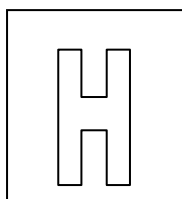


Candidate Name: _____

Class Adm No

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2017 Preliminary Examination II

Pre-University 3

H2 CHEMISTRY

9647/03

Paper 3 Free Response

15th Sept 2017

2 hours

Candidates answer on separate paper.

Additional materials: Answer Paper

Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

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

Write in dark blue or black pen.

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

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

Answer any **four** questions.

A Data Booklet is provided.

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

You are reminded of the need for good English and clear presentation in your answers.

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.

Question	1	2	3	4	5	Total
Marks	20	20	20	20	20	80

- 1 (a) Graphite is a naturally-occurring form of crystalline carbon and is found in metamorphic and igneous rocks. Graphite is extremely soft and cleaves with very light pressure yet it is extremely resistant to heat and nearly inert in contact with almost any other material. These extreme properties give it a wide range of uses in metallurgy and manufacturing.

(i) With reference to the structure, account for the following properties of graphite.

- Soft
- Heat resistant and inert

[3]

Graphite has a **giant covalent structure**(;). The bonding between the layers is **weak temporary dipole – induced dipole forces**(;) which can be **easily overcome**d, allowing the layers to **slide over** each other easily and thus graphite is soft.

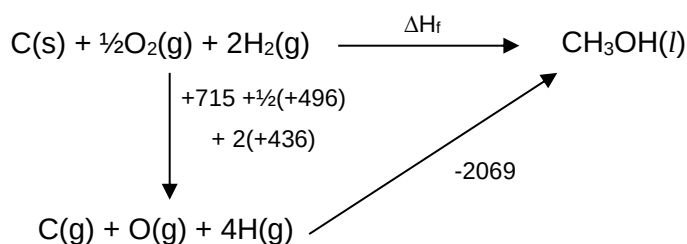
Large amount of thermal energy is required to break the **strong covalent bonds**(;) between the carbon atoms within the layers which account for its resistance to heat.

(ii) The following table shows some thermochemistry data.

Reaction	$\Delta H / \text{kJ mol}^{-1}$
Standard enthalpy change of atomisation of carbon	+715
Enthalpy change of $4\text{H(g)} + \text{O(g)} + \text{C(g)} \rightarrow \text{CH}_3\text{OH(l)}$	-2069

With the use of relevant data from the *Data Booklet* and the above information, calculate the enthalpy change of formation of methanol.

[3]



$$\Delta H_f = +715 + \frac{1}{2}(+496) + 2(+436) + (-2069) = -234 \text{ kJ mol}^{-1}$$

- (b) A butane burner is used to heat the air in a hot air balloon. The hot air balloon has a volume of 2.1 m^3 and its volume does not change when the enclosed air is heated.

(i) Using the ideal gas equation, calculate the amount of gas molecules the balloon contains at temperature 800 K and a pressure of $1.0 \times 10^6 \text{ Pa}$.

[1]

$$pV = nRT$$

$$1.0 \times 10^6 \times 2.1 = n \times 8.31 \times 800$$

$$n = 316 \text{ mol}$$

- (ii) Hence calculate the mass of air it contains, assuming an average relative molecular mass of 29. [1]

$$\text{Mass} = 315.9 \times 29 = 9160\text{g}$$

- (iii) The standard enthalpy change of combustion of butane is $-2877.5 \text{ kJ mol}^{-1}$. It requires 1.0 J of energy to raise the temperature of 1.0 g of air by 1.0 K. Using your answer in (b)(ii), calculate the mass of butane that needs to be burnt to raise the temperature of the air in the balloon by 20 K. Assume that the hot air balloon is a closed system. [2]

$$Q = mc\Delta T = 9160 \times 1.0 \times 20 = 183213 \text{ J}$$

$$\Delta H = - \frac{Q}{\text{Amt of butane}} \times \text{coeff}$$

$$-2877.5 = - \frac{183213 \div 1000}{\text{amt of butane}} \times 1$$

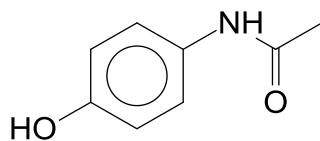
$$\text{Amount of butane} = 0.06367 \text{ mol}$$

$$\text{Mass of butane} = 0.06367 \times (4 \times 12.0 + 1.0 \times 10) = 3.69\text{g}$$

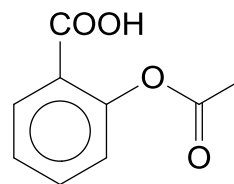
- (iv) The actual mass of butane that needs to be burnt to raise the temperature of the air in the balloon by 20 K was found to be 3.81 g. Suggest why this differs from your answer in (b) (iii). [1]

More butane needs to be burnt due to heat loss.

- (c) Paracetamol and aspirin are effective at pain and fever relief due to their ability to dissolve quickly in the blood stream and are soluble in fatty compounds found in cell membrane.



Paracetamol



Aspirin

- (i) Account for these properties based on the structure and bonding of aspirin. [2]

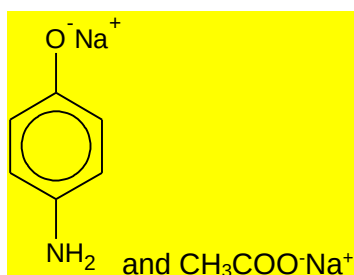
Aspirin has a simple molecular structure. The presence of COOH forms ion-dipole interactions (when hydrolysed to form COO^-) / hydrogen bonding with water.

The presence of benzene ring forms favourable van der Waals' forces with the fatty compounds which results in the solubility.

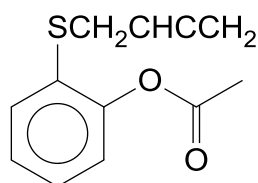
- (ii) One of the pain relievers cause more stomach irritation than the other. With reference to the functional groups present, suggest and explain the pain reliever that you will recommend to someone who suffers from gastric bleeding. [2]

Paracetamol causes less stomach irritation and is recommended(;) as the acidic -COOH group of aspirin will attack the lining of the stomach walls, causing irritation.(;)

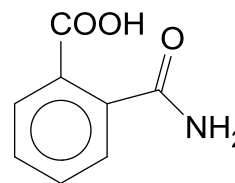
- (iii) Write the structural formula of the organic product(s) formed when paracetamol tablet is refluxed with sodium hydroxide. [2]



- (iv) Extensive research has been made to improve the effectiveness of the pain-relievers. Two proposals were made to modify aspirin.



Drug A



Drug B

Given that the melting points of Drugs **A** and **B** are 179°C and 154°C respectively, account for the melting point in terms of structure and bonding. [2]

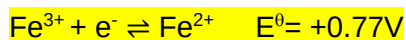
Both drugs have simple molecular structure. Drug A has a higher melting point as the van der Waals' forces of attraction is more extensive and stronger than the hydrogen bonding in Drug B. More energy is needed to overcome the stronger van der Waals' forces of attraction between Drug A.

- (v) State the relative solubility of Drugs **A** and **B** in water. [1]

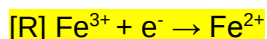
Drug A is less soluble in water than drug B.

- 2 Halogens and their compounds can be toxic but some are essential for the human body's functioning and are used in daily products. The oxidising power of chlorine allows it to act as a good disinfectant.

(a) With the use of *Data Booklet*, explain why FeCl_3 exists but FeI_3 does not. [4]

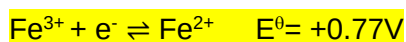


For FeCl_3 , initial species present: Fe^{3+} and Cl^-

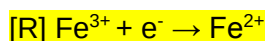
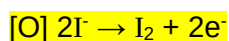


$$E^0_{\text{cell}} = +0.77 - (+1.36) = -0.59\text{V} < 0$$

Hence, the species cannot undergo further redox. Thus FeCl_3 exists.



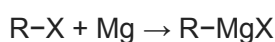
For FeI_3 , initial species present: Fe^{3+} and I^-



$$E^0_{\text{cell}} = +0.77 - (+0.54) = +0.23\text{V} > 0$$

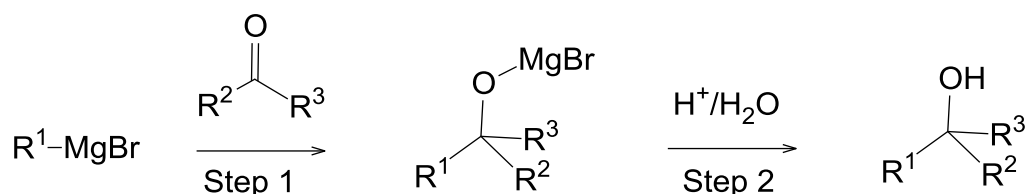
Hence, the species can undergo further redox to form Fe^{2+} and I_2 . Thus FeI_3 does not exist.

- (b) Grignard reaction is an important reaction which helps in lengthening the carbon chain. A Grignard reagent has a general formula of R-MgX where R is an alkyl or aryl group and is formed via the reaction of an alkyl or alkyl halide with magnesium powder.

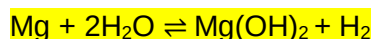


Grignard reagent

Carbonyl compounds react with Grignard reagent to increase the carbon chain.



- (i) In the formation of Grignard reagent, it is important to carry out the reaction in a dry environment. Suggest a reason. [1]



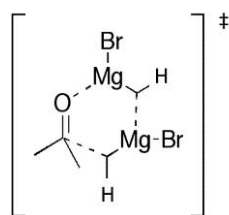
Mg reacts in the presence of water to form magnesium hydroxide and H_2 gas. OR
Grignard reagent can react with water to form the respective alkane.

- (ii) It was observed that the reaction to form the Grignard reagent is very slow at the start when magnesium powder is added to the alkyl halide in diethyl ether solvent. Suggest a reason. [1]

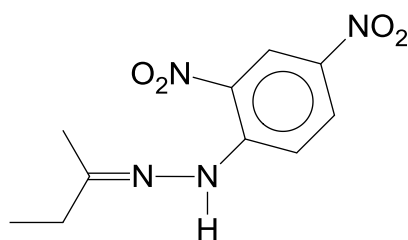
There is an unreactive layer of magnesium oxide coated on the exterior.

- (iii) The addition of the Grignard reagent to the carbonyl typically proceeds through a six-membered ring transition state. For the reaction of each molecule of carbonyl compound, two molecules of Grignard reagents are involved in the formation of the transition state.

Suggest the transition state of Step 1 for the reaction between propanone and CH_3MgBr shown above. [1]

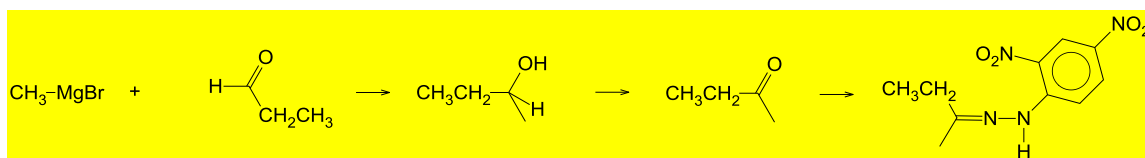


- (iv) Suggest a four-step synthesis of compound **Q**. State the reagents and conditions for each stage and draw structures of the intermediate organic products. The first two steps should involve the use of Grignard reaction between CH_3MgBr and a relevant carbonyl compound.



Compound Q

[5]



- (c) (i) Describe what is observed when NaCl and NaBr reacts with concentrated sulfuric acid respectively. In each case, suggest the products of the reaction and write equations where appropriate. [2]



White fumes of HCl (g) produced. (.)



Orange-brown fumes (mixture of Br_2 and HBr) obtained. (.)

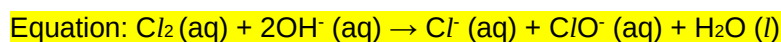
- (ii) Explain any difference in their reactions with concentrated sulfuric acid. [1]

The ease of oxidation of halide ions increases from Cl^- to Br^- . Hence, Br^- is oxidised to Br_2 and Cl^- is not oxidised at all.

- (d) When cold aqueous sodium hydroxide is added to a yellowish-green solution of chlorine in trichloromethane and shaken together, two immiscible colourless layers (aqueous layer and organic layer) were observed.

- (i) State the type of reaction and give an equation, including state symbols, for this reaction. [2]

Type of reaction: disproportionation of chlorine

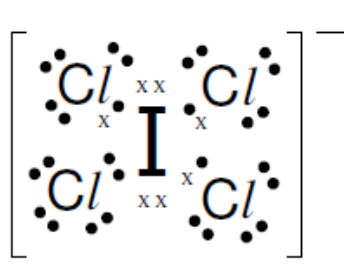


- (ii) Assuming that the starting reagents were added in stoichiometric ratio, suggest the chemical species found in the two immiscible colourless layers respectively. [2]

Aqueous layer: $\text{Cl}^- (\text{aq}) + \text{ClO}^- (\text{aq})$

Organic Layer: CHCl_3

- (e) One of the compounds that may be formed between chlorine and iodine is iodine tetrachloride, ICl_4 . Construct a 'dot-and-cross diagram' to show the arrangement of electrons in ICl_4 . [1]



[Total: 20]

- 3 (a) Hunsdiecker reaction is the organic reaction of silver salts of carboxylic acids with halogens to give organic halides.

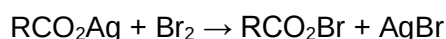
The overall reaction is:



The reaction mechanism of the Hunsdiecker reaction is believed to involve organic radical intermediates.

The steps involved in the reaction mechanism are as follows:

1. The silver salt of the carboxylic acid quickly reacts with bromine to form the acyl hypohalite intermediate, RCO_2Br .



2. The initiation step involves the formation of two radicals from the acyl hypohalite intermediate. One of which is bromine radical.
3. The first step of propagation involves the removal of CO_2 from the radical formed in step 2, forming $\text{R}\bullet$ and CO_2 .
4. $\text{R}\bullet$ recombines with the acyl hypohalite intermediate to form the desired organic halide.

- (i) Write equations to illustrate the reaction mechanism of Hunsdiecker reaction. [3]



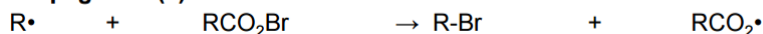
Initiation



Propagation (I)



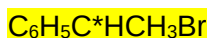
Propagation (II)



Termination



- (ii) Draw the structure of the organic product formed when $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{COOAg}$ reacts with Br_2 . [1]



- (iii) The product in (a)(ii) displays optical isomerism as it has a chiral centre. Explain the term *chiral centre* and label the chiral centre in (a)(ii) with an asterix(*) sign. [2]

A chiral centre is a **C atom bonded to four different substituents.**

- (iv) Chlorine and iodine can be used in place of bromine to react with silver salts of carboxylic acids.

A student wanted to compare the rate of reaction of iodine reacting with silver salts of carboxylic acids with that of bromine. However, he did not label the apparatus and ended up not able to tell which apparatus has the iodine-containing and bromine-containing organic products.

Describe a chemical test which can allow the student to derive correctly the apparatus with the iodine-containing and bromine-containing organic products respectively. Include the observations, if any. [4]

Add NaOH to the respective solutions, followed by HNO₃. Add AgNO₃(aq).

The solution containing a cream precipitate has the bromine-containing product while the solution containing a yellow precipitate has the iodine-containing product.

Add concentrated NH₃ to the respective solutions.

The cream precipitate will dissolve in the concentrated NH₃ while the yellow precipitate will not dissolve in the concentrated NH₃.

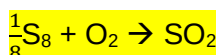
- (b) Write the equations and state the observations of the following reactions, where appropriate.

- Reaction between sodium and oxygen
- Reaction between sulfur and oxygen

[4]



Na burns in oxygen with an orange flame.

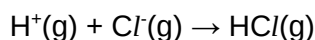


S burns with a blue flame to form SO₂.

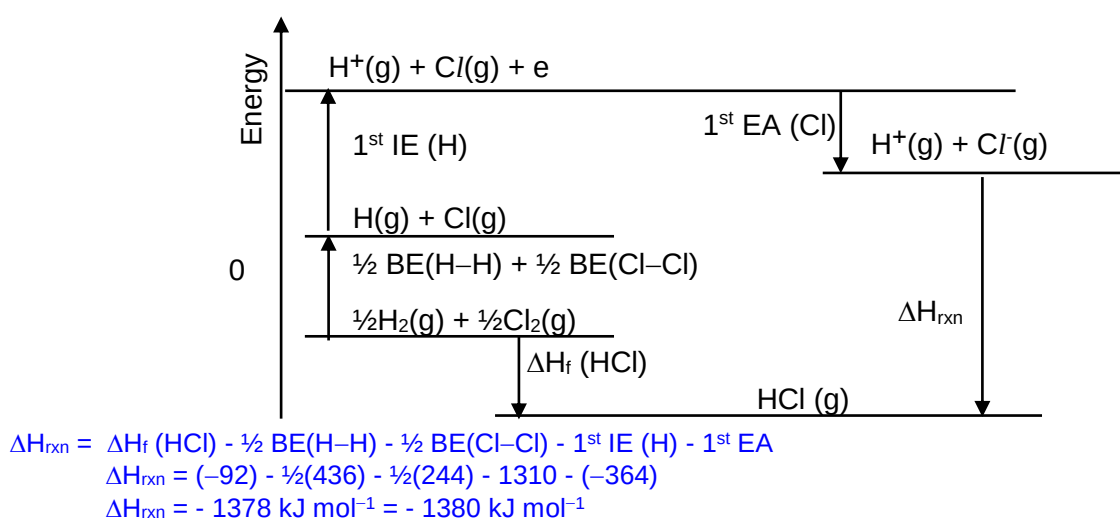
- (c) (i) The following table shows some thermochemistry data.

Reaction	$\Delta H / \text{kJ mol}^{-1}$
enthalpy change of formation of HCl(g)	-92
first electron affinity of Cl(g)	-364

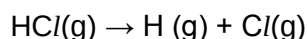
Using the following data, and relevant data from the *Data Booklet*, construct an energy level diagram to calculate the standard enthalpy change for the following reaction.



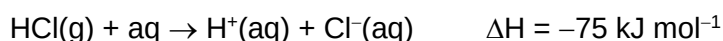
[4]



- (ii) The following reaction is expected to be an endothermic reaction.



However, the following reaction is an exothermic reaction.



Explain the above observations.

[2]

The first reaction involves bond breaking only while the second reaction involves forming ion-dipole interactions between H^+ and water molecules and Cl^- and water molecules. Energy is evolved in the formation of ion-dipole interactions which can more than compensate the heat absorbed to break the H-Cl bond in the gaseous state and to ionise the H atom, thus resulting in the enthalpy change of reaction is exothermic.

[Total: 20]

- 4 (a) (i) Heating compound **P**, $C_{10}H_{12}O_3$, with dilute sulfuric acid yields compound **Q**, $C_9H_{12}O_2$, and methanoic acid.

On treatment with dilute nitric acid, compound **Q** forms compound **R** with the formula $C_9H_{11}NO_4$. Compound **Q** also reacts with aqueous bromine to form compound **S**, $C_9H_9O_2Br_3$.

Heating compound **R** with tin in concentrated hydrochloric acid, followed by adding excess aqueous sodium hydroxide to the product gives compound **T**, $C_9H_{12}NO_2Na$.

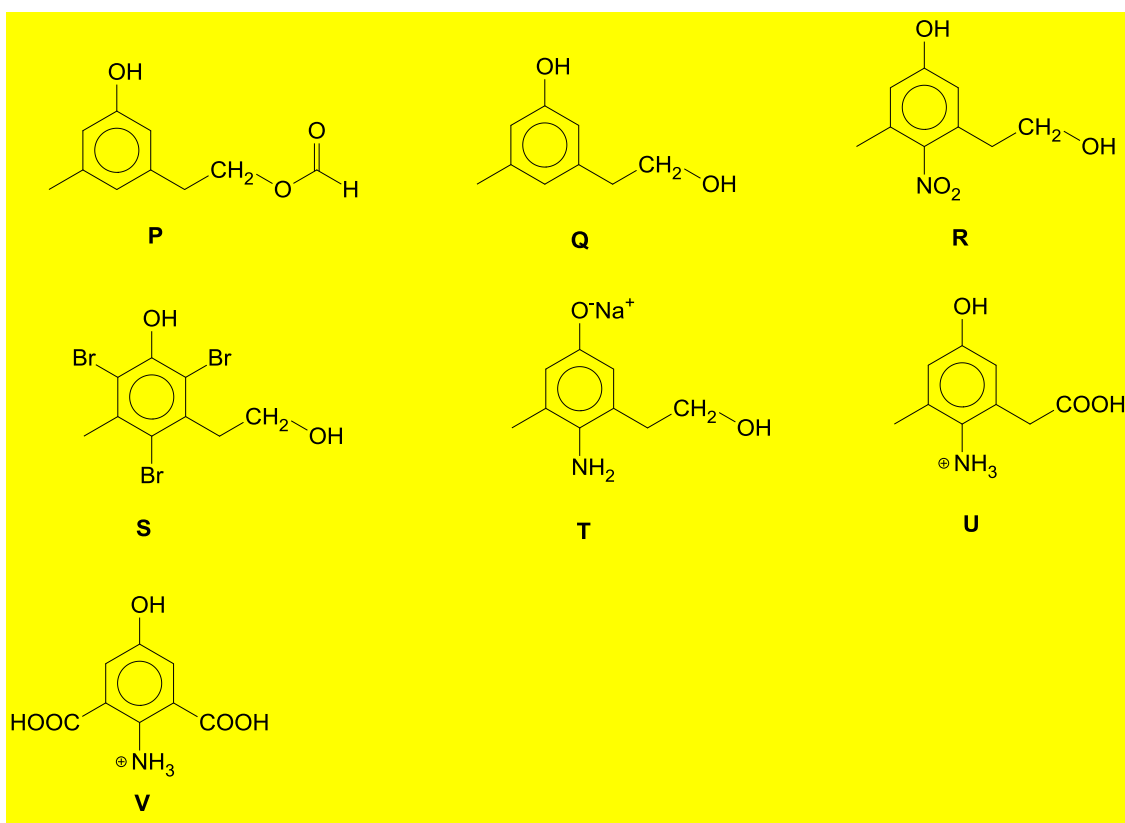
Compound **T** turns hot acidified potassium dichromate solution green and forms compound **U**, $C_9H_{12}NO_3$. 1 mole of compound **U** reacts with 3 moles of aqueous sodium hydroxide. Compound **T** reacts with hot acidified potassium manganate(VII) and forms compound **V**, $C_8H_8NO_5$.

Suggest structures for compounds **P–V** and give an account of the chemistry involved.

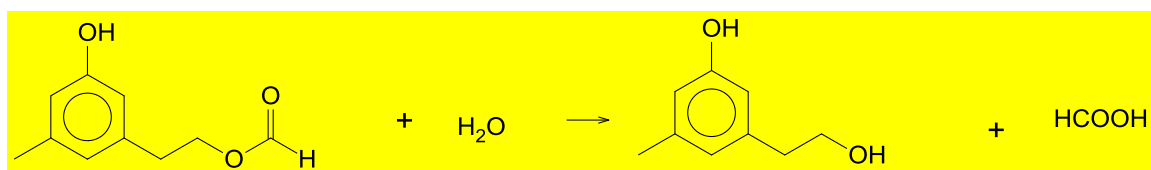
[14]

Observation	Deduction
Heating compound P which has the formula, $C_{10}H_{12}O_3$, with dilute sulfuric acid yields compound Q , $C_9H_{12}O_2$, and methanoic acid	P is an ester P undergoes acidic hydrolysis.
On treatment with dilute nitric acid, compound Q forms compound R	Q contains phenol Q undergoes electrophilic substitution.
Compound Q also reacts with aqueous bromine to form compound S , $C_9H_9O_2Br_3$	Q contains phenol Br is substituted at 2,4 and 6 position in S . Q undergoes electrophilic substitution.
Heating compound R with tin in concentrated hydrochloric acid	Reduction of nitro group to $-NH_2$ R contains $-NO_2$
Adding excess aqueous sodium hydroxide to the product gives compound T , $C_9H_{12}NO_2Na$.	Acid-base reaction Phenoxide ion is produced
Compound T turns hot acidified potassium dichromate solution green and forms compound U , $C_9H_{12}NO_3$.	Oxidation Primary alcohol is present in T Phenoxide ion is acidified and revert to phenol in U

1 mole of compound U reacts with 3 moles of aqueous sodium hydroxide.	U contains 3 acidic groups(1 phenol,1 ammonium salt group and 1 carboxylic acid group).
Compound T reacts with hot acidified potassium manganate(VII) and forms compound V , $C_8H_8NO_5$.	Oxidation



(ii) Write the equation for the reaction of compound **P** being heated with dilute sulfuric acid.[1]



(b) Ester is an organic molecule which has many uses. Esters with low molecular masses are commonly used as fragrances and are found in essential oils. Phosphoesters form the backbone of DNA molecules.

(i) Given that methyl methanoate and ethyl methanoate are the simplest esters available, suggest a chemical test which can distinguish the two compounds. [3]

To separate solutions of methyl methanoate and ethyl methanoate, add $NaOH(aq)$ and heat it, followed by adding $I_2(aq)$. The solution that forms a yellow precipitate contains

ethyl methanoate while the solution that contains methyl methanoate does not form yellow precipitate.

- (ii) Acyl chlorides and esters are both derivatives of carboxylic acids.

Compare and account for the acidity of methyl methanoate and ethanoyl chloride. [2]

Ethanoyl chloride is more acidic than methyl methanoate(;) as it hydrolyses in water to form HCl which is a strong acid(;).

[Total: 20]

- 5 Vehicle frames are usually made from aluminium as it is lightweight and strong. However, the aluminium frames have to be made more resistant to corrosion as certain parts could be exposed to rainwater and acidic gases in vehicle exhaust.

The industrial process for the anodising of aluminium uses an inert platinum cathode and aqueous sulfuric acid as the electrolyte.

- (a) Explain, in terms of the electrode reactions, how a piece of aluminium metal could be anodised to be more resistant to corrosion. [3]

at the Pt cathode: $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$

at the Al anode:



Overall reaction: $2\text{Al}(\text{s}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow \text{Al}_2\text{O}_3(\text{s}) + 3\text{H}_2(\text{g});$

- (b) A current of 0.30 mA was switched on for 1 hour to anodise an aluminium frame.

Calculate the amount of Al_2O_3 produced from the anodisation. [3]

$$Q = It$$

$$Q = 0.30 \times 10^{-3} \times 3600 = 1.08 \text{ C}$$

$$Q = nF$$

$$\text{No. of mol of electrons transferred, } n = Q / F = 1.08 / 96500 = 1.12 \times 10^{-5} \text{ mol};$$

[Turn over



For every 12 mol of electron transferred, 2 mol of Al_2O_3 is produced ;

No. of mol of Al oxidised = $1.12 \times 10^{-5} \div 6 = 1.87 \times 10^{-6} \text{ mol}$;

- (c) *Use of the Data Booklet is relevant to this question.*

Explain, stating any observations, how the electrode reactions would be different if

- (i) the electrolyte was contaminated with copper(II) sulfate. [2]

The cathode reaction will instead be the reduction of Cu^{2+} ions to copper solid.



The platinum cathode will be coated with a pink / orange / brown layer of copper ;

- (ii) the aluminium electrode was replaced with another platinum electrode. [2]

Platinum is inert and does not get oxidised. Water is oxidised to oxygen gas.



Effervescence of a colourless gas at the anode; (which relights a glowing splint)

- (d) Infra-red (IR) spectroscopy is a common technique used to identify functional groups in organic compounds and to study how the functional groups are affected by other substances. When a beam of IR light of varying energies is shone at an organic compound, its functional groups can absorb certain energies characteristic to it. The energy of IR light is measured in wavenumbers, $\tilde{\nu}$, and is expressed as the reciprocal of its wavelength, λ , with units of cm^{-1} .

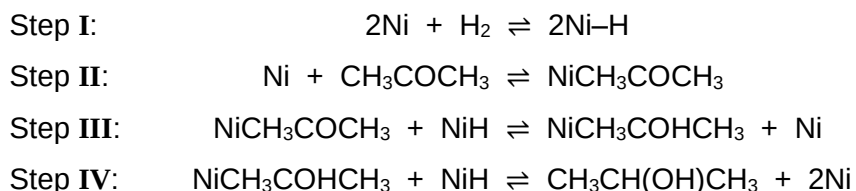
$$\tilde{\nu} = \frac{1}{\lambda}$$

For example, carbonyl functional groups absorb IR light at the wavenumber range of 1680 to 1750 cm^{-1} , while alkyl groups absorb IR light at a wavenumber range of 2840 to 3095 cm^{-1} .

The gas-phase kinetics and mechanism of the hydrogenation of propanone using nickel catalyst was studied using IR spectroscopy. Dissociative adsorption of hydrogen gas on solid nickel is known to occur readily (step I). The adsorption of propanone gas onto the nickel catalyst was identified by a wavenumber peaking at 1620 cm^{-1} . The shift in wavenumber from 1680 to 1620 cm^{-1} confirms that it is the C=O functional group that is adsorbed onto the nickel catalyst and not the methyl groups (step II). However, no wavenumber shift corresponding to

the alcohol functional group of the product, propan-2-ol, was found. This indicates that when the product is formed, it immediately desorbed from the catalyst (step IV).

Hence, the proposed mechanism for this reaction is as follows.



When the experiment was conducted in a closed vessel of fixed volume at a constant temperature of 363 K, the following data was recorded.

Experiment	Partial pressure of hydrogen / kPa	Partial pressure of propanone / kPa	Relative rate
1	0.5	2.5	1
2	1	2.5	2
3	4	5	16
4	10	5	16
5	50	5	16

- (i) Nickel is acting as a *heterogeneous* catalyst in this reaction.

Define the term *heterogeneous*.

[1]

The catalyst used is in a different phase / physical state from the reactants. ;

- (ii) Based on experiments 1 to 3, determine the order of reaction with respect to hydrogen and with respect to propanone.

Hence, deduce the rate equation for the hydrogenation of propanone.

[3]

$$\text{Rate} = k[\text{H}_2]^m[\text{propanone}]^n$$

By comparing experiments 1 and 2,

When partial pressure (concentration) of hydrogen doubled and propanone kept constant, rate doubled.

Reaction is first order with respect to hydrogen, $m = 1$;

By comparing experiments 2 and 3,

$$\frac{\text{rate of expt 3}}{\text{rate of expt 2}} = \frac{k[\text{H}_2]^1[\text{propanone}]^n}{k[\text{H}_2]^1[\text{propanone}]^n}$$

$$\frac{16}{2} = (4)^1 \times \frac{5}{2.5}^n$$

$$2^n = 2$$

$$n = 1$$

Reaction is first order with respect to propanone, $n = 1$;

$$\text{Rate} = k[\text{H}_2][\text{CH}_3\text{COCH}_3] \quad \text{or} \quad \text{rate} = k p_{\text{H}_2} p_{\text{CH}_3\text{COCH}_3} ;$$

- (iii) Based on your answer in (ii), state which step in the proposed mechanism is the rate-determining step. [1]

Step 4. ;

Explanation (not needed)

If slow step is

$$\text{step 1: rate} = k [\text{H}_2]^1 \quad \text{X}$$

$$\text{step 2: rate} = k [\text{CH}_3\text{COCH}_3]^1 \quad \text{X}$$

$$\text{step 3: rate} = k [\text{H}_2]^{0.5} [\text{CH}_3\text{COCH}_3]^1 \quad \text{X}$$

$$\text{step 4: rate} = k [\text{H}_2] [\text{CH}_3\text{COCH}_3]^1 \quad (\text{consistent})$$

Write the expression for K_c for steps 1 to 3, ignoring Ni as it is in solid state. Re-express the rate equation for step 4 in terms of the actual reactants and not leave it in terms of the intermediates.

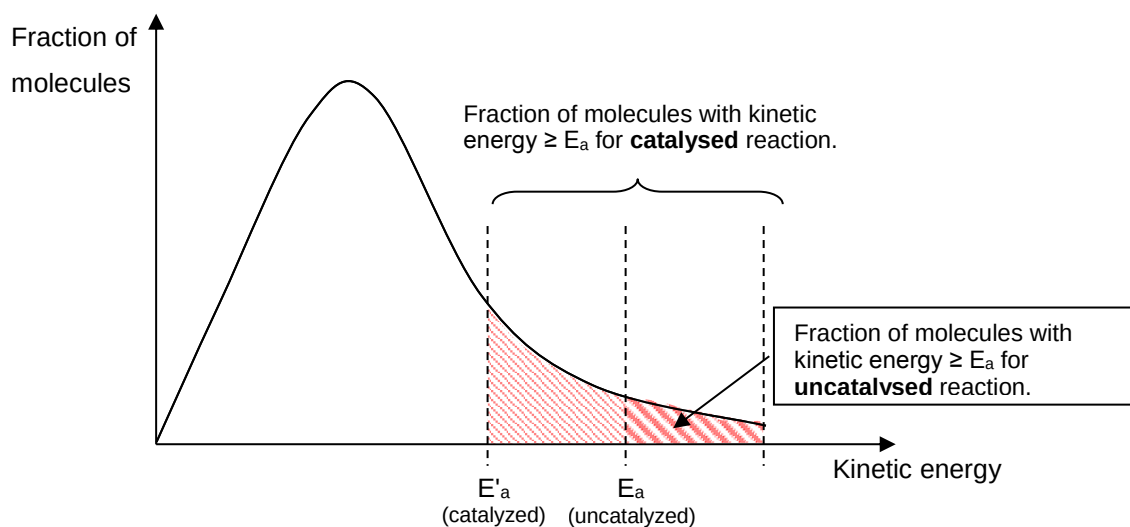
- (iv) Suggest a reason why the catalyst has to be used in the powdered form. [1]

The powdered form provides a larger surface area which increases the frequency of effective collisions, speeding up the reaction. ;

- (v) Hence, or otherwise, suggest a reason why the rate of reaction stopped increasing in experiments 4 and 5 when the partial pressure of hydrogen exceeded 4 kPa. [1]

The hydrogen gas concentration (substrate concentration) exceeded the available catalyst surface area for adsorption / reaction to take place. ;

- (vi) Sketch an energy distribution diagram to explain how the rate of the reaction would have been different without the use of a catalyst. [3]



; (1 m for diagram and labels)

- A catalyst provides an **alternative reaction path with lower activation energy (E'_a)** than that for the uncatalysed reaction (E_a).
- Without a catalyst, **fraction of molecules containing energy greater than the activation energy decreases**
- The **frequency of effective collisions is lower without a catalyst.**
- Hence, **rate of reaction decreases.**

;; (0-1 pt = 0m ; 2-3 pts = 1m, all 4 pts = 2m)

[Total: 20]

END OF PAPER

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