	RAFFLES INSTIT 2018 YEAR 6 PR Higher 2	UTION ELIMINARY EXAMINATION	
CANDIDATE NAME			
CLASS		INDEX NUMBER	
CHEMIST Paper 2 Str	RY ructured Question	S	9729/02 11 September 2018 2 hours
Candidates a	answer on the Questi	on Paper.	2 110013

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not open this question booklet until you are told to do so.

Write your name, class and index number in the spaces provided at the top of this page. Write in dark blue or black pen in the spaces provided. You may use a soft pencil for any diagrams, graphs or rough working. Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

A Data Booklet is provided. Do not write anything in it.

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

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

For Examiner's Use	
1	/ 8
2	/ 13
3	/ 16
4	/ 13
5	/ 10
6	/ 15
Total	/ 75

This document consists of 23 printed pages.

Å

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

1 Gemstones such as amethysts, pearls and malachites contain compounds of main group and transition elements.

Fig. 1.1 shows the logarithm of the ionisation energies, \log (IE), for the outermost ten electrons in an atom of an element **X**, which has atomic number smaller than 20.



Fig. 1.1

- (a) Deduce which Group in the Periodic Table X belongs to and state the identity of X. Explain your answer.
 [3]
- (b) The colour of amethyst is caused by the presence of compounds containing manganese and iron.

Explain why the first ionisation energies of manganese and iron are similar.

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

Malachites contain copper(II) carbonate while pearls contain calcium carbonate. Predict whether calcium carbonate or copper(II) carbonate has a higher decomposition temperature. Explain your answer.

[Total: 8]

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2 (a) Polycyclic aromatic hydrocarbons (PAHs) are potential carcinogens.

Anthracene is an example of a PAH and its Kekulé structure is shown in Fig. 2.1.

Fig. 2.1

- (i) A compound is aromatic if it satisfies the following criteria:
 - it is a cyclic planar molecule,
 - it has a delocalised π electron system, and
 - it has $(4n + 2) \pi$ electrons, where n is an integer.

By considering the hybridisation of the carbon atoms in anthracene and the criteria for aromaticity, explain why anthracene is aromatic.

[3]

(ii) The enthalpy change of hydrogenation of cyclohexene to cyclohexane is -118 kJ mol^{-1} .



Using the Kekulé structure given in Fig. 2.1, calculate the enthalpy change of complete hydrogenation of anthracene, ΔH_1 .

[1]

(iii) Fig. 2.2 is the actual representation of anthracene.



Fig. 2.2

Complete the energy level diagram below using the data in Table 2.1. Hence, calculate the actual value for the enthalpy change of complete hydrogenation of anthracene, ΔH_2 .



Table 2.1

 $\Delta H_2 = \dots \qquad [3]$

(iv) Using your answers to (a)(ii) and (a)(iii), calculate the resonance energy of anthracene.

(b) Table 2.2 shows some information on anthracene and other PAHs found in smoked fish.

РАН	structure	mean concentration (C _m) / ppm	Toxicity Equivalency Factor (TEF)
anthracene C ₁₄ H ₁₀	$\hat{O}\hat{O}\hat{O}$	0.029	0.01
chrysene C ₁₈ H ₁₂		0.135	0.01
benzo[a]pyrene C ₂₀ H ₁₂		0.204	1.00

Table 2.2

(i) The carcinogenic toxic equivalent (TEQ) of PAHs in smoked fish can be calculated using equation 2.1.

TEQ = Sum of $[C_m (in ppm) \times TEF]$ ----- equation 2.1

Using equation 2.1 and the data from Table 2.2, calculate the TEQ of smoked fish.

[1]

(ii) For an average person, the excess cancer risk (ECR) resulting from exposure to PAHs through smoked fish consumption can be determined using equation 2.2.

$$ECR = \frac{TEQ}{body \text{ weight in } kg} \times 1.37 \times 10^{-3} \text{ ----- equation } 2.2$$

Given that the acceptable ECR value set by United States Environmental Protection Agency is 1.0×10^{-6} , use equation 2.2 to determine the ECR value due to the consumption of smoked fish by a 70 kg person. Hence, state whether the person is at risk of cancer.

(c) Phenolphthalein is formed when phenol undergoes electrophilic substitution with phthalic anhydride.

The overall equation for the reaction is shown below.



(i) As phenolphthalein is a carcinogen, it has been replaced by thymolphthalein, which can be formed by a similar reaction between thymol and phthalic anhydride.

By using the structure of thymol as shown below, draw the structure of thymolphthalein.



thymol

(ii) Explain whether thymol or phenol undergoes electrophilic substitution more readily.

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[1]

(d) Phenolphthalein indicator is colourless. Under basic conditions, phenolphthalein undergoes dissociation to form its conjugate base, which is pink in colour.

The conjugate base of phenolphthalein is found to be A and not B.



Explain why the structure of **A** is more stable than that of **B**.

 [1]

[Total: 13]

For

examiner's use **3 (a)** Acid derivatives, RCOY, are compounds formed when the –OH group of carboxylic acid is replaced by a different group (Y). They have the general structure as shown below.

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Acid derivatives undergo nucleophilic acyl substitution, with the general mechanism shown below:



The mechanism involves the heterolytic fission of the C-Y bond, resulting in Y leaving with a pair of electrons as Y^- . Y^- is called the leaving group.

When RCOY undergoes nucleophilic acyl substitution, one factor that affects its reactivity is the basicity of Y^- . In general, the stronger Y^- is as a Lewis base, the poorer it is as a leaving group. This results in RCOY being less reactive towards nucleophilic acyl substitution.

(i) Suggest why strong Lewis bases are poor leaving groups.

......[1]

Table 3.1 shows the four most common types of acid derivatives and the pK_b of Y⁻.

functional group	example of acid derivative	leaving group, Y⁻	p <i>K</i> ₀ of Y⁻
acyl chloride	ethanoyl chloride	C <i>l</i> ⁻	21
ester	o methyl ethanoate	CH₃O⁻	-2
acid anhydride	ethanoic anhydride	CH₃COO⁻	9
amide	O NH ₂ ethanamide	NH₂ [−]	-24

(ii) A student proposed two reactions to synthesise methyl ethanoate using methoxide ions.



Reaction 2



With reference to the pK_b values given in Table 3.1, explain why reaction **1** is a better method to synthesise methyl ethanoate than reaction **2**.

(b) Methyl ethanoate can also be synthesised from methanol and ethanoic acid. The reaction is reversible and does not go to completion.

Reaction 3 $CH_3OH(I) + CH_3COOH(I) \rightleftharpoons CH_3COOCH_3(I) + H_2O(I)$

Table 3.2 shows the densities and molar masses of methanol and ethanoic acid.

Table 3.2

compound	density / g cm ⁻³	molar mass / g mol ⁻¹
methanol	0.792	32.0
ethanoic acid	1.05	60.0

To determine the equilibrium constant, K_c , for this reaction, a student mixed 20.0 cm³ of ethanoic acid with 20.0 cm³ of methanol, and left the mixture to stand for one week to reach equilibrium.

 5.0 cm^3 of the equilibrium mixture was pipetted out and added to 100 cm^3 of ice-cold water in a conical flask. The resultant mixture required 16.80 cm³ of 0.500 mol dm⁻³ aqueous NaOH for complete reaction.

(i) Calculate the initial amount of methanol used in the reaction.

(ii) Calculate the amount of ethanoic acid present in the equilibrium mixture. Assume that the total volume of the equilibrium mixture is 40.0 cm³.

[2]

[1]

(iii) Write an expression for the K_c of reaction **3**.

(iv)	Given that the initial amount of ethanoic acid used is 0.350 mol, calculate a value
	for K _c .

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[2]

(v) Explain why 5.0 cm³ of the equilibrium mixture was added to 100 cm³ of ice-cold water before it was titrated against aqueous NaOH.

.....[2]

(c) Methyl ethanoate and ethyl methanoate are isomers. Suggest a simple chemical test which can distinguish between them. Write equations for the reactions that occur for the ester that gives the positive test.

[3]

(d) Compounds **P** and **Q** are solids at room temperature and are insoluble in water. They have the structures shown below.





compound **Q**

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A student added some **Q** to **P** by mistake. Outline how **P** can be separated from **Q**. Briefly explain your answer.

[2] [Total: 16]

14

- **4** Magnesium sulfate heptahydrate, MgSO₄•7H₂O, commonly called Epsom salt, has been traditionally used as a component of bath salts.
 - (a) The standard enthalpy change of the following reaction, ΔH_r^{\ominus} , cannot be determined directly.

 $MgSO_4(s) + 7H_2O(I) \longrightarrow MgSO_4 \cdot 7H_2O(s) \qquad \Delta H_r^{\ominus}$

An experiment was performed to determine the standard enthalpy change of solution, ΔH_{sol}^{\ominus} , of anhydrous MgSO₄ and Hess' Law was then used to calculate ΔH_{r}^{\ominus} .

The experimental procedure involved using a data logger to measure the temperature of the mixture when 7.500 g of anhydrous $MgSO_4$ was added to 100 cm³ of water in a Styrofoam cup at t = 75 s.

A graph of temperature against time was plotted.



(ii) Determine the maximum temperature change of the reaction, ΔT , from the graph. Show all construction lines and working clearly.

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[2]

(iii) Using your answer to (a)(ii), calculate the experimental ΔH_{sol}^{\ominus} of anhydrous MgSO₄. You may assume that the density of the solution is 1 g cm⁻³ and its specific heat capacity is 4.18 J g⁻¹ K⁻¹.

[2]

(iv) The actual value of ΔH_{sol}^{\ominus} of anhydrous MgSO₄ is -88.0 kJ mol⁻¹. Other than the assumptions made above, give a reason for the discrepancy between this value and your answer in (a)(iii).

Hence, suggest a possible improvement to the experimental procedure.

(v) The ΔH_{sol}^{\ominus} of hydrated magnesium sulfate, MgSO₄•7H₂O, is +16.0 kJ mol⁻¹. Using the ΔH_{sol}^{\ominus} of anhydrous MgSO₄ given in (a)(iv), calculate ΔH_{r}^{\ominus} .

Table 5.1

standard enthalpy change of formation of anhydrous MgSO ₄ , ΔH_{f}^{\ominus} (MgSO ₄ (s))	–1278 kJ mol ^{–1}
lattice energy of anhydrous MgSO ₄	–2705 kJ mol ^{–1}
standard enthalpy change of atomisation of Mg(s), $\Delta H_{at}^{\ominus}(Mg(s))$	+148 kJ mol ⁻¹

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[4]

[Total: 13]

5 (a) Use of the Data Booklet is relevant to this question.

The Ag⁺(aq)/Ag(s) half-cell was connected to the $Cu^{2+}(aq)/Cu(s)$ half-cell, and the standard e.m.f. was measured.

(i) Draw a fully labelled diagram to show the set-up for measuring the standard e.m.f. of the above cell.

In your diagram, show clearly the direction of the electron flow in the external circuit.

(ii) Calculate the E^{\ominus}_{cell} for this set-up.

[1]

[3]

For examiner's use

(iii) With the aid of equations, state what is observed in the $Cu^{2+}(aq)/Cu(s)$ half-cell when NH₃(aq) is added slowly to it, until in excess.

[3]

(iv) Predict and explain how the E_{cell} changes after the addition of NH₃(aq).

(b) The zinc-silver oxide alkaline battery is available in small sizes as button cells and the overall cell reaction is shown below.

 $Zn(s) + Ag_2O(s) \longrightarrow ZnO(s) + 2Ag(s)$ $E^{\ominus}_{cell} = +1.60 \text{ V}$

Calculate the ΔG^{\ominus} for the above reaction.

[1]

For examiner's use

[Total: 10]

6 In 1969, a large meteorite fell in the village of Murchison, Australia. Over the years, more than 30 different amino acids have been identified in the meteorite by multiple studies. Some of these amino acids are commonly found in proteins, while others are unusual because they are not found in proteins.

20

The structures of three of the amino acids found in the Murchison meteorite are given in Table 4.1.

amino acid three letter code	structure of fully protonated amino acid
ams	
msr	O HO NH ₃ ⁺
his	HO NH3 ⁺ O NH ⁺ H

Table 4.1

(a) Which two of the three amino acids in Table 4.1 are **not** found in proteins? With reference to their structures, explain your answer.



(b) It was suggested that alien organisms could synthesise a dipeptide of the structure *his*-*msr*. Draw the structure of this dipeptide in the space below.

[1]

The p K_a values of the acidic groups at 25 °C in the fully protonated *his* are labelled below.



- fully protonated his
- (c) (i) Calculate the pK_b values of N^① and N^③ in the fully **deprotonated** *his* and write them in the boxes below.

[1]



(iv) Explain why N[®] is **not** basic.

10 cm³ of 0.1 mol dm⁻³ of the fully **deprotonated** *his* was titrated against 0.1 mol dm⁻³ HC*l*(aq) from a burette. The titration curve is shown below.



- (d) Fill in the boxes above with the correct pH values and HC*l* volumes. [2]
- (e) Calculate the pH after 6.0 cm^3 of HCl(aq) was added from the burette.

- Draw the structures of the major species present at points **Y** and **Z** of the titration. (i) For examiner's use major species at point Y major species at point Z
- (ii) The isoelectric point of an amino acid can be defined as the pH at which the amino acid exists predominantly as zwitterions (with no net charge).

By considering your answer in (f)(i), mark the isoelectric point of his with an "X" on the titration curve. [1]

[Total: 15]

(f)

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[2]