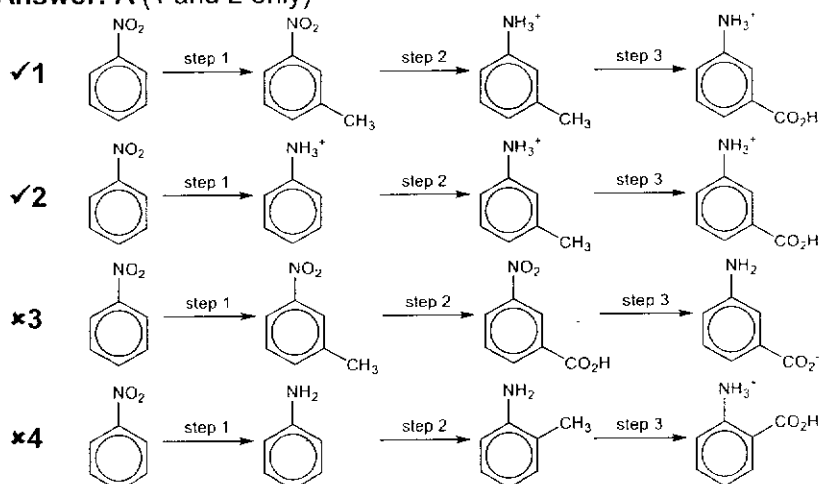
If the reaction is an S_N2 reaction, there will be an inversion of stereochemistry, which causes rotation of plane polarised light in the opposite direction (**reject option B**).

24 Answer: D

For $AgX(s)$ to be formed, the alkyl halide has to undergo hydrolysis first so that the free halide ion can be formed.

The rate of hydrolysis is determined by the strength of the C–X bond.

Note: Options A, B and C are correct factual statements, but they do not explain the observation given in the question.

25 Answer: A (1 and 2 only)**26 Answer: D (1 only)**

✗1 DIBP does not have $-\text{COCH}_3$ and $-\text{CH}(\text{OH})\text{CH}_3$ group present in the structure to give a positive iodoform test.

✓2 The ester undergoes acid hydrolysis first and the primary alcohol formed undergoes oxidation, decolourising purple KMnO_4 .

✓3 The ester undergoes acid hydrolysis and the 1,2-dibenzoic acid which requires 2 mol of NaOH for complete neutralisation.

27 Answer: C

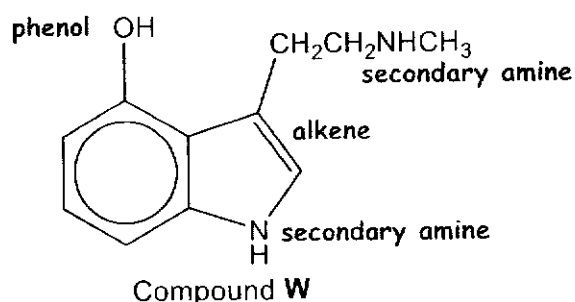
Compound **A** is an amide which is neutral.

Compounds **B**, **C** and **D** are secondary amines.

Compound **B** has an electron-withdrawing C/ group which makes the lone pair on the N less available for protonation.

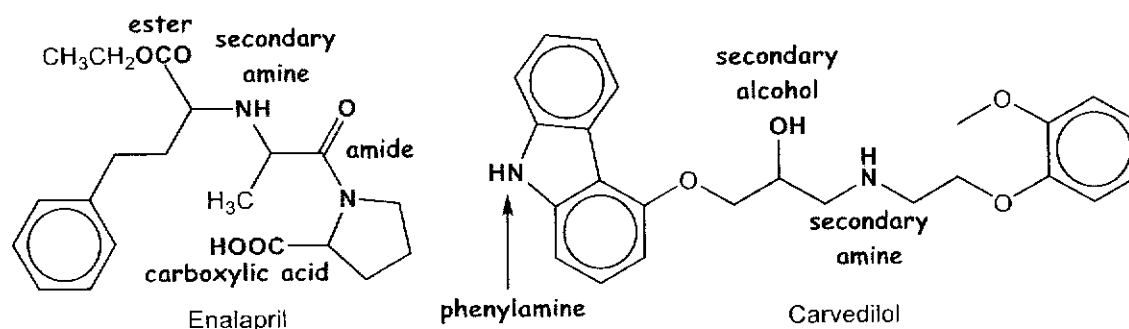
Due to p-p orbital overlap, the lone pair on N in compound **D** is delocalised into the C=C alkene, making it less available for protonation.

28 Answer: B (2, 3 and 4)



- ✗1 The acidic group (phenol) is more acidic than ethanol, and thus will have a lower pK_a .
- ✓2 The acidic phenol group will react with bases, and the alkaline amine group on the side chain will react with acids.
- ✓3 The amines will react with CH_3COCl to form the amide and white fumes of HCl .
- ✓4 Due to p-p orbital overlap, the lone pair on O in phenol is delocalised into the benzene ring, making phenol a weaker nucleophile for condensation to take place during ester formation.

29 Answer: A (1 and 2)



- ✓1 The phenylamine in Carvedilol will decolourise orange $\text{Br}_2(\text{aq})$.
- ✓2 The carboxylic acid in Enalapril will form $\text{CO}_2(\text{g})$ with aqueous sodium carbonate.
- ✗3 The primary alcohol formed after acid hydrolysis of Enalapril and the secondary alcohol in Carvedilol will decolourise purple $\text{KMnO}_4(\text{aq})$.

30 Answer: B

Only option B is able to account for all the fragments generated by the two enzymes. All the other options have one fragment (either from the first or second enzyme) missing.

- ✗A missing the fragment tyr-leu-leu from the first enzyme
- ✗C missing the fragment leu-try from the second enzyme
- ✗D missing the fragment tyr-ala from the first enzyme



JURONG PIONEER JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2021

CHEMISTRY

9729/02

Higher 2

15 September 2021

Paper 2 Structured Questions

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use	
1	14
2	20
3	11
4	15
5	15
Penalty (delete accordingly)	
Bond linkages	-1 / NA
Significant figures & units	-1 / NA
Total	75

This document consists of 17 printed pages and 1 blank page.

Answer **all** the questions.

For
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1 (a) The reducing agent LiAlH_4 can be synthesised by reacting aluminium chloride with lithium hydride, LiH .

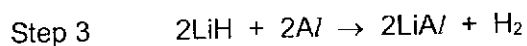
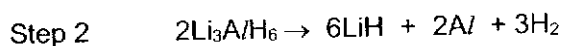
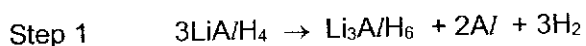
(i) Lithium hydride contains the ions Li^+ and H^- . State the electronic configuration of these two ions.

Li^+ H^- [1]

(ii) Explain why Li^+ ion has a smaller radius than H^- ion.

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

(iii) LiAlH_4 decomposes slowly according to the mechanism below.



Use the above mechanism to deduce the overall equation for this decomposition.

..... [1]

(iv) $\text{LiAl}(s)$ has a melting point of 718°C and conduct electricity when in solid and molten states.

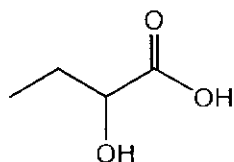
Suggest the structure and describe the type of bonding for $\text{LiAl}(s)$.

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

(v) Assuming the same packing arrangement of atoms, suggest why $\text{LiAl}(s)$ has a lower density than $\text{Al}(s)$.

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

- (b) Two students try to prepare 2-hydroxybutanoic acid in the laboratory.

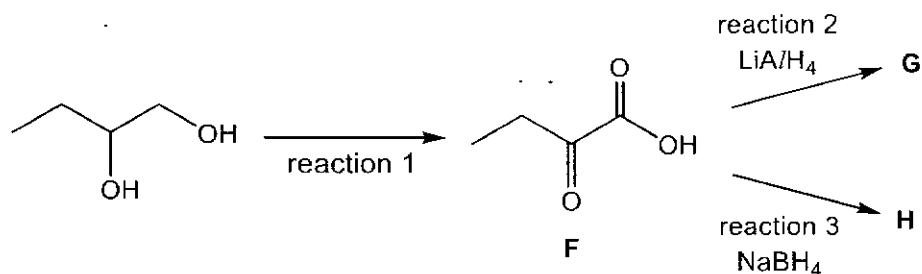


2-hydroxybutanoic acid

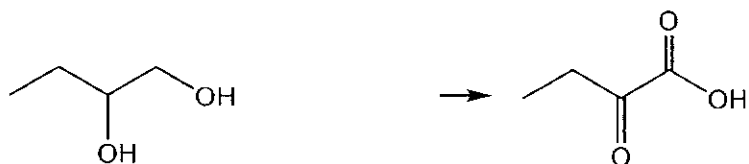
Both students oxidise butane-1,2-diol to form **F** in reaction 1.

One student then reduces **F** using LiAlH_4 . **G** is formed.

The other student reduces **F** using NaBH_4 . **H** is formed.



- (i) Complete the equation to show the conversion of butane-1,2-diol to **F** in reaction 1. Use $[\text{O}]$ to balance your equation.



[1]

- (ii) Only one of the students successfully prepares 2-hydroxybutanoic acid. Identify which compound, **G** or **H**, is 2-hydroxybutanoic acid and explain the difference between reactions 2 and 3.

.....

.....

.....

[2]

- (c) Draw a labelled diagram to show how hydrogen bonding occurs between two molecules of butane-1,2-diol.

[2]

(d) Like butane-1,2-diol, compound **J** contains only carbon, hydrogen and oxygen.

The following information of **J** is known.

- **J** has a M_r of 192 and does not rotate plane polarised light.
- Complete combustion of 4.32 g of compound **J** produces 5.94 g of CO_2 and 1.62 g of H_2O .
- 1 mole of **J** requires 3 moles of dilute NaOH for complete neutralisation.

Calculate the C:H ratio and deduce the molecular formula of **J**.

Hence, suggest a possible structure for **J**.

For
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[3]

[Total: 14]

2 (a) Concentrated sulfuric acid is a versatile reagent.

- (i) When solid NaCl reacts with concentrated sulfuric acid, white fumes of HCl(g) and sodium hydrogen sulfate, NaHSO₄, are formed.

However, when solid NaI reacts with concentrated sulfuric acid, purple fumes of I₂(g) and hydrogen sulfide gas, H₂S(g), are also formed.

State the role of concentrated sulfuric acid in each reaction. Explain how you arrive at your answer.

- reaction of solid NaCl with conc. H₂SO₄

role of conc. H₂SO₄

explanation

.....

- reaction of solid NaI with conc. H₂SO₄

role of conc. H₂SO₄

explanation

.....

[3]

- (ii) Suggest why NaCl and NaI differ in their reactions with concentrated sulfuric acid.

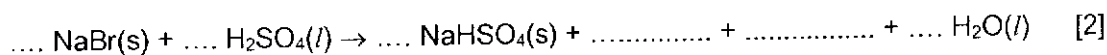
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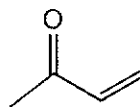
[1]

- (iii) The addition of concentrated sulfuric acid to solid sodium bromide, NaBr, produces reddish brown fumes and an acidic gas that decolourises acidified potassium manganate(VII) solution. This acidic gas is a significant contributor to acid rain.

Complete the equation to show the reaction of concentrated sulfuric acid with sodium bromide.



(b) Butenone is shown.

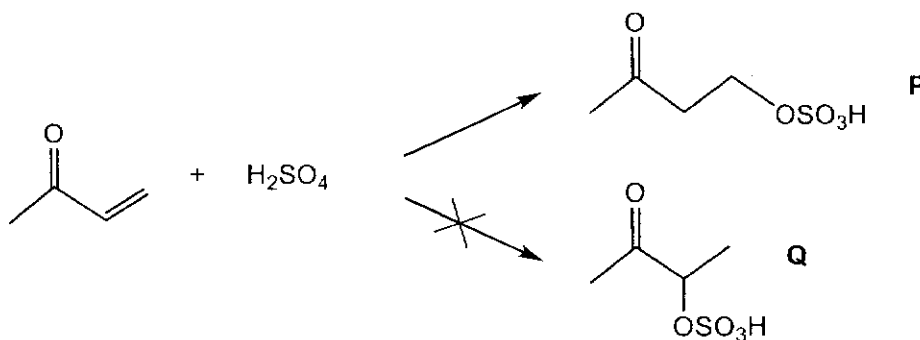


(i) By reference to the bonding, suggest why the $\text{H}_2\text{C}=\text{C}-\text{C}=\text{O}$ part of the molecule is planar.

.....
.....

[1]

(ii) When mixed with concentrated sulfuric acid, butenone undergoes electrophilic addition reaction to give isomer **P** rather than isomer **Q**.



Complete Fig. 2.1 to suggest a mechanism for this reaction. Include any dipoles, lone pairs and curly arrows to the movement of electron pairs.

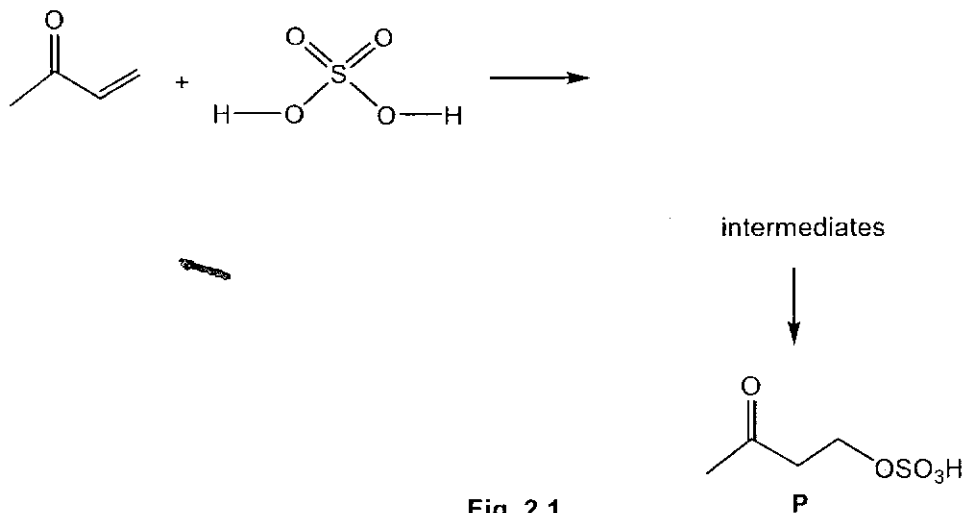


Fig. 2.1

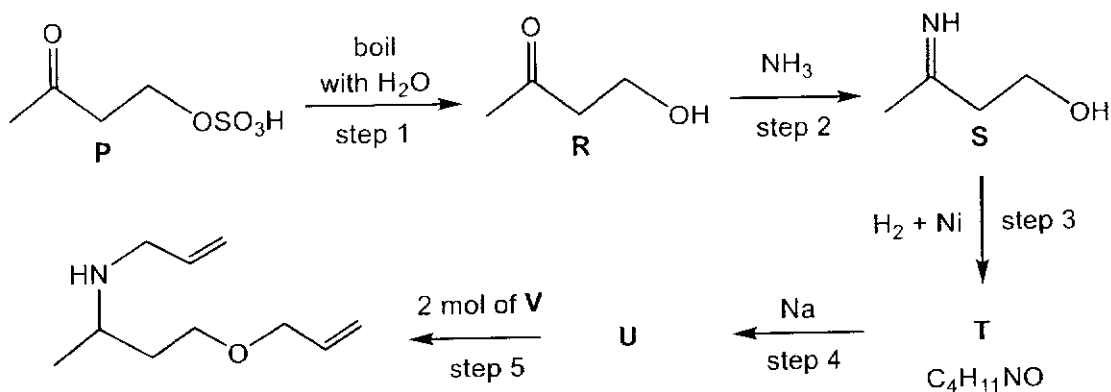
[2]

(iii) With reference to the mechanism you have drawn in (b)(ii), explain why isomer **Q** is not produced.

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[1]

- (c) When isomer **P** is boiled in water, alcohol **R** is obtained, which undergo further reactions as shown below.



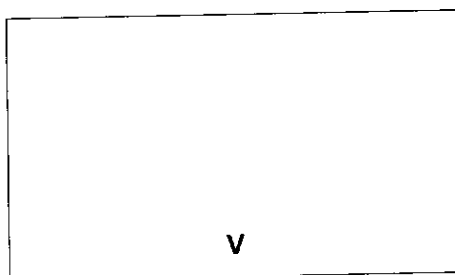
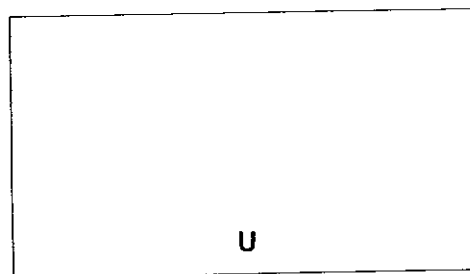
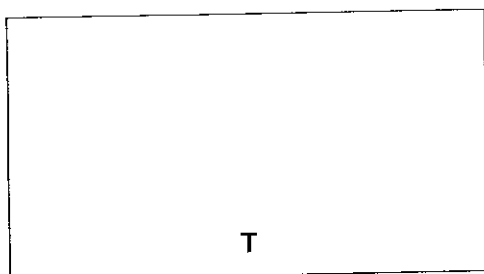
- (i) Name the *types of reaction* that occur during each of the steps 1 and 2.

step 1

step 2

[2]

- (ii) Draw the structures of **T**, **U** and **V**.



[3]

- (iii) In step 3, Ni was used as a heterogeneous catalyst. Explain how this *type* of catalysis works.

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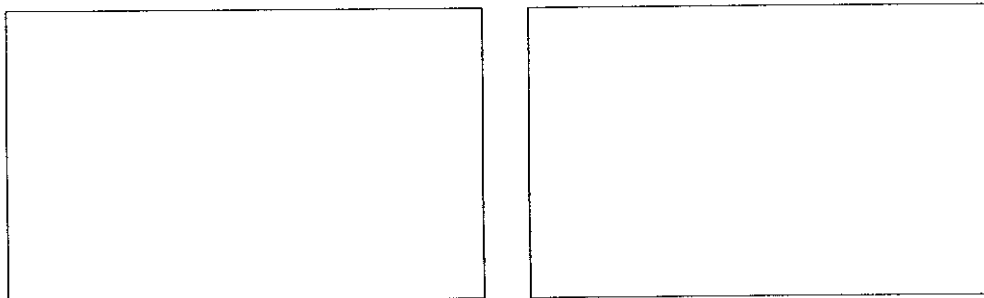
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[2]

- (iv) **S** exists as a mixture of two stereoisomers.
Draw the structure of each stereoisomer of **S** and explain how this type of isomerism arise.

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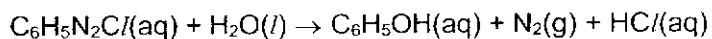


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[3]

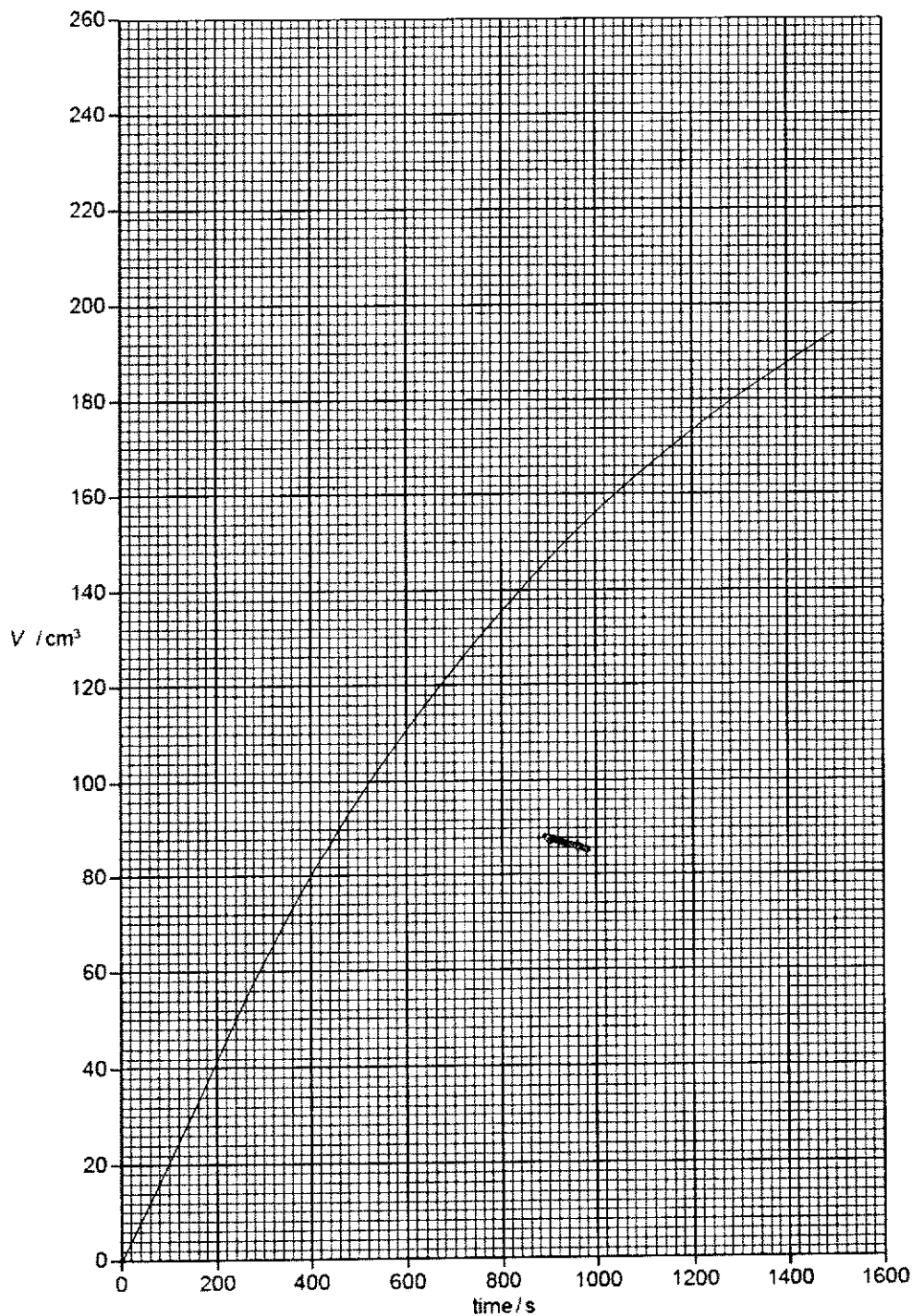
[Total: 20]

- 3 Benzenediazonium chloride, $C_6H_5N_2Cl$, is readily hydrolysed at temperatures above $5\text{ }^\circ\text{C}$.



Some chemists investigate the rate of this hydrolysis reaction. They measure the volume of nitrogen gas, V , produced over time, t .

The volume of the solution used in the experiment is 100 cm^3 and the final volume of gas produced, V_{final} , is found to be 252 cm^3 at $45\text{ }^\circ\text{C}$ and 101 kPa .



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- (a) (i) By determining two half-lives, show the reaction is first order with respect to $[\text{C}_6\text{H}_5\text{N}_2\text{C}]$. Show all your working, and draw clearly any construction lines on your graph.

.....
.....

[2]

- (ii) Calculate the rate constant, k , for this reaction. Include units in your answer.

[2]

- (iii) Why is it not possible to determine the order with respect to water?

.....
.....

[1]

- (b) (i) The progress of the reaction in this experiment can also be followed using a pH meter.

Using relevant information in the question, calculate the pH of the solution at the end of the reaction.

[3]

- (ii) Besides gas collection and measuring pH, suggest one other method with which the chemists could measure the progress of the reaction.

.....
.....

[1]

- (c) The chemists carried out the reaction at several temperatures and plotted a graph of $\ln k$ against $\frac{1}{T}$ as shown in Fig. 3.2.

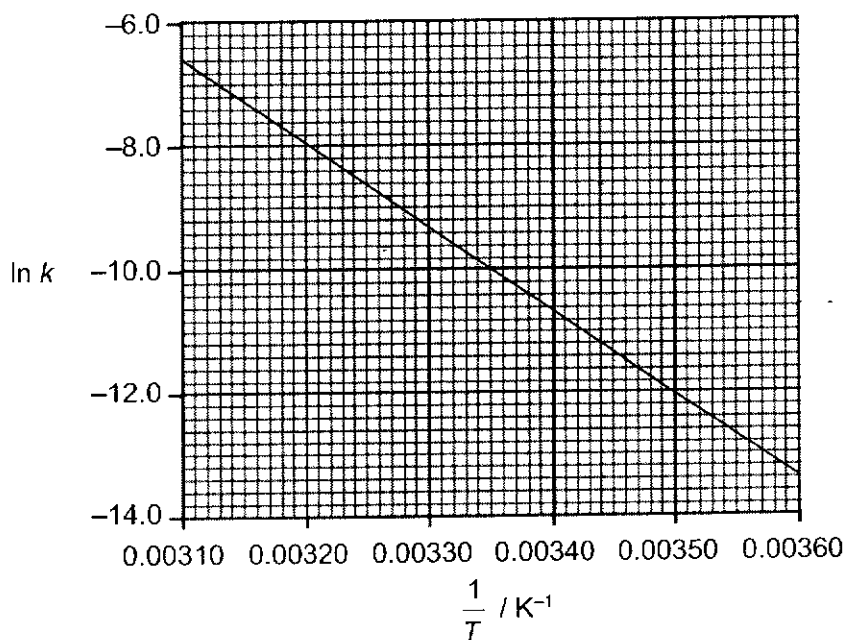


Fig. 3.2

The activation energy, E_a , is related to temperature T by the following equation.

$$k = Ae^{-\frac{E_a}{RT}} \quad \text{where } A \text{ is the pre-exponential factor}$$

Use the graph in Fig. 3.2 to determine a value for E_a . Show all your working.

[2]

[Total: 11]

4 (a) Aluminium reacts with chlorine to form aluminium chloride. At low temperatures, solid aluminium chloride has the formula of Al_2Cl_6 .

(i) Draw a displayed formula of Al_2Cl_6 to illustrate the different types of bonding present.

[1]

(ii) The following enthalpy changes are useful for this question.

enthalpy change of formation of $Al_2Cl_6(s)$ $= -1401 \text{ kJ mol}^{-1}$

enthalpy change of atomisation of $Al(s)$ $= +326 \text{ kJ mol}^{-1}$

enthalpy change of sublimation of $Al_2Cl_6(s) \rightarrow Al_2Cl_6(g)$ $= +116 \text{ kJ mol}^{-1}$

Using relevant data in the *Data Booklet* and the information given in the list above, complete the energy level diagram in Fig. 4.1 which can be used to calculate the average bond energy of the $Al-Cl$ bond in Al_2Cl_6 .

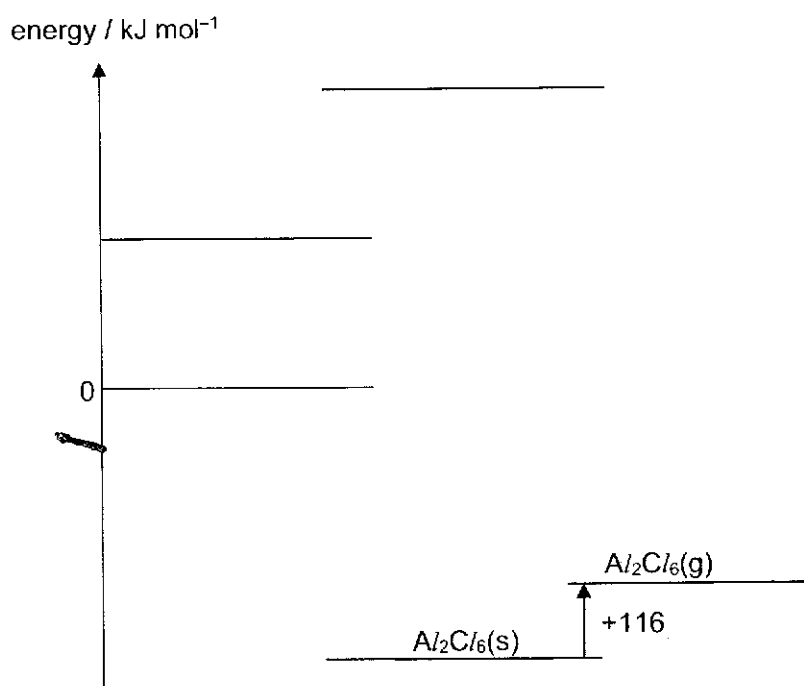


Fig. 4.1

[2]

(iii) Calculate a value for average bond energy of $Al-Cl$ in Al_2Cl_6 .

[2]

- (iv) When solid Al_2Cl_6 dissolves in water, a weakly acidic solution is obtained. Explain the observations and write an equation for the formation of the acidic solution. Suggest the pH of the resulting solution.

.....

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[3]

- (b) In an electrolytic cell, a current of 0.250 A is passed through a concentrated solution of $FeCl_x$, producing iron metal and chlorine gas.

- (i) With reference to E^\ominus values in the *Data Booklet*, explain why chlorine gas instead of oxygen gas is produced at the anode.

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[2]

- (ii) When the cell operates for 2 hours, 0.521 g of iron is deposited at one of the electrodes. Determine the value of x in $FeCl_x$.

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.....

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[2]

- 5 A refrigerant is a working fluid used in the refrigeration cycle of air conditioning systems and heat pumps where in most cases, they undergo a repeated phase transition from a liquid to a gas and back again. However, refrigerants are heavily regulated due to their toxicity, flammability and the contribution to ozone depletion and climate change.

Some common refrigerants, together with their properties, are listed below.

Table 5.1

code	chemicals	boiling point / °C	toxicity	flammability	ozone depletion potential
R-11	CCl_3F	24	low	non-flammable	1.00
R-12	CCl_2F_2	-30	low	non-flammable	1.00
R-22	$CHClF_2$	-41	low	non-flammable	0.055
R-32	CH_2F_2	-52	low	low flammability	0
R-290	$CH_3CH_2CH_3$	-42	low	high flammability	0
R-717	NH_3	-33	high	low flammability	0
R-1130	$CHCl=CHCl$	60	low	non-flammable	0

- (a) In the 1920s, refrigeration and air conditioning systems used compounds such as ammonia and propane as refrigerants. However, in the early 1970s, chlorofluorocarbon gases (CFCs) such as R-11, R-12 and R-22 dominated the market of refrigerants.

Based on the information in Table 5.1, suggest **one** reason for the widespread use of CFCs?

..... [1]

- (b) One consideration for a good refrigerant is to have a low vapour pressure.

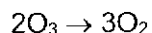
Based on this consideration, together with the data in Table 5.1, state which of these compounds, R-11 (CCl_3F) or R-717 (NH_3), is a better refrigerant. Explain your choice.

.....

 [3]

- (c) In the year 1981, R-11 (CCl_3F) and R-12 (CCl_2F_2) were banned by Montreal Protocol due to its destructive effect on the ozone layer.

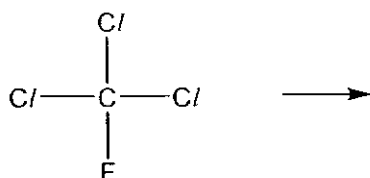
In the stratosphere where there is a strong presence of ultra-violet light, ozone, O_3 , is believed to be destroyed by chlorine *radicals* from CFCs.



- (i) Explain what is meant by the term *radical*.

.....
 [1]

- (ii) Using curly arrows, show the formation of a chlorine radical from one R-11 (CCl_3F) molecule for the first step of the mechanism.



Name the type of bond breaking: [2]

- (iii) Propose the propagation steps involving chlorine radical and ozone. There is no need to show curly arrows in your equations.

First propagation step:

Second propagation step: [2]

- (iv) Propose one possible termination step for the mechanism.

..... [1]

- (v) With reference to your answer in (c)(ii) and quoting appropriate data from *Data Booklet*, explain why R-32 (CH_2F_2) does not deplete ozone layer, as compared to other CFCs, such as R-11 (CCl_3F) or R-12 (CCl_2F_2).

.....

 [2]

(vi) Suggest a reason why R-1130 (CHCl=CHCl) does not deplete ozone layer as compared to other CFCs.

.....
.....
.....

[1]

(d) Hydrocarbons, such as R-290 (CH₃CH₂CH₃), have been long used as refrigerants before they were replaced by the CFCs.

After the Montreal Protocol and the banning of most CFCs, hydrocarbons regain popularity, replacing the CFCs since they do not destroy the ozone layer.

Suggest **one** additional advantage and **one** potential hazard of using R-290 instead of CFCs as refrigerant.

advantage:

potential hazard:

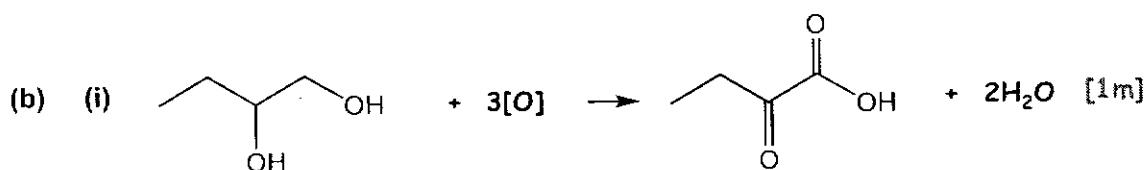
[2]

[Total: 15]

END OF PAPER

Mark Scheme for JC2 H2 Chemistry (9729) Preliminary Examination Paper 2

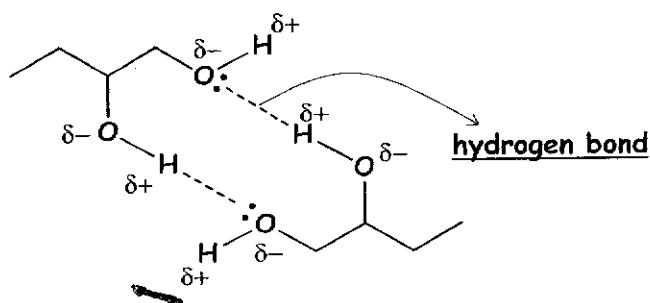
- 1 (a) (i) $\text{Li}^+ : 1s^2$ $\text{H}^- : 1s^2$ [1m] for both
- (ii) Both have same number of quantum shells and no shielding by inner shell electrons. Li^+ has a larger nuclear charge/more protons and hence smaller radius. [1m]
- (iii) $\text{LiAlH}_4 \rightarrow \text{LiAl} + 2\text{H}_2$ [1m]
- (iv) LiAl has giant metallic structure. [1m]
Large amount of heat energy is required to overcome the strong electrostatic attraction between a lattice of cations and delocalised electrons. [1m]
- (v) The effect of a smaller A_r is more significant than that of a smaller volume of Li atom due to its smaller (atomic) radius. [1m]



(ii) H is 2-hydroxybutanoic acid. [1m]

NaBH_4 reduces ketone only while LiAlH_4 reduce both ketone and carboxylic acid, forming back butane-1,2-diol [1m]

(c)



[1m] dotted lines between O and H for two hydrogen bonds
[1m] dipoles on 2 O-H, lone pair on O + label "hydrogen bond" for one hydrogen bond

(d)

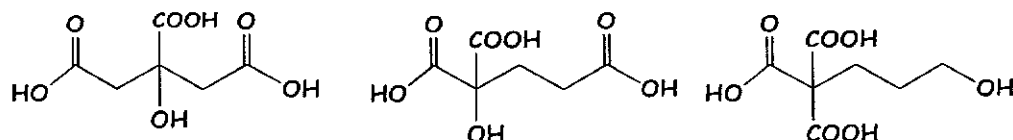
	J	CO_2	H_2O
Amount/mol	$\frac{4.32}{192} = 0.0225$	$\frac{5.94}{44.0} = 0.135$	$\frac{1.62}{18.0} = 0.0900$
Mol ratio	$\frac{0.0225}{0.0225} = 1$	$\frac{0.135}{0.0225} = 6$	$\frac{0.0900}{0.0225} = 4$

Mole ratio of J : C : H = 1 : 6 : 8 [1m] accept "3 : 4"

Let molecular formula of J be $\text{C}_6\text{H}_8\text{O}_x$.

$6(12.0) + 8(1.0) + 16.0x = 192.0 \Rightarrow x = 7 \therefore$ molecular formula is $\text{C}_6\text{H}_8\text{O}_7$. [1m]

Since J : NaOH = 1 : 3, J has 3 $-\text{COOH}$ groups. [1m] for any achiral $\text{C}_6\text{H}_8\text{O}_7$ e.g.



- 2 (a) (i) • reaction of solid NaCl with conc. H_2SO_4
 role of conc. H_2SO_4 : **Bronsted acid** (✓)
 explanation: H_2SO_4 donates a H^+ to form HSO_4^- OR Cl^- accepts a H^+ to form HCl . [1m]
- reaction of solid NaI with conc. H_2SO_4
 role of conc. H_2SO_4 : **Oxidising agent** (✓)
 explanation: O.S. of I increases from -1 in NaI to 0 in I_2 OR O.S. of S decreases from +6 in H_2SO_4 to -2 in H_2S . [1m]
- 2(✓): [1m]

(ii) HI/I-/NaI is a stronger reducing agent than HCl/Cl-/NaCl. [1m]

(iii) $2\text{NaBr(s)} + 3\text{H}_2\text{SO}_4(\text{l}) \rightarrow 2\text{NaHSO}_4(\text{s}) + \text{Br}_2(\text{g}) + \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$

[1m] for $\text{Br}_2 + \text{SO}_2$; [1m] for balanced eqn

(b) (i) There is p-p orbital overlap between C of C=O bond and the adjacent C of C=C. [1m]

(ii)

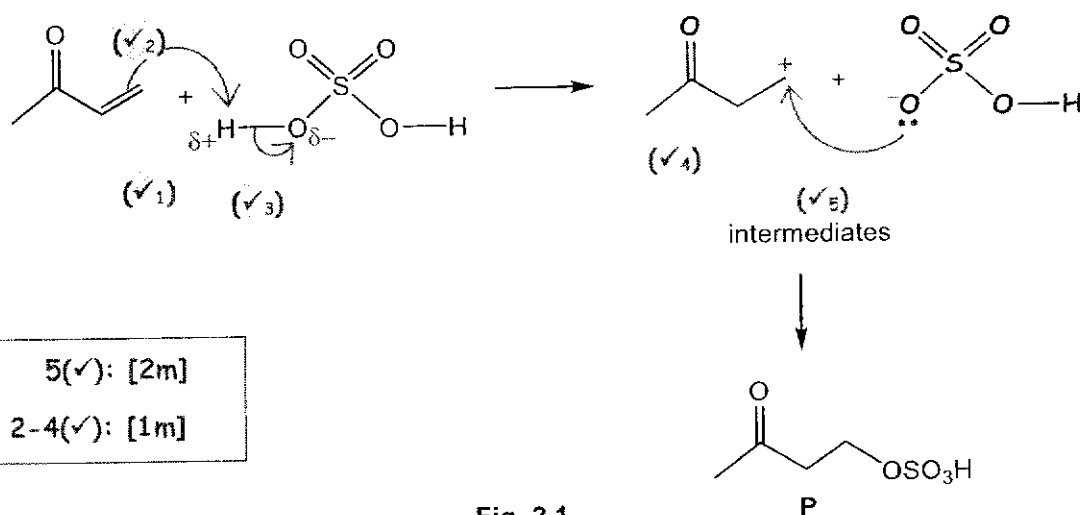
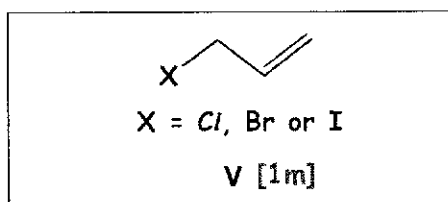
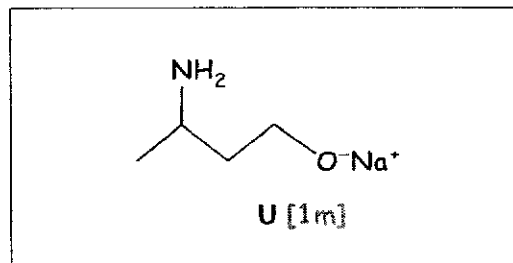
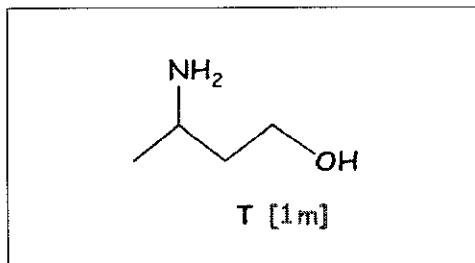


Fig. 2.1

(iii) Electron-withdrawing C=O in the secondary carbocation that forms Q intensifies the positive charge, making it less stable and less readily formed than the primary carbocation that forms P. [1m]

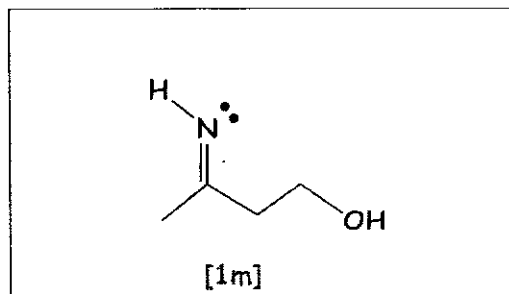
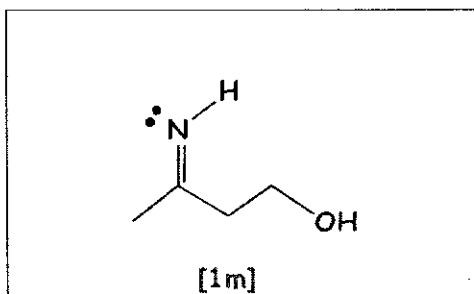
- (c) (i) step 1: hydrolysis/ nucleophilic substitution [1m]
 step 2: condensation [1m]

(ii)



- (iii) When the reactants are adsorbed on the catalyst surface (✓), the bonds in the reactants are weakened (✓) which lowers E_a . Surface concentration of reactants also increases. Thus, the rate of the reaction increases (✓). The products are desorbed (✓) from the catalyst surface, making it available for adsorption of new reactant molecules. 4(✓): [2m]; 2-3(✓): [1m]

(iv)



Cis-trans isomerism arises due to restricted rotation about the C=N bond which has two different groups attached to each C and N [1m]

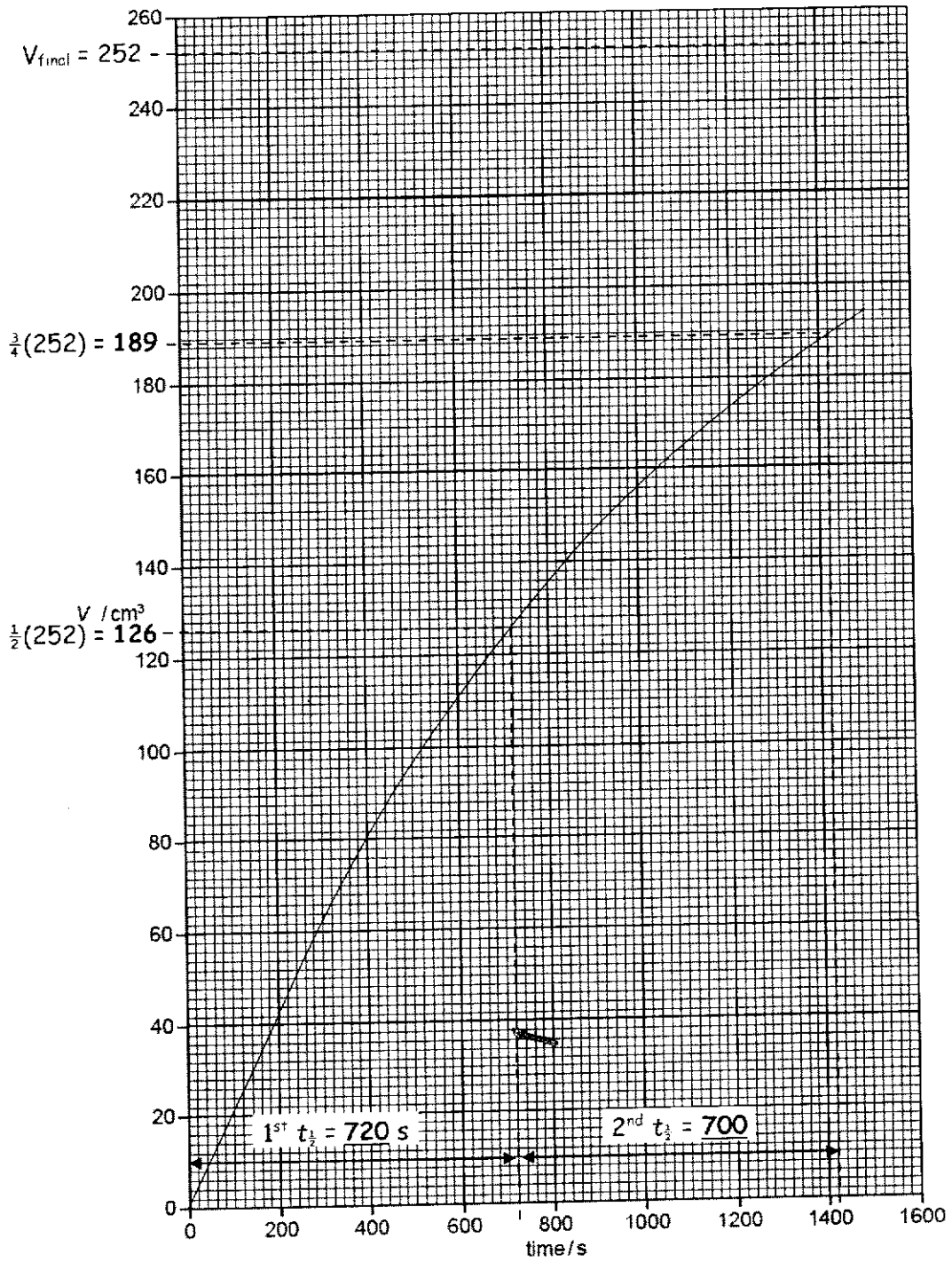


Fig. 3.1

- (a) (i) [1m] for 2 correctly read $t_{\frac{1}{2}}$ values clearly indicated on graph
Half-lives are approximately constant so the reaction is first order wrt $[C_6H_5N_2Cl]$ [1m]

(ii) rate = $k [C_6H_5N_2Cl]$

Average $t_{\frac{1}{2}} = \frac{1}{2} (720 + 700) = 710$ s

$k = \frac{\ln 2}{710} = \underline{9.76 \times 10^{-4} \text{ s}^{-1}}$ [1m] 3sf; ecf $t_{\frac{1}{2}}$ from (a)(i); [1m] units

- (iii) Water is a solvent so it is in large excess. Thus only a small proportion of water is reacted and hence concentration of water remains effectively constant throughout the progress of the reaction. [1m]

(b) (i) $n(N_2) = \frac{(101 \times 10^3)(252 \times 10^{-6})}{(8.31)(45 + 273)} = 9.63 \times 10^{-3} \text{ mol}$ [1m]

Since $HCl \equiv N_2$,

$[H^+] = [HCl] = \frac{9.63 \times 10^{-3}}{\frac{100}{1000}} = 0.0963 \text{ mol dm}^{-3}$ [1m] ecf from $n(N_2)$

$pH = -\lg 0.0963 = \underline{1.02}$ [1m] ecf from $[H^+]$

- (ii) [1m] for any of the following methods

- Use an electronic weighing balance to measure the mass of the solution at various time intervals
- Use a conductivity meter to measure the conductivity of the solution due to production of H^+ and Cl^- at various time intervals
- Titrate quenched samples taken from the main reaction mixture at various time intervals with $NaOH(aq)$ of known concentration

(c)

$k = Ae^{-\frac{E_a}{RT}}$

$\ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T} \right)$

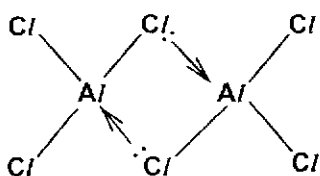
gradient = $-\frac{E_a}{R} = \frac{(-6.60) - (-13.40)}{0.00310 - 0.00360} = \underline{-13600 \text{ K}^{-1}}$ [1m]

$E_a = \text{gradient} \times (-R)$

= $\underline{(-13600) \times (-8.31)}$

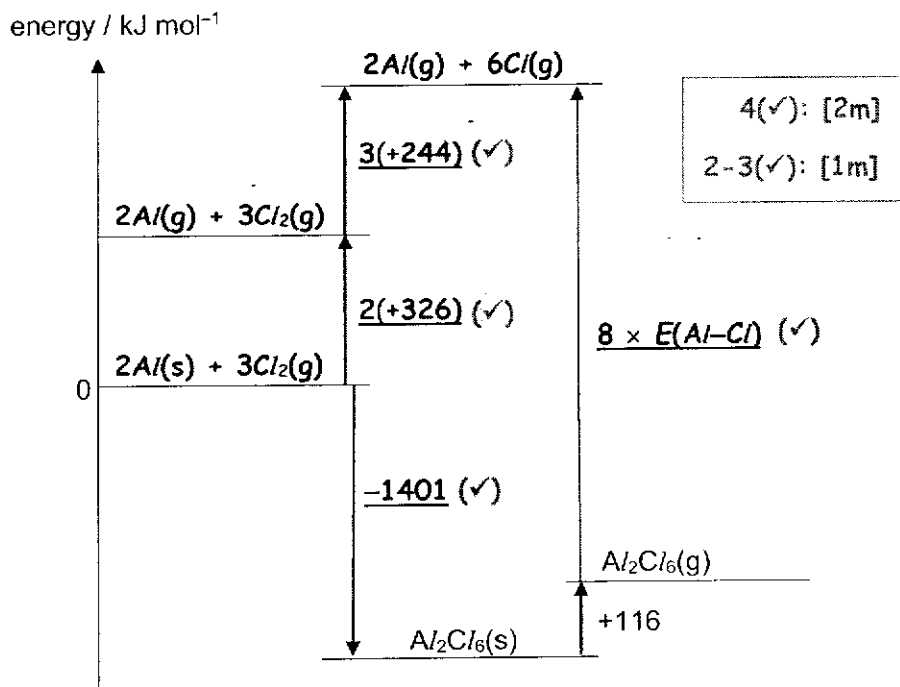
= $\underline{+113\,000 \text{ J mol}^{-1}}$ or $\underline{+113 \text{ kJ mol}^{-1}}$ [1m] 3sf + units; ecf from gradient

4 (a) (i)



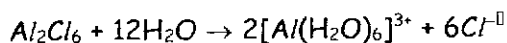
[1m] correct displayed structure with two dative bonds (represented by $Cl \rightarrow Al$; lone pair not required)

(ii)

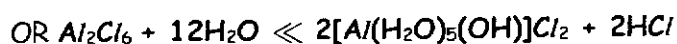
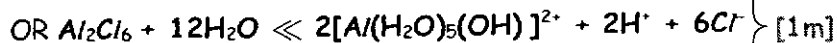


(iii) $8E(\text{Al-Cl}) = -(+116) - (-1401) + 2(+326) + 3(+244)$ [1m] ecf from multiplier
 $E(\text{Al-Cl}) = +334 \text{ kJ mol}^{-1}$ [1m] 3sf

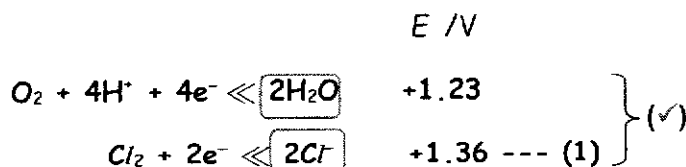
(iv) Al_2Cl_6 dissolves in water to form $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ in water.



Since Al^{3+} has a high charge density (✓), $\text{Al}_2\text{Cl}_6/[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ undergoes partial hydrolysis (✓) in water. Al^{3+} polarises the coordinated H_2O molecule and weakens the O-H bond (✓) which breaks to release H^+ , giving rise to a weakly acidic solution of pH 3 (✓). 4(✓): [2m]; 2-3(✓): [1m]



- (b) (i)
- Cl^-
- anion and
- H_2O
- molecules are attracted to the anode.



High $[Cl^-]$ shifts the position of equilibrium (1) to the left (\checkmark), making $E(Cl_2/Cl^-)$ less positive (or more negative) than $E(O_2/H_2O)/+1.23V$ (\checkmark).

So Cl^- is more easily oxidised than H_2O , producing Cl_2 gas instead of O_2 gas. (\checkmark) award only with mention of shift in position of equilibrium

4(\checkmark): [2m]; 2-3(\checkmark): [1m]

- (ii)
- $I \times t = n_e \times F$

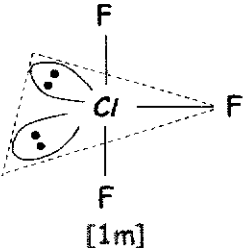
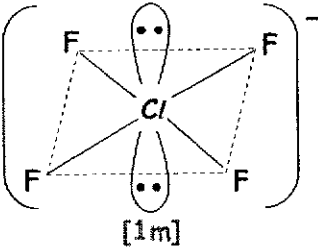
$$0.250 \times (2 \times 60 \times 60) = n_e \times 96500$$

$$n_e, \text{ amount of } e^- = \underline{0.0187} \text{ mol [1m]}$$

$$\text{Amount of Fe} = \frac{0.521}{55.8} = 0.00934 \text{ mol}$$

$$\text{Since } n(\text{Fe}) : n_e = 0.00934 : 0.0187 = 1 : 2 \quad \left. \vphantom{\text{Since } n(\text{Fe}) : n_e} \right\} [1m]$$

$$x = \underline{2}$$

(c) CF_3	$[CF_4]^-$
 <p>shape: trigonal planar <u>trigonal planar</u> (\checkmark)</p>	 <p>shape: <u>square planar</u> (\checkmark)</p>

- 5 (a) CFCs are
- non-toxic / non-flammable
- . [1m]

- (b)
- R-11 / CCl_3F
- is a
- better
- refrigerant. [1m]

From Table 5.1, CCl_3F has a higher boiling point than NH_3 so CCl_3F has stronger IMF.

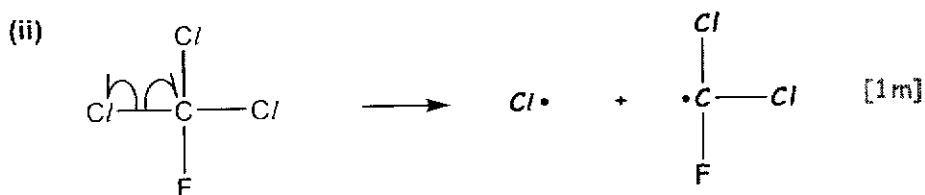
Both CCl_3F and NH_3 have simple covalent structures.

Due to greater number of electrons per (CCl_3F) molecule (\checkmark), more energy (\checkmark^*) is needed to overcome the stronger (\checkmark^*) instantaneous dipole-induced dipole interaction between CCl_3F molecules (\checkmark) than the weaker hydrogen bonds between NH_3 molecules (\checkmark). Thus, CCl_3F is less easily vaporised and has lower vapour pressure than NH_3 .

4(\checkmark): [2m]; 2-3(\checkmark): [1m]

(\checkmark^*) stronger + more energy

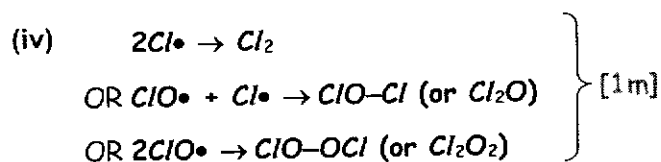
(c) (i) A radical is a species with unpaired electron(s) [1m]



Name the type of bond breaking: homolytic fission [1m]

(iii) First propagation step: $Cl\cdot + O_3 \rightarrow ClO\cdot + O_2$ [1m]

Second propagation step: $ClO\cdot + O_3 \rightarrow 2O_2 + Cl\cdot$ [1m]



(v) $E(C-F) = +485 \text{ kJ mol}^{-1}$; $E(C-Cl) = +340 \text{ kJ mol}^{-1}$ (✓)

Since $E(C-F) > E(C-Cl)$, C-F bond is stronger (✓) than C-Cl bond and will not be broken by UV light (✓). Thus, no F radical will be produced (✓) and hence no depletion of ozone layer by R-32.

OR

Atomic radius of F = 0.072 nm; atomic radius of Cl = 0.099 nm (✓)

Since F has a smaller radius than Cl, C-F bond is shorter and stronger (✓) than C-Cl bond and will not be broken by UV light (✓). Thus, no F radical will be produced (✓) and hence no depletion of ozone layer by R-32.

4(✓): [2m]; 2-3(✓): [1m]

(v) p-p orbital overlap results in the delocalisation of lone pair of electrons on Cl into the adjacent π electron cloud of the C=C bond. This imparts a partial double bond character in C-Cl bond and strengthens C-Cl bond. Thus, it will not break under UV light to give a Cl radical. [1m]

(d) advantage: Propane is easy to produce/ readily available/ inert. [1m]

potential hazard: It is highly flammable. [1m]



JURONG PIONEER JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2021

CHEMISTRY

9729/03

Higher 2

20 September 2021

Paper 3 Free Response Questions

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
 Write in dark blue or black pen on both sides of the paper.
 You may use a HB pencil for any diagrams or graphs.
 Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at end of this booklet. The question number must be clearly shown.

Section A

Answer **all** questions.

Section B

Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
 A *Data Booklet* is provided.

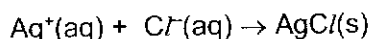
At the end of the examination, fasten all your work securely together.
 The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use	
1	20
2	20
3	20
4 or 5	20
Penalty (delete accordingly)	
Lack 3sf in final answer	-1 / NA
Missing/wrong units in final ans	-1 / NA
Bond linkages	-1 / NA
Total	80

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- (c) The presence of halide ions in natural water sources such as rivers and lakes are usually detected using aqueous ammonia and aqueous silver nitrate.

The following equation shows the precipitation of AgCl ,



Thermodynamic quantity	Value
$K_{\text{sp}}(\text{AgCl})$	$1.8 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$
$\Delta S_{\text{ppt}}(\text{AgCl})$	$-410 \text{ J mol}^{-1} \text{ K}^{-1}$
$\Delta H_{\text{hyd}}(\text{Ag}^+)$	-473 kJ mol^{-1}
$\Delta H_{\text{hyd}}(\text{Cl}^-)$	-378 kJ mol^{-1}

Table 1.1

- (i) 5 cm^3 of $0.0100 \text{ mol dm}^{-3}$ of silver nitrate is added to a 30 cm^3 sample of river water containing chloride ions.

What is the minimum concentration, in mol dm^{-3} , of chloride ions present in the river water when the first trace of precipitate appears? [2]

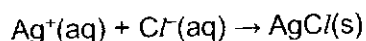
- (ii) To another sample of river water, aqueous silver nitrate is added, followed by excess aqueous ammonia. A cream precipitate is formed which is partially soluble in excess.

Suggest the identity of the precipitate and thus identify the halide present in this sample of river water. [1]

- (iii) When a precipitate is formed, ΔG_{ppt} is given by the following expression.

$$\Delta G_{\text{ppt}} = RT \ln K_{\text{sp}}$$

Using appropriate data in Table 1.1, calculate ΔG_{ppt} , in kJ mol^{-1} , and hence ΔH_{ppt} for the precipitation of AgCl at room temperature.



- (iv) Using your answer in (c)(iii) and data in Table 1.1, calculate the lattice energy for AgCl . [2]

- (v) The theoretical lattice energy for AgCl is found to be -770 kJ mol^{-1} .

State and explain the reason for the difference between the theoretical value and your answer in (c)(iv). [2]

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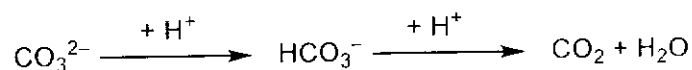
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- 2 (a) Aqueous sodium carbonate reacts with H^+ in two stages.



0.200 mol dm^{-3} nitric acid was added gradually to a 20.0 cm^3 solution containing both Na_2CO_3 and $NaHCO_3$. The changes in pH are monitored as shown in **Figure 2.1**.

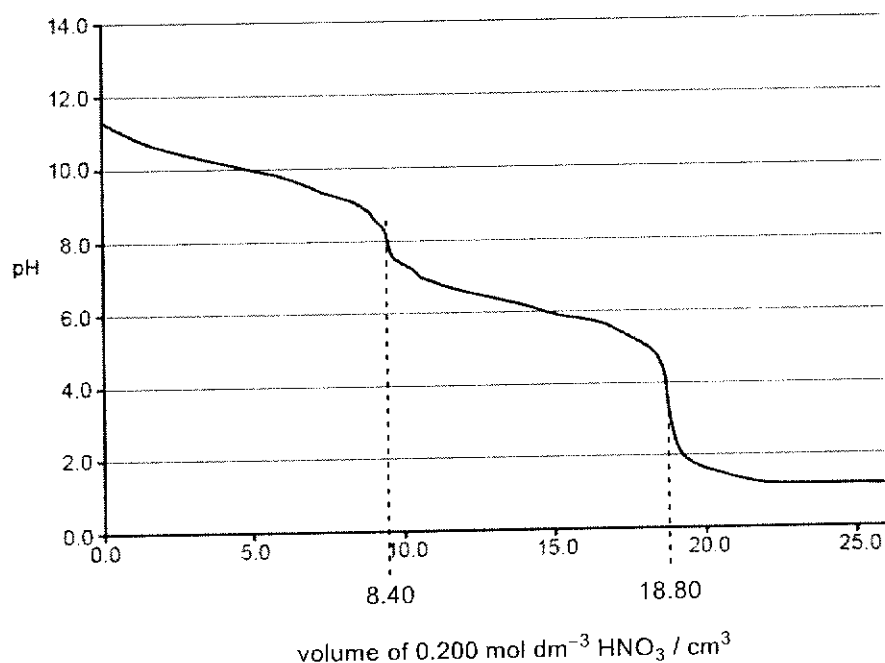


Figure 2.1

- (i) A list of indicators and their pK_a values is given in **Table 2.1**.

indicator	thymol blue	methyl yellow	methyl red	cresol red	thymolphthalein
pK_a	1.7	3.1	5.1	8.3	9.2

Table 2.1

From **Table 2.1**, state and explain which two indicators are suitable to determine the two end-points in **Figure 2.1**. [2]

- (ii) Calculate the concentration, in $g\ dm^{-3}$, of sodium carbonate and sodium hydrogencarbonate present in the original solution. [4]

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- (b) Wines contain a mixture of organic acids, including dicarboxylic acids such as tartaric acid. These acids produce a prickling sensation on the tongue during wine-tasting.

Dicarboxylic acids ionise in stages.

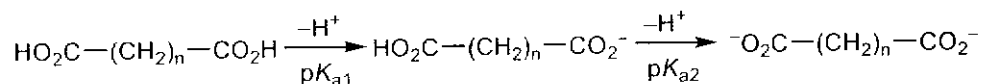


Table 2.2 compares the $\text{p}K_a$ values of two dicarboxylic acids, tartaric acid and succinic acid.

Acid	Formula	$\text{p}K_{a1}$	$\text{p}K_{a2}$
Tartaric	$\begin{array}{c} \text{OH} \quad \text{H} \\ \quad \\ \text{HO}_2\text{C}-\text{C}-\text{C}-\text{CO}_2\text{H} \\ \quad \\ \text{H} \quad \text{OH} \end{array}$	2.95	4.25
Succinic	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{HO}_2\text{C}-\text{C}-\text{C}-\text{CO}_2\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	4.20	5.60

Table 2.2

- (i) Explain why the $\text{p}K_{a2}$ values are higher than $\text{p}K_{a1}$ values for both acids. [1]
- (ii) By considering the structure of the respective monoanions, explain why succinic acid has a higher $\text{p}K_{a1}$ value than tartaric acid. [2]
- (iii) An amphiprotic species is one that reacts with both an acid and a base. The monoanion of a dicarboxylic acid, $\text{HO}_2\text{C}-(\text{CH}_2)_n-\text{CO}_2^-$, is an amphiprotic species.

The pH of an amphiprotic species is given by the following expression.

$$\text{pH} = \frac{1}{2} (\text{p}K_{a1} + \text{p}K_{a2})$$

Using tartaric acid as an example, write two equations to show that its monocarboxylate ion is an amphiprotic species. [2]

- (iv) The pH–volume added curve when 55 cm^3 of 0.20 mol dm^{-3} aqueous NaOH is added to 25.0 cm^3 of 0.20 mol dm^{-3} tartaric acid is shown in **Figure 2.2**.

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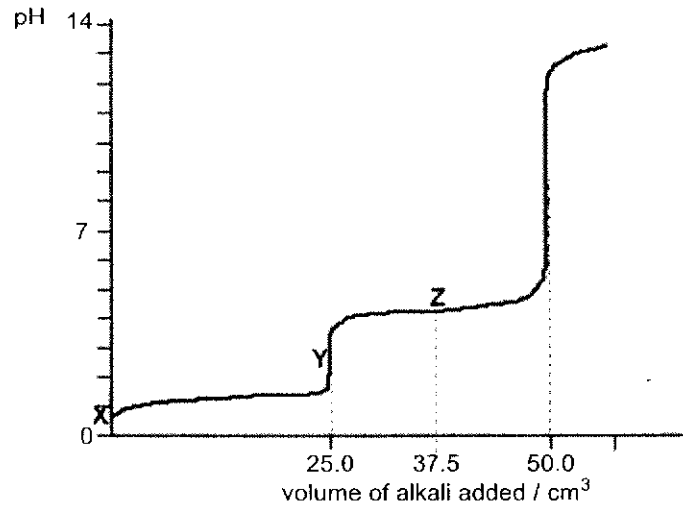


Figure 2.2

Using **Figure 2.2** and the data from **Table 2.2**, determine the pH at points **X**, **Y** and **Z**.

[3]

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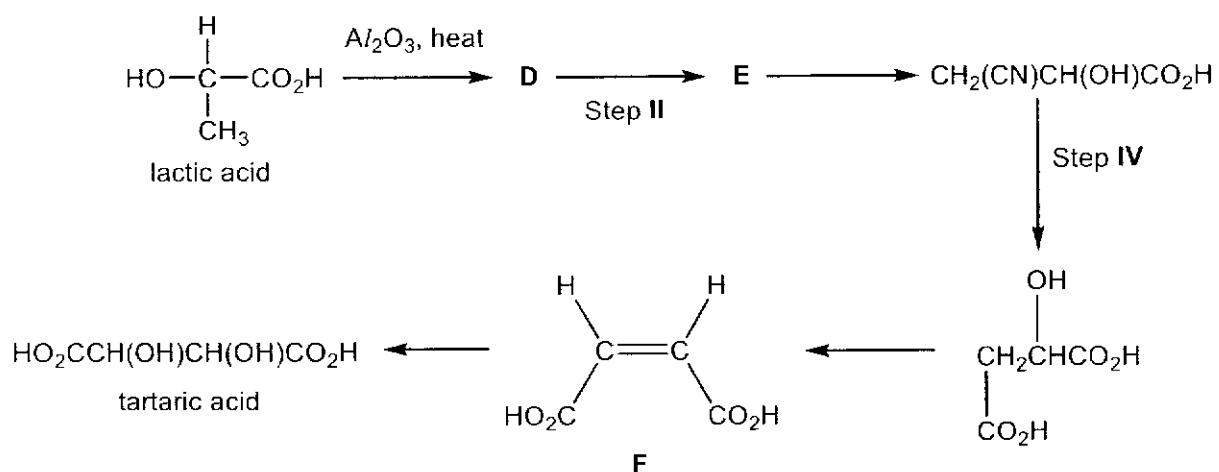
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- (c) Tartaric acid can be synthesised from lactic acid in the laboratory via the following reaction sequence.



- (i) Suggest the structural formulae of **D** and **E**. [2]
- (ii) Give the reagents and conditions for steps **II** and **IV**. [2]
- (iii) Suggest a simple chemical test to confirm that all of compound **F** has been converted to tartaric acid. [2]

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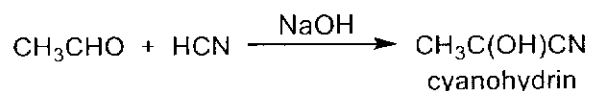
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- 3 (a) Nitrogen can be introduced into organic compounds by reacting a carbonyl group with a weak acid such as HCN in the presence of a base to form a cyanohydrin.

An example of such reaction is shown using ethanol as an example.



The kinetics of this reaction was studied by monitoring the initial rate when the concentration of ethanal and NaOH are varied while using excess HCN.

HCN is used in excess for all experiments.

experiment	initial concentration of / mol dm ⁻³		initial rate of cyanohydrin formation / mol dm ⁻³ s ⁻¹
	CH ₃ CHO	NaOH	
1	1.25×10^{-2}	1.25×10^{-4}	1.15×10^{-14}
2	2.50×10^{-2}	1.25×10^{-4}	2.30×10^{-14}
3	3.75×10^{-2}	2.50×10^{-4}	6.90×10^{-14}

Table 3.1

- (i) State and explain why NaOH is needed in the reaction of CH₃CHO and HCN. [2]
- (ii) Use the data in Table 3.1 to determine the order of reaction with respect to CH₃CHO and NaOH. [2]

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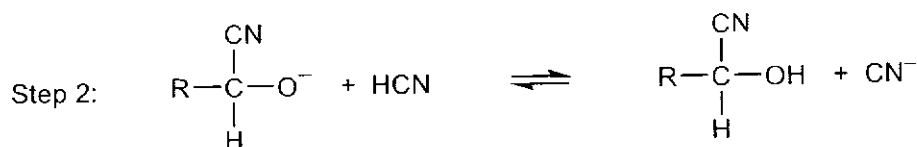
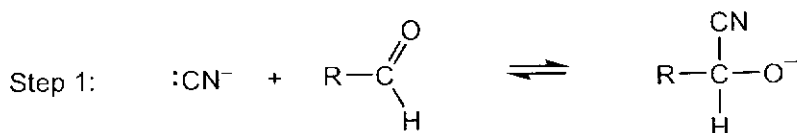
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- (b) The uncatalysed addition of HCN to a carbonyl group to give a cyanohydrin proceeds by two steps.



The rate equation for the formation of cyanohydrin is as follows:

$$\text{rate} = k[\text{carbonyl compound}][\text{CN}^-]$$

The overall reaction is an equilibrium, and the value of the equilibrium constant, K_c , has been measured under identical experimental conditions for a number of carbonyl compounds.

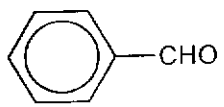
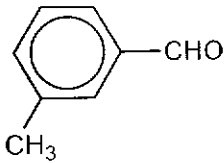
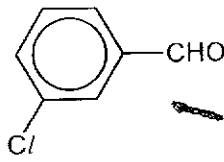
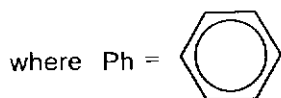
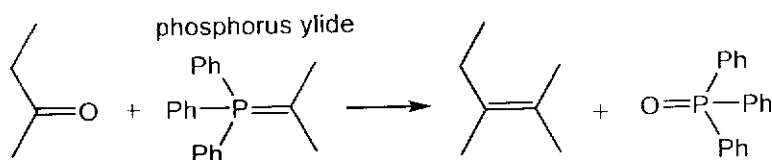
	carbonyl compound	$K_c = \frac{[\text{cyanohydrin}]}{[\text{carbonyl compound}][\text{HCN}]}$ / mol ⁻¹ dm ³
I		210
II		175
III		500

Table 3.2

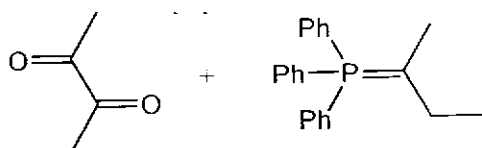
- (i) Which is the rate-determining step of the reaction? [1]
- (ii) By considering the mechanism for the reaction of the carbonyl compound with HCN, account for the different values of K_c shown in Table 3.2. [3]

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- (c) A phosphorous ylide is used in the Wittig reaction which converts a carbonyl compound to an alkene. An example of a Wittig reaction is shown below.



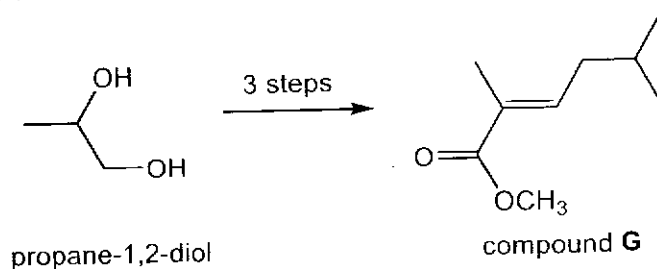
- (i) Suggest the structure formed when 1 mole of the following carbonyl compound reacts with 2 moles of the phosphorous ylide via the Wittig reaction.



Hence, suggest the number of stereoisomers that can be formed.

[2]

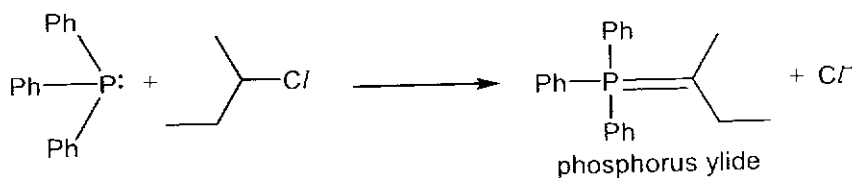
- (ii) Using the Wittig reaction as one of the steps in a three-step synthesis route, suggest suitable reagents and conditions to synthesise compound **G** from propane-1,2-diol.



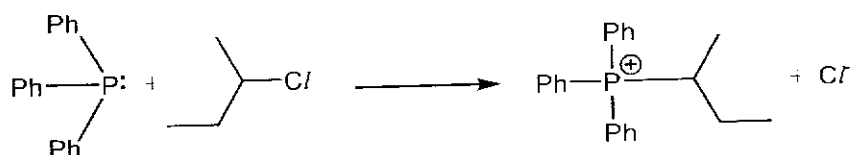
In your answer, include the structure of the intermediates formed.

[5]

A phosphorous ylide is formed by reacting a suitable phosphine and an alkyl halide. An example of a phosphorous ylide is given below.



- (iii) The initial structure of the ylide formed carries a positive charge as shown.



By considering the type of reaction that occurred, give one reason why the reaction occurs more readily with $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{Cl}$ than with $\text{CH}_3\text{CH}_2\text{CHClCH}_3$.

[1]

- (iv) By considering the structure of the phosphorous ylide given, explain why Ph_3N cannot be used for the formation of the ylide.

[1]

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(d) Arenes undergo electrophilic substitution reactions.

The position of substitution during the electrophilic substitution of arenes can be explained based on the stability of the carbocationic arenium ion.

An example involving the bromination of methylbenzene is shown in **Figure 3.1**.

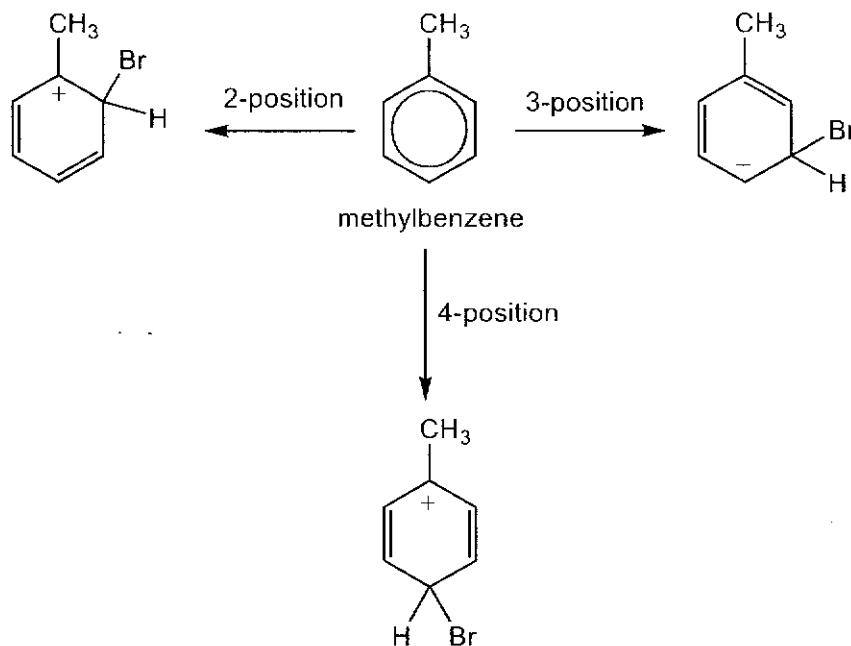


Figure 3.1

(i) Based on the stability of the carbocationic arenium ions, suggest why the methyl group directs incoming electrophiles to the 2- and 4-positions in preference to the 3-position. [2]

(ii) Draw the structure of the product formed when benzaldehyde undergoes bromination. [1]

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[Total: 20]

Section B

Answer **one** question from this section.

4 Carbon, "the building block of life", combines with hydrogen and oxygen to form compounds that make up living things.

For
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Use

(a) Dinitrogen oxide, N_2O , has a molecular shape similar to that of carbon dioxide, CO_2 .

(i) Draw the dot-and-cross diagram for N_2O . [1]

(ii) Predict, with reasons, which of the two compounds, N_2O or CO_2 , has a lower boiling point. [2]

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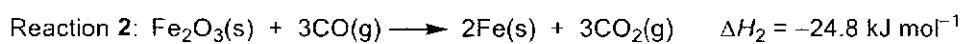
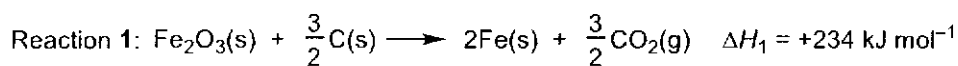
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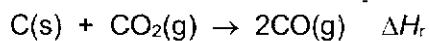
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- (b) Either carbon or carbon monoxide can bring about the reduction of iron(III) oxide in a blast furnace.



- (i) By considering the thermodynamic spontaneity of the two reactions, state and explain which reaction is more favoured at low temperatures. [3]
- (ii) The carbon monoxide is formed by the following reaction:



Calculate ΔH_f for this reaction. [2]

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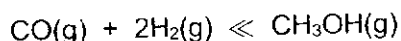
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- (c) A commercial production of methanol involves the reaction of carbon monoxide with hydrogen gas at 7500 kPa.

One of the steps in the production as shown below is carried out at 7500 kPa.



- (i) The reaction was carried out in the laboratory. After the reaction reached equilibrium, the mixture of gases contained 38.0 g of hydrogen, 462 g of carbon monoxide and 7200 g of methanol.

Calculate the mole fraction of each gas in the mixture.

[2]

- (ii) Write an expression for the equilibrium constant, K_p , for the reaction.

Using your answer in (c)(i), calculate a value for K_p , stating its units.

[2]

- (iii) Compound **J** has molecular formula $\text{C}_8\text{H}_9\text{N}$ and is soluble in dilute HCl solution. When compound **J** is reacted with steam in the presence of catalyst at high temperature and pressure, two possible isomeric organic products, **L** and **M** are formed. One mole of **J** requires 4 moles of aqueous bromine for reaction.

Compound **L** is optically active but not **M**. Compound **L** reacts with alkaline aqueous iodine to form yellow precipitate.

Separate samples of **J**, **L** and **M** reacts with hot concentrated KMnO_4 to form the same product **Q**, $\text{C}_7\text{H}_7\text{O}_2\text{N}$, which is a crystalline solid upon evaporation.

Deduce the structures of **J**, **L**, **M** and **Q**. Explain your reasoning.

[8]

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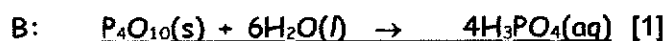
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1 (a)

	Deductions
B is soluble in water	Not MgO, Al ₂ O ₃ , SiO ₂
Aq. solution of B reacts with Na ₂ CO ₃ in 2:3 ratio to form CO ₂ (g)	Aq. solution of <u>B is acidic</u> (✓) Since the reacting ratio is 2:3, the acid formed must be tribasic ∴ <u>B is P₄O₁₀/P₄O₆</u> [1]
C is soluble in water	Not MgO and Al ₂ O ₃ , SiO ₂
Aq. solution of C reacts with NH ₄ ⁺ to give NH ₃ (g)	Aq. solution of <u>C is basic</u> (✓) ∴ <u>C is Na₂O</u> [1]
A reacts with both B and C	<u>A is amphoteric</u> (✓) ∴ <u>A is Al₂O₃</u> [1]

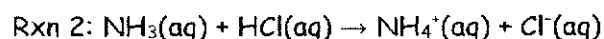
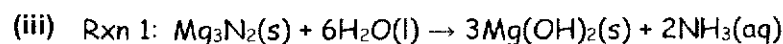
2-3✓: 1m

Equations for reaction with water:

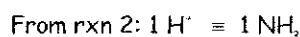
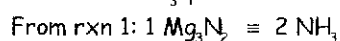


Mg²⁺ has the same charge but a smaller ionic radius hence a higher charge density than Ba²⁺. Thus Mg²⁺ polarises the large NH₂⁻ anion more. (✓) This weakens the N-H bond in the Mg(NH₂)₂ more (✓) and thus a lower temperature is needed to decompose magnesium amide.

4✓: 2m; 2-3✓: 1m



$$\text{Amount of acid} = \frac{12.0}{1000} \times 0.50 = 0.00600 \text{ mol}$$

Amount of NH₃ produced from reaction with air = 0.00600 mol

$$\text{Amount of Mg}_3\text{N}_2 \text{ formed} = \frac{0.00600}{2} = 0.00300 \text{ mol} \quad [1]$$

$$\text{Mass of Mg}_3\text{N}_2 \text{ in 1.00 g sample} = 0.00300 \times 100.9 = 0.303 \text{ g}$$

$$\begin{aligned} \therefore \text{percentage of Mg}_3\text{N}_2 \text{ in 1.00 g sample} &= \frac{0.303}{1.00} \times 100 \\ &= 30.3\% \quad [1] \end{aligned}$$

1 (c) (i) Precipitate formed is AgCl.

$$\begin{aligned} [\text{Ag}^+] \text{ at point of mixing} &= \frac{0.0100 \times 5}{30 + 5} & [1] \\ &= 1.428 \times 10^{-3} \text{ mol dm}^{-3} \end{aligned}$$

$$[\text{Cl}^-] \text{ at point of mixing} = \frac{[\text{Cl}^-]_{\text{initial}} \times 30}{30 + 5}$$

For precipitation to take place: ionic product (AgCl) $\geq K_{\text{sp}}(\text{AgCl})$

$$\text{ionic product} = (1.428 \times 10^{-3}) \left(\frac{[\text{Cl}^-]_{\text{initial}} \times 30}{30 + 5} \right) \geq 1.8 \times 10^{-10}$$

$$\therefore [\text{Cl}^-]_{\text{initial}} \geq \underline{1.47 \times 10^{-7} \text{ mol dm}^{-3}} \quad [1]$$

(ii) Cream ppt is AgBr, halide present is Br⁻.

$$\begin{aligned} \text{(iii)} \quad \Delta G &= (8.31)(298) \ln(1.8 \times 10^{-10}) \\ &= -5.56 \times 10^4 \text{ J mol}^{-1} \\ &= \underline{-55.6 \text{ kJ mol}^{-1}} & [1] \end{aligned}$$

$$\text{Using } \Delta G_{\text{ppt}}^{\ominus} = \Delta H_{\text{ppt}}^{\ominus} - T \Delta S_{\text{ppt}}^{\ominus}$$

$$-5.56 \times 10^4 = \Delta H_{\text{ppt}}^{\ominus} - (298)(-410)$$

$$\therefore \Delta H_{\text{ppt}}^{\ominus} = \underline{-178000 \text{ J mol}^{-1} / -178 \text{ kJ mol}^{-1}} \quad [1]$$

(iv) Since $\Delta H_{\text{ppt}}^{\ominus} = -178 \text{ kJ mol}^{-1}$, hence $\Delta H_{\text{soln}}^{\ominus} = \underline{+178 \text{ kJ mol}^{-1}}$ [1]

$$\text{Since } \Delta H_{\text{soln}} = -LE + \sum \Delta H_{\text{hyd}}(\text{ions})$$

$$+178 = -LE + (-473) + (-378)$$

$$\therefore LE = \underline{-1030 \text{ kJ mol}^{-1}} \quad [1]$$

(v) This difference indicates that AgCl is not purely ionic / there exists covalent character in the ionic bond in AgCl. [1]

The electronegative difference between Ag and Cl is so small that complete transfer of an electron from the silver to the chlorine is not possible. [1]

OR

Cl^- has a large anion radius allowing it to be readily polarised by Ag^+ ions. [1]

[Total: 20]

2 (a) (i) Indicator for first end point: cresol red

Indicator for second end point: methyl yellow [1] – for both indicators

pK_a of indicator matches the pH change at equivalence point [1]

OR

Equivalence point pH lies within working range of the indicator [1]

(ii) Since CO_3^{2-} the stronger base, it will react with acid first.

Rxn at first end point: $\text{CO}_3^{2-}(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{HCO}_3^-(\text{aq})$

$$\text{amount of } \text{H}^+ = \frac{8.40}{1000} \times 0.200 = 0.00168 \text{ mol}$$

Since $1 \text{ CO}_3^{2-} \equiv 1 \text{ H}^+$

$$\text{amount of } \text{CO}_3^{2-} \text{ in } 20.0 \text{ cm}^3 \text{ solution} = 0.00168 \text{ mol} \quad [1]$$

$$[\text{Na}_2\text{CO}_3] = 0.00168 \times \frac{1000}{20.0} \times 106 = 8.90 \text{ g dm}^{-3} \quad [1]$$

Rxn at second end point: $\text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{CO}_2 + \text{H}_2\text{O}$

$$\begin{aligned} \text{Vol. of acid reacting with } \text{HCO}_3^- \text{ formed from } \text{CO}_3^{2-} \\ = 8.40 \text{ cm}^3 \end{aligned}$$

$$\begin{aligned} \text{Vol. of acid reacting with } \text{HCO}_3^- \text{ originally in solution} \\ = (18.80 - 8.40) - 8.40 = 2.00 \text{ cm}^3 \end{aligned}$$

$$\begin{aligned} \text{amount of acid reacting} &= \frac{2.00}{1000} \times 0.200 \\ &= 4.00 \times 10^{-4} \text{ mol} \quad [1] \\ &= \text{amount of } \text{HCO}_3^- \text{ originally in solution} \end{aligned}$$

$$\begin{aligned} \therefore [\text{HCO}_3^-] \text{ originally in solution} &= 4.00 \times 10^{-4} \times \frac{1000}{20.0} \times 84.0 \\ &= 1.68 \text{ g dm}^{-3} \quad [1] \end{aligned}$$

OR

$$\begin{aligned} \text{Vol. of acid used to react with total amount of } \text{HCO}_3^- \\ = 18.80 - 8.40 = 10.40 \text{ cm}^3 \end{aligned}$$

$$\begin{aligned} \text{Total amount of acid used} &= \text{Total amount of } \text{HCO}_3^- \text{ present} \\ &= \frac{10.40}{1000} \times 0.200 \\ &= 0.00208 \text{ mol} \end{aligned}$$

At first end point, $1 \text{ CO}_3^{2-} \equiv 1 \text{ HCO}_3^-$

$$\begin{aligned} \text{Amount of } \text{HCO}_3^- \text{ formed from } \text{CO}_3^{2-} &= 0.00168 \text{ mol} \\ \text{original amount of } \text{HCO}_3^- &= 0.00208 - 0.00168 \\ &= 4.00 \times 10^{-4} \text{ mol} \quad [1] \end{aligned}$$

$$\begin{aligned} [\text{HCO}_3^-] \text{ originally in solution} &= 4.00 \times 10^{-4} \times \frac{1000}{20.0} \times 84.0 \\ &= 1.68 \text{ g dm}^{-3} \quad [1] \end{aligned}$$

- 2 (b) (i) It is more difficult/energy required to remove a positively charged H⁺ ion from anion than a neutral molecule due to greater electrostatic attraction. [1]

OR

Doubly charged anion is more unstable than a singly charged anion. [1]

- (ii) A higher pK_{a1} value for succinic acid implies it is the weaker acid than malonic acid, indicating the anion of succinic acid is less stable/anion of tartaric acid is more stable (✓)₁.

Any one of the following reasons:

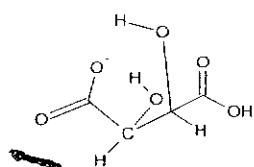
- Two electron-withdrawing -OH groups that helps to disperse the negative charge on O⁻ in the monoanion of tartaric acid (✓)₂, making it more stable.

There is electron-donating alkyl group that intensifies the negative charge on O⁻ in the monoanion of succinic acid, (✓)₃ making it less stable.

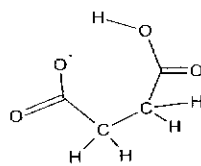
- Monoanion of tartaric acid can form (more extensive) intramolecular hydrogen bonding forming 5- or 6-membered rings. (✓)₂

Monoanion of succinic acid cannot form (have less extensive) intramolecular hydrogen bond as it forms an unstable 7-membered ring. (✓)₃

structural formulae of mono-anions



Monoanion formed from tartaric acid



Monoanion formed from succinic acid

3✓: 2m; 2✓: 1m

- (iii) $\text{HO}_2\text{CCH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2^- + \text{H}^+ \rightarrow \text{HO}_2\text{CCH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2\text{H}$ [1]
 $\text{HO}_2\text{CCH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2^- + \text{OH}^- \rightarrow ^-\text{O}_2\text{CCH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2^- + \text{H}_2\text{O}$ [1]

Accept also :



- 2 (b) (vi) At point X: initial pH of tartaric acid (weak acid)

$$\begin{aligned} [\text{H}^+] &= \sqrt{K_a \times [\text{acid}]} \\ &= \sqrt{(10^{-2.95})(0.20)} \\ &= 0.0150 \text{ mol dm}^{-3} \\ \text{pH} &= -\lg 0.0150 = 1.82 \quad [1] \end{aligned}$$

At point Y: pH of amphiprotic species $^-\text{O}_2\text{C}(\text{CH}(\text{OH}))_2(\text{CO}_2\text{H})$

$$\begin{aligned} \text{pH} &= \frac{1}{2}(pK_{a1} + pK_{a2}) \\ &= \frac{1}{2}(2.95 + 4.25) = 3.60 \quad [1] \end{aligned}$$

At point Z: solution is at maximum buffering capacity when $[\text{O}_2\text{C}(\text{CH}(\text{OH}))_2(\text{CO}_2\text{H})] = [\text{O}_2\text{C}(\text{CH}(\text{OH}))_2(\text{CO}_2^-)]$

$$\text{pH} = pK_{a2} = 4.25 \quad [1]$$

- (c) (i) D: $\text{CH}_2=\text{CHCO}_2\text{H}$ [1]



- (ii) Step II: $\text{Br}_2(\text{aq})$ [1]



- (iii) Use aqueous bromine to test the reaction mixture. [1]

If aqueous bromine remains orange, reaction is complete. / If orange aqueous bromine decolourises, reaction is incomplete. [1]

[Total: 20]

- 3 (a) (i) NaOH is required to generate the nucleophile CN^- . [1]

HCN is a weak acid/ionises only partially. Thus $[\text{CN}^-]$ is low and reaction is slow. [1]

- (ii) Comparing experiments 1 and 2:

When $[\text{CH}_3\text{CHO}]$ increases by 2x, rate increases by 2x
 $\rightarrow \text{rate} \propto [\text{CH}_3\text{CHO}]$

\therefore order of reaction wrt CH_3CHO is 1. [1]

Comparing experiments 1 and 3:

Let rate = $k[\text{CH}_3\text{CHO}][\text{NaOH}]^a$

$$\frac{1.15 \times 10^{-14}}{6.90 \times 10^{-14}} = \frac{k(1.25 \times 10^{-2})(1.25 \times 10^{-4})^a}{k(3.75 \times 10^{-2})(2.50 \times 10^{-4})^a}$$

$\therefore a =$ order of reaction wrt NaOH = 1 [1]

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- 3 (b) (i) The rate equation defines the slow step and shows that there is only 1 molecule of carbonyl compound and one CN^- involved.

Hence, the rate-determining step is Step 1.

- (ii) The bigger K_c value indicates position of equilibrium to form the cyanohydrin compound lies more to the right, compound is more susceptible to nucleophilic substitution. [1]

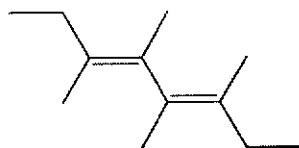
Comparing reactions I and II:

The electron donating $-\text{CH}_3$ group make the carbonyl C less electron deficient, thus less susceptible to nucleophilic attack. [1]

Comparing reactions I and III:

The electron withdrawing/electronegative $-\text{Cl}$ group makes the carbonyl C more electron deficient, thus more susceptible to nucleophilic attack. [1]

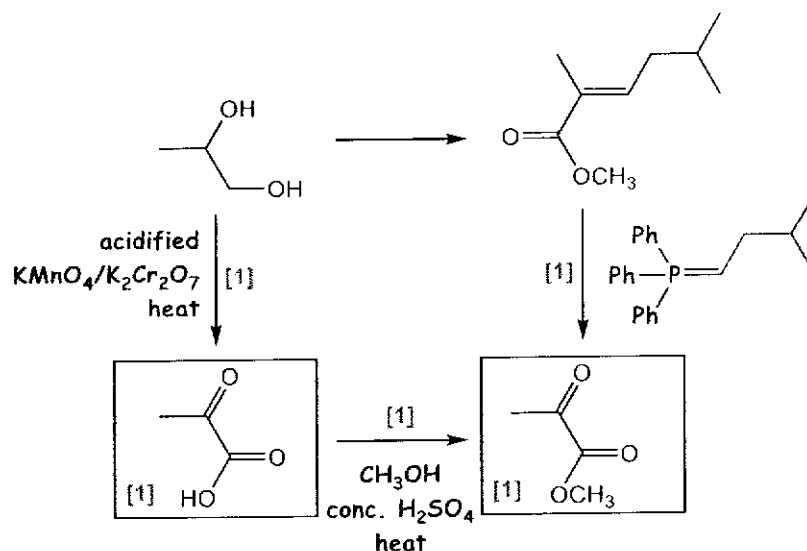
- (c) (i) The product formed:



[1]

Since the product has two $\text{C}=\text{C}$ double bonds, total number of isomers formed $2^2 = \underline{4}$. [1]

- (ii)



- (iii) There is less steric hindrance from the primary alkyl halide compared to a secondary alkyl halide. [1]

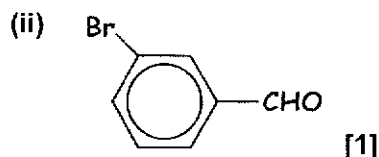
OR

There is one less electron-donating alkyl group in the primary alkyl halide hence the C is less δ^+ and is more susceptible to nucleophilic attack. [1]

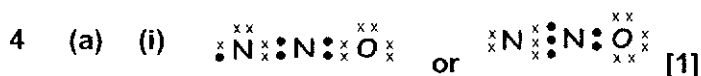
3 (c) (iv) N cannot expand octet/have more than 8 valence electrons because N does not have energetically accessible/low-lying vacant (3)d orbitals to accept the electrons. [1]

(d) (i) The tertiary carbocation formed/one more electron-donating CH₃ group attached to the C⁺ (✓) when the Br⁺ electrophile is substituted at the 2- and 4-positions is more stable (✓) as the the positive charge on C⁺ is more dispersed (✓), stabilising the carbocation.

3✓: 2m; 2✓: 1m



[Total: 20]



(ii) CO₂ has lower boiling point. (✓)

Both have simple covalent structure. However, more energy (✓) is required to overcome the stronger permanent dipole-permanent dipole attractions between N₂O molecules (✓) compared to the weaker instantaneous dipole-induced dipole attractions between CO₂ molecules. (✓)

4✓: 2m; 2-3✓: 1m

(b) (i) Considering the spontaneity of the two reactions using the relationship $\Delta G = \Delta H - T\Delta S$

$$\text{For reaction 2: } \Delta G = \underbrace{\Delta H}_{-ve} - T \underbrace{\Delta S}_0$$

ΔS for reaction 2 is negligible/approximately zero since there is (no change in the number of moles of gas). As such, the reaction is enthalpy driven. Since ΔH is negative, ΔG is always negative. Thus, lowering temperature will have no impact on ΔG for reaction 2. [1]

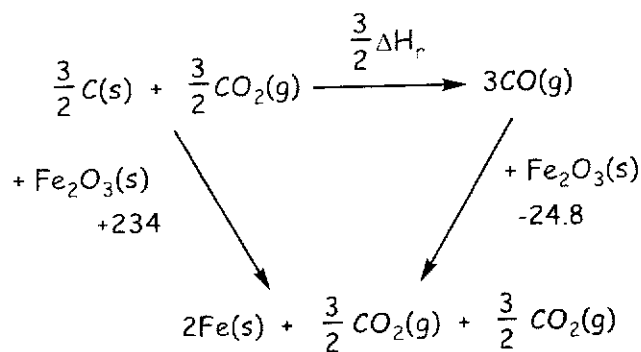
$$\text{For reaction 1: } \Delta G = \underbrace{\Delta H}_{+ve} - T \underbrace{\Delta S}_{+ve}$$

ΔS for reaction 1 is positive since there is (an increase in the number of moles of gas). However, since ΔH is positive, the reaction is only spontaneous at high temperatures. [1]

As such, at lower temperatures, reaction 2 is favoured. [1]

For
Examiner's
Use

(ii)



$$\begin{aligned}
 \therefore \Delta H_r &= \frac{2}{3} \times [(+234) - (-24.8)] && [1] \text{ - or from balanced cycle} \\
 &= \underline{+173 \text{ kJ mol}^{-1}} && [1]
 \end{aligned}$$

(c) (i)

$$\text{amount of } H_2 = \frac{38.0}{2} = 19.0 \text{ mol}$$

$$\text{amount of } CO = \frac{462}{28} = 16.5 \text{ mol}$$

$$\text{amount of } CH_3OH = \frac{7200}{32} = 225 \text{ mol}$$

$$\therefore \text{Total amount of gas} = 19.0 + 16.5 + 225 = \underline{260.5 \text{ mol}} \quad [1]$$

$$\text{mole fraction of } H_2 = \frac{19.0}{260.5} = \underline{0.0729}$$

$$\text{mole fraction of } CO = \frac{16.5}{260.5} = \underline{0.0633}$$

$$\text{mole fraction of } CH_3OH = \frac{225}{260.5} = \underline{0.864}$$

[1]

(ii)

$$K_p = \frac{P_{CH_3OH}}{(P_{CO})(P_{H_2})^2} \quad [1]$$

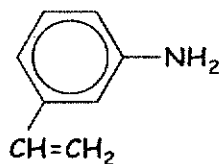
$$= \frac{0.864 \times 7500}{(0.0633 \times 7500)(0.0729 \times 7500)^2}$$

$$= \underline{4.57 \times 10^{-11} \text{ kPa}^{-2}} \quad [1] \text{ - units}$$

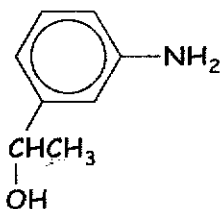
4 (d)

	Type of reaction	Deductions
J has MF C_8H_9N		$C:H \approx 1:1$, <u>benzene ring present in J</u> (✓) – mark under phenylamine.
J is soluble in dilute HCl	<u>Acid-base</u> (✓)	<u>J is an amine</u> (✓).
J reacted with steam in the presence of catalyst at high temp. and pressure	<u>Electrophilic addition</u> (✓a)	<u>J contains an alkene</u> (✓b). <u>L and M are alcohols</u> (✓).
J reacts with 4 mol of $Br_2(aq)$	<u>Electrophilic addition</u> (✓a) <u>Electrophilic substitution</u> (✓)	<u>J contains an alkene</u> (✓b). <u>J is phenylamine</u> (✓). 2,4,6-position relative to amine group is unsubstituted
L is optically active		<u>L contains a chiral C</u> (✓).
L reacts with alkaline $I_2(aq)$	<u>Triiodomethane / Iodoform test / oxidation</u> (✓)	<u>L contains $-CH(OH)CH_3$</u> (✓)
J, L and M reacts with acidified $KMnO_4$ to form Q $C_7H_8O_2N$	<u>oxidation</u> (✓)	<u>Q contains $-CO_2H$ group / benzoic acid</u> (✓)
Q $C_7H_8O_2N$ (crystalline solid)	<u>Intra-molecular acid-base</u> (✓)	<u>Q is a ionic salt</u> (✓)

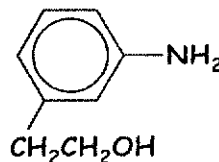
15-12 ✓: 5m; 10-11 ✓: 4m; 7-9 ✓: 3m; 4-6 ✓: 2m; 2-3 ✓: 1m



compound J [1]

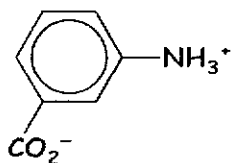


compound L



compound M

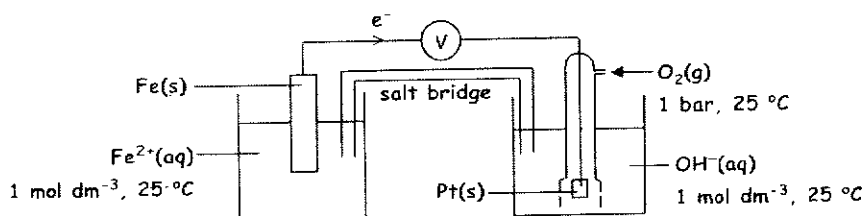
[1]



compound Q [1]

[Total: 20]

5 (a) (i)

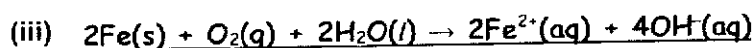
[1] for each correctly drawn half-cell *mark for temp only once

[1] for salt bridge and voltmeter

[1] for electron flow

Minus 1m if "1 mol dm⁻³ H₂O" is stated

(ii)
$$E_{\text{cell}}^{\ominus} = +0.40 - (-0.44) = +0.84 \text{ V}$$

Do not accept if "Fe(OH)₂" is used to balance eqn

(iv)
$$\Delta G = -nFE = -(4)(96500)(+0.84) = -324000 \text{ J mol}^{-1}$$
$$= -324 \text{ kJ mol}^{-1} \quad [1]$$

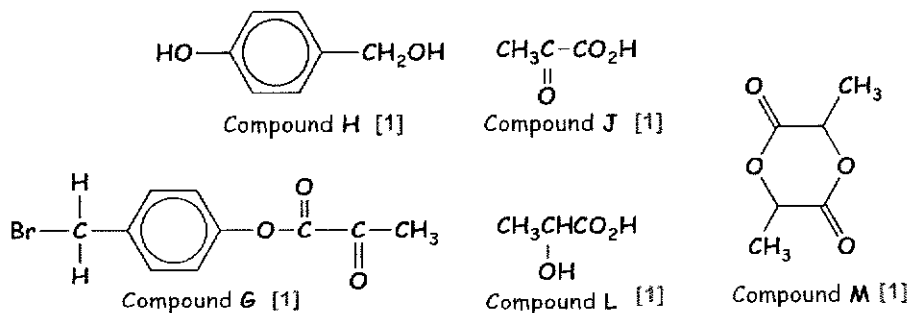
Since $\Delta G < 0$, reaction is energetically feasible. [1](v) NaOH reacts with Fe²⁺ to form Fe(OH)₂ that reduces [Fe²⁺]. (✓)This causes the position of equilibrium for Fe²⁺ + 2e⁻ ⇌ Fe to shift left (✓), E(Fe²⁺/Fe) to be less positive and thus E_{cell} to be more positive. (✓)This will result in a more negative ΔG value, thus reaction becomes more feasible. (✓)

4✓: 2m; 2-3✓: 1m

(b)

	Type of reaction	Deductions
G boiled with NaOH gives H and J	Alkaline hydrolysis (✓) Nucleophilic substitution (✓)	G is an ester (✓) G is an alkyl halide (✓)
H $C_7H_8O_2$ forms violet colouration with neutral ferric chloride		C:H \approx 1:1, <u>benzene ring present in H</u> (✓) – mark under phenol. H is a phenol (✓)
1 mole of H reacts with 2 moles of Br_2 to form a symmetrical product.	Electrophilic substitution (✓)	H is 1,4-disubstituted (✓)
J + $NaHCO_3$ forms gas	Acid-carbonate reaction (✓)	J is a carboxylic acid (✓)
J + aq. alkaline I_2 gives yellow ppt and K	Iodoform test (✓)	J contains $-CH(OH)CH_3$ or $-COCH_3$ group (✓)
J heated with $H_2(g)$ and Ni forms L	Reduction (✓)	J is a ketone (✓) L is an alcohol (✓)
Heat L in acid catalyst forms M	condensation (✓)	M is an ester (✓)

14-17 ✓: 5m; 10-13 ✓: 4m; 7-9 ✓: 3m; 4-6 ✓: 2m; 2-3 ✓: 1m



[Total: 20]

