RAFFLES INSTITUTION
2018 Year 5 Promotion Examination

HIGHER 2

CHEMISTRY 9729

28 September 2018

2 hours 40 minutes

Additional Materials: Multiple Choice Answer Sheet
Data Booklet
Writing Paper

READ THESE INSTRUCTIONS FIRST

DO NOT open this booklet until you are told to do so.

Write your name and civics tutorial group in the spaces provided on the OMR sheet, cover sheets on pages **2** and **14** and writing paper.

This paper consists of three sections **A**, **B** and **C**.

Section A (15 marks) consists of 15 multiple-choice questions.
Answer this section first. The OMR sheet will be collected after the **first 30 minutes.**
Record your answers to this section in soft pencil on the separate OMR Answer Sheet.

Section B (35 marks) consists of 3 structured questions.
Answers to this section are to be written in the spaces provided in the question paper.

Section C (40 marks) consists of 3 free-response questions.
Answers to this section are to be written on the writing paper provided. You are to begin each question on a fresh page of paper.

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.

Write in dark blue or black pen. You may be subjected to penalty for writing answers in pencil.

At the end of the examination, fasten your answers to Section **C** and the cover sheet on page **2** securely together.

Answers to Sections **B** and **C** are to be handed in **separately**.

This document consists of **23** printed pages.

C

RAFFLES INSTITUTION
2018 Year 5 Promotion Examination
H2 Chemistry

COVER SHEET

Name: ( )	**Class:**

For Examiner's Use Only

Section	Marks
C1	/ 11
C2	/ 15
C3	/ 14

Fasten your answers to Section **C** and this cover sheet securely together.

Section A (15 marks)

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

1 When sulfur is boiled with sodium hydroxide solution, the initial reaction results in the formation of S^{2-} and SO_3^{2-} ions.

What is the mole ratio of S : S^{2-} : SO_3^{2-} in the balanced equation for this reaction?

A 2 : 1 : 1 **B** 3 : 2 : 1

C 3 : 1 : 2 **D** 4 : 1 : 3

2 In an experiment, 10 cm^3 of a gaseous compound, $C_xH_yS_z$, was exploded with 100 cm^3 of oxygen (in excess). One of the products is SO_2(g). After cooling to room temperature, the volume of the gaseous mixture was found to be 90 cm^3, but this decreased to 70 cm^3 when the mixture was bubbled through aqueous alkali.

What is the molecular formula of this compound?

A $C_6H_4S_2$ **B** $C_2H_6S_2$ **C** C_2H_6S **D** CH_4S

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

Iron and nickel are transition metals which often form ions with a charge of 2+.

Which statement concerning the atoms and ions of these two elements is correct?

A Ni^{2+} ion has a smaller ionic radius than Fe^{2+} ion.

B Ni atom has a lower first ionisation energy than Fe atom.

C Fe^{2+} ion and Ni atom are isoelectronic.

D In the same electric field, Ni^{2+} ion will be deflected more than Fe^{2+} ion.

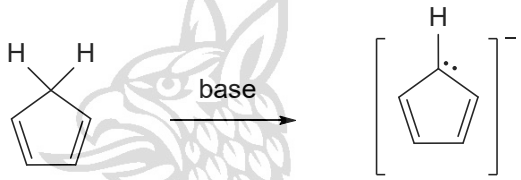
4 *Use of the Data Booklet is relevant to this question.*

Paramagnetism is a form of magnetism exhibited by species which contain unpaired electrons. These species can be attracted by an external magnetic field.

Which of the following species is **not** paramagnetic?

A Cl^+ **B** V^{3+} **C** O^- **D** Cu^+

5 Cyclopentadiene is an organic molecule with a structure as shown below. In the presence of a base, one of its hydrogens can be removed to form the planar cyclopentadienyl anion which is stabilised by resonance.



cyclopentadiene cyclopentadienyl anion

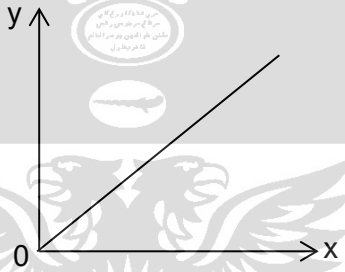
Which statement about these species are correct?

1 Cyclopentadiene is a planar molecule.
2 All carbon atoms in cyclopentadienyl anion are sp^2 hybridised.
3 The carbon-carbon bonds in the cyclopentadienyl anion are of different lengths.

A 1 only **B** 2 only

C 3 only **D** 2 and 3 only

6 Which of the following correctly represents ideal gas behaviour as shown by the graph?



	y-axis	x-axis	variable(s) held constant
A	p	V	n and T
B	p	$\frac{1}{T}$	n and V
C	pV	p	n and T
D	pV	T	n

7 Which class of reaction always has a positive enthalpy change?

A atomisation

B combustion

C formation

D solution

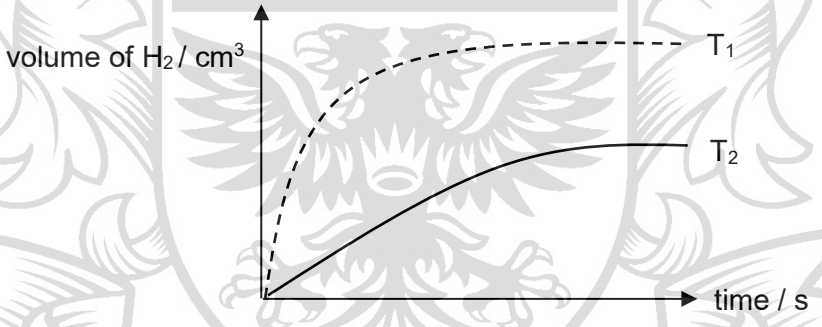
8 Which equation represents a reaction that is spontaneous at all temperatures?

A	$Q(g) \rightarrow R(s) + 2S(g)$	$\Delta H > 0$
B	$2T(s) + 3U(g) \rightarrow 4V(aq)$	$\Delta H < 0$
C	$2W(l) \rightarrow X(g)$	$\Delta H < 0$
D	$Y(g) \rightarrow Z(g)$	$\Delta H > 0$

9 The reaction of graphite and steam is shown below.

$$C(s) + H_2O(g) \rightleftharpoons H_2(g) + CO(g)$$

The graph below represents the volume of hydrogen gas formed at two different temperatures, T_1 and T_2, with the same initial amount of reactants.



Which statement about the reaction is correct?

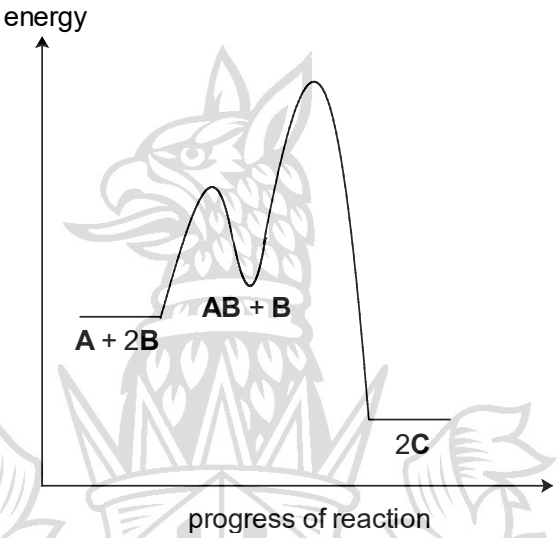
A The forward reaction is exothermic.

B The addition of more carbon will shift the position of equilibrium to the right.

C The equilibrium constant, K_c, increases with increasing temperature.

D The temperature T_2 is greater than T_1.

10 The energy profile of a chemical reaction, **A** + 2**B** ⟶ 2**C**, is shown below.



What can be deduced from the energy profile?

1 The reaction is second order with respect to **B**.
2 The rate determining step is a bimolecular reaction.
3 The reaction is a catalysed reaction.

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

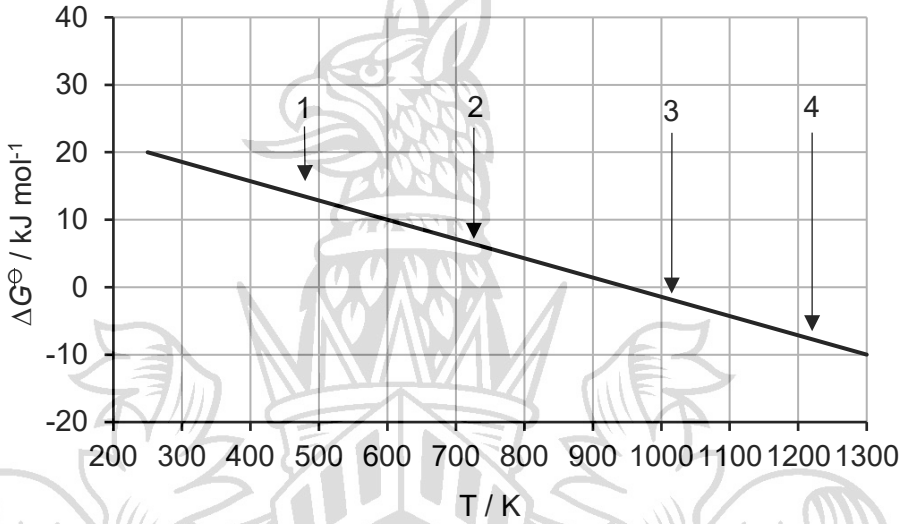
11 Lead is the final product formed by a series of changes in which the rate-determining step is the radioactive decay of uranium-238. This radioactive decay is a first-order reaction with a half-life of 4.5 x 10^9 years.

How long would it take for a rock sample, originally lead-free, to contain a molar proportion of uranium to lead of 1 : 3?

A 1.5 x 10^9 years
B 2.25 x 10^9 years
C 9.0 x 10^9 years
D 1.35 x 10^9 years

12 The graph shows how $\Delta G^{\ominus}$ changes with temperature for the reaction shown.

$$\mathbf{W}(g) + \mathbf{X}(g) \rightleftharpoons \mathbf{Y}(g) + \mathbf{Z}(g)$$



Equimolar amounts of **W** and **X** were introduced into a sealed container and allowed to reach equilibrium.

At which points will the equilibrium concentration of **X** be **smaller** than that of **Y**?

A 1 and 2 only

B 1 only

C 2, 3 and 4 only

D 3 and 4 only

13 PCl_5 can be prepared from the chlorination of PCl_3.

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

Equal amounts of reactants with a total initial pressure p were reacted in a sealed vessel at constant temperature.

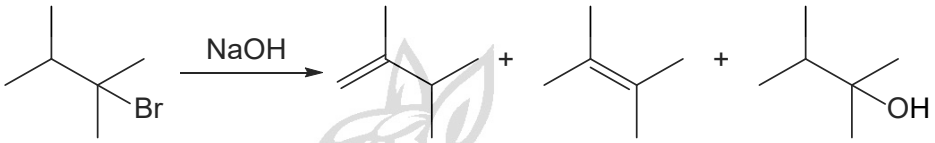
The equilibrium partial pressure of PCl_5 was found to be $\frac{1}{5}$ p.

What is the value of equilibrium constant, K_p, at this temperature?

A $\frac{5}{16p}$ **B** $\frac{20}{9p}$

C $\frac{3p}{2}$ **D** $\frac{3p}{50}$

14 What types of reactions are shown below?



1. condensation
2. elimination
3. oxidation
4. substitution

A 2 and 4 only **B** 2 and 3 only

C 1, 2 and 4 only **D** 3 and 4 only

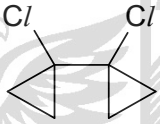
15 In the presence of light, chlorocyclopropane reacts with liquid bromine to form a mixture of products.

chlorocyclopropane

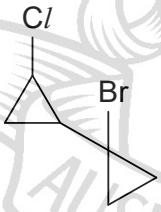
Which of the following compounds is **not** a possible product in this reaction?

A

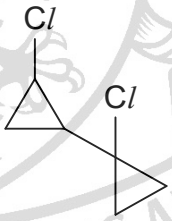
B



C



D



- END OF SECTION A -

Section C (40 marks)

This section consists of **three** questions. Answer **all** questions from this section.
Begin each question on a **fresh page of paper**.

C1 When heated, butane reacts with chlorine to form 1-chlorobutane as one of the products. The equation for the reaction is shown below.

$$CH_3CH_2CH_2CH_3(g) + Cl_2(g) \longrightarrow CH_3CH_2CH_2CH_2Cl(g) + HCl(g)$$

(a) Explain why $CH_3CH_2CH_2CH_3$ has a lower boiling point than $CH_3CH_2CH_2CH_2Cl$. [2]

(b) With reference to the *Data Booklet*, calculate ΔH_r for this reaction. Hence, explain why the above reaction is spontaneous. [2]

(c) Describe the mechanism for the above reaction. [3]

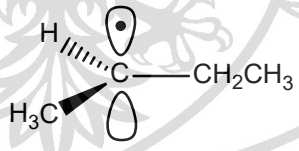
(d) If all hydrogen atoms were equally reactive, the mono-chlorination of butane should yield 1-chlorobutane and 2-chlorobutane in the ratio of 3:2.

(i) Give a reason to account for the ratio obtained. [1]

However, the experimental yield of 1-chlorobutane is lower than expected. In an experiment, 1-chlorobutane was found to constitute 30% of the mono-chlorobutanes formed.

(ii) Using the information given, compare the relative reactivities of the hydrogen atoms in butane. Explain your answer. [1]

(e) In the production of 2-chlorobutane by free radical substitution, the product mixture obtained is a racemic mixture. It is proposed that the free radical exists in the following structure.



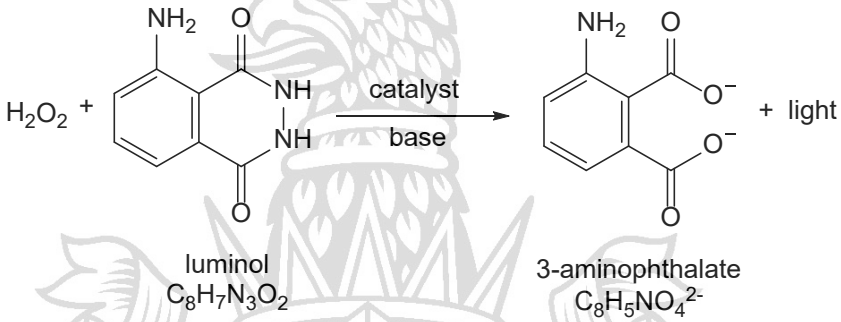
(i) Draw the enantiomers of 2-chlorobutane. [1]

(ii) Explain why the 2-chlorobutane is formed as a racemic mixture. [1]

[Total: 11]

C2 Chemiluminescence is the emission of light as a result of a chemical reaction, for example, the reactions used in glow sticks.

Luminol is a common chemiluminescent reagent. In the presence of a base and a catalyst, H_2O_2 oxidises luminol to form 3-aminophthalate with the emission of an intense blue glow.



luminol
$C_8H_7N_3O_2$

3-aminophthalate
$C_8H_5NO_4^{2-}$

(a) Write a half-equation for the oxidation of luminol to 3-aminophthalate under basic conditions. Nitrogen gas is one of the products. [1]

The following solutions were prepared to conduct a chemiluminescent clock reaction. Horseradish peroxidase (HRP) was used as the catalyst.

FA 1 contains luminol, uric acid (UA) and HRP prepared in a basic solution.
FA 2 is H_2O_2 solution.

Reaction (1) $H_2O_2 + UA \xrightarrow{HRP} UA^* + \text{other products}$

Reaction (2) $H_2O_2 + \text{luminol} \xrightarrow{HRP} \text{3-aminophthalate} + \text{light}$

When **FA 1** and **FA 2** are mixed together, UA is preferentially oxidised by H_2O_2 in Reaction (1). After the UA is completely oxidised, Reaction (2) begins, giving off a sudden flash of light. The time delay, *T*, is the time taken for the flash of light to be observed after **FA 1** and **FA 2** are mixed.

For the first experiment, 2.5 cm^3 of **FA 1** and 2.0 cm^3 of **FA 2** were mixed and the time delay, *T*, was recorded using a stopwatch.

(b) **(i)** Calculate the percentage uncertainty (or error) associated with preparing the first sample if 10 cm^3 measuring cylinders were used to measure the volumes of **FA 1** and **FA 2**. The uncertainty in the volume measured using a 10 cm^3 measuring cylinder is ±0.2 cm^3. [1]

(ii) Suggest how the percentage uncertainty (or error) calculated in **(b)(i)** can be reduced. [1]

(iii) Besides the measurement of volumes, identify another possible source of error in this experiment. [1]

The experiment was repeated with varying concentrations of UA, HRP and H_2O_2, and the following results were obtained.

Experiment	[UA] / x 10^{-5} mol dm^{-3}	[HRP] / x 10^{-7} mol dm^{-3}	[H_2O_2] / x 10^{-5} mol dm^{-3}	T / s
1	3.00	2.65	4.0	450
2	3.00	1.33	4.0	900
3	1.00	1.33	4.0	300
4	0.50	1.33	2.0	150

(c) In Experiments 2 and 3, the concentrations of HRP and H_2O_2 were kept constant. Explain why this was necessary. [1]

(d) The relationship between the initial rate of Reaction (1) and the time delay, T, is given by

$$\text{initial rate} \approx \frac{[UA]}{T}$$

(i) By calculating the initial rate, or otherwise, use the above data to deduce the order of Reaction (1) with respect to UA, HRP and H_2O_2. Show your reasoning clearly. [3]

(ii) Write down the rate equation for Reaction (1) and state the units of the rate constant. [2]

(iii) Sketch a graph to show how the concentration of HRP changes with time in Experiment 1. Briefly describe any key features of the graph. [2]

(e) A partial mechanism for Reaction (1) is proposed below. X, Y and UA* are intermediates.

Step 1 $H_2O_2 + HRP \rightarrow X$
Step 2 $X + UA \rightarrow Y + UA^*$
Step 3 $Y + UA \rightarrow HRP + UA^*$

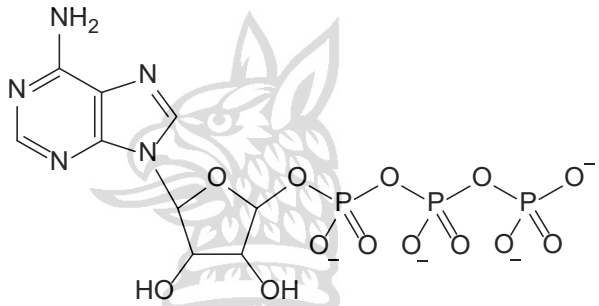
Explain fully how HRP acts as a homogeneous catalyst in this reaction, using evidence from the partial mechanism. [2]

(f) Outline how you would determine the effect of temperature on the rate of this reaction.

You are provided with the same **FA 1** and **FA 2** solutions as described above. [1]

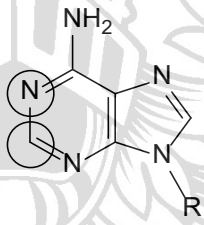
[Total: 15]

C3 Adenosine triphosphate, ATP, is an important biomolecule which provides energy to drive various processes in living cells, such as muscular contraction.



adenosine triphosphate

(a) ATP contains a bicyclic ring, adenine, which has the following structure.



adenine

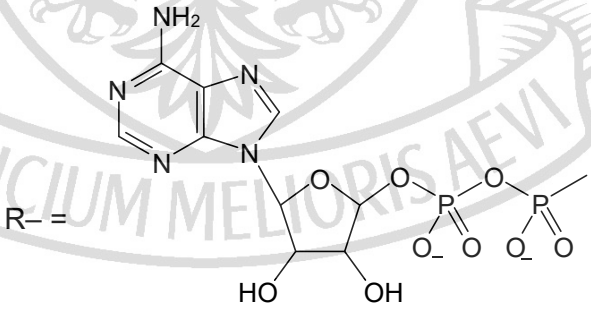
State the hybridisation for each of the circled C and N atoms. Briefly explain your answer for the C atom. [3]

(b) A student suggested that ATP hydrolysis releases energy due to the breaking of the "high energy" P–O bond. However, bond breaking is an endothermic process.

The equation for the standard enthalpy change of ATP hydrolysis is as follows.

$$[R\text{–}O\text{–}PO_3]^{4-}(aq) + H_2O(l) \xrightarrow{\Delta H^{\ominus}_{hydrolysis}(ATP)} [R\text{–}O]^{3-}(aq) + H^+(aq) + [PO_3\text{–}OH]^{2-}(aq)$$

where $[R\text{–}O\text{–}PO_3]^{4-}$ represents ATP and R represents the following structure.



You are provided with the following information:

$[R–O–PO_3]^{4–}(g) \rightarrow [R–O]^{3–}(g) + PO_3^{–}(g)$	$\Delta H_1^{\ominus} = +206$ kJ mol^{-1}
$H_2O(g) \rightarrow H^+(g) + OH^–(g)$	$\Delta H_2^{\ominus} = +1626$ kJ mol^{-1}
$PO_3^{–}(g) + OH^–(g) \rightarrow [PO_3–OH]^{2–}(g)$	$\Delta H_3^{\ominus} = –288$ kJ mol^{-1}

Standard enthalpy changes of hydration of

$H^+(g)$	$\Delta H^{\ominus}_{hyd} = –1091$ kJ mol^{-1}
$[R–O–PO_3]^{4–}(g)$	$\Delta H^{\ominus}_{hyd} = –84.0$ kJ mol^{-1}
$[R–O]^{3–}(g)$	$\Delta H^{\ominus}_{hyd} = –122$ kJ mol^{-1}
$[PO_3–OH]^{2–}(g)$	$\Delta H^{\ominus}_{hyd} = –484$ kJ mol^{-1}

Standard enthalpy change of vaporisation of water

$H_2O(l) \rightarrow H_2O(g)$ $\quad \Delta H^{\ominus}_{vap} = +40.7$ kJ mol^{-1}

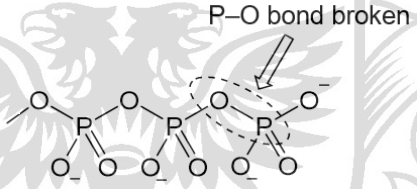
(i) Explain why the standard enthalpy change of hydration of $H^+(g)$ is exothermic but the standard enthalpy change of vaporisation of water is endothermic. [2]

(ii) By drawing an appropriate energy cycle, calculate $\Delta H^{\ominus}_{hydrolysis}$(ATP).

$$[R–O–PO_3]^{4–}(aq) + H_2O(l) \xrightarrow{\Delta H^{\ominus}_{hydrolysis}(ATP)} [R–O]^{3–}(aq) + H^+(aq) + [PO_3–OH]^{2–}(aq)$$

[4]

(c) The process represented by $\Delta H_1^{\ominus}$ involves the breaking of the P–O bond in ATP as shown in the diagram below. However $\Delta H_1^{\ominus}$ has a **smaller magnitude** than the bond energy of the P–O bond found in the *Data Booklet*, 340 kJ mol^{-1}. By considering the structure of the triphosphate group below, suggest a reason to explain why. [1]



(d) **(i)** The $\Delta S^{\ominus}$ of the hydrolysis of ATP is +7.7 J mol^{-1} K^{-1}. Comment on the **sign** of $\Delta S^{\ominus}$. [1]

(ii) The maximum work done by a chemical reaction is given by $\Delta G^{\ominus}$. Use your answer in **(b)(ii)** to determine the maximum work done by the hydrolysis of ATP under standard conditions. [1]

(iii) In living organisms, the maximum work done by the hydrolysis of ATP is more exergonic than that calculated in **(d)(ii)**. Suggest a possible reason and explain why. [2]

[Total: 14]

RAFFLES INSTITUTION
2018 Year 5 Promotion Examination
H2 Chemistry

COVER SHEET

Name:	( )	**Class:**

For Examiner's Use Only

Section		**Marks**
A		**/ 15**
B	**B1**	**/ 13**
	B2	**/ 10**
	B3	**/ 12**
C	**C1**	**/ 11**
	C2	**/ 15**
	C3	**/ 14**
Promotional Examination	**Total**	**/ 90**
	Percentage	**/ 100**
	Grade	

Section B (35 marks)

This section consists of **three** questions.
Answer **all** the questions in this section in the spaces provided.

B1 The value of the equilibrium constant, K_c, for the following reaction is determined using a titration procedure.

$$Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s) \qquad \Delta H < 0$$

25.0 cm^3 of 0.100 mol dm^{-3} Fe^{2+} solution is mixed with 25.0 cm^3 of 0.100 mol dm^{-3} Ag^+ solution in a volumetric flask. The mixture is shaken and left to stand for 30 minutes to reach equilibrium.

Using a pipette, 25.0 cm^3 of the equilibrium mixture is transferred into a conical flask, *while ensuring that the Ag solid at the bottom of the volumetric flask is not disturbed*.

The concentration of Ag^+ in the 25.0 cm^3 equilibrium mixture is determined by titration with KSCN solution of a suitable concentration. The titration reaction is as follows.

$$Ag^{+}(aq) + SCN^{-}(aq) \longrightarrow AgSCN(s)$$

When $Ag^+(aq)$ has completely reacted, the addition of one excess drop of SCN^- then reacts with Fe^{3+} as shown below.

$$Fe^{3+}(aq) + SCN^{-}(aq) \longrightarrow FeSCN^{2+}(aq)$$

(a) Write the K_c expression for the reaction between Fe^{2+} and Ag^+.

[1]

(b) The concentration of Ag^+ in the equilibrium mixture is expected to be 0.045 mol dm^{-3}.

You are to prepare a suitable concentration of KSCN solution in a 250 cm^3 volumetric flask that is to be used for titration with 25.0 cm^3 of the equilibrium mixture.

You may assume that the following are provided.

3 g solid KSCN
deionised water
the apparatus normally found in a school or college laboratory

(i) Calculate a suitable mass of solid KSCN to be used, stating any assumptions made.

[2]

(ii) Describe a practical sequence for the preparation of KSCN solution from the solid KSCN provided.

....

....

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....

....

....[3]

(c) A student accidentally transferred some of the Ag solid from the equilibrium mixture when using the pipette. Suggest two reasons how this would lead to inaccurate titration results.

……

……

……

……

……[2]

(d) The colours of the following aqueous ions or solids are given.

Species	**Colour**
$Fe^{2+}(aq)$	pale green
$Ag^{+}(aq)$	colourless
$Fe^{3+}(aq)$	yellow
$SCN^{-}(aq)$	colourless
AgSCN(s)	white
$FeSCN^{2+}(aq)$	blood red

With the aid of the above information, suggest the colour change at the end-point of the titration.

……[1]

(e) The concentration of Ag^{+} in the equilibrium mixture was verified to be 0.045 mol dm^{-3}.

Using your expression in **(a)**, calculate the value of the equilibrium constant, K_c.

Value of K_c = ……
[2]

(f) Another equilibrium mixture is prepared at a higher temperature using the same procedure.

Explain how the higher temperature will affect the concentration of Ag^+ in the equilibrium mixture.

……

……

……

……[2]

[Total: 13]

B2 Isomerism is commonly observed in organic compounds.

(a) What is meant by the term *constitutional isomers*?

……

……[1]

(b) There are several compounds with the molecular formula C_3H_6O.
Information about three such compounds is given below.

Compound **P**
- It is a symmetrical molecule with a C=O bond.

Compound **Q**
- It is a cyclic compound with no double bonds.
- Hydrogen bonding exists between its molecules.

Compound **R**
- It is a cyclic compound with no double bonds.
- Hydrogen bonding **does not** exist between its molecules.
- It exists as a pair of enantiomers.

Give the skeletal formulae of compounds **P**, **Q** and **R** in the boxes below.

P	**Q**	**R**

[3]

(c) Oxetane is another compound with molecular formula C_3H_6O.
It has the following structure.

(i) State the number of electron pairs around the O atom.

……..…… [1]

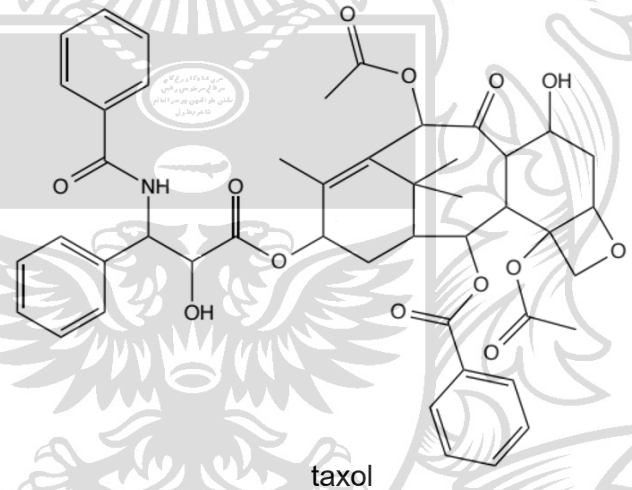
(ii) Suggest a value for the C–O–C bond angle observed in oxetane and briefly explain your answer.

……..

……..

……..…… [2]

(iii) Taxol is a natural compound which contains an oxetane ring.



taxol

State the number of chiral carbons present in taxol.

……..…… [1]

(d) Stereoisomerism is another type of isomerism commonly observed in organic compounds.

But-2-ene exists as a pair of stereoisomers.

Give the structures of the two isomers of but-2-ene and explain how these two isomers arise.

……

……

…… [2]

[Total: 10]

B3 *Use of the Data Booklet is relevant to this question.*

This question is about carbon dioxide, its impact on the environment as well as its applications in industry.

(a) Dry ice, which is solid CO_2, can be added to water to create a dense mist for stage effects. Calculate the density, in g cm^{-3}, of CO_2 gas at room temperature and pressure.

[1]

(b) Molar heat capacity is the quantity of energy needed to raise the temperature of 1 mol of a substance by 1 K.

The molar heat capacity of the various components of dry air at 298 K and 1 atm is given below.

gas	molar heat capacity / J mol^{-1} K^{-1}	% composition by volume
N_2	29.12	78.1
O_2	29.38	20.9
CO_2	36.94	0.04
noble gases	20.79	0.96

Using the data given, calculate the molar heat capacity of dry air at 298 K and 1 atm.

[1]

(c) In places with high humidity, it is common to hear people commenting that "*the air is really heavy today!*".

At a given temperature and pressure, do you agree that a fixed volume of moist air is denser than the same volume of dry air?

……

……

……[2]

(d) Decaffeinated coffee has been gaining wider commercial interest due to the increasing number of coffee drinkers who wish to limit their caffeine intake for health reasons.

Dichloromethane, CH_2Cl_2, and supercritical CO_2 are two commonly-used solvents for the extraction of caffeine.

Supercritical CO_2 exists at temperatures above 31.1°C and pressures above 72.9 atm. Supercritical CO_2, though a gas, behaves like a liquid.

(i) Draw the dot-and-cross diagram for CH_2Cl_2.

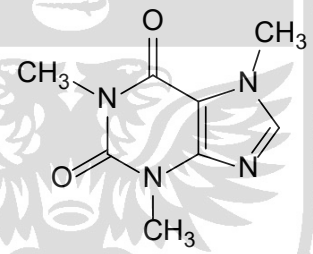
[1]

(ii) Suggest whether the C*l*–C–C*l* bond angle is smaller than, equal to, or larger than H–C–H bond angle.

……..

……..…. [1]

The structure of caffeine is given below.



caffeine

(iii) Explain, in terms of intermolecular forces, which of the two solvents (CH_2Cl_2 or supercritical CO_2) might be a better solvent for caffeine.

……..

……..

……..

……..…. [2]

(iv) Suggest one advantage of extracting caffeine using supercritical CO_2 over CH_2Cl_2.

……..…… [1]

(e) Soft drink manufacturers force carbon dioxide to dissolve in water to produce carbonated water with the 'fizzy' characteristic. The carbonic acid, H_2CO_3, produced then partially dissociates to produce H^+ ions.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

(i) H^+ ions do not exist in isolation in water. They bond to water molecules to form hydronium ions, H_3O^+.

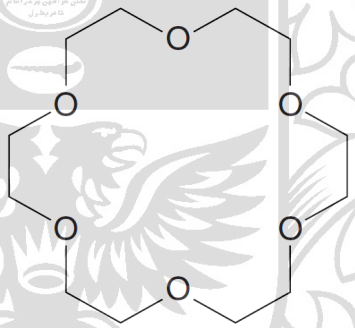
Predict and explain the shape of the hydronium ion.

……..……...

……..…… [2]

(ii) The hydronium ion, H_3O^+, may be solvated inside the macrocyclic 18-crown-6 molecule shown.

Draw **one** hydronium ion inside the macrocycle, showing how it is attached to the ring.



[1]

[Total: 12]

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