

## DUNMAN HIGH SCHOOL Preliminary Examination 2018 Year 6

# H1 CHEMISTRY

Paper 2 Structured Questions

8873/02 13 September 2018

2 hours

Candidates answer on the Question Paper. Additional Materials: Data Booklet

### READ THESE INSTRUCTIONS FIRST

Write your index number and name 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.

Section A Answer all the questions.

Section B Answer one question.

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								
P1		P2 Section A		P2 Section B		Total	%	
	Q1	Q2	Q3	Q4	Q5	Q6		
30	13	9	20	18	20	20	/ 110	

#### Section A

Answer **all** the questions from this section, in the spaces provided.

**1** (a) Group 1 elements are strong reducing agents. State and explain the trend of reducing power of Group 1 elements down the Group.

[3]

Reducing power of Group 1 elements *increases* down the group.

<u>Number of filled principle quantum shell increases</u> and <u>valence electrons are</u> increasingly further away from the nucleus

Valence electrons are <u>less strongly attracted</u> to the nucleus and <u>smaller amount</u> <u>of energy</u> is needed to remove the valence electron so it is <u>more easily oxidised</u>.

(b) Group 1 elements and its compounds have many uses. Sodium hydrogencarbonate (NaHCO<sub>3</sub>) is often used to treat ant stings which contains methanoic acid (HCOOH), a weak acid.

Write an equation for the dissociation of methanoic acid in water. Indicate which species are the acid, the base and their conjugate pairs in the reaction.

[2]

#### $HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$

Acid: HCOOH Conjugate base: HCOO<sup>-</sup> Base: H<sub>2</sub>O Conjugate acid: H<sub>3</sub>O<sup>+</sup>

- (c) When the ant bites, it injects a solution containing 50 % by volume of unionised methanoic acid. A typical ant may inject around  $6.0 \times 10^{-3}$  cm<sup>3</sup> of this solution.
  - (i) Given that the density of methanoic acid is 1.2 g cm<sup>-3</sup>, what is the amount (in moles) of methanoic acid that a typical ant injects?

[1]

volume of HCOOH =  $6.0 \times 10^{-3} \times 0.5$ =  $3.0 \times 10^{-3} \text{ cm}^3$ 

mass of HCOOH =  $3.0 \times 10^{-3} \times 1.2$ = 0.00360 g

no of moles of HCOOH =  $\frac{0.00360}{46.0}$ 

= <u>7.83 x 10<sup>-5</sup> mol</u> (3 s.f.)

As soon as the methanoic acid is injected, it dissolves in water in the body to produce a solution of methanoic acid with pH 2.43.

(ii) Assuming that it dissolves fully in 1.0 cm<sup>3</sup> of water in the body, calculate the concentration of the methanoic acid solution that is formed initially. You may ignore the volume of methanoic acid injected in this calculation.

[1]

$$[HCOOH] = \frac{7.826 \times 10^{-5}}{0.001}$$
  
= 7.83 x 10^{-2} mol dm<sup>-3</sup> (3 s.f.)

(iii) Calculate the percentage of methanoic acid molecules which have dissociated in 1.0 cm<sup>3</sup> of water.

$$[H^+] = 10^{-2.43}$$
  
= 3.7154 x 10^{-3} mol dm<sup>-3</sup> (5 s.f.)  
percentage = [H^+]  
[HCOOH] x 100%  
= 3.72 x 10^3  
7.826 x 10<sup>-2</sup> x 100%  
= 4.75 % (3 s.f.)

- (d) A student was given an unlabelled bottle and was told that it contained pure sample of one of the following three compounds.
  - methanol
  - methanal
  - propanone
  - (i) State the reagent used for a chemical test that could show that the sample can be either methanal and propanone but **not** methanol. Describe what would be observed.

[2]

[2]

#### Reagent: 2,4–DNPH

Observations: orange precipitate observed.

(ii) Describe one chemical test that could distinguish between methanal and propanone.

[2]

Add **Tollens' reagent and warm** to both samples. Only methanal will form **black/ grey solid** or **silver mirror** 

OR

Add **Fehling's solution and warm** to both samples. Only methanal will form **reddish**– **brown precipitate**.

OR

Add **<u>alkaline aqueous iodine and warm</u>** to both samples. Only propanone will form **<u>yellow precipitate</u>**.

[Total: 13]

- 2 A sequence of reactions starting from compound A is shown below.
  - (a) Draw the structures of compounds A, B, C, D, E and F in the boxes below.



(c) The alcohol CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH, used as the reagent in reaction VII above, can be converted into CH<sub>3</sub>CH=CH<sub>2</sub>. How may this conversion be achieved in a laboratory?
[1]

Add <u>excess concentrated  $H_2SO_4$ </u> to a sample of  $CH_3CH_2CH_2OH$  and <u>heat</u>.

[Total: 9]

[2]

**3 (a)** Pure hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>, was long believed to be unstable. Its decomposition follows a first order reaction.

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$$

(i) Sketch a graph of  $[H_2O_2]$  against time to show that the reaction is first order with respect to  $H_2O_2$ .



(ii) As H<sub>2</sub>O<sub>2</sub> decomposes slowly at room temperature, catalysts such as platinum metal are often added to lower the activation energy to increase the rate of reaction.

With reference to the information provided below, sketch the energy profile diagram showing the catalysed reaction only.

enthalpy change of	-196 kJ mol <sup>-1</sup>
the decomposition	
activation energy	+75 kJ mol <sup>-1</sup>
(without catalyst)	
activation energy	+49 kJ mol <sup>-1</sup>
(with catalyst)	

[2]



- (b) In the presence of UV light,  $H_2O_2$  decomposes to form hydroxyl free radicals, •OH.
  - (i) Draw the 'dot-and-cross' diagram for  $H_2O_2$ .

(ii) Using relevant bond energy values from the *Data Booklet*, suggest the relative rate of the formation of •C*l* from chlorine gas as compared that of •OH from hydrogen peroxide.

[2]

[1]

From the *Data Booklet*, Bond energy of O–O = 150 kJ mol<sup>-1</sup> Bond energy of Cl–Cl = 244 kJ mol<sup>-1</sup>

Ease of cleavage of bond: O-O > Cl-Cl

Rate of formation of •OH radicals is <u>faster</u> than •Cl.

(iii) Propylamine, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, may be formed via the following reaction pathway involving free radical substitution in the first step.

 $CH_{3}CH_{2}CH_{3} \xrightarrow{\text{Step I}} CH_{3}CH_{2}CH_{2}Cl \xrightarrow{\text{Step II}} CH_{3}CH_{2}CH_{2}NH_{2}$ 

Name the type of reaction occurring in **Step II**. State the reagent and conditions required for this step.

[2]

Type of reaction: (Nucleophilic) Substitution

Reagent: <u>NH<sub>3</sub> in excess</u> Condition: <u>in ethanol, heat in sealed tube</u> (iv) As the yield from the reaction in (b)(iii) is low, propose a 3-step synthetic route to produce propylamine from ethene instead. Show clearly the reagents and conditions as well as the intermediates involved.

[3]

$$H_{2}C = CH_{2} \xrightarrow{HCl(g)} CH_{3}CH_{2}CI \xrightarrow{alcoholic} CH_{3}CH_{2}CN \xrightarrow{LiA/H_{4} in} CH_{3}CH_{2}CN \xrightarrow{dry ether} CH_{3}CH_{2}CH_{2}NH_{2}$$

(c) The kinetics of the reaction between hydrogen peroxide and iodide ions in acidic solution was studied.

$$H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$$

Four separate experiments were carried out to determine the relative rates by varying the concentrations of the reactants. The results obtained are given in the table below.

Expt	[H <sub>2</sub> O <sub>2</sub> ] / mol dm <sup>-3</sup>	[I <sup>_</sup> ] / mol dm <sup>-3</sup>	[H <sup>+</sup> ] / mol dm <sup>-3</sup>	relative rate
1	0.03	0.03	0.03	1.0
2	0.05	0.03	0.03	1.6
3	0.05	0.01	0.06	0.53
4	0.03	0.01	0.03	0.33

(i) With reference to the overall equation given above, write the oxidation and reduction half-equations.

 $[O]: 2I^- \rightarrow I_2 + 2e^- \\ [R]: H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ 

(ii) Use the data to deduce the orders of reaction with respect to H<sub>2</sub>O<sub>2</sub>, I<sup>−</sup> and H<sup>+</sup>. Show your working clearly.

[3]

[2]

Comparing Experiments 1 and 2,  $[H_2O_2]$  increases by 1.6 times as rate also increases by 1.6 times whilst keeping [I<sup>-</sup>] and [H<sup>+</sup>] constant.

 $\Rightarrow$  Order of reaction with respect to H<sub>2</sub>O<sub>2</sub> is <u>1</u>.

Comparing Experiments 1 and 4,  $[I^-]$  increases by 3 times as rate also increases by 3 times whilst keeping  $[H_2O_2]$  and  $[H^+]$  constant.

 $\Rightarrow$  Order of reaction with respect to I<sup>-</sup> is <u>1</u>.

Comparing Experiments 2 and 3, as  $[H_2O_2]$  is constant while  $[I^-]$  decreases by 3 times and  $[H^+]$  increases by 2 times, rate decreases by 3 times. Hence, change in  $[H^+]$  does not affect the rate.

 $\Rightarrow$  Order of reaction with respect to H<sup>+</sup> is **0**.

(iii) Hence, write the rate equation and state the units of the rate constant.

[2]

rate =  $k[H_2O_2][I^-]$ 

Units of rate constant = **mol**<sup>-1</sup> **dm**<sup>3</sup> **s**<sup>-1</sup>

(iv) Unreacted iodide ions may be easily separated from the reaction mixture by adding silver nitrate solution, followed by filtration. State the identity and colour of the precipitate formed.

[1]

AgI and yellow ppt.

[Total : 20]

- **4** Isoprene, **E**, is an organic compound that could be used to synthesise limonene, which is commonly used in fragrances.
  - (a) E can be synthesised from 3–methylbut–1–ene, A, in a 4–step process as follows.



(i) **B** is a major product of step **I**.

Draw the structures of compounds **B**, **C** and **D**.



(ii) Hydrogen chloride, the reagent in step I, is commonly used in organic synthesis.

State and explain how the thermal stabilities of hydrogen halides varies down the Group.

Thermal stability of hydrogen halides decreases down the group

Down the group,

**Bond energy decreases** [BE (H–F) > BE (H–Cl) > BE (H–Br) > BE (H–I)]. **Covalent bond strength** also **decreases** [H–F > H–Cl > H–Br > H–I]. Hence hydrogen halides decompose more readily down the group.

(b) The following reaction shows an alternative route to form an intermediate for the synthesis of isoprene.



(i) State the reagents and conditions of **step 1** which will result in formation of compounds **F** and **G**.

Limited Cl<sub>2</sub>, uv

- (ii) Predict the ratio in which **F** and **G** will be formed.
  - **F** : **G** 6 : 1

[3]

[2]

[1]

(c) The bar chart below shows the second ionisation energy (2<sup>nd</sup> IE) of nine consecutive elements (J to R) in Periods 2 and 3 of the Periodic Table.



(i) Write an equation for the second ionisation energy of element **J**.

 $J^+(g) \rightarrow J^{2+}(g) + e^-$ 

Electronic configuration:

(ii) Identify element N.

Na

[1]

[1]

(iii) Using your answers in (c)(i), (c)(ii) and the electronic configurations of the species involved, explain the significantly higher 2<sup>nd</sup> IE of N compared to O.

N<sup>2+</sup> (1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>);

[2]

O<sup>2+</sup> ([Ne]3s<sup>1</sup>)

The 3<sup>rd</sup> ionisation energy of **N** involves the removal of a <u>2p</u> electron

The 3<sup>rd</sup> ionisation energy of **O** involves the removal of a <u>3s</u> electron

A <u>larger amount of energy</u> is required to remove the <u>2p</u> electron in  $N^{2+}$  which is in an <u>inner quantum shell</u> compared to <u>3s</u> electron in  $O^{2+}$ .

Hence 3<sup>rd</sup> ionisation energy of **N** is significantly higher than that of **O**.

- (d) The Periodic Table shows the element, Helium, placed at the top of Group 18.
  - (i) Suggest why the element Helium could be placed at the top of Group 2.

Helium has <u>2 valence electrons</u> like all other Group 2 elements.

(ii) Suggest why the element Helium is not placed at the top of Group 2, by comparing **one** physical property. Explain your answer.

[2]

[1]

Helium atoms are held by <u>weak instantaneous dipole induced dipole</u> <u>interactions</u> while within group 2 elements exist <u>strong electrostatic forces</u> <u>of attraction between cations and a sea of delocalised electrons</u>.

Hence, helium has <u>low melting/boiling point</u> and it <u>exist as a gas</u> while group 2 elements has <u>high melting/boiling point and exist as a solid</u> at room temperature.

OR

Hence, <u>helium</u> is a <u>non-conductor of electricity</u> due to (<u>absence of</u> <u>mobile/delocalised electrons</u>) while <u>group 2 elements</u> are <u>good conductor</u> of <u>electricity</u> due to (<u>presence of delocalised electrons</u>).

- (e)  $Al_2O_3$ , SiO<sub>2</sub> and P<sub>4</sub>O<sub>10</sub> are oxides of Period 3 elements.
  - (i) Explain why both  $Al_2O_3$  and  $SiO_2$  are insoluble in water.

[2]

 $Al_2O_3$  is insoluble in water due to a <u>very exothermic lattice energy</u> and hence, it is very <u>difficult to break down the ionic lattice structure</u>.

 $SiO_2$  is insoluble in water due to <u>strong and extensive covalent bonds</u> <u>between Si and O atoms</u>.

(ii) Explain, with the aid of an equation, the reaction of  $P_4O_{10}$  with water.

[2]

 $\mathsf{P}_4\mathsf{O}_{10}$  is  $\underline{\textbf{covalent}}$  in nature and reacts  $\underline{\textbf{readily}}$  with water to form an  $\underline{\textbf{acidic}}$  solution.

 $\mathsf{P}_4\mathsf{O}_{10}(\mathsf{s}) + \mathsf{6H}_2\mathsf{O}(l) \rightarrow \mathsf{4H}_3\mathsf{PO}_4(\mathsf{aq})$ 

[Total: 18]

#### Section B

Answer **one** question from this section, in the spaces provided.

**5** Levocarnitine is a quaternary ammonium compound involved in metabolism in most mammals.



- (a) A kinetic study on the RuCl<sub>3</sub> catalysed reaction between levocarnitine and bromamine-T was carried out in aqueous hydrochloric acid.
  - (i) The following equilibrium exists for  $RuCl_3$  in aqueous hydrochloric acid.

$$[\operatorname{Ru}Cl_5(\operatorname{H}_2\operatorname{O})]^{2-} + \operatorname{C}l^- \rightleftharpoons [\operatorname{Ru}Cl_6]^{3-} + \operatorname{H}_2\operatorname{O}$$

Explain why  $[RuCl_6]^{3-}$  is likely to be the reactive species instead of  $[RuCl_5(H_2O)]^{2-}$  in this study.

[1]

By Le Chatelier's Principle, the presence of <u>chloride ions from aqueous HC/</u> will shift the <u>position of equilibrium to the right</u>, favouring the formation of  $[RuCl_6]^{3-}$ .

(ii) Levocarnitine is converted into the following product by bromamine-T.



State the type of reaction that levocarnitine had undergone and explain your answer in terms of changes in oxidation number.

[2]

#### **Oxidation**

The oxidation number of <u>carbon</u> (bonded to -OH group) <u>increased from 0 in</u> <u>levocarnitine</u> to <u>+2 in the product</u>. (b) A series of experiments were carried out at different temperatures under first order conditions with respect to bromamine-T.

The value of the observed rate constant, *k*, for the catalysed reaction was determined at each temperature and the results are summarised in the table below.

k	temperature, T
/ 10⁴ s⁻¹	/ K
1.82	293
3.00	303
4.62	313
7.30	323

The activation energy,  $E_a$ , and the pre-exponential factor, A, which is a constant, for the reaction can be determined from the equation.

$$k = Ae^{\frac{-E_a}{RT}}$$

*R* is the molar gas constant.

T is the reaction temperature in kelvin.

*k* is the observed rate constant at a chosen temperature.

(i) Calculate the values of ln k and  $\frac{1}{\tau}$  for each of the experiments above.

[2]

<i>k</i> / 10⁴ s⁻¹	ln <i>k</i>	temperature, T / K	$\frac{1}{T}$ / K <sup>-1</sup>
1.82	9.81	293	0.00341
3.00	10.3	303	0.00330
4.62	10.7	313	0.00319
7.30	11.2	323	0.00310

(ii) Hence plot a graph of ln *k* against  $\frac{1}{T}$  and determine  $E_a$  from the gradient of the best-fit line which is  $\frac{-E_a}{R}$ .

[4]



Gradient =  $\frac{-E_a}{R}$  = -4380.1 K Hence  $E_a$  = 36399 J mol<sup>-1</sup> = <u>36.4 kJ mol<sup>-1</sup></u>

(iii) State the effect of temperature on the rate of the reaction and explain your answer with the aid of a Boltzmann distribution curve.

[4]



When temperature of the reaction increases,

- <u>average kinetic energy</u> of reactant particles increases
- there are more reactant particles with energy  $\geq E_a$
- <u>number of effective collisions per unit time</u> / <u>frequency</u> of effective collisions increases
- rate of reaction increases, since the <u>rate of reaction is proportional to the</u> <u>frequency of effective collisions</u>

Tosyl chlorides (TsC*l*) are often used to convert alcohols into alkyl tosylates which undergo substitution reactions. An example of this application is given below.



(c) Consider the reaction scheme below involving an alkyl tosylate N.



(i) State the functional group(s) present in the starting material, M.

Primary alcohol and alkene

(ii) Describe what will be observed when **M** is heated with acidified potassium dichromate(VI) and draw the structure of the organic product formed.

[2]

[2]

Orange acidified potassium dichromate(VI) turns green.



(iii) Draw the structures of the compounds N, P and Q.



[Total: 20]

- 6 Methanoic acid is the simplest carboxylic acid and is an important intermediate in chemical synthesis. It occurs naturally and is found notably in ants.
  - (a) (i) Methanoic acid is a *weak acid*. What do you understand by the term in *italics*? [2]

An acid is a compound which is a **proton donor**. A weak acid is an acid which only **partially dissociates** in water to release proton.

(ii) The acid dissociation constant,  $K_a$ , for methanoic acid is  $1.6 \times 10^{-4}$  mol dm<sup>-3</sup>. Calculate the pH of a 0.100 mol dm<sup>-3</sup> solution of methanoic acid, given that  $[H^+] = \sqrt{K_a \times [HCOOH]}$ .

[2]

$$[H^+] = \sqrt{1.6 \times 10^{-4} \times 0.100}$$
  
= 4.00 × 10<sup>-3</sup> mol dm<sup>-3</sup>  
pH = -log (4.00 × 10<sup>-3</sup>)  
= 2.40 (3 sf)

(iii) A solution comprising methanoic acid and sodium methanoate can function as a buffer solution. With the aid of a balanced equation, describe how this buffer solution can resist pH changes when a small amount of sulfuric acid is added. [2]

 $H^+ + HCOO^- \rightarrow HCOOH$ 

When a small amount of sulfuric acid is added, methanoate will react with and **remove the acid to form methanoic acid**. This ensures that the pH of the solution is maintained **fairly constant**.

- (b) The energy contents of methanoic acid can be determined by means of calorimetric experiments. These experiments are usually carried out using polystyrene cup in a normal school laboratory. The standard enthalpy change of neutralisation can also be determined.
  - (i) Define what is meant by the *standard enthalpy change of neutralisation*.

[1]

Standard enthalpy change of neutralisation is the energy evolved when one mole of water is formed when an acid is completely neutralised by a base under standard conditions.

(ii) Write a balanced chemical equation for the neutralisation of methanoic acid with potassium hydroxide.

[1]

 $HCOOH + KOH \rightarrow HCOO^{-}K^{+} + H_2O$ 

(iii) How would you expect the enthalpy change of neutralisation in (b)(ii) to compare with the enthalpy change of neutralisation of nitric acid with potassium hydroxide? Explain your answer.

[2]

The enthalpy change of neutralisation in (b)(ii) will be less exothermic. Some of the heat evolved as a result of the neutralisation is absorbed by the dissociation of methanoic acid, a weak acid. Hence, less heat should be evolved.

(iv) Suggest a suitable indicator for the titration between methanoic acid and potassium hydroxide.

[1]

Phenolphthalein or any other suitable indicator (e.g. thymol blue)

(v) Draw the structure of polystyrene (with at least three repeating units) given that the monomer styrene has the structure as shown below.



[1]



(c) Enthalpy change of reaction 1,  $\Delta H_1$ , can be determined using enthalpy change of reaction 2,  $\Delta H_2$ , and enthalpy change of reaction 3,  $\Delta H_3$ , in the energy cycle below.



When 6.2 g of  $Na_2O(s)$  is dissolved in 250 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> HC*l*(aq), the temperature of the solution rose by 17 °C.

(i) Using the cycle above, calculate  $\Delta H_2$ .

No. of mol of Na<sub>2</sub>O =  $\frac{6.2}{(23 \times 2+16)}$  = 0.100 mol (exact) No. of mol of HC*l* = 0.25 × 1.0 = 0.250 mol

Since n <sub>Na2O</sub>: n <sub>HCl</sub> = 1:2, HCl is in excess. This means that 0.200 mol of  $H_2O$  was formed.

q = mc∆T = 250 × 4.18 × 17 = 17765 J

$$\Delta H_2 = \frac{17765}{0.200} \times 2 = -177650 \text{ J mol}^{-1} = -178 \text{ kJ mol}^{-1} (3 \text{ sf})$$

(ii) The enthalpy change of neutralisation between NaOH(aq) and HC*l*(aq) is known to be -57.3 kJ mol<sup>-1</sup>. Calculate  $\Delta H_1$ .

By Hess' Law,  $\Delta H_1 = -177.65 - (2)(-57.3)$  $= -63.1 \text{ kJ mol}^{-1} (3 \text{ sf})$ 

(d) The German company BASF is a world leader in the production of methanoic acid. It has an efficient process of producing methanoic acid from methyl methanoate. The process is described below.

#### Step 1:

Methyl methanoate is mixed with water and allowed to react to produce methanol and methanoic acid.

#### Step 2:

Methanol is reacted with carbon monoxide and a catalyst to produce methanoic acid.

(i) State the type of reaction occurring in Step 1.

[1]

[3]

[1]

#### Step 1: Hydrolysis

- 18
- (ii) Suggest why a catalyst is used in Step 2.

[1]

A catalyst is required to **speed up the reaction** because carbon monoxide has a very **strong triple bond** which must be weakened / broken in order for the reaction to occur.

(iii) Methanol produced using the process can also be used to produce dimethyl ether which is an alternative fuel to diesel.



Draw the displayed formulae of compounds A and B.

[2]



[Total: 20]