

CHEMISTRY

Paper 2 Structured Questions

Candidates answer on the Question Paper Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, CT group, centre number and index number clearly in the spaces above.

Write in dark blue or black pen.

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

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

Answer all questions in the spaces provided in the Question Paper.

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

A Data Booklet is provided.

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.

For Examiner's Use		
1	/ 19	
2	/ 11	
3	/ 11	
4	/ 11	
5	/ 15	
6	/8	
Deductions		
Total	/ 75	

Calculator Model:

9729/02

12 September 2018

2 hours

1 (a) Describe and explain the trend in thermal stability of Group 17 hydrides, HF to HI, by referring to relevant bond energies from the *Data Booklet*.

(b) The very low acid strength of HF was frequently explained by the same reasoning in (a). However, the dissociation of HF in aqueous solution

 $HF(aq) \rightarrow H^{+}(aq) + F^{-}(aq) \Delta H_{dissociation}$

involves a cycle of steps. Hence, a whole series of enthalpy changes should be considered, one of which is the enthalpy change of hydration.

(i) Explain, with the aid of an equation, what is meant by standard enthalpy change of hydration for F^- ion.

	•••
[2]

(ii) Fig. 1.1 shows an incomplete energy level diagram to represent the cycle of steps involved in the dissociation of HF.



Fig. 1.1

Complete Fig. 1.1 by incorporating the following data and relevant data from the *Data Booklet*. Draw arrows and label each level with the appropriate formulae.

electron affinity for F(g)	= –328 kJ mol ^{–1}	
enthalpy change of hydration for H ⁺ (g)	= –1091 kJ mol⁻¹	
enthalpy change of hydration for F-(g)	= –515 kJ mol ^{–1}	
· · · · · · · · · · · · · · · · · · ·		[3]

(iii) Use your completed energy level diagram to calculate $\Delta H_{\text{dissociation}}$ for HF.

[1]

(c) (i) Explain why two HF molecules can form a hydrogen bond between them.

(ii) When we measure the distance between a hydrogen nucleus and a fluorine nucleus in solid HF, two H to F 'bond distances' are found: 0.092 nm and 0.163 nm.

Draw a diagram containing two HF molecules, showing why there are two different 'bond distances'. Name and label which bond has 'bond distance' 0.092 nm, which has 'bond distance' 0.163 nm.

[2]

(d) Nitrogen also forms hydrides, such as hydrogen azide, HN₃, and ammonia, NH₃.

 HN_3 has two bond angles: 104.5° and 180°.

Suggest a dot-and-cross diagram for HN₃.

(e) NH_3 is produced from N_2 and H_2 in the presence of a catalyst.

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

(i) State and explain how the entropy will change when N_2 and H_2 react.

 	 [2]

(ii) Write an expression for K_p for the above equilibrium.

[1]

(iii) In an experiment, N_2 and H_2 are placed in a sealed reactor in the molar ratio 1:3. The reactor is maintained at a temperature of 750 K. At equilibrium, 20% of N_2 is converted to NH_3 , and the total pressure is 20.0 Mpa.

Calculate a value for K_p for the equilibrium, stating its units. (1 MPa = 10⁶ Pa)

[Total: 19]

2 In addition to carbon and hydrogen, organic compounds commonly contain other elements covalently bonded in their molecules.

A strategy to identify these other elements in the compounds is to convert them to ionic forms so that these can be detected subsequently by qualitative tests.

(a) State the *type of reaction* that a chloroalkane can be subjected to so as to convert the chlorine present to chloride ions. Give the reagents and conditions for the reaction.

type of reaction:

reagents and conditions:[1]

"Sodium fusion" is an approach which uses the above strategy for the detection of other elements, in particular, halogens, nitrogen and/or sulfur, in organic compounds. The procedure is outlined below.

- 1. A sample of sodium metal is gently heated in a small boiling tube until molten.
- 2. The organic compound is added to the boiling tube a little at a time. Effervescence of hydrogen is observed immediately if the organic compound contains "active hydrogen".
- 3. The boiling tube is heated gently at first, then strongly while the "fusion reaction" between sodium and the organic compound occurs. During this process, other elements in the organic compound are converted to ions such as those in Table 2.1 and ionic sodium compounds are formed.
- 4. The contents of the hot boiling tube are completely emptied into a beaker of water. The "fusion reaction" is quenched because any excess sodium reacts with the water.
- 5. The contents of the beaker are filtered.
- 6. The filtrate is tested for relevant ions qualitatively.

Table 2.1

element(s) other than carbon and hydrogen in organic compound	ion after "fusion reaction"
chlorine	chloride, C <i>l</i> ⁻
bromine	bromide, Br⁻
both nitrogen and sulfur	thiocyanate, SCN⁻
nitrogen in the absence of sulfur	cyanide, CN⁻
sulfur in the absence of nitrogen	sulfide, S²⁻

(b) (i) Suggest two different functional groups which may be present in organic compounds containing "active hydrogen", leading to effervescence in step 2.

.....[1]

(ii) One reason that sodium is used is that the sodium ion in the filtrate does not interfere with the tests in step 6.

Using **relevant** data from Table 2.2 about sodium, suggest another **two** reasons why sodium is used for the "fusion reaction".

density	0.97 g cm ⁻³
melting point	98 C
standard redox potential, <i>E</i> [⊖] (Na⁺/Na)	-2.71 V

.....

Table 2.2

- (c) In step 6, to test for the sulfide ion, the reagent sodium nitroprusside is added to the filtrate. A positive test is indicated by the appearance of a violet colouration owing to the formation of compound A, which contains an octahedral complex ion containing Fe²⁺.
 - (i) Explain why compound A is coloured.

 (ii) Compound A contains the following composition by mass.

element	Na	Fe	С	Ν	0	S
percentage by mass	27.1	16.4	17.7	24.7	4.7	9.4

Determine the empirical formula of compound **A**.

[2]

(iii) The complex ion in compound **A** contains two different ligands, one of which is found in Table 2.1.

Suggest the formula of the **other** ligand, given that this ligand forms only one bond with the central Fe^{2+} ion. Information from other parts of (c) may be relevant.

.....[1]

(d) **B** ($M_r = 77.1$) is an optically active organic compound. In addition to carbon and hydrogen, **B** contains only element(s) in Table 2.1. **B** underwent "sodium fusion" and its filtrate gave a blood-red complex on addition of aqueous Fe³⁺.

Suggest the structure of compound **B**, given that it is non-cyclic and contains only single bonds. Assume that all elements show their usual valencies.

[1]

[Total: 11]

3 (a) Ethyl diazoethanoate, D, reacts with water to give compound E, and nitrogen.

$$N_2CHCO_2CH_2CH_3(aq) + H_2O(l) \rightarrow HOCH_2CO_2CH_2CH_3(aq) + N_2(g)$$

D E

When 2.50×10^{-3} mol of **D** was added into water, the volume of nitrogen gas evolved at intervals of time after the start of the reaction were measured at 293 K, 1 atm. The experiment results were plotted in the graph below.



(iii) Calculate the rate constant for this reaction at 293 K, stating its units.

(b) The rate of this reaction, using 1.00 mol dm⁻³ of solution **D**, was measured at 293 K in the presence of nitric acid. The results for a series of pH values are shown in Table 3.1.

experiment	pН	initial rate / mol dm ⁻³ min ⁻¹
1	2.0	2.69 × 10 ⁻²
2	2.3	1.35 × 10 ^{−2}
3	2.4	1.07 × 10 ⁻²

- Table 3.1
- (i) Using the information in Table 3.1, deduce the order of reaction with respect to $H^+(aq)$, and hence write the rate equation for this reaction.

 	[2]

(ii) The overall reaction between **D** and water is shown below:



This reaction occurs via a three-step mechanism in the presence of H⁺(aq).

 In the first step, the lone pair of electrons on the negatively charged nitrogen forms a new π bond with the positively charge nitrogen and simultaneously, the C=N π bond attacks H⁺(aq) to form a new σ bond to give intermediate F.



- In the second step, water reacts with F, giving the protonated form of E and N₂.
- In the third step, H⁺(aq) is lost to give **E**.

Illustrate the mechanism for this reaction, showing any relevant lone pairs, dipoles and charges, and indicating the movement of electron pairs with curly arrows. Label the slow step in your mechanism.

[3]

[Total: 11]

4 (a) (i) The p K_a values for the two successive dissociation of H₂C₂O₄ at 25 °C are: $pK_{a1} = 1.23$; $pK_{a2} = 4.19$.

A small quantity of $H_2C_2O_4$ is usually found in fabrics as dye fixatives, a substance used to set dyes on fabrics. A dye having a density of 1.50 g cm⁻³ contains *x* % by mass of $H_2C_2O_4$.

The pH of the dye is found to be 1.27. Ignoring the second dissociation for $H_2C_2O_4$ and assuming that the acidity of the dye arises only from $H_2C_2O_4$, determine the value of *x*.

(ii) When 25.0 cm³ of the dye is titrated with 0.100 mol dm⁻³ NaOH(aq), the pH at the second equivalence point is greater than 7.

With the aid of a relevant equation, explain this observation.

 (b) The following scheme illustrates a series of reactions involving $Fe^{3+}(aq)$.



- **5** Substituted benzaldehydes serve as important intermediates in the production of medicines, agricultural chemicals, and functional polymers.
 - (a) Describe the mechanism for the nitration of benzaldehyde, showing clearly how the **major** mono-substituted product is formed. Include curly arrows showing the movement of electrons, charges and any relevant lone pairs.

(b) In 1994, H. Goda et. al. reported a method for the synthesis of some halo-substituted benzaldehydes from benzaldehyde. The synthetic scheme showing the relative position of the halogen, X, to the group already on the benzene ring, is shown in Fig. 5.1.



(i) Using your knowledge of the orientating effect of groups in aromatic substitution reactions, explain the significance of the author's work.

.....[1]

(ii) The O-methyloxime derivative formed in step 1 is able to exhibit cis-trans isomerism.

Explain why this is so.



(c) Fig. 5.2 shows a possible reaction sequence with 2-chlorobenzaldehyde as the starting material.



Fig. 5.2

(d) Tollens' reagent which consists of the diamminesilver(I) complex, [Ag(NH₃)₂]⁺, is a commonly used reagent to test for the presence of aliphatic aldehydes and benzaldehydes.

With the aid of half-equations, write a balanced equation for the reaction of benzaldehyde, C_6H_5CHO , and $[Ag(NH_3)_2]^+$.

In this reaction, the oxidation number of the carbonyl carbon in benzaldhyde changes from +1 to +3.

Oxidation half-equation: Reduction half-equation: Overall equation: [2]

(e) In linear complexes such as the $[Ag(NH_3)_2]^+$ complex, the ligands approach the central metal ion along the z-axis. This causes the d-orbitals of the central metal ion to split into three energy levels as shown in Fig. 5.3.



(i) Draw the shapes of the $d_{x^2-y^2}$ and d_{yz} orbitals. Label your drawings clearly.

[2]

(ii) By considering the shape and orientation of the *d*-orbitals, suggest the identities of the highest and lowest energy *d*-orbitals in a linear complex.

Highest energy *d*-orbital: Lowest energy *d*-orbitals: and [1] [Total: 15]

6 Glucose, C₆H₁₂O₆, is the most abundant monosaccharide in nature and has great potential for application in fuel cell. Glucose alkaline fuel cell is a promising power source for portable electronic equipment. The set-up is illustrated in Fig. 6.1.



Fig. 6.1

At the anode, glucose is oxidised to carbonate ions, CO_3^{2-} , in an alkaline medium while at the cathode, oxygen gas is reduced. The value of E^{e}_{cell} is +0.85 V. The overall reaction occurring in the fuel cell is given below:

 $C_{6}H_{12}O_{6} + 6O_{2} + 12OH^{-} \rightarrow 6CO_{3}^{2-} + 12H_{2}O$

(a) (i) Deduce the number of moles of electrons exchanged per mole of glucose in the fuel cell.

(ii) Hence, calculate the standard Gibbs free energy change, ΔG° , for the overall reaction.

(iii) Determine the value for the E^{θ} of the CO₃^{2-/} C₆H₁₂O₆ electrode reaction.

- [1]
- (iv) Using your answer in (a)(ii) and the following data, calculate ΔH° and ΔS° for the overall reaction.

Compound	∆ <i>H</i> ^e f / kJ mol ⁻¹
C ₆ H ₁₂ O ₆	-1270
OH-	-230
CO3 ²⁻	-670
H ₂ O	-286

Table 6.1

(b) In the fuel cell, glucose molecules are adsorbed on the nickel anode surface prior to oxidation to carbonate ions. Fig. 6.2 shows how E_{cell} varies with the concentration of glucose.





Explain the shape of the graph.

(c) Suggest a possible advantage of using the glucose fuel cell compared to a hydrogen fuel cell.

.....[1] [Total: 8]

END OF PAPER