

NAME

CHEMISTRY

Paper 3 Free Response

CT GROUP

18S

9729/03 2 October 2018 1 hour

Candidates answer on separate paper.

Additional Materials: Answer Paper, Graph Paper, Cover Page and Data Booklet.

READ THESE INSTRUCTIONS FIRST

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

Write in dark blue or black pen.

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

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

Section A Question 1 is a compulsory question.

Section B

Answer only **<u>one</u>** question from this section.

Begin each question on a <u>new piece</u> of paper.

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

A Data Booklet is provided.

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.

At the end of the examination, fasten all your work securely together, together with the cover page.

Section A

Question 1 is a **compulsory** question. All candidates should answer this question.

1 (a) The Haber process is the main industrial procedure for the production of ammonia from nitrogen and hydrogen.

$$N_2(g) + 3H_2(g) = 2NH_3(g)$$

- (i) State Le Chatelier's Principle.
- (ii) The optimal operating temperature for the Haber process is 450 °C. Use the following values to calculate the ΔG_r° at 450 °C.

 $\Delta H_{\rm r}^{\,\rm e}$ = - 92.0 kJ mol⁻¹ $\Delta S_{\rm r}^{\,\rm e}$ = - 199 J K⁻¹ mol⁻¹

- (iii) Calculate the value of the equilibrium constant for the Haber process at the same temperature using $\Delta G_r^{e} = RT \ln K$. Explain the significance of your answer in terms of the yield of the process. [2]
- (iv) State the usual operating pressure (in atm) required for the Haber process and explain why it is necessary for an acceptable yield in the industrial procedure. [2]
- (b) Disinfecting solutions often contain hypochlorous acid, HOC*l*, which can react with alkenes via electrophilic addition.

When hypochlorous acid reacts with but-1-ene, the major product obtained is 1-chlorobutan-2-ol.



1-chlorobutan-2-ol

- (i) Deduce which atom in the HOC*l* molecule is the electrophilic site responsible for the product shown. [1]
- (ii) Describe the mechanism of the reaction between HOC*l* and but-1-ene to form 1-chlorobutan-2-ol, including curly arrows, lone pairs and dipoles where appropriate.
 [2]
- (iii) The product of the reaction, 1-chlorobutan-2-ol, exists as a mixture of stereoisomers. State the type of isomerism that occurs and briefly explain how and in what proportion the stereoisomers were formed. [3]

[1]

[1]

(iv) Compounds A, B and C have the same molecular formula C_8H_8 . All three compounds possess a six-membered ring each.

When all three compounds undergo oxidative cleavage separately, only one organic compound is formed in each case, as shown in Table 1.1.





Suggest the structures of **A**, **B** and **C**.

[3]

- (c) (i) Sketch on the same axes, the trend for the atomic radii and ionic radii of the Period 3 elements from Na to Cl. [2]
 - (ii) Explain the shape of each of your sketches in (c)(i) as fully as you can. Comparison between the two sketches is not required.
 [3]

[Total: 20]

Section B

Answer **one** question from this section.

2 Proteases are enzymes that can break down particular bonds that are present in protein molecules. In such reactions, proteins are called 'substrates'.

Consider the following section of a protein substrate that can be acted on by a protease.



- (a) (i) Explain the term *bond energy*.
 - Quote all relevant data from the *Data Booklet* to suggest, with reasoning, which bond is broken by the protease in the above section of the protein substrate. You may ignore any bonds to R.

ĊH₂

(b) **P** is a product of the above enzymatic reaction. **P** can dissociate in water to form **Q**.



In terms of the Bronsted-Lowry theory of acids and bases, identify the role of **P** in the forward reaction and that of **Q** in the reverse reaction. Briefly explain your answer. [2]

(c) The kinetics of a reaction between a protease enzyme and a substrate, casein, were studied in a temperature-controlled water bath.

enzyme	+	substrate	\rightarrow	products	+	enzyme	(1)
(protease)		(casein)				(protease)	

(i) One of the products, **T**, forms a blue colouration when reacted with a chemical called Folin's reagent. Suggest how you would monitor the rate of reaction (1) over time. [1]

[1]

Time /min	[casein] /mol dm ⁻³			
0	0.1000			
1.5	0.0850			
4.3	0.0640			
6.5	0.0495			
10.1	0.0345			
15.4	0.0180			

The following table shows [casein] at various times.

- (ii) Plot these data on suitable axes and, showing all your working and drawing clearly any construction lines on your graph, use it to determine:
 - the order of reaction with respect to [casein]; and
 - the initial rate, in mol dm⁻³ min⁻¹.

[4]

(d) The activity of proteases can be significantly affected by the presence of certain inorganic salts, such as magnesium chloride.

By constructing a Born-Haber cycle that shows *all individual processes*, calculate the lattice energy of magnesium chloride using data from the table below, together with relevant data from the *Data Booklet*.

Enthalpy change of formation of magnesium chloride / kJ mol ⁻¹	-642
Electron affinity of Cl / kJ mol ⁻¹	-349
Enthalpy change of atomisation of magnesium / kJ mol ⁻¹	+120

[4]

- (e) Product **T**, from part (c), contains the elements carbon, hydrogen, nitrogen and oxygen only. A series of experiments were carried out to determine its identity.
 - (i) When 1.176 g of purified T was burnt in excess oxygen, 2.573 g of carbon dioxide and 0.643 g of water were formed. Calculate the mass of carbon and hydrogen, respectively, in 1.176 g of T.
 - (ii) In a separate reaction, all the nitrogen in a fresh 1.176 g sample of **T** was converted into ammonia. All the ammonia produced was then absorbed in a beaker containing 80.0 cm³ of 0.100 mol dm⁻³ hydrochloric acid. The remaining hydrochloric acid required 22.10 cm³ of 0.0700 mol dm⁻³ sodium hydroxide solution for neutralisation.

Calculate the mass of nitrogen in 1.176 g of T.

(iii) Hence, using your answers to (e)(i) and (e)(ii), deduce the empirical formula of T. [2]

[Total: 20]

[2]

- **3 (a)** Ozone in the upper atmosphere is formed and destroyed naturally such that a dynamic equilibrium exists.
 - (i) What do you understand by the term *dynamic equilibrium*? [1]
 - (ii) The typical ozone concentration over Earth's surface is about 300 Dobson units (DU). Each DU is defined to be a thickness of 0.01 mm formed by a particular gas present in the atmosphere if it were compressed over a certain area at standard temperature and pressure.

Calculate the number of molecules of ozone that would typically be present over an area of 1.0 m^2 on the Earth's surface. Assume that ozone behaves ideally. [3]

(b) In the 1970s, chlorofluorocarbons (CFCs), widely used as refrigerants, are found to be a major cause of ozone depletion. Due to their long lifetime, they migrate to the upper atmosphere where ultraviolet radiation breaks the C–C/ bonds forming C/• radicals.

The mechanism below shows how Cl• radicals may catalyse ozone (O₃) destruction.

 $\begin{array}{lll} Cl \bullet (g) \ + \ O_3 (g) \ \longrightarrow \ Cl O \bullet (g) \ + \ O_2 (g) & \text{slow} & E_a = 2.1 \text{ kJ mol}^{-1} \\ Cl O \bullet (g) \ + \ O \bullet (g) \ \longrightarrow \ Cl \bullet (g) \ + \ O_2 (g) & \text{fast} \end{array}$

(i) Write an equation for the overall reaction shown by the above mechanism. [1]

[1]

- (ii) Write the rate equation for the overall reaction.
- (iii) Sketch a labelled reaction pathway diagram for the mechanism, given that the overall reaction is exothermic. [2]
- (iv) Recent studies suggest that the mechanism may actually involve the reaction of $C/O \cdot$ to form Cl_2O_2 . Draw the dot-and-cross diagram of a Cl_2O_2 molecule. [1]
- (v) A natural cause of ozone destruction is nitrogen monoxide, •NO, which catalyses the reaction via a similar mechanism with an activation energy of 11.9 kJ mol⁻¹.

Explain which catalyst is more effective for ozone destruction. [1]

In 1987, the world signed the Montreal Protocol to eliminate CFCs. Since then, chemists have sought to prepare new compounds as replacements. However in 2017, researchers concluded there is no ideal compound as yet that combined low environment impact with desirable refrigerant properties.

(c) The earliest strategy was to replace a C–C*l* bond in a CFC with a C–H bond, forming a hydrochlorofluorocarbon (HCFC). However, a disadvantage of HCFC is increased flammability affecting safety.

Suggest one physical property of HCFCs that would also be different from CFCs, and explain why it is different. [2]

- (d) The next replacement was hydrofluorocarbons (HFCs). One HFC used now in refrigerators and car air-conditioners is HFC-134a, where 134 is its code number.
 - (i) The molecular formula for a HFC can be obtained by adding 90 to its code number to get a three-digit number, in which:
 - the first digit is the number of C atoms
 - the second digit is the number of H atoms, and
 - the third digit is the number of F atoms.

Write the molecular formula of HFC-134.

- (ii) The suffix "a" in the code indicates a specific isomer of HFC-134. Draw the two isomers of HFC-134 and state the type of isomerism observed. [2]
- (e) Unfortunately, HFCs are found to be greenhouse gases. Another new class of refrigerants, hydrofluoroolefins (HFOs), is introduced for their lower impact on global warming.

An example is HFO-1234yf:

H₂C C F

- (i) Give the IUPAC name for HFO-1234yf.
- (ii) Describe a simple chemical test to distinguish between HFO-1234yf and HFC-134a, stating the reagents and expected observations for each compound. [2]
- (iii) HFO-1234yf could react via the pathway below to form trifluoroethanoic acid, which may pose a risk to the environment.



trifluoroethanoic acid

Name the types of reaction that occur for step 1 and step 2. [2]

[Total: 20]

~END OF PAPER~



[1]