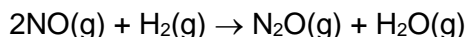


2016 H2 Chemistry Prelim Exam Paper 3 Suggested Answers

- 1 (a) At high temperatures NO reacts with H₂ to produce nitrous oxide, N₂O, a greenhouse gas.



To study the kinetics of this reaction at 820 °C, initial rates for the formation of N₂O were measured using various initial partial pressures of NO and H₂.

Experiment	Initial pressure / kPa		Initial rate of production of N ₂ O / kPa s ⁻¹
	P_{NO}	P_{H_2}	
1	16	8	1.15×10^{-2}
2	8	8	2.87×10^{-3}
3	8	24	8.60×10^{-3}

- (i) Deduce the rate equation in terms of partial pressure. [3]

Comparing expts 2 and 3,
 Rate increases by 3 times when the P_{H_2} increases by 3 times.
 Order of reaction with respect to H₂ is 1.
 Comparing expts 1 and 2,
 Rate increases by 4 times when P_{NO} increases by 2 times.
 Order of reaction with respect to NO is 2.
 Hence rate = $k(P_{\text{NO}})^2 P_{\text{H}_2}$

- (ii) Using the rate equation and the information in the table above, calculate a value for the rate constant, giving its units. [2]

Using data from expt 1:
 $1.15 \times 10^{-2} = k(16)^2(8)$
 $k = 5.62 \times 10^{-6}$
 unit = (kPa)⁻² s⁻¹

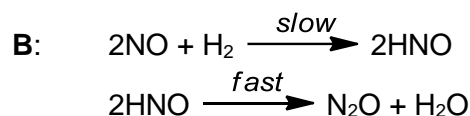
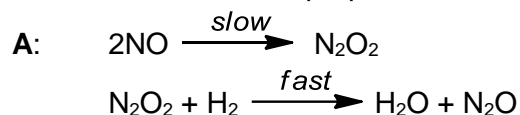
- (iii) Hence, calculate the initial rate at which NO reacts when 25 kPa of NO and 12.5 kPa of H₂ are mixed at 820 °C. [1]

rate = $5.62 \times 10^{-6} \times 25^2 \times 12.5 = 4.39 \times 10^{-2} \text{ kPa s}^{-1}$ (ecf)
 rate of disappearance of NO = $2 \times 4.39 \times 10^{-2} = 8.78 \times 10^{-2} \text{ kPa s}^{-1}$

- (iv) Write the rate equation for the reaction when NO is used in large excess. Hence, determine the time elapsed to reduce the partial pressure of H₂ to half of its initial value, if 100 kPa of NO and 1 kPa of H₂ are mixed at 820 °C. [3]

Rate = $k'P_{\text{H}_2}$
 Since $P_{\text{NO}} \gg P_{\text{H}_2}$,
 $k' = k(P_{\text{NO}})^2$
 $= 5.62 \times 10^{-6} \times (100)^2$ (ecf)
 $= 5.62 \times 10^{-2}$
 $t_{1/2} = \ln 2 / k'$
 $= 12.3 \text{ s}$

(v) Two mechanisms, **A** and **B** are proposed below.



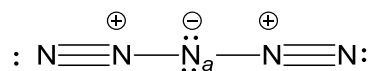
Which mechanism is consistent with the rate equation obtained in (a)(i). Explain your answer. [1]

B

The molecularity of the reactants in the slow step is 2 with respect to NO and 1 with respect to H₂. It is consistent with the experimentally-determined order of reaction with respect to each reactant.

(b) Polynitrogen compounds have great potential for being used as high energy density materials. They are thermodynamically unstable. Huge amounts of energy are released from their decomposition or reactions leading to more stable products.

(i) The polynitrogen species, N₅⁺ was first isolated in 1999. One of its resonance forms is shown below.



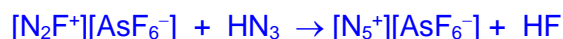
State the bond angle and molecular shape around nitrogen labelled a. [1]

Bond angle: any value between 105° and 109°

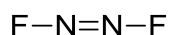
Shape: bent

(ii) The synthesis of a white ionic solid, [N₅⁺][AsF₆⁻], was achieved by reacting [N₂F⁺][AsF₆⁻] with hydrazoic acid, HN₃, in liquid HF at -78 °C.

Write a balanced equation for this reaction. [1]

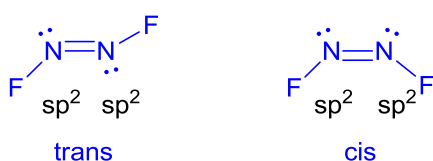


(iii) [N₂F⁺][AsF₆⁻] was first prepared by reacting N₂F₂ with the strong Lewis acid, AsF₅. N₂F₂ has the following structure and exhibits cis-trans isomerism.



Draw the cis-trans isomers of N₂F₂, including all lone pairs and suggest an appropriate hybridisation for each nitrogen atom in N₂F₂.

[2]



All lone pairs shown
All sp² correctly labelled

- (c) Nitrogen is found in all organisms, primarily in amino acids which made up proteins.

Isoleucine, $\text{NH}_2\text{CH}(\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3)\text{CO}_2\text{H}$ is an α -amino acid where the amino group and carboxylic acid group are separated by one carbon. It is a constituent amino acid in many protein molecules. Isoleucine can exist as different stereoisomers.

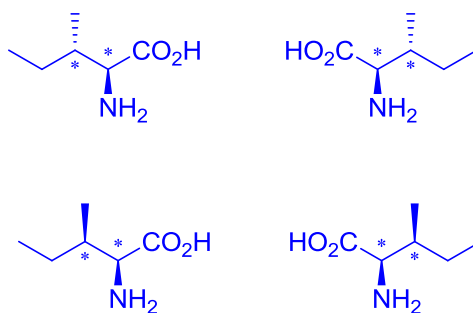
- (i) State the reagents and conditions needed to break protein down into its constituent amino acids. [1]

$\text{H}_2\text{SO}_4(\text{aq})$ or $\text{NaOH}(\text{aq})$
Heat

- (ii) Define the term *stereoisomers*. [1]

Molecules with same structural formula but different arrangement of atoms in space.

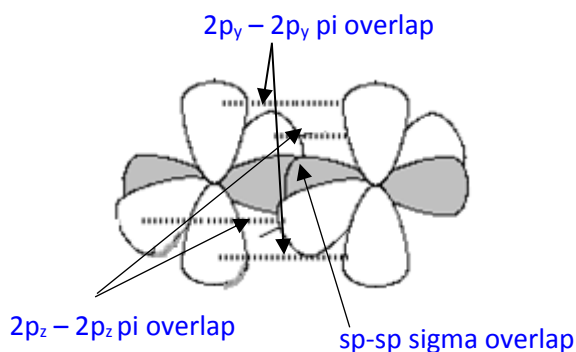
- (iii) There are four optical isomers of isoleucine. Draw the structures of these four stereoisomers of isoleucine, indicating clearly the chiral centres. [2]



Two chiral centres correctly labelled in one structure

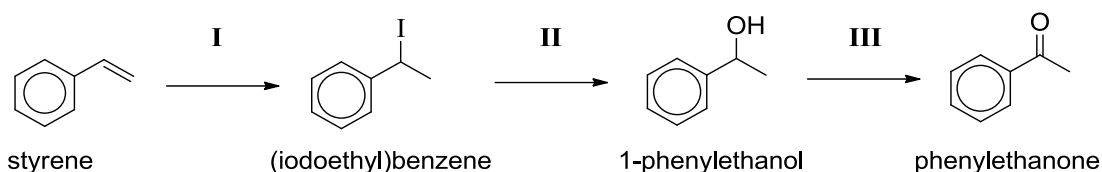
- (d) 3-amino-3-methyl-1butyne, $\text{CH}\equiv\text{CCNH}_2(\text{CH}_3)_2$ is used as the starting material to make other chemicals.

Draw a labelled diagram to show the orbitals that form $\text{C}\equiv\text{C}$ in an alkyne. [2]



[Total: 20]

- 2 (a) Styrene (phenylethene) is a useful organic intermediate used for the synthesis of many products. For instance, styrene is able to undergo the reaction shown below:



- (i) State the reagents and conditions required for reactions I, II and III. [3]

I: HI(g) , room temperature
(ignore state symbol unless it's given as aqueous state)

II: NaOH(aq) , heat

III: $\text{K}_2\text{Cr}_2\text{O}_7\text{(aq)}$, $\text{H}_2\text{SO}_4\text{(aq)}$, heat

- (ii) By considering the substituent(s) attached to the carbonyl group, give two reasons for the lower reactivity of phenylethanone towards nucleophiles compared to propanone, CH_3COCH_3 . [2]

Steric hindrance of the bulky phenyl group makes it harder for the nucleophile to approach.

The p-orbitals of the carbonyl carbon overlap with the π orbitals of the benzene ring OR Electrons from the benzene ring delocalise to the carbonyl carbon, making it less electron-deficient and hence less susceptible to nucleophilic attack.

- (iii) Suggest a simple chemical test to distinguish between (iodoethyl)benzene and iodobenzene, $\text{C}_6\text{H}_5\text{I}$. State the observations for each compound. [2]

NaOH(aq) , heat,
followed by excess $\text{HNO}_3\text{(aq)}$ and $\text{AgNO}_3\text{(aq)}$
(iodoethyl)benzene forms yellow precipitate
iodobenzene does not form yellow precipitate

- (iv) The solubility of (iodoethyl)benzene in water was found to be 32.1 mg dm^{-3} . Explain why (iodoethyl)benzene has such a low solubility in water. [2]

The predominant interactions between (iodoethyl)benzene molecules are dispersion forces.

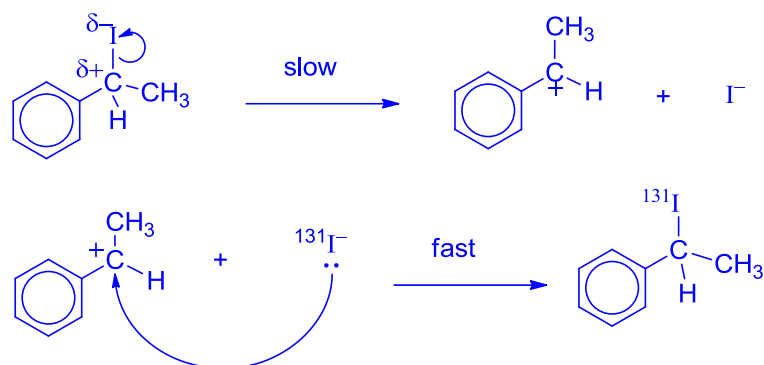
Weak dipole-induced dipole interactions formed between (iodoethyl)benzene and water release insufficient energy to overcome the strong hydrogen bonding in water.

- (b) (Iodoethyl)benzene exists as a pair of enantiomers **A** and **B**.

An optically pure sample containing only isomer **A** dissolved in hexane underwent a nucleophilic substitution reaction with a solution containing radioactive iodide ions, $^{131}\text{I}^-$. After the reaction, 75% of the (iodoethyl)benzene is incorporated with radioactive iodide.

An investigation into the kinetics of the reaction revealed that the rate of reaction was independent of the concentration of $^{131}\text{I}^-$.

- (i) Describe the mechanism for the reaction of (iodoethyl)benzene with $^{131}\text{I}^-$. In your answer, clearly label the ^{131}I , and include any relevant charges, curly arrows and dipoles or lone pairs of electrons that you consider important in this mechanism. [2]

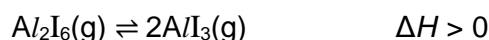


- (ii) Calculate the percentage of (iodoethyl)benzene that exists as enantiomer **B** incorporated with ^{131}I in the product mixture. [1]

Since 75% of **A** reacted, 25% of **A** remained unreacted.
percentage of enantiomer **B** = $75 / 2$
= 37.5%

- (c) The term 'tri-iodide' refers to molecules that contain three iodine atoms in their molecular formula, such as nitrogen tri-iodide, NI_3 , and aluminium tri-iodide, AlI_3 .

AlI_3 has a simple molecular structure. In the gas phase, it dimerises readily to form the dimer Al_2I_6 . The two species are related by the equilibrium shown below.



- (i) A 10.0 g sample of Al_2I_6 was allowed to vapourise in a 2 dm^3 vessel at 400°C . Calculate the initial pressure of Al_2I_6 . [2]

$$\begin{aligned} P_{\text{Al}_2\text{I}_6} &= \frac{nRT}{V} \\ &= \frac{\left(\frac{10.0}{816}\right)(8.31)(673)}{2 \times 10^{-3}} \\ &= 34300 \text{ Pa} \end{aligned}$$

- (ii) Given that the degree of dissociation (α) of Al_2I_6 was 0.35, find the K_p value for the equilibrium at 400°C . [2]

$$\begin{aligned} P_{\text{Al}_2\text{I}_6} \text{ (after dissociation)} &= 0.65 \times 34300 \text{ (ecf)} \\ &= 22300 \text{ Pa} \\ P_{\text{AlI}_3} &= 2 \times 0.35 \times 34300 \text{ (ecf)} \\ &= 24000 \text{ Pa} \\ K_p &= \frac{(P_{\text{AlI}_3})^2}{P_{\text{Al}_2\text{I}_6}} = \frac{24000^2}{22300} \\ &= 25800 \text{ Pa} \end{aligned}$$

- (iii) Explain the effect on the degree of dissociation of Al_2I_6 for each of the changes below.

- The reaction was carried out at 300°C .
- A sample of $\text{Ar}(\text{g})$ was introduced into a 1 dm^3 vessel containing $\text{AlI}_3(\text{g})$ and $\text{Al}_2\text{I}_6(\text{g})$ at 400°C . [2]

When the temperature is decreased, the backward exothermic reaction is favoured. Hence, the position of equilibrium will shift to the left and degree of dissociation decreases.

While total pressure in the vessel increases as number of moles of gases increases with injection of inert Ar(g), mole fraction and partial pressure of the $\text{Al}_3(\text{g})$ and $\text{Al}_2\text{I}_6(\text{g})$ remain constant. Hence there is no shift in the position of equilibrium and no change in the degree of dissociation.

- (d) The table below shows the boiling points of PCl_3 and PF_5 .

Compound	Boiling Point / °C
PCl_3	76.1
PF_5	– 84.6

Explain why PCl_3 has a higher boiling point than PF_5 .

[2]

PCl_3 molecules are held by dipole-dipole interactions, PF_5 molecules are held by dispersion forces. Hence more energy is needed to overcome the stronger dipole-dipole interactions in PCl_3 .

[Total: 20]

- 3 (a) Lead(II) nitrate decomposes on heating in the same way as magnesium nitrate. By using relevant data from the *Data Booklet*, predict and explain which of the two nitrates, lead(II) nitrate or magnesium nitrate, would have a higher decomposition temperature. [2]

$\text{Pb}(\text{NO}_3)_2$ has the higher decomposition temperature.
Both Mg^{2+} and Pb^{2+} have the same ionic charge (2+) but ionic radius of Pb^{2+} is larger than that of Mg^{2+}
Charge density of Pb^{2+} is lower (or polarising power of Pb^{2+} is lower)
Electron cloud of NO_3^- is distorted to a smaller extent by Pb^{2+}
 $\Rightarrow \text{Pb}(\text{NO}_3)_2$ has a higher thermal stability and thus a higher decomposition temperature.

- (b) The halogens are reactive elements and are involved in many reactions.

- (i) When chlorine is bubbled through cold sodium hydroxide solution, followed by an excess of acidified silver nitrate solution, only $\frac{1}{2}$ of the chlorine which has dissolved is precipitated as silver chloride. When the sodium hydroxide solution is hot, up to $\frac{5}{6}$ of the chlorine can be precipitated. Explain the observations with the aid of relevant equations. [3]

Precipitation: $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$

With cold $\text{NaOH}(\text{aq})$:

$\text{Cl}_2(\text{g}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{NaClO}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

Molar ratio of $\text{Cl}^- : \text{ClO}^- = 1:1$

$\frac{1}{2}$ of the chlorine is precipitated as AgCl .

With hot NaOH(aq):



Molar ratio of $\text{Cl}^- : \text{ClO}_3^- = 5:1$

$\frac{5}{6}$ of the chlorine is precipitated as AgCl.

- (ii) When chromium is made to react with chlorine, the main product of the reaction is CrCl_3 . However, when chromium is made to separately react with other halogens such as fluorine and iodine, the main products are CrF_4 and CrI_2 . By reference to relevant E^\ominus values, what can you conclude about the relative oxidising ability of the halogens? [2]

Correct E^\ominus data for F_2 , Cl_2 and I_2



Oxidising power: $\text{F}_2 > \text{Cl}_2 > \text{I}_2$ as $E^\ominus(\text{X}_2/\text{X}^-)$ is less positive down the group.

Correct O.N. of Cr in all three compounds

F_2 is the strongest oxidising agent and oxidises Cr to CrF_4 , where the oxidation state of Cr in CrF_4 is +4.

Cl_2 is less oxidising than F_2 and oxidises Cr to CrCl_3 , where the oxidation state of Cr in CrCl_3 is +3.

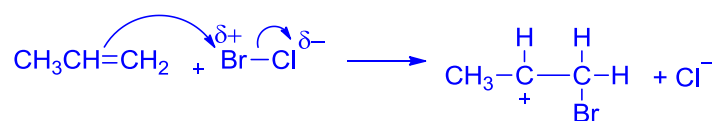
Iodine is the weakest oxidising agent and oxidises Cr to CrI_2 , where the oxidation state of Cr in CrI_2 is +2.

The halogens also form many interhalogen compounds in which two different halogens are combined. Interhalogen compounds like BrCl have similar properties to the halogens.

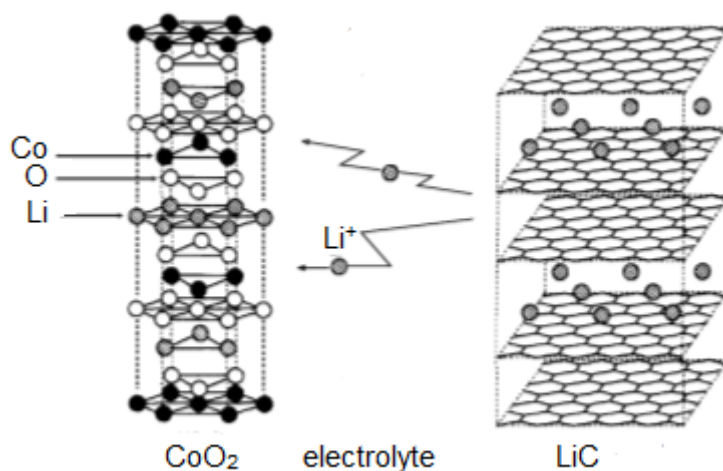
- (iii) Suggest an equation for the reaction that occurs between BrCl and aqueous KI. [1]



- (iv) BrCl reacts with alkenes faster than the pure halogens such as Cl_2 and Br_2 . Show the slow step of the reaction between BrCl and propene. [1]



- (c) A lithium-ion battery is a rechargeable battery. In a fully charged battery, lithium ions occupy the tiny spaces in graphite to form LiC . During discharge, lithium ions are produced which migrate through the electrolyte while at the same time, graphite is being regenerated. In the other electrode, lithium ions react with CoO_2 to form LiCoO_2 .



- (i) Write equations for the electrode reactions occurring at the anode and cathode during discharge. [2]



- (ii) Hence, write an equation for the overall reaction that occurs during discharge. [1]

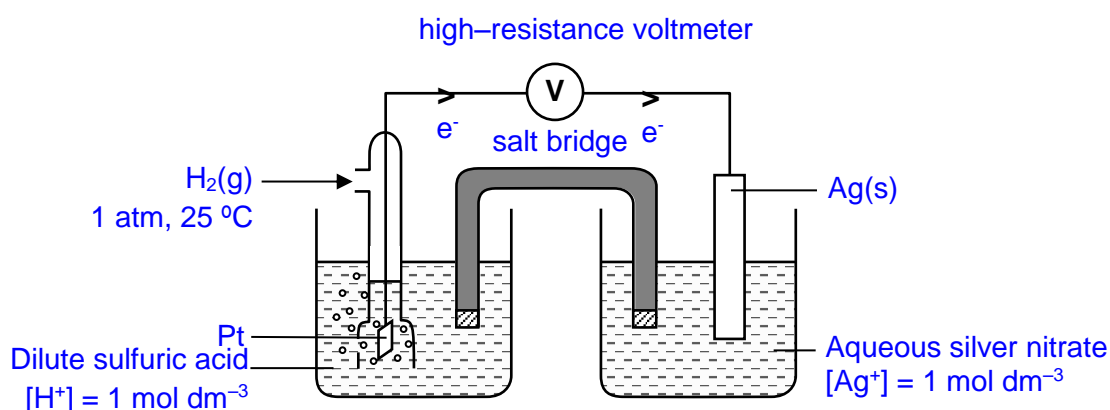


- (iii) By determining the oxidation numbers of the relevant elements, identify the elements that have been oxidised and reduced. [1]

C is oxidised as O.N. increased from -1 in LiC to 0 in C.

Co is reduced as O.N. decreased from +4 in CoO₂ to +3 in LiCoO₂.

- (d) (i) With reference to the *Data Booklet*, draw a fully labelled diagram showing how you could measure the standard electrode potential for the Ag⁺/Ag system. Indicate the direction of electron flow. [2]



- (ii) The electrode potential, E and the concentration of silver ions in solution under non-standard conditions are related by the following equation.

$$E = 0.80 - 0.03 \lg \frac{1}{[\text{Ag}^+(\text{aq})]^2}$$

The solubility product constant of AgCl is $K_{\text{sp}} = 1.8 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$. Using the equation given above, calculate the electrode potential at 298 K of a half-cell formed by

- (I) a Ag electrode immersed in a saturated solution of AgCl .

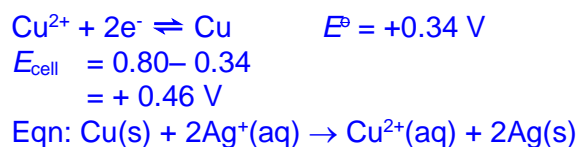
$$\begin{aligned} [\text{Ag}^+] &= \sqrt{1.8 \times 10^{-10}} \\ &= 1.3 \times 10^{-5} \text{ mol dm}^{-3} \\ E &= 0.80 - 0.03 \lg \frac{1}{(1.3 \times 10^{-5})^2} \\ &= +0.51 \text{ V} \end{aligned}$$

- (II) a Ag electrode immersed in a 0.5 mol dm^{-3} solution of KCl containing some AgCl precipitate.

$$\begin{aligned} [\text{Ag}^+] &= \frac{1.8 \times 10^{-10}}{0.5} \\ &= 3.6 \times 10^{-10} \text{ mol dm}^{-3} \\ E &= 0.80 - 0.03 \lg \frac{1}{(3.6 \times 10^{-10})^2} \\ &= +0.23 \text{ V} \end{aligned}$$

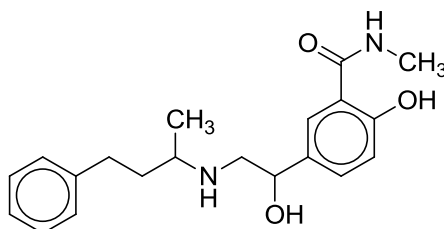
[3]

- (iii) A cell is made by connecting the half-cell in (d)(i) to a standard Cu^{2+}/Cu half-cell. By reference to relevant data from the Data Booklet, calculate the cell emf and write an equation (with state symbols) for the reaction that has occurred. [2]



[Total: 20]

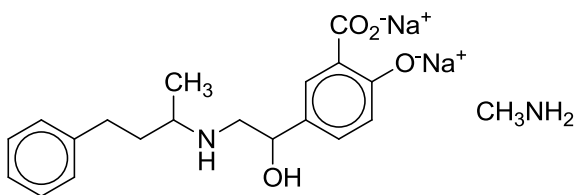
- 4 (a) Compound **G** has the structure shown.



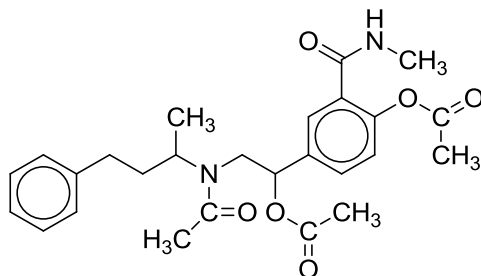
Give the structures of the organic compounds formed by compound **G** under the following conditions.

(i) NaOH(aq), reflux

[2]

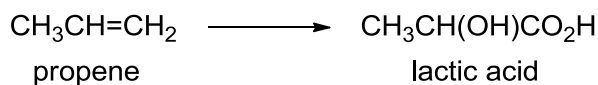
(ii) Excess CH_3COCl , room temperature

[2]



(b) Lactic acid can be used in food products as pH regulators or as a food preservative. It can also be used as a flavouring agent.

(i) Suggest reagents and conditions needed to convert propene into 2-hydroxypropanoic acid (commonly known as lactic acid) in no more than 3 steps. Give the structures of the intermediates.

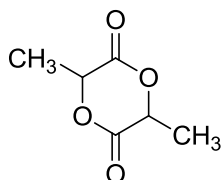


[3]

Step I: Cold KMnO_4 / NaOH(aq) Step II: $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{H}_2\text{SO}_4(\text{aq})$, refluxStep III: $\text{NaBH}_4(\text{alc})$, reflux

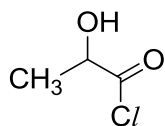
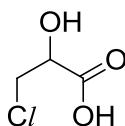
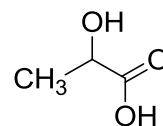
(ii) When lactic acid is refluxed with concentrated sulfuric acid, compound **H** with the molecular formula of $\text{C}_6\text{H}_8\text{O}_4$ is formed. It does not react with sodium. Give the structural formula of **H**.

[1]



(iii) Describe and explain the relative acidity of the following three compounds.

[2]

**A****B**

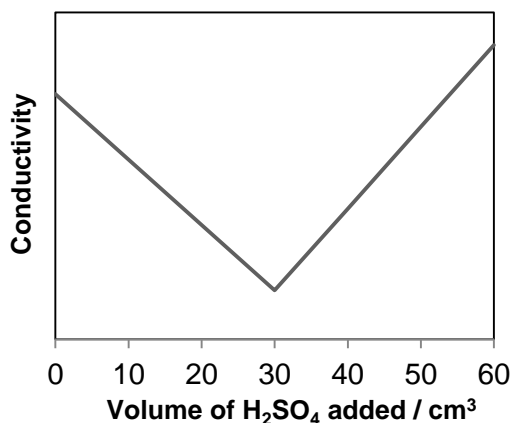
lactic acid

Compound **A** is the most acidic and lactic acid is the least acidic.

A contains the acyl chloride which hydrolyses readily in water to produce a strong acid HCl.

Presence of Cl atom in **B** exerts an electron-withdrawing inductive effect which produces a more stable anion than the anion formed from lactic acid.

- (c) Experiment 1 is conducted in which the conductivity of 25 cm³ of Ba(OH)₂ solution is monitored as it is titrated with 0.10 mol dm⁻³ of aqueous H₂SO₄. The data collected from the experiment is plotted in the graph below.



- (i) The conductivity of the Ba(OH)₂ solution decreases as the volume of 0.10 mol dm⁻³ H₂SO₄ is added from 0 cm³ to 30 cm³.

Identify the chemical species that enable the solution to conduct electricity as the first 30 cm³ of H₂SO₄ (aq) is added. Hence explain why the conductivity decreases. [2]

Species: Ba²⁺(aq) and OH⁻(aq)

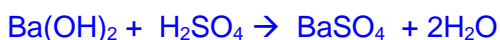
As the titration proceeds before the equivalence point,

OH⁻(aq) is removed by neutralisation to form H₂O(l).

Ba²⁺(aq) is removed by precipitation to form BaSO₄(s).

Thus there are less mobile charge carriers, and conductivity decreases.

- (ii) Using the information in the graph, calculate the initial concentration of Ba(OH)₂. [1]



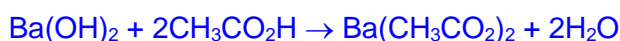
$$n_{\text{Ba(OH)}_2} = n_{\text{H}_2\text{SO}_4}$$

$$\text{No. of moles of Ba(OH)}_2 = 30/1000 \times 0.10 \\ = 0.003 \text{ mol}$$

$$\text{Concentration of Ba(OH)}_2 = 0.003 / 0.025 \\ = 0.12 \text{ mol dm}^{-3}$$

- (d) In Experiment 2, another 25 cm³ sample of 0.10 mol dm⁻³ aqueous Ba(OH)₂ is mixed with 80 cm³ of 0.10 mol dm⁻³ of ethanoic acid to form solution **A**. Barium ethanoate, Ba(CH₃CO₂)₂ is the product of the reaction. The acid dissociation constant, *K*_a, of ethanoic acid is 1.7 × 10⁻⁵ mol dm⁻³. Calculate the pH of the solution **A**. [3]

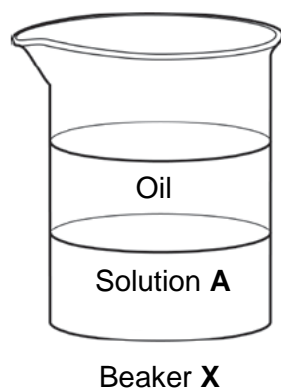
$$K_a = [\text{H}^+] [\text{CH}_3\text{CO}_2^-] / [\text{CH}_3\text{CO}_2\text{H}]$$



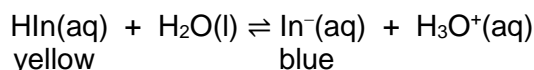
$$\text{New } [\text{CH}_3\text{CO}_2\text{H}] = (80 - 50)/1000 \times 0.10 / 0.105$$

$$\begin{aligned}
 &= 0.0286 \text{ mol dm}^{-3} \\
 \text{New } [\text{CH}_3\text{CO}_2^-] &= 2 \times 25/1000 \times 0.10 / 0.105 \\
 &= 0.0476 \text{ mol dm}^{-3} \\
 0.0476[\text{H}^+]/0.0286 &= 1.7 \times 10^{-5} \\
 [\text{H}^+] &= 1.02 \times 10^{-5} \text{ mol dm}^{-3} \\
 \text{pH} &= -\lg(1.02 \times 10^{-5}) \\
 &= 4.99
 \end{aligned}$$

- (e) Half of the solution **A** formed in (d) is added to beaker **X** where there is a layer of colourless oil as shown in the figure below.



The indicator HIn is a weak acid with a $\text{p}K_{\text{a}}$ value of 6.0. It reacts with water as represented in the equation below.



A small amount of indicator HIn is added into beaker **X**. The mixtures are stirred well and the two layers are allowed to separate.

Assume the pH of solution **A** is unaffected by the presence of colourless oil.

- (i) State the colour observed in the oil layer of beaker **X**. Explain the observation in terms of acid-base equilibrium and inter-molecular interactions.

[2]

The oil layer is yellow in colour.

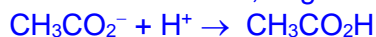
Solution **A** is of pH 4.99, acid form of indicator HIn(aq) predominates since $\text{pH} < \text{p}K_{\text{a}}$. Since HIn is a neutral (uncharged) molecule, some of it can dissolve better in the oil layer because of dispersion forces (or dipole-induced dipole or dipole-dipole interactions) with the oil molecules

- (ii) A few drops of aqueous sodium hydroxide and hydrochloric acid are added to the beaker **X** successively and stirred well. Explain with the aid of equation(s) why there is no change in the colour of the oil layer after each addition. [2]

On addition of NaOH, large reservoir of $\text{CH}_3\text{CO}_2\text{H}$ removes the OH^- added.



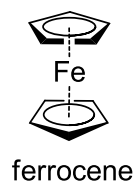
On addition of HCl, large reservoir of CH_3CO_2^- removes the H^+ added.



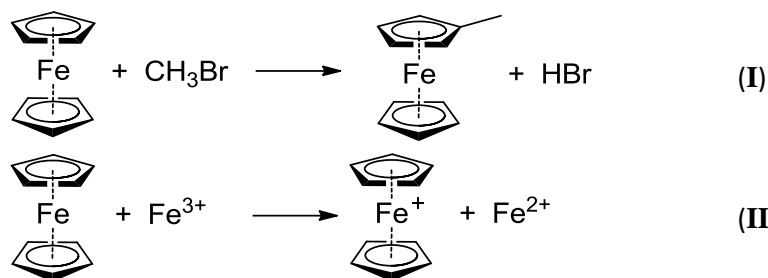
$[\text{H}^+]$ remains unchanged, the HIn form still predominates and is soluble in the oil layer

[Total: 20]

- 5 (a) Ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$, is an orange solid. In this complex, C_5H_5^- is the ligand and it donates π electrons from the ring to the vacant 3d orbital of Fe. The structure of ferrocene is given below.



Ferrocene can undergo a series of different reactions and some are analogues of organic reactions. Two reactions of ferrocene are shown below:



- (i) State the types of reaction for reactions I and II. [1]

I: electrophilic substitution

II: redox

- (ii) State the oxidation number of Fe in ferrocene and hence its electronic configuration. [1]

Oxidation Number of Fe: +2

Electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

- (iii) Suggest why Ferrocene is a coloured complex. [2]

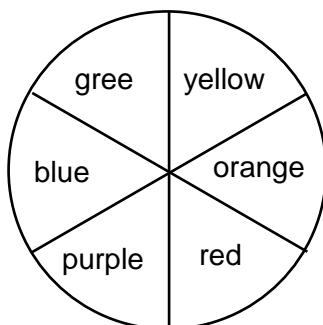
In the presence of ligands, 3d orbitals of iron are split into 2 groups with slightly different energy (d-d splitting).

A 3d electron from the lower energy group is promoted to the higher energy group (d-d transition)

by absorbing energy from the visible region of the electromagnetic spectrum.

Colour observed is complementary to the colour absorbed.

- (iv) The complementary colours are illustrated with the following colour wheel.



Aqueous Fe^{2+} ion is green in colour, suggest and explain if water causes a larger split between the two groups of 3d orbitals as compared to C_5H_5^- . [2]

C_5H_5^- causes a larger 3d orbital split.

With water as the ligand, electromagnetic waves with energy corresponding to red is absorbed which has a lower energy than blue, which is absorbed when C_5H_5^- is the ligand.

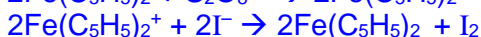
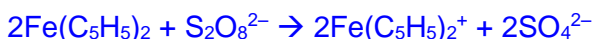
- (v) By considering reaction II, suggest if $E^\ominus(\text{Fe}(\text{C}_5\text{H}_5)_2^+|\text{Fe}(\text{C}_5\text{H}_5)_2)$ is more positive or less positive than $E^\ominus(\text{Fe}^{3+}|\text{Fe}^{2+})$. Explain your answer. [1]

$E^\ominus(\text{Fe}(\text{C}_5\text{H}_5)_2^+|\text{Fe}(\text{C}_5\text{H}_5)_2)$ is less positive than $E^\ominus(\text{Fe}^{3+}|\text{Fe}^{2+})$.

In reaction II ferrocene has been oxidised by Fe^{3+} , thus $E^\ominus(\text{Fe}(\text{C}_5\text{H}_5)_2^+|\text{Fe}(\text{C}_5\text{H}_5)_2)$ has a less positive E^\ominus value than $E^\ominus(\text{Fe}^{3+}|\text{Fe}^{2+})$ since $E^\ominus_{\text{cell}} = E^\ominus_{\text{reduced}} - E^\ominus_{\text{oxidised}} > 0$.

- (vi) The reaction between $\text{S}_2\text{O}_8^{2-}$ and I^- is slow in the absence of catalyst. Ferrocene can be a suitable catalyst for this reaction between $\text{S}_2\text{O}_8^{2-}$ and I^- .

Explain with the aid of equations how it works. You may use $\text{Fe}(\text{C}_5\text{H}_5)_2$ to represent ferrocene. [2]



Without the catalyst, the reaction has a high activation energy due to collisions between ions of the same charge.

In the presence of catalyst, collisions between ions of the same charge are avoided hence it lowers the activation energy.

- (vii) By considering your answers to (v) and (vi), suggest a range of values for $E^\ominus(\text{Fe}(\text{C}_5\text{H}_5)_2^+|\text{Fe}(\text{C}_5\text{H}_5)_2)$. [1]

$$+0.54\text{V} < E^\ominus(\text{Fe}(\text{C}_5\text{H}_5)_2^+|\text{Fe}(\text{C}_5\text{H}_5)_2) < +0.77\text{V}$$

- (b) Ephedrine, $\text{C}_{10}\text{H}_{15}\text{NO}$, is a drug used to prevent low blood pressure during spinal anaesthesia. It is optically active and has 2 chiral centres.

When Ephedrine is heated with acidified potassium manganate(VII), it gives benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ as one of the products. When it is heated with acidified potassium dichromate(VI), it gives **P**. **P** gives an orange precipitate when treated with 2,4-dinitrophenylhydrazine but it has no reaction with Tollens' reagent.

When Ephedrine is heated with equimolar CH_3Cl , it gives **Q**, $\text{C}_{11}\text{H}_{17}\text{NO}$ as the major product. When it is heated with excess CH_3Cl , it gives **R**, $\text{C}_{12}\text{H}_{20}\text{NOCl}$ as the major product.

Deduce the structures of Ephedrine, **P**, **Q** and **R**. Explain your answer. [7]

Ephedrine has 2 chiral centres, it has two carbon atoms attached to four different groups.

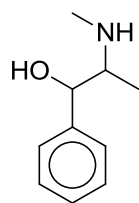
Ephedrine undergoes side-chain oxidation of benzene with hot acidified potassium manganate to give benzoic acid, it contains mono-substituted benzene with a benzylic hydrogen.

P undergoes condensation with 2,4-dinitrophenylhydrazine, it suggests it contains either aldehyde or ketone functional groups. Since it does not react with Tollens' reagent, it must be a ketone.

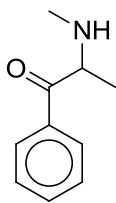
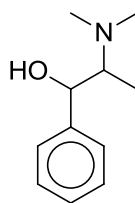
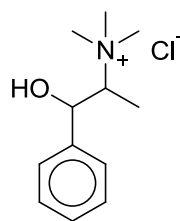
Hence, Ephedrine contains a secondary alcohol since it can be oxidised by dichromate to form a ketone.

Ephedrine undergoes nucleophilic substitution with CH_3Cl to form **Q**. It contains an amine group.

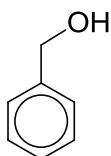
When Ephedrine is reacted with excess CH_3Cl , two methyl groups have been incorporated in **R** as confirmed by the change in the molecular formula, hence it contains secondary amine group.



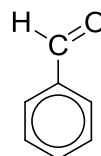
Ephedrine

**P****Q****R**

(c) Draw a labelled diagram to show how benzaldehyde can be synthesised from phenylmethanol in a laboratory.

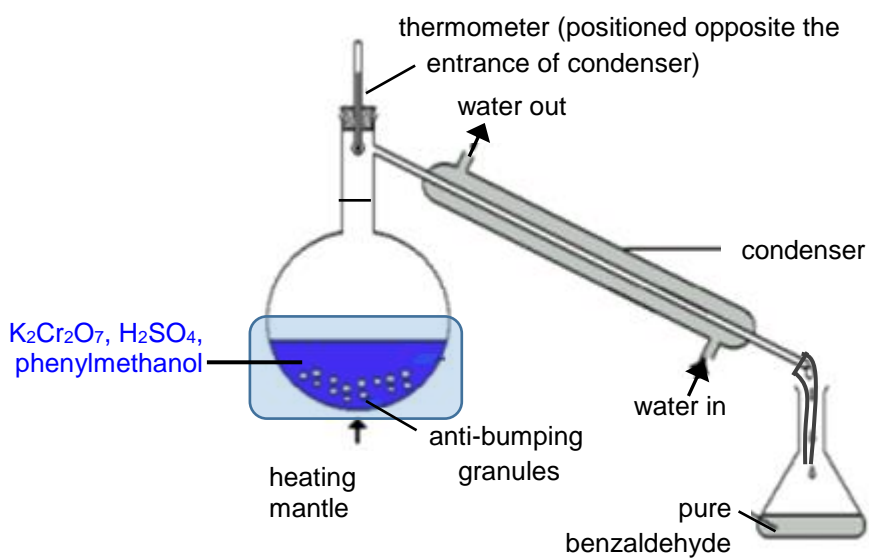


phenylmethanol



benzaldehyde

[3]



[Total: 20]