ANDERSON JUNIOR COLLEGE

Promotional Examinations 2012

CHEMISTRY **9647/01**

Higher 2 **3 October 2012**

Paper 1 Multiple Choice **45 minutes**

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the Multiple Choice Answer Sheet.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.

Multiple Choice Answer Sheet

Write your name, PDG and NRIC/FIN number, including the reference letter.

Shade the NRIC / FIN number.

Exam Title: JC1 Promotional Examination

Exam Details: H2 Chem / Paper 1

Date: 03/10/2012

This document consists of **10** printed pages.

Section A

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

1 Bones contain a complex mixture of calcium salts, protein and other material. When a bone is strongly heated in a current of air, the only residue is calcium oxide.

From a sample of 50.0 g of bone, 14.0 g of calcium oxide were obtained.

What is the percentage by mass of calcium in the bone?

A 10.0 % **B** 14.0 % **C** 20.0 % **D** 23.3%

2 0.35 g of $\mathbf{A}_2CO_3$ (a carbonate of **A**) is found to react completely with 50 cm^3 of 0.10 mol dm^{-3} hydrochloric acid.

What is the relative atomic mass of **A**?

A 10 **B** 40 **C** 80 **D** 140

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

Sodium percarbonate, $(Na_2CO_3)_x.y(H_2O_2)$, is an oxidising agent found in home and laundry cleaning products.

On acidification, 15.0 cm^3 of 0.100 mol dm^{-3} sodium percarbonate produces 72 cm^3 of carbon dioxide at r.t.p..

In another experiment, 10.0 cm^3 of 0.050 mol dm^{-3} sodium percarbonate requires 12.0 cm^3 of 0.0500 mol dm^{-3} acidified $KMnO_4$ for complete reaction. Given that

$$2MnO_4^- + 5H_2O_2 + 6H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

What is the ratio of $\frac{x}{y}$?

A $\frac{1}{3}$ **B** $\frac{3}{1}$ **C** $\frac{3}{2}$ **D** $\frac{2}{3}$

4 Which ion has more electrons than protons and more protons than neutrons?
$[H={}^{1}_{1}H; D={}^{2}_{1}H; O={}^{16}_{8}O]$

A D^-

B D_3O^+

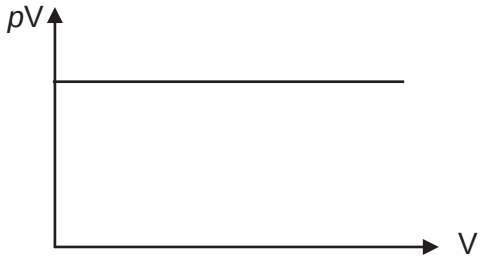
C OD^-

D OH^-

5 Consider fixed mass of an ideal gas at a constant temperature and occupy a vessel of volume V at a pressure *p*.

Which graph does not show the correct relationship between *p* and V for this gas?

A



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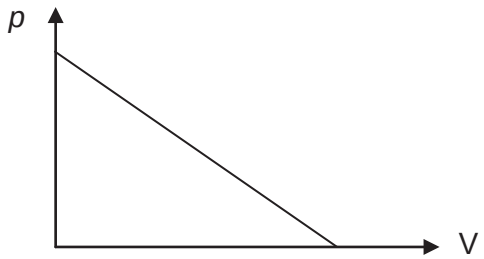

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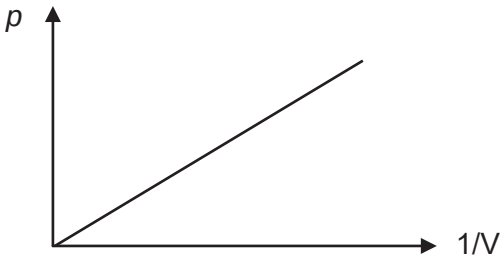

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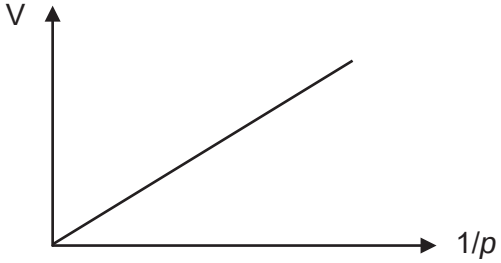


6 Which of the following is not a planar molecule?

A BCl_3

B ICl_3

C $CH_2=C=CH_2$

D $CH_2=CH–CH=CH_2$

7 Which of the following statements describes a phenomenon which cannot be explained by hydrogen bonding?

A Ice has a lower density than water at 0 ^{o}C.

B The boiling point of alcohols increases with increasing relative molecular mass.

C Ethanoic acid molecules form dimers when dissolved in benzene.

D Ammonia, NH_3 is more soluble than phosphine, PH_3 in water.

8 Which of the following is true about sodium chloride?

A It can act as an electrolyte in molten form.

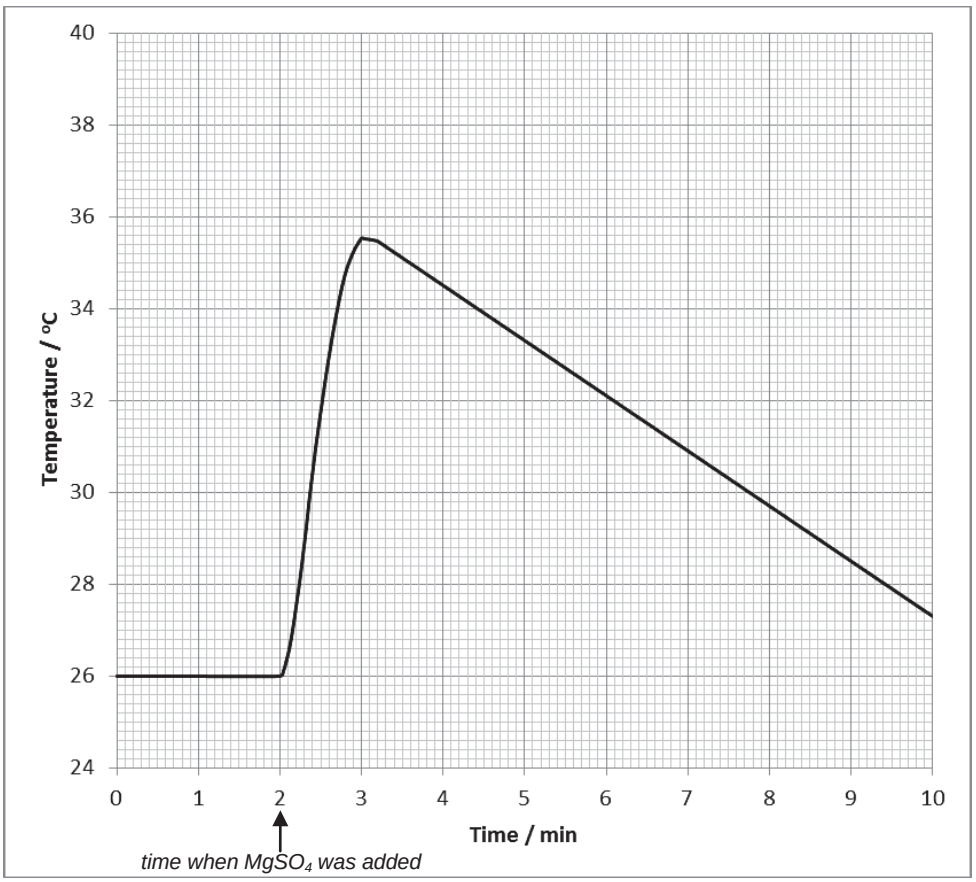
B It is soluble in cyclohexane.

C It is malleable and ductile.

D It has a solid lattice where each Na^+ is surrounded by one Cl^-.

9 A student conducted an experiment to determine the enthalpy change of solution of $MgSO_4$ in water. 9.00 g of solid $MgSO_4$ was added to 150 g of water and the temperature of the solution was noted at various time intervals.

Using the data obtained from the experiment, the following graph was obtained. The specific heat capacity of water is 4.18 kJ kg^{-1} K^{-1}.



What is the enthalpy change of solution of $MgSO_4$ based on the data obtained from the experiment?

A +79.9 kJ mol^{-1}

B –80.5 kJ mol^{-1}

C –90.6 kJ mol^{-1}

D +91.2 kJ mol^{-1}

10 Which of the following is a correct statement about the effect of a catalyst on a reversible reaction?

A It increases the speed of the colliding particles.

B It increases the rate constant of the reaction in both directions.

C It increases the number of collisions between the reactant particles.

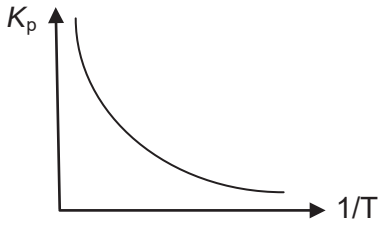
D It increases the yield of product in a reversible reaction.

11 The mechanism for the iodination of propanone in aqueous acid is thought to be as follows.

What are the orders of reaction with respect to iodine and propanone?

	iodine	propanone
A	0	1
B	0	2
C	1	0
D	1	1

12 The equilibrium constant, K_p for the reaction: 2**J**(g) + **K**(g) $\rightleftharpoons$ **L**(g) varies with temperature T as shown in the diagram below.



What conclusion can be drawn regarding the above reaction?

A The equilibrium mixture contains a higher proportion of **L** at lower temperatures.

B The equilibrium mixture contains a higher proportion of **L** at lower pressures.

C The reverse reaction is endothermic.

D Introducing an inert gas at constant *p* and T will cause the position of equilibrium to shift left.

13 At body temperature of 37 °C, K_w has a value of 2.4×10^{-14}.

What is the concentration of OH^- if the pH of blood is 7.4 under these conditions?

A 7.00×10^{-7} **B** 6.03×10^{-7} **C** 2.51×10^{-7} **D** 3.98×10^{-8}

14 An acidic buffer can be prepared by mixing aqueous solutions of benzoic acid and sodium benzoate.

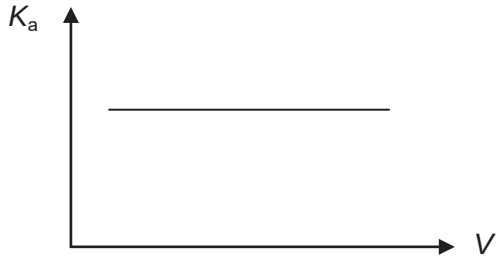
What is the pH of an aqueous solution containing 0.1 mol dm^{-3} sodium benzoate and 0.01 mol dm^{-3} benzoic acid?
[K_a (benzoic acid) = 6×10^{-5} mol dm^{-3}]

A 3.22 **B** 4.22 **C** 4.78 **D** 5.22

15 A 1 mol sample of ethanoic acid is diluted at constant temperature to a volume *V*.

Which diagram shows how K_a, the acid dissociation constant, varies with *V*?

A



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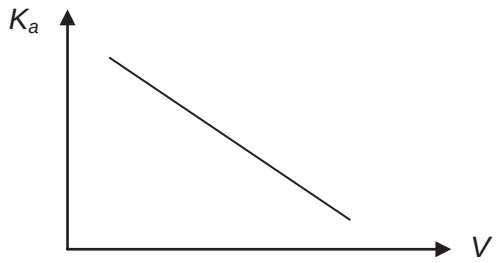

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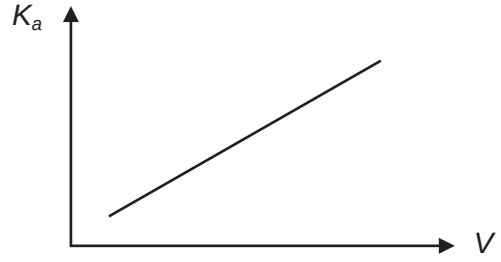
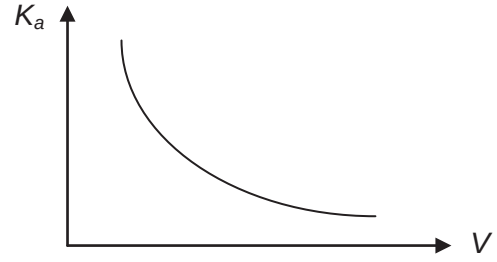


D



16 Public swimming pools are often chlorinated to kill bacteria. As an alternative to chlorination, silver ions can be used in a concentration of not more than 10^{-6} mol dm^{-3} and not less than 10^{-7} mol dm^{-3} of silver ions.

Which compound would, in saturated solution, provide the necessary concentration of silver ions?

	compound	solubility product
A	AgBr	5×10^{-13} mol^2 dm^{-6}
B	AgC*l*	2×10^{-10} mol^2 dm^{-6}
C	$AgIO_3$	2×10^{-8} mol^2 dm^{-6}
D	Ag_2CO_3	5×10^{-12} mol^3 dm^{-9}

17 Which hydrocarbon can form a monochloro–substitution derivative which shows **both** chirality and *cis–trans* isomerism?

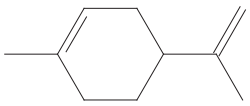
A $CH_3CH=CH_2$

B $(CH_3)_2C=CH_2$

C $CH_3CH=C(CH_3)_2$

D $CH_3CH=CHCH_2CH_3$

18 Limonene is a constituent of lemon oil and is a useful starting material for the manufacture of perfumes.



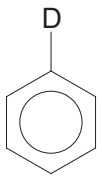
limonene

How many chiral centres are there in the compound formed by reacting limonene with cold acidified potassium manganate(VII)?

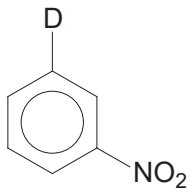
A 2 **B** 3 **C** 4 **D** 5

19 Deuterium, D, is a heavy isotope of hydrogen. Deuteriobenzene is reacted with a mixture of nitric acid and sulfuric acid under controlled conditions, so that only mononitration takes place.

Assuming that the carbon–deuterium bond is broken as easily as a carbon–hydrogen bond, which proportion of the nitrated products will be 3–nitrodeuteriobenzene?



deuteriobenzene

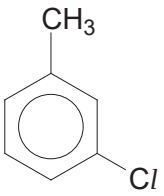


3-nitrodeuteriobenzene

A 16 % **B** 20 % **C** 33 % **D** 45 %

20 Which compound **cannot** be made directly from methylbenzene?

A



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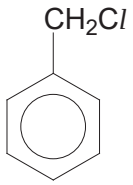

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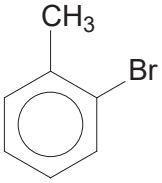
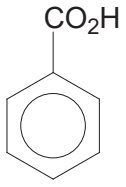


D



Section B

For each of the question in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct.)

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

21 Which of the following has the same numbers of atoms as 500 cm^3 of 0.5 mol dm^{-3} HCl at standard temperature and pressure?

1 65.5 g of Xe

2 10.2 g of Al_2O_3

3 11.2 dm^3 of O_3

22 A 30 cm^3 mixture of gaseous hydrocarbons **R** and **S**, in the ratio of 1:2, was sparked with an excess of oxygen. After cooling to room temperature, 100 cm^3 of the residual gas was absorbed by sodium hydroxide.

Which of the following pairs of hydrocarbons could be **R** and **S**?

	R	S
1	C_2H_6	C_4H_8
2	C_4H_{12}	C_3H_6
3	C_3H_8	C_2H_4

23 The equations for three reactions involving Cl_2, SO_2 and H_2S are given below.

I $Cl_2(g) + 2H_2O(l) + SO_2(g) \longrightarrow 2HCl(aq) + H_2SO_4(aq)$

II $Cl_2(g) + H_2S(g) \longrightarrow 2HCl(g) + S(s)$

III $SO_2(g) + 2H_2S(g) \longrightarrow 2H_2O(l) + 3S(s)$

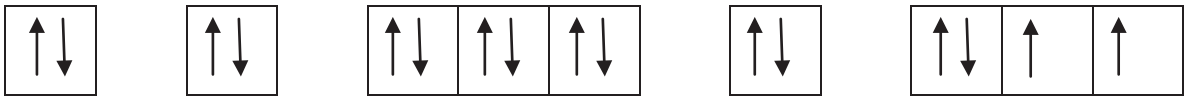
Which of the following deductions can be made from the information above?

1 Cl_2 is the weakest reducing agent.

2 H_2S is the strongest reducing agent.

3 The oxidation number of S changes from –2 in H_2S to 0 in S for reaction **II**.

24 A species **U** has the following electronic configuration.



What could **U** be?

1 Ar^{2-} ion

2 S atom

3 Cl^{+} ion

25 In which sequence are the molecules quoted in order of increasing bond angle within the molecules?

1 H_2O CCl_4 SO_3

2 SF_6 H_2O CO_2

3 NH_3 BCl_3 $BeCl_2$

26 Which class of reaction always has an exothermic enthalpy change?

1 Combustion

2 Neutralisation

3 Electron affinity

27 In which processes will ΔS be positive?

1 $CO_2(s) \longrightarrow CO_2(g)$

2 $N_2O_4(g) \longrightarrow 2NO_2(g)$

3 $CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$

28 Which set of solutions of equal volume when mixed will give an acidic buffer?

1 0.05 mol dm^{-3} HCl and 0.10 mol dm^{-3} CH_3CO_2Na

2 0.10 mol dm^{-3} CH_3CO_2H and 0.10 mol dm^{-3} NaOH

3 0.10 mol dm^{-3} CH_3CO_2H and 0.05 mol dm^{-3} $Ca(OH)_2$

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

29 Using a colorimeter, the following reaction is studied by finding the time taken for the coloured reactant, **V**, to decolourise. The reaction is catalysed by **X**.

$$\mathbf{V} + \mathbf{W} \xrightarrow{\mathbf{X}} \mathbf{Y} + \mathbf{Z}$$

The following results were obtained.

Experiment	Volume of **V** added / cm^3	Volume of **W** added / cm^3	Volume of **X** added / cm^3	Volume of H_2O added / cm^3	Time taken for colour of **V** to disappear / s
1	5	5	5	10	40
2	5	20	10	15	10
3	10	20	10	10	20
4	10	20	5	15	40

Which of the following deductions can be made from the information above?

1 The reaction is first order with respect to **X**.

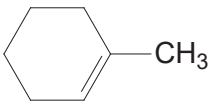
2 **W** is not involved in the rate–determining step.

3 The overall order of the reaction is 3.

30 A hydrocarbon, on heating with an excess of hot concentrated acidic $KMnO_4(aq)$, produces $HO_2CCH_2CH_2CH_2COCH_3$.

What could the hydrocarbon be?

1



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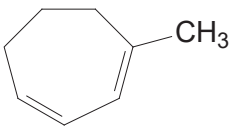

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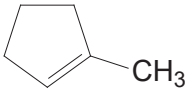


Question Number	*Key*	*Question Number*	*Key*
1	**C**	16	**A**
2	**B**	17	**D**
3	**D**	18	**C**
4	**D**	19	**C**
5	**B**	20	**A**
6	**C**	21	**B**
7	**B**	22	**B**
8	**A**	23	**A**
9	**C**	24	**C**
10	**B**	25	**A**
11	**A**	26	**B**
12	**D**	27	**B**
13	**B**	28	**D**
14	**D**	29	**D**
15	**A**	30	**C**

1 **C**

$$n(CaO) \text{ obtained} = \frac{14.0}{(40.1+16.0)}$$
$$= 0.250 \text{ mol}$$
$$= n(Ca) \text{ in bone}$$

$$\text{mass of Ca in bone} = 0.250 \times 40.1$$
$$= 10.0 \text{ g}$$

$$\% \text{ by mass of Ca in bone} = \frac{10.0}{50.0} \times 100\%$$
$$= \mathbf{20.0\ \%}$$

2 **B**

$$\mathbf{A}_2CO_3 + 2HCl \rightarrow 2\mathbf{A}Cl + CO_2 + H_2O$$

$$n(HCl) \text{ used} = \frac{50}{1000}(0.10) = 0.00500 \text{ mol}$$

$$n(\mathbf{A}_2CO_3) \text{ reacted} = \tfrac{1}{2}\, n(HCl) \text{ used}$$
$$= 0.00250 \text{ mol}$$

$$\text{Molar mass of } \mathbf{A}_2CO_3 = \frac{0.35}{0.00250}$$
$$= 140 \text{ g mol}^{-1}$$

$$A_r \text{ of } \mathbf{A} = \frac{140 - [12.0 + 3(16.0)]}{2}$$
$$= \mathbf{40.0}$$

FYI: **A** is likley to be K. The A_r calculated is higher than that of K because the $\mathbf{A}_2CO_3$ may not be pure and hence the amount of HCl used is lower than expected. A more accurate way to determine the A_r of **A** is to collect the volume of CO_2 evolved and use it to determine the amount of CO_2.

3 **D**

$$Na_2CO_3 + 2H^+ \longrightarrow 2Na^+ + CO_2 + H_2O$$

$n(Na_2CO_3) = n(CO_2) = 67.2/22400 = 0.003$ mol
$n(\text{sodium percarbonate}) = 15.0/1000 \times 0.100 = 0.0015$ mol
$n(\text{sodium percarbonate}) : n(Na_2CO_3)$

1	:	x
0.0015	:	0.003

Thus, x = **2**

$n(KMnO_4^-) = 12.0/1000 \times 0.0500 = 0.0006$ mol
$n(H_2O_2) = 5/2 \times 0.0006 = 0.0015$ mol
$n(\text{sodium percarbonate}) = 10.0/1000 \times 0.050 = 0.0005$ mol
$n(\text{sodium percarbonate}) : n(H_2O_2)$

1	:	y
0.0005	:	0.0015

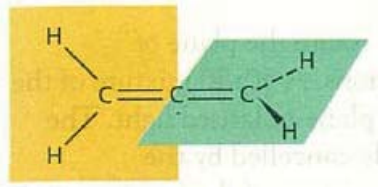
Thus, y = **3**

$$\text{ratio of } \frac{x}{y} = \frac{2}{3}$$

4 more electrons than protons => anion (option **A**, **C** and **D**) **D**
more protons than neutrons => must contain H in it based on given elements (Why?)
=> **D**

5 For a fixed mass of gas at a constant temperature, pV = constant **B**
Hence, pV is a constant at all V (or p). p is directly proportional to 1/V and vice-versa.

6 **C**

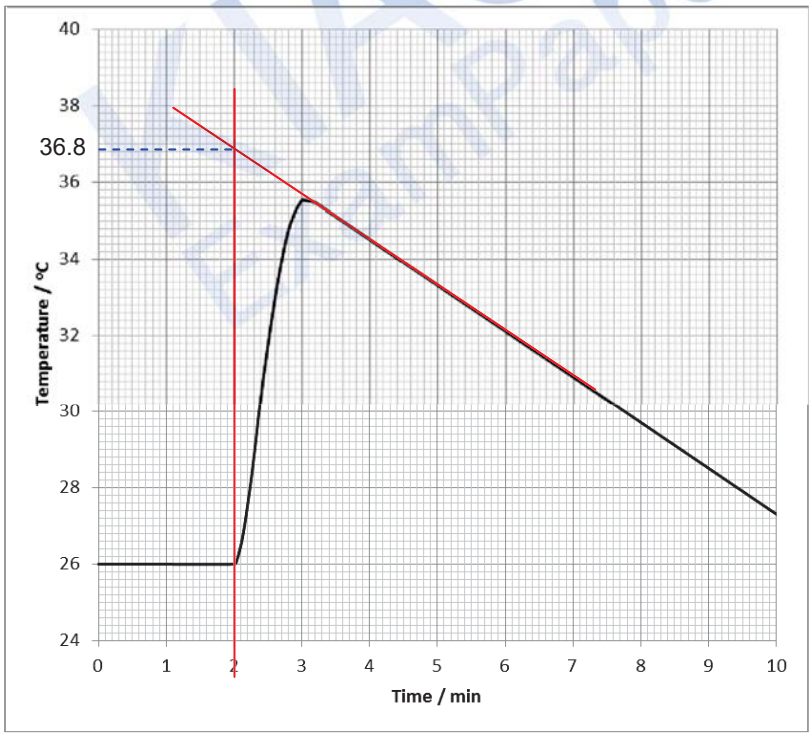
A	trigonal planar	planar
B	T–shaped	planar
C	linear wrt central C atom and trigonal planar wrt terminal C atoms	
D	trigonal planar wrt each C atom	planar

7 The boiling point of alcohols increases with increasing M_r is due to the <u>larger electron cloud size</u> (greater ease of distortion and stronger van der Waals'). **B**

8 NaC*l* has a giant ionic lattice structure with strong electrostatic forces of attraction between Na^+ and Cl^- ions. **A**

A In the molten form, ions are free to move and hence can be a charge carrier.
B It is soluble in water (polar solvent) due to strong ion–dipole interactions.
C Metal is malleable and ductile (structure can change the shape without fracturing) due to the sea of delocalised electrons which shield the cations from repelling each other. In ionic solid, stress will cause the ions of alternating charges to be displaced to produce contact between the like charges. The repulsion between these ions make the crystal fall apart.
D Each Na^+ is surrounded by 6 Cl^- and vice–versa.

9 **C**



T_{max} at time = 2 min is <u>36.8°C</u>

Using q = mcΔT
= (150/1000)(4.18)(36.8 – 26)
= 6.77 kJ
n($MgSO_4$) = 9.00 / 120.4
= 0.07475 mol
$\therefore \Delta H_{sol}$ = –q/n
= –6.77 / 0.07475
= **–90.6 kJ mol^{-1}**

10 A catalyst increases the rate of achieving equilibrium by increasing both the rate of forward and reverse reaction to the same extent. The yield remains unchanged as the position of equilibrium is not affected. **B**

11 From the 3rd step (fast), you can conclude that I_2 does not affect the rate of reaction and order of reaction wrt I_2 is **0**. (narrow to options **A** and **B**) **A**
As the r.d.s. (slow) is not the 1st step, you have to consider all steps preceding the slow step for the rate law. Since the [intermediate] is dependent on [CH_3COCH_3] and [H^+], order of reaction wrt propanone is **1**.

12 From graph, K_p decreases as 1/T increases, i.e. K_p decreases as T decreases. **D**
$\Rightarrow p_{reactants}$ increases as T decreases (since $K_p \alpha \frac{p_{products}}{p_{reactants}}$)
$\Rightarrow$ at lower temperatures, the position of equilibrium [2**J**(g) + **K**(g) $\rightleftharpoons$ **L**(g)] shifts **left**
$\Rightarrow$ since lower temperatures favour exothermic reaction, the reverse reaction is **exothermic**

A: The equilibrium mixture contains a lower proportion of **L** at lower temperatures.
B: At lower pressures, position of equilibrium shifts **left** (i.e. favours the side with greater no. of moles of gaseous molecules). Thus, the equilibrium mixture contains a lower proportion of **L**.
C: The reverse reaction is exothermic.
D: Introducing an **inert** gas at constant (total) pressure (P_T) increases n_T.
Since p = n/n_T x P_T, at constant P_T & larger n_T, partial pressures, p of **J**(g), **K**(g) & **L**(g) decrease.

$$2\mathbf{J}(g) + \mathbf{K}(g) \rightleftharpoons \mathbf{L}(g)$$

Position of equilibrium shifts left as the decrease in partial pressures on the LHS is greater than that on the RHS (3 moles of gaseous species on LHS vs. 1 mole of gaseous species on RHS).

13 pH = 7.4 **B**
$[OH^-] = \frac{2.4 \times 10^{-14}}{10^{-7.4}}$ = **6.03 x 10^{-7} mol dm^{-3}**

14 **D**
$K_a = \frac{[H^+][C_6H_5COO^-]}{C_6H_5COOH}$
$6 \times 10^{-5} = [H^+]\frac{0.1}{0.01}$
$[H^+] = 6 \times 10^{-6}$
pH = **5.22**

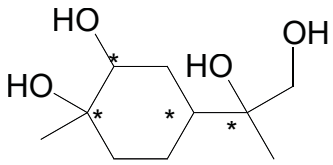
15 K_a is temperature dependent. Hence an increase in V (dilution) will not have any impact on the value of K_a. **A**

16 **A**

	compound	$[Ag^+]$ in saturated solution
A	AgBr	$[Ag^+] = \text{solubility} = \sqrt{5x10^{-13}} = 7.07 \times 10^{-7}$ mol dm^{-3}
B	AgC*l*	$[Ag^+] = \text{solubility} = \sqrt{2x10^{-10}} = 1.41 \times 10^{-5}$ mol dm^{-3}
C	$AgIO_3$	$[Ag^+] = \text{solubility} = \sqrt{2x10^{-8}} = 1.41 \times 10^{-4}$ mol dm^{-3}
D	Ag_2CO_3	$[Ag^+] = 2 \times \text{solubility} = \left(\frac{5x10^{-12}}{4}\right)^{\frac{1}{3}} = 2.15 \times 10^{-4}$ mol dm^{-3}

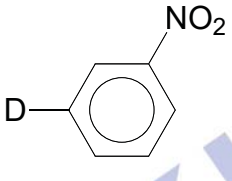
17 Options **A** and **B** will not be able to exhibit *cis–trans* isomerism even after monochloro–substitution due to presence of the $=CH_2$ group. **D**
Option **C** will not have chiral carbon even after monochloro substitution due to $-CH_3$ groups having at least 2 identical H atoms.

18 **C**

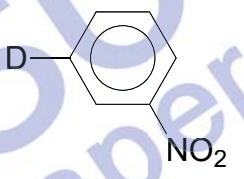


On reaction with cold $KMnO_4$, will be formed. There will be 4 chiral carbons present and the no. of stereoisomers is 2^4 (16).

19 Each poistion on the benzene ring has equal probability of being substituted by $-NO_2$ group (including the C atom bonded to D). Hence the chance of having the $-NO_2$ group substituted on the 3rd C wrt the C atom bonded to D is 2 x 16.7%. **C**



is the same as



20 $-CH_3$ group is 2,4–directing. **A**

21 **B**

$$n(HCl) = \frac{500}{1000}(0.5)$$
$$= 0.250 \text{ mol}$$
$$\text{no. of atoms} = 2 \times n(HCl)$$
$$= 0.500 \text{ mol}$$

	amount of substance present	no. of atoms
1	$n(Xe) = \frac{65.5}{131} = 0.500$	1 x 0.5 = 0.50
2	$n(Al_2O_3) = \frac{10.2}{2(27.0)+3(16.0)} = 0.100$	5 x 0.1 = 0.50
3	$n(O_3) = \frac{11.2}{22.4} = 0.500$	3 x 0.5 = 1.50

22 **R** : **S** **B**

1 : 2

10 : 20 (volume of mixture = 30 cm^3)

Let **R** be C_xH_y & **S** be $C_{x'}H_{y'}$.

$$\underset{10}{C_xH_y} + (x + y/4)\,O_2 \longrightarrow \underset{10x}{x\,CO_2} + y/2\,H_2O$$

$$\underset{20}{C_{x'}H_{y'}} + (x' + y'/4)\,O_2 \longrightarrow \underset{20x'}{x'\,CO_2} + y'/2\,H_2O$$

$10x + 20x' = 100$

$\underline{x + 2x' = 10}$

Thus, only options 1 & 2 are correct.

23 In the 1st reaction, SO_2 reduces Cl_2 to HCl and hence Cl_2 is a weaker reducing agent. **A**
In the 2nd reaction, H_2S reduces Cl_2 to HCl and hence Cl_2 is a weaker reducing agent.
In the 3rd reaction, H_2S (-2) reduces SO_2 (+4) to S (0) and hence SO_2 is a weaker reducing agent.

24 Electronic configuration shown has 16 e, hence **U** could be any atom or ion containing 16 e. **C**

25

1	bent (104.5°)	tetrhedral (109.5°)	trigonal planar (120°)	**A**
2	cctahedral (90°)	bent (104.5°)	linear (180°)	
3	trigonal pyramidal (107°)	trigonal planar (120°)	linear (180°)	

26 **1**: Combustion is always exothermic **B**
2: Neutralisation is always exothermic
3: The 2nd electron affinity is always endothermic.

27 **1**: $CO_2(s) \rightarrow CO_2(g)$; increase in no. of gaseous particles; $\Delta S > 0$ **B**
2: $N_2O_4(g) \rightarrow 2NO_2(g)$; increase in no. of gaseous particles $\Delta S > 0$
3: $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$; decrease in no. of gaseous particles $\Delta S < 0$

28

1 0.05 mol dm^{-3} HCl and 0.10 mol dm^{-3} CH_3CO_2Na **D**
$\Rightarrow$ 0.05 mol dm^{-3} weak acid and 0.05 mol dm^{-3} CH_3CO_2Na present (buffer)

2 0.10 mol dm^{-3} CH_3CO_2H and 0.10 mol dm^{-3} NaOH
$\Rightarrow$ only a salt of weak acid present (not buffer)

3 0.10 mol dm^{-3} CH_3CO_2H and 0.05 mol dm^{-3} $Ca(OH)_2$
$\Rightarrow$ only a salt of weak acid left (not buffer)

29 Please note that the total volume in Experiment 1 is half of that in the other experiments (25 cm^3 compared to 50 cm^3). So it is easier if the **volumes in Experiment 1 are re–based to 50 cm^3** as shown so as to facilitate data comparison. (note that by doing so, concentration of each reactants used remain the same) **D**
Do not to double the time!

In this method, the rate of reaction is measured in terms of the rate at which the concentration of **V** changes

$$\text{rate of reaction } \alpha \frac{\text{concentration of V added}}{\text{time taken for colour of V to disappear}}$$

Expt	Vol of **V** added / cm^3	Vol of **W** added / cm^3	Vol of **X** added / cm^3	Vol of H_2O added / cm^3	Time taken for colour of **J** to disappear / s	Rate of reaction / mol dm^{-3} s^{-1}
1	**10**	**10**	**10**	**20**	40	0.005
2	5	20	10	15	10	0.010
3	10	20	10	10	20	0.010
4	10	20	5	15	40	0.005

Comparing expt 1 & 3,
doubling volume of **K** doubles the rate, reaction is first order w.r.t. **W**.

Comparing expt 3 & 4,
Halving volume of **Y** halves the rate, reaction is first order w.r.t. **X**.

Comparing expt 2 & 3,
doubling volume of **J** did not change the rate, reaction is zero order w.r.t. **V**.

30 $CH_3CO(CH_2)_4CO_2H$ will be formed for option 1. **C**

NAME:_____ PDG:_____ Register No:____

ANDERSON JUNIOR COLLEGE

Promotional Examinations 2012

CHEMISTRY **9647/02**

Higher 2 **3 October 2012**

Paper 2 Structured & Free Response Questions **2 hours 15 minutes**

Candidates answer Section A on the Question Paper.

Additional Materials: Data Booklet
Writing paper

READ THESE INSTRUCTIONS FIRST

Write your name, PDG and register number on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A
Answer **all**the questions.

Section B
Answer **all** questions on separate writing paper.
Begin each question on a fresh sheet of paper.

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				
Paper 2	1		Paper 1	/ 30
	2			
	3		Paper 2	/ 90
	4			
	5		Final Marks	/ 120
	6			/ 100
	7		Grade	

This document consists of **14**printed pages.

Section A

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

1 Planning (P)

The solubility of cerium(IV) sulfate, at a particular temperature, is defined as: the mass of cerium(IV) sulfate that will dissolve in and just **saturate** 100 g of solvent at that temperature.

In a saturated solution of cerium(IV) sulfate, the following equilibrium is established.

$$Ce(SO_4)_2(s) \rightleftharpoons Ce^{4+}(aq) + 2SO_4^{2-}(aq)$$

(a) A student was asked to conduct an experiment to determine the solubility of cerium(IV) sulfate crystals in water under standard conditions.

The student then carried out the following procedure.

Step 1 Using a 100 cm^3 measuring cylinder, measure approximately 50 cm^3 of water into a 250 cm^3 conical flask.

Step 2 Add solid $Ce(SO_4)_2$ into the flask.

Step 3 Stopper and shake the flask to dissolve the solid.

Step 4 Continue adding and shaking until a saturated solution is obtained.

Step 5 Leave the flask to stand at room temperature for some time, shaking the flask intermittently.

Step 6 Filter the mixture, using a dry filter paper and dry filter funnel, into a pre–weighed dry beaker, to obtain the saturated solution.

Step 7 Pour about 10 cm^3 of the saturated solution into a pre–weighed crucible.

Step 8 Record the mass of the solution and the crucible.

Step 9 Dry the $Ce(SO_4)_2$ solid and crucible in the oven to evaporate the water.

Step 10 Cool the $Ce(SO_4)_2$ solid and crucible in a desiccator.

Step 11 Reweigh the crucible with the crystals of $Ce(SO_4)_2$ formed.

(i) Suggest how the student can ensure that the solution in Step 4 is saturated.

……

……

(ii) Suggest why it is necessary to leave the flask to stand for some time at room temperature in Step 5.

……

……

……

(iii) The student collected the following data from the experiment.

mass of empty crucible	/ g	***a***
mass of the crucible and solution	/g	***b***
mass of the crucible and $Ce(SO_4)_2$ crystals	/g	***c***

Use the data above, to calculate the solubility of cerium(IV) sulfate in water.

(iv) Suggest one significant modification to the given procedure to ensure the reliability of the results.

……

……

[5]

(b) Cerium(IV) sulfate crystals also dissolve in dilute sulfuric acid, H_2SO_4.

(i) By considering the ions present in a solution of cerium(IV) sulfate in sulfuric acid, predict and explain how the solubility of the cerium(IV) sulfate will be affected by the concentration of the acid.

Prediction: ……

Explanation: ……

……

(ii) On the following axes, sketch how the solubility of cerium(IV) sulfate changes with the concentration of sulfuric acid.

[3]

[Total: 8]

2 **(a)** In an experiment to identify an oxide of nitrogen, 0.1 mol of the oxide is mixed with an excess of hydrogen and passed over a catalyst at a suitable temperature.

$$N_xO_y \xrightarrow[\text{catalyst}]{H_2(g)} xNH_3 + yH_2O$$

The ammonia produced is neutralised by 100 cm^3 of 2.0 mol dm^{-3} of hydrochloric acid. The water produced weighs 7.20 g.

(i) What is the formula of the oxide of nitrogen?

formula of the oxide of nitrogen ……

(ii) Hence, state, in terms of the change in oxidation number, whether the oxide of nitrogen is oxidised or reduced in the above reaction.

……

……

[2]

(b) Nitrous oxide, N_2O, can be produced by heating a solution of sulfamic acid, H_2NSO_3H and nitric acid. Sulfuric acid and water are the other by–products.

(i) Write a balanced equation for the production of nitrous oxide using this method.

……

In the laboratory, nitric acid is reduced to nitrous oxide by reacting it with a mixture of hydrochloric acid and tin(II) chloride solution.

$$2HNO_3 + 8HCl + 4SnCl_2 \longrightarrow 4SnCl_4 + N_2O + 5H_2O$$

The resulting solution requires 20.0 cm^3 of 0.10 mol dm^{-3} of Fe^{2+} to completely reduce the Sn^{4+}present to Sn^{2+}.

(ii) Write a balanced ionic equation for the reaction between Fe^{2+} and Sn^{4+}.

……

(iii) Hence calculate the volume of nitrous oxide produced under standard conditions.

volume of nitrous oxide produced ……

In the N_2O molecule, the central atom is nitrogen. The molecule contains a dative covalent bond.

(iv) Draw the 'dot–and–cross' diagram for N_2O. Include lone pairs in your diagram.

(v) Hence, state the shape of N_2O molecule.

……

(vi) The molecules of nitrous oxide contain similar number of electrons as atoms of argon. Their boiling points differ widely, however.

Suggest an explanation for the difference in boiling points.

……

……

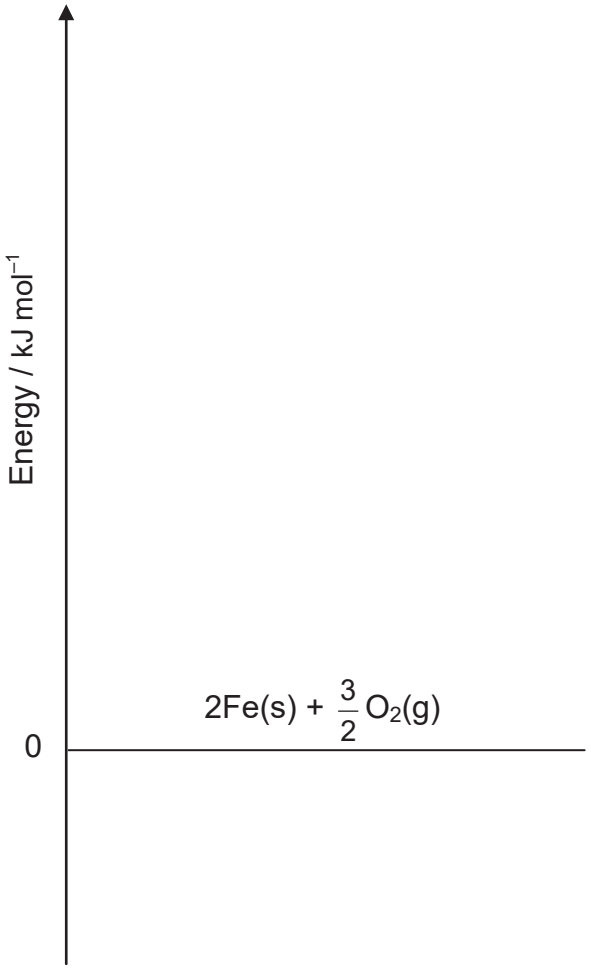
……

[6]
[Total: 8]

3 **(a)** Iron(III) oxide, which is found in the mineral haematite, is the main source of iron for the steel industry. It is a reddish brown solid and has the formula Fe_2O_3.

By using relevant data from the *Data Booklet* and the following data, construct a labeled Born–Haber cycle on the **energy level diagram** below, showing clearly all the enthalpy changes involved and the chemical species at each stage.

first electron affinity of oxygen	–141kJ mol^{-1}
second electron affinity of oxygen	+844 kJ mol^{-1}
enthalpy change of atomisation of iron	+414 kJ mol^{-1}
enthalpy change of formation of iron(III) oxide	–824 kJ mol^{-1}



Hence, use it to calculate the lattice energy of iron(III) oxide.

lattice energy of iron(III) oxide ……

[5]

(b) Iron(III) oxide is also called rust since it is formed from the reaction of iron and oxygen in the presence of moisture in the process of rusting.

$$2Fe(s) + \frac{3}{2}O_2(g) \longrightarrow Fe_2O_3(s)$$

The standard entropy change, $\Delta S^{\ominus}$, for this reaction is –275 J K^{-1} mol^{-1}.

(i) Explain why the entropy change of the above reaction is negative.

……

……

(ii) Using the data given above and in **(a)**, calculate $\Delta G^{\ominus}$ for this reaction.

$\Delta G^{\ominus}$ = ……

(iii) Hence, explain why rusting occurs at room temperature.

……

……

[3]

[Total: 8]

4 The extent of unsaturation in a fatty acid is known as the iodine value and may be determined by the amount of iodine that can be added to a fatty acid.
An acidified solution of iodine monochloride, IC*l*, can be used to estimate the unsaturation of fats and oils.

A 0.20 g sample of an unsaturated acid, **E**, $C_8H_{10}O_2$, was treated with 25.0 cm^3 (an excess) of 0.20 mol dm^{-3} IC*l* solution. The excess of IC*l* reagent was determined by adding 20.0 cm^3 of KI solution and titrating the I_2 formed with 12.5 cm^3 of 0.10 mol dm^{-3} $Na_2S_2O_3$ solution.

$$ICl + I^- + H_2O \longrightarrow I_2 + Cl^- + H_2O$$
$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

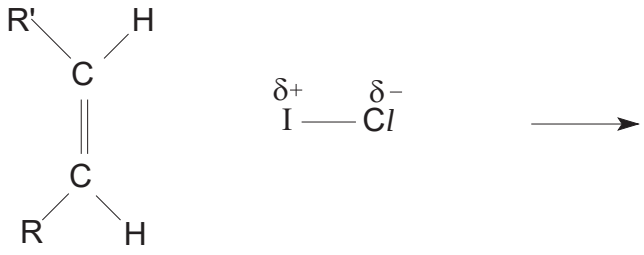
(a) Use the titration data given to determine the number of carbon–carbon double bonds in acid **E**.

number of carbon–carbon double bonds in acid**E** ……
[3]

(b) Hence, suggest a possible**unbranched** structure for acid **E**.

[1]

(c) Representing the formula of acid **E** by the abbreviated structure R–CH=CH–R', complete the mechanism for the reaction between **E** and I*Cl*, including curly arrows showing the movement of electrons, and all charges.



E

[2]
[Total: 6]

Section B

Answer **all** questions from this section on separate writing paper.

5 **(a)** At 25°C, a flask is filled with 4.36 x 10^3 Pa of pure $H_2S(g)$. Solid NH_4HS is then added until there is an excess of unreacted solid remaining, and the following dynamic equilibrium is set up:

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

(i) Given that the partial pressure of NH_3 at equilibrium is 3.30 x 10^4 Pa, calculate the value for K_p.

(ii) The numerical value of K_p increases when temperature is increased to 30°C.

Predict, with reasoning, how the position of equilibrium might change if there were an increase in

1. the volume of the flask
2. the temperature

[6]

(b) In another experiment, NH_3 and H_2S gases are introduced into an empty 10 dm^3 flask at 25°C. The initial partial pressure of each gas is 5.07 x 10^4 Pa.

Using your answer from **(a)(i)**, calculate the mass of NH_4HS that is present when equilibrium is established.

[3]

(c) H_2S can ionise in stages.

$$H_2S \xrightarrow[pK_{a1}]{-H^+} HS^- \xrightarrow[pK_{a2}]{-H^+} S^{2-}$$

In an experiment, 50.0 cm^3 of 0.10 $moldm^{-3}$ solution of H_2S, was titrated with 0.25 $moldm^{-3}$ NaOH.

At 25°C, the first acid dissociation constant, K_{a1}, of H_2S is 9.1 x 10^{-8} $moldm^{-3}$.

(i) Calculate the pH of a 0.10 $moldm^{-3}$ solution of H_2S (ignore the effect of pK_{a2} on the pH).

(ii) Calculate the volume of NaOH required for complete neutralisation of H_2S in the above experiment. Hence calculate the concentration of the salt, Na_2S, formed.

The pH at the second equivalence point is found to be 12.4.

(iii) Write an equation to show why the pH is greater than 7.

(iv) Using the pH at the second equivalence point, calculate the value of the first base dissociation constant, K_{b1}, of S^{2-}.

Hence, determine the value of the second acid dissociation constant, K_{a2}, of H_2S.

(v) Suggest a reason for the difference in values of K_{a1} and K_{a2} of H_2S.

(vi) Using appropriate values from above, sketch the pH curve of this titration.

[9]

(d) Explain, using equations, why a solution containing H_2S and NaHS can act as a buffer solution.

[2]

[Total: 20]

6 3–methylpentane can react with chlorine via free radical substitution to produce a mixture of **four**monochlorinated products.

(a) Draw the structural formula of the four monochlorinated products formed from 3–methylpentane and predict the ratio in which these products are formed. You may assume that the reaction occurs at the same rate at all carbon atoms.

[5]

(b) Name and describe the reaction mechanism to produce **one** of the monochlorinated products, labelling each step in the mechanism appropriately.

[3]

(c) Different halogens used will result in different rates of free radical substitution of 3–methylpentane. Rate of reaction for different halogens used is as shown in descending order:

$$F_2 > Cl_2 > Br_2 > I_2$$

By quoting suitable *bond energies* from the *Data Booklet*, explain why the *initiation step* for free radical substitution is **not** the rate–determining step.

[2]

(d) Explain whether the following step occurs in the free radical substitution mechanism:

$$(CH_3CH_2)_2CHCH_3 + Cl\bullet \longrightarrow (CH_3CH_2)_2CClCH_3 + H\bullet$$

[1]

(e) Compound **F** is a **dichlorinated** product of 3–methylpentane which does not exhibit any optical activity. When **F** undergoes elimination, it produces two compounds, **G** and **H** which have the same formula, C_6H_{10}.

When compound **G**, with structural formula of $CH_3CH=C(CH_3)CH=CH_2$, is oxidised by hot concentrated $KMnO_4$, three different carbon–containing products are formed.

(i) Indicate the type of isomerism shown in compound**G**.

(ii) Suggest the three carbon–containing products obtained from oxidation of compound **G**.

(iii) Based on the structure of **G**, suggest a likely structure for compound **F** and explain why it does not exhibit any optical activity.

(iv) Hence, deduce the structure of compound **H**.

[6]

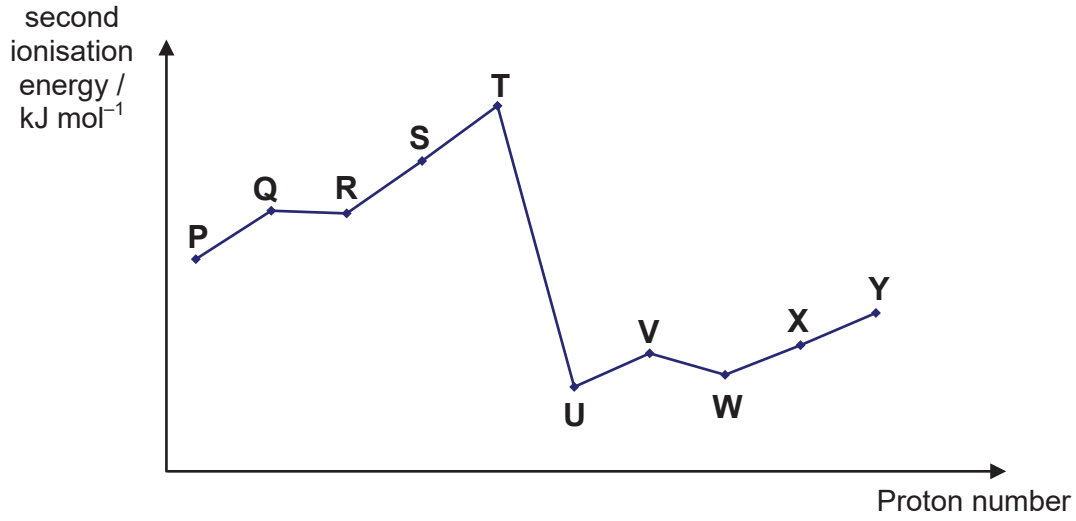
(f) 2–chloropentane undergoes the following synthesis route.

Identify the reagents and conditions at each step of the synthesis route, and draw the structural formula of the intermediate**J**.

[3]

[Total: 20]

7 **(a)** Oxygen is a Period 2 element. The second ionisation energies of ten successive elements **P** to **Y** in both Periods 2 and 3 of the Periodic Table are shown below:



(i) Identifythe letter that represents oxygen.

(ii) Element **P** and **X** are in the same Group.

Explain why the second ionisation energy of **X** is found to be lower than that of **P**.

(iii) Identify the Group in the Periodic Table to which element **V** belongs. Hence, suggest the formula of a compound that element **V** will form with oxygen.

(iv) Element **X** can form more than one stable chlorides.

State the formula of **one** of the chlorides formed. Draw the structural formula of the chloride formed by **X**and indicate clearly the bond angle about **X**.

(v) In general, ionisation energy increases across a period. However, there are some the discontinuities in the graph shown above. One of the exceptions in the general trend occurs between elements **Q** and **R**.

Using the electronic configurations of $\mathbf{Q}^+$ and $\mathbf{R}^+$, explain why the second ionisation energy of **Q** is higher than that of **R**.

[9]

(b) Both oxygen and sulfur are Group VI elements. Explain each of the following observations.

(i) The boiling point of H_2O is higher than that of H_2S. Draw a diagram to illustrate your answer.

(ii) The bond angle in H_2O is larger than that in H_2S.

[3]

(c) Oxygen has many industrial uses. One of the major uses of oxygen is in the manufacture of sodium peroxide, Na_2O_2. Na_2O_2 is used in submarines for absorbing atmospheric carbon dioxide and regenerating oxygen. The reaction produces sodium carbonate as a by–product.

$$2Na_2O_2(s) + 2CO_2(g) \longrightarrow 2Na_2CO_3(s) + O_2(g)$$

(i) State the oxidation number of oxygen in each of the following compounds:

I Na_2O_2
II Na_2CO_3
III O_2

(ii) Hence, identify the type of reaction that took place in the above reaction.

(iii) Describe the bonding in Na_2O_2 and explain why it can act as an electrical insulator. Includea 'dot–and–cross' diagram in your answer.

[5]

(d) A sample of sodium peroxide was completely reacted with excess carbon dioxide. The sodium carbonate formed was thenreacted with 50.0 cm^3 of 1.50 mol dm^{-3} hydrochloric acid (in excess). Any carbon dioxide in the solution was removed.

10.0 cm^3 of the resultant solution required 23.0 cm^3 of 0.50 mol dm^{-3} sodium hydroxide for neutralisation.

Calculate the mass of the sodium peroxide in the sample.

[3]
[Total: 20]

1 (a) (i) A saturated solution is formed when no more $Ce(SO_4)_2$ can dissolve in water and undissolved $Ce(SO_4)_2$ solid remains in the solution. [1]

(ii) This is to ensure that the equilibrium is reached at room temperature/to allow the mixture to equilibrate to room temperature.
as the solubility of $Ce(SO_4)_2$ changes with temperature [1]

(iii)

mass of empty crucible	/ g	***a***
mass of the crucible and solution	/ g	***b***
mass of the crucible and $Ce(SO_4)_2$ crystals	/ g	***c***

mass of water that evaporated = (b – c) g

mass of $Ce(SO_4)_2$ formed after heating = (c –a) g [1]

solubility of $Ce(SO_4)_2$ in 100g of water = $\frac{100}{(b-c)}$ x (c – a) g [1]

(iv) Repeat the heat–cool–weigh process (Step 9 – 11) until a constant mass is obtained. [1]

accept: Carry out the dissolving of cerium(IV) sulfate crystals (step 1 – 5) in a temperature–controlled water bath.

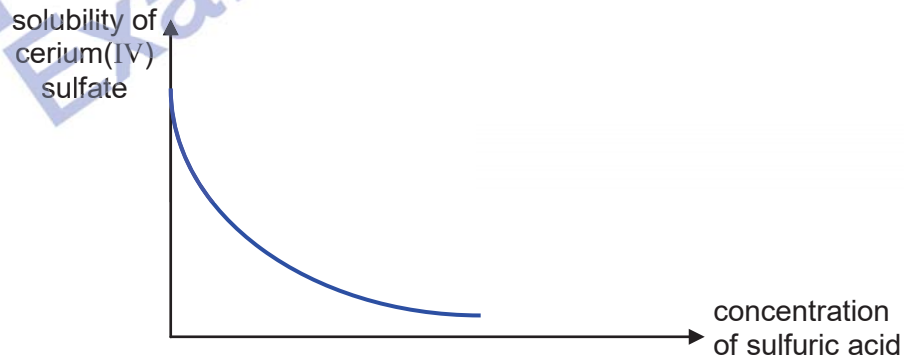
(b) (i) Prediction: Solubility of $Ce(SO_4)_2$ decreases with increasing $[H_2SO_4]$. [1]

Explanation: [1]

$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$$
$$Ce(SO_4)_2(s) \rightleftharpoons Ce^{4+}(aq) + 2SO_4^{2-}(aq) \text{——(1)}$$

With the increase in $[SO_4^{2-}]$ due to the H_2SO_4, the position of equilibrium (1) will shift to the left. This will result in less $Ce(SO_4)_2$ dissolving in H_2SO_4/ decrease in the solubility of $Ce(SO_4)_2$.

(ii) [1]



Also accept straight line with negative gradient.
Line must touch the y–axis, but not the x–axis.

2 (a) (i) $N_xO_y \xrightarrow[\text{catalyst}]{H_2(g)} xNH_3 + yH_2O$ [1]

$nH_2O = \frac{7.20}{18.0}$
= 0.400 mol
$nNH_3 = nHCl$
= 0.1 x 2.0
= 0.200 mol

$\frac{n_{H_2O}}{n_{N_xO_y}} = \frac{y}{1}$ y = 4

$\frac{n_{NH_3}}{n_{N_xO_y}} = \frac{x}{1}$ x = 2

Formula of $N_xO_y = N_2O_4$

(ii) Nitrogen is reduced as the oxidation number of nitrogen decreases from +4 in N_2O_4 to –3 in NH_3. [1]

Note: Explanation must involve change in oxidation number. Passing over $H_2(g)$ / increase in H atoms are not acceptable.

(b) (i) $HNO_3 + NH_2SO_3H \longrightarrow H_2SO_4 + N_2O + H_2O$ [1]

(ii) $2Fe^{2+} + Sn^{4+} \longrightarrow 2Fe^{3+} + Sn^{2+}$ [1]

(iii) $n(Sn^{4+}) = ½\ n(Fe^{2+})$
= 0.5 x 20/1000 x 0.10
= 0.00100 mol

$2HNO_3 + 8HCl + 4SnCl_2 \longrightarrow 4SnCl_4 + N_2O + 5H_2O$
nN_2O = 0.25 x 0.00100 mol
= 2.50×10^{-4} mol
Vol of $N_2O = 2.50 \times 10^{-4} \times 24\ dm^3$
= $6.00 \times 10^{-3}\ dm^3$
= **6.00 cm^3** [1]

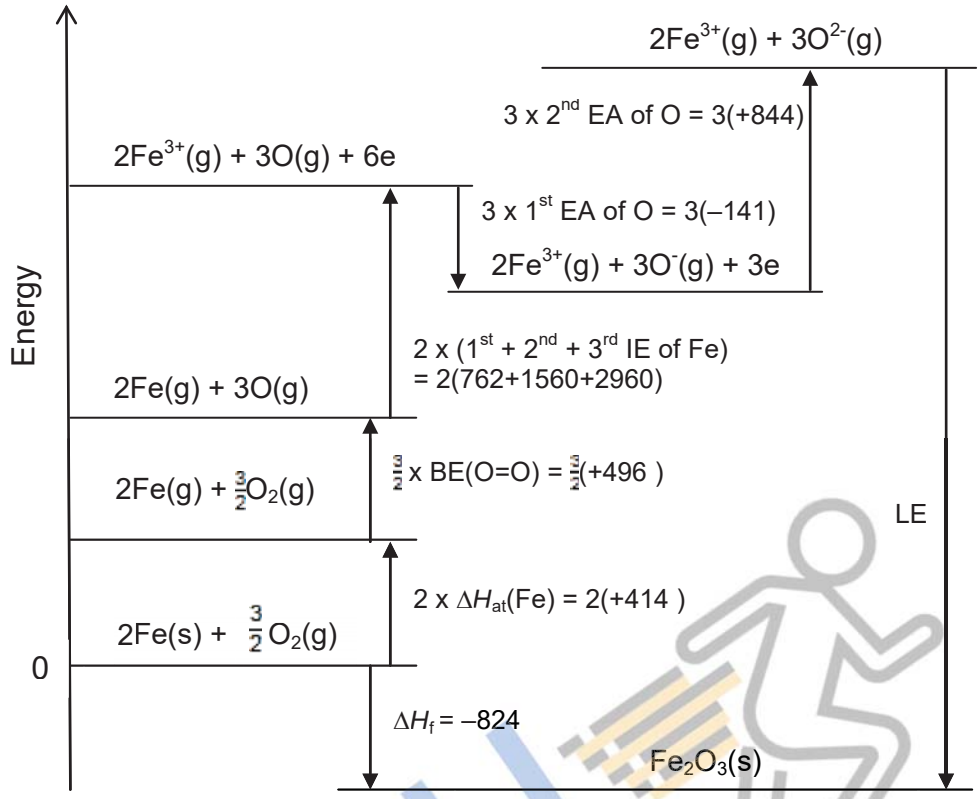
(iv) [1]

(v) Shape: **linear** (2bp 0lp) [1]

(vi) Nitrous oxide is a polar molecule while argon is monoatomic resulting in stronger permanent dipole–permanent dipole attractions between the N_2O molecules. Hence more energy is required to overcome these attractions, thus the boiling point is higher. [1]

(accept explanation in terms of surface area of N_2O being larger; more extensive id–id due to triatomic molecule)

3 (a) [5]



By Hess Law,

$\Delta H_f = 2 \times \Delta H_{at}(Fe) + \frac{3}{2} \times BE(O=O) + 2 \times (1^{st} + 2^{nd} + 3^{rd}$ IE of Fe)
$+ 3 \times 1^{st}$ EA of O + 3 x 2^{nd} EA of O + LE

$-824 = 2(414) + \frac{3}{2}(496) + 2(762+1560+2960) + 3(-141) + 3(844) + LE$

LE = –15069 kJ mol^{-1}

[1] each: for any 2 arrows (with correct equation, state symbols, arrows, labelling of ΔH), max 3 marks
[1]: correctly apply Hess' Law
[1]: correct L.E.

(b) (i) Decrease in disorder due to <u>decrease in number of gaseous particles</u>. [1]
OrDecrease in disorder due to the formation of <u>solid</u>.

(ii) $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ [1]
$= (-824 \times 10^3) - (298)(-275)$
$= -7.42 \times 10^5$ J mol^{-1}
$=$ **–742 kJ mol^{-1}**

(iii) $\Delta G^{\ominus}$ is <u>negative</u>, reaction is <u>spontaneous</u>. [1]

4 **(a)** $n(S_2O_3^{2-})$ used $= \frac{12.5}{1000} \times 0.10$

$= 1.25 \times 10^{-3}$ mol

$n(I_2)$ formed $= \frac{1}{2}(1.25 \times 10^{-3})$

$= 6.25 \times 10^{-4}$ mol

$= n(ICl)$ in excess [1]

$n(ICl)$ reacted with E $= \frac{25.0}{1000} \times 0.20 - 6.25 \times 10^{-4}$

$= 4.38 \times 10^{-3}$ mol

$n(\mathbf{E})$ reacted $= \frac{0.20}{8(12.0) + 10(1.0) + 2(16.0)}$

$= 1.45 \times 10^{-3}$ mol [1]

Let x be the number of C=C present in **E**

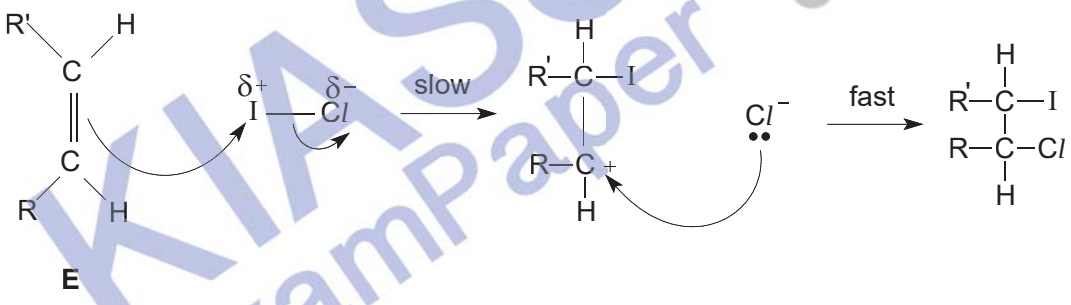
$\frac{n_{ICl} \text{ reacted}}{n_E} = \frac{x}{1}$

$\frac{4.38 \times 10^{-3}}{1.45 \times 10^{-3}} = x$

$x = \mathbf{3}$ [1]

(b) Any 8–carbon chain acid with 3 C=C and satisfy molecular formula given [1]
e.g. $CH_2{=}CHCH{=}CHCH{=}CHCH_2CO_2H$

(c) (electrophilic addition) [2]



[1]: correct electrons movement
[1]: correct charges and intermediate, slow & fast step

5 (a) (i)

	$NH_4HS(s)$	$\rightleftharpoons$	$NH_3(g)$	+	$H_2S(g)$
initial p / Pa			0		**4.36×10^3**
change in p / Pa			*+ 3.30×10^4*		*+ 3.30×10^4*
p at eqm / Pa			**3.30×10^4**		3.736×10^4

Solid NH_4HS added will change P.O.E. to shift right and hence more NH_3 and H_2S will be formed.

Eqm partial pressure of $H_2S = 4.36 \times 10^3 + 3.30 \times 10^4$
$= 3.736 \times 10^4$ Pa [1]

$K_p = (p_{H2S})(p_{NH3})$
$= (3.736 \times 10^4)(3.30 \times 10^4)$
$=$ **1.23×10^9 Pa^2** [1]

(ii) 1. the volume

When volume is increased, pressure decreases. This will shift the position of equilibrium to the right in order to increase pressure by producing more gas molecules. [2]

[1]:POE shifts right
[1]: correct explanation

2. the temperature

Since K_p increases with temperature, the forward reaction is endothermic. When the temperature is increased, the forward endothermic reaction is favoured. The position of equilibrium will shift to the right in order to reduce temperature by absorbing extra heat. [2]

[1]: identify forward reaction is endothermic
[1]: POE shifts right

(b)

	$NH_4HS(s)$	$\rightleftharpoons$	$NH_3(g)$	+	$H_2S(g)$
initial p / Pa			5.07×10^4		5.07×10^4
change in p / Pa			$-x$		$-x$
p at eqm / Pa			**$5.07 \times 10^4 - x$**		**$5.07 \times 10^4 - x$**

Let the partial pressure of NH_3 reacted be x.

Since T remain at 25 °C, $K_p = 1.23 \times 10^9$
$(5.07 \times 10^4 - x)^2 = 1.23 \times 10^9$
$x = 1.563 \times 10^4$ Pa [1]

Number of moles of NH_3 that reacted $= \frac{pV}{RT} = \frac{1.563 \times 10^4 \times 10 \times 10^{-3}}{8.31 \times 298}$
$= 0.06312$ mol [1]

Since number of moles of NH_3 reacted = number of moles of NH_4HS reacted,
mass of $NH_4HS = 0.06312 \times 51.1 =$ **3.23 g** [1]

Alternatively,
Equilibrium partial pressure of each gas = $\sqrt{(1.23 \times 10^9)}$
$= 3.507 \times 10^4$ Pa
Partial pressure of each gas that reacted = $5.07 \times 10^4 - 3.507 \times 10^4$
$= 1.563 \times 10^4$ Pa

(c) **(i)**

$$K_a = \frac{[H^+][HS^-]}{[H_2S]} = \frac{[H^+]^2}{[H_2S]}$$

$$9.1 \times 10^{-8} \approx \frac{[H^+]^2}{0.10}$$

$[H^+] = 9.54 \times 10^{-5}$ moldm^{-3}

$pH = -\log_{10}[H^+]$

$= -\log_{10}(9.54 \times 10^{-5})$ = **4.02** [1]

(ii) $n_{H2S} = 0.05 \times 0.10 = 5 \times 10^{-3}$ mol

Since n_{H2S}:n_{NaOH} is 1:2, $n_{NaOH} = 0.01$ mol

Vol. of NaOH required for complete neutralization = 0.01/0.25

= 0.04 dm^3 = **40 cm^3** [1]

Since n_{H2S}:n_{salt} is 1:1, $n_{salt} = 5 \times 10^{-3}$ mol

[salt] = 5×10^{-3}/ 0.09 = **0.0556 moldm^{-3}** [1]

(iii) $\mathbf{S^{2-} + H_2O \rightleftharpoons HS^- + OH^-}$ [1]

(iv)

	S^{2-}	+ H_2O	$\rightleftharpoons$	HS^-	+ OH^-
initial conc / mol dm^{-3}	0.05556			0	0
change in conc / mol dm^{-3}	$-10^{-1.6}$			$+10^{-1.6}$	$+10^{-1.6}$
eqm conc / mol dm^{-3}	0.03044			0.02512	0.02512

pOH = 14 – 12.4 = 1.6

$[OH^-] = 10^{-1.6}$ = 0.02512 mol dm^{-3}

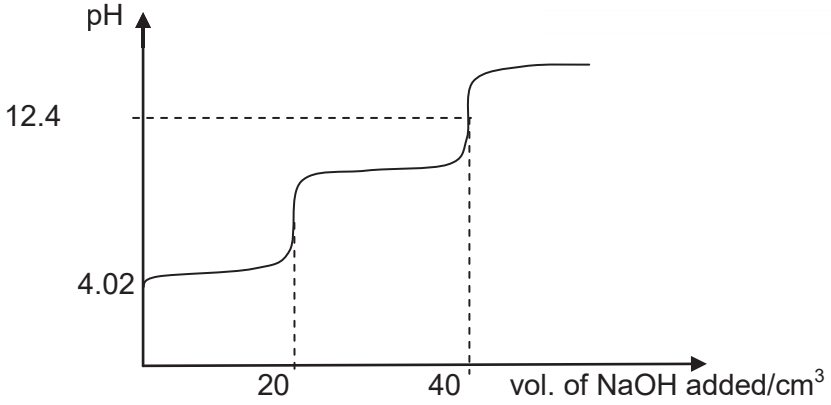
$[S^{2-}]_{eqm}$ = 0.0556 – 0.02512 = 0.03044 mol dm^{-3} [1]

$$K_{b1}(S^{2-}) = \frac{[OH^-][HS^-]}{[S^{2-}]} = \frac{0.02512^2}{0.03044} = \mathbf{0.0207\ mol\ dm^{-3}}$$ [1]

$$K_{a2}(H_2S) = \frac{10^{-14}}{K_{b1}} = \mathbf{4.82 \times 10^{-13}\ mol\ dm^{-3}}$$

(v) K_{a2} is a smaller value than K_{a1}. For K_{a1}, it involves losing a H^+ ion from a neutral H_2S molecule. For K_{a2}, it involves losing a H^+ ion from a negatively–charged ion and this is more difficult due to the electrostatic attraction between the oppositely charged ions. [1]

(vi) [2]



[1]: shape of graph, correct labelled axes, showing 2 equivalence points
[1]: indicates values of initial pH, volume and pH at 2nd equivalence point

(d) When small amount of H^+ is added,

$HS^- + H^+ \longrightarrow H_2S$ [1]

When small amount of OH^- is added,

$H_2S + OH^- \longrightarrow HS^- + H_2O$ [1]

Hence pH remains relatively constant

6 **(a)**

monochlorinated product	relative ratio
$CH_3CH_2CH(CH_2Cl)CH_2CH_3$	3
$CH_3CH_2CCl(CH_3)CH_2CH_3$	1
$CH_3CH_2CH(CH_3)CHClCH_3$	4
$CH_3CH_2CH(CH_3)CH_2CH_2Cl$	6

[5]

[1] each: correct structure
[1]: correct ratio

(b) Free radical substitution [3]

Initiation:
$Cl–Cl \rightarrow 2Cl\bullet$
Propagation:
$Cl\bullet + CH_3CH_2CH(CH_3)CH_2CH_3 \rightarrow \bullet CH_2CH_2CH(CH_3)CH_2CH_3 + HCl$
$\bullet CH_2CH_2CH(CH_3)CH_2CH_3 + Cl–Cl \rightarrow Cl\bullet + CH_3CH_2CH(CH_3)CH_2CH_2Cl$
Termination:
$CH_3CH_2CH(CH_3)CH_2CH_2\bullet + Cl\bullet \rightarrow CH_3CH_2CH(CH_3)CH_2CH_2Cl$
$2Cl\bullet \rightarrow Cl–Cl$

[1] : correct labelling and name of mechanism
[1] : correct propagation steps
[1] : correct initiation and termination steps

(c) [2]
F–F Bond energy = 158 $kJmol^{-1}$
Cl–Cl Bond energy = 244 $kJmol^{-1}$
Br–Br Bond energy = 193 $kJmol^{-1}$
I–I Bond energy = 151 $kJmol^{-1}$
If initiation stage is the rate–determining step, bond energies of the halogens are the activation energies for the initiation stage and hence rate of free radical substitution should be as follows:
$I_2 > F_2 > Br_2 > Cl_2$
Since rate of substitution of different halogens does not follow this trend, the rate determining step for free radical substitution cannot be the initiation stage.

[1]: correctly quoted B.E.
[1]: recognise that order of reactivity based on B.E.

(d) No. H• radical is too unstable to exist. [1]
(accept explanation in terms of ΔH is endothermic)

(e) **(i)** geometrical isomerism [1]

(ii) **CH_3COOH**, **$CH_3COCOOH$**, **CO_2** [2]
2 correct structures – 1M, 3 correct structures – 2M

(iii) **F ≡$CH_3CHClCH(CH_3)CHClCH_3$** [1]
It has a plane of symmetry within the molecule and hence does not display any optical activity even though it has 2 chiral centers. [1]

(iv) **$CH_2=CHCH(CH_3)CH=CH_2$** [1]

(f) Step I: Ethanolic KOH, heat under reflux [1]
Step II: cold, acidic/alkaline $KMnO_4$ [1]
Intermediate**J**: $CH_3CH=CHCH_2CH_3$. [1]

7 (a) (i) Element **Q** [1]

(ii) Electronic configuration of $\mathbf{P}^+$: $1s^2 2s^2 2p^2$ [2]
Electronic configuration of $\mathbf{X}^+$: $1s^2 2s^2 2p^6 3s^2 3p^2$

The election removed from $\mathbf{P}^+$ is from 2p orbital, whereas the electron removed from X^+ is from 3p orbital which is at a higher energy level [1], much lesser energy is required to remove electron from $\mathbf{X}^+$ than from $\mathbf{P}^+$ and hence a lower second ionisation energy [1]. **Or**

The election removed from $\mathbf{P}^+$ is from 2p orbital, whereas the electron removed from $\mathbf{X}^+$ is from 3p orbital. Since valence e^- in $\mathbf{X}^+$is further away from the nucleus than $\mathbf{P}^+$, it experiences a weakerattraction bythe nucleus [1]. Much lesser energy is required to remove electron from $\mathbf{X}^+$ than from $\mathbf{P}^+$ and hence a lower second ionisation energy [1].

(iii) Group III [1]
$\mathbf{V}_2O_3$ [1]

(iv) $\mathbf{X}Cl_3$ / $\mathbf{X}Cl_5$ [2]

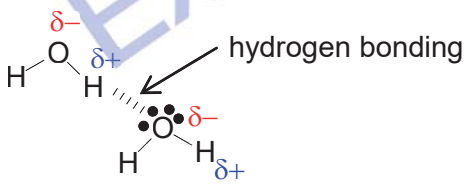
or

[1]: correct formula of chloride
[1]:correct structure with bond angles

(v) Electronic configuration of $\mathbf{Q}^+$: $1s^2 2s^2 2p^3$ [1]
Electronic configuration of $\mathbf{R}^+$: $1s^2 2s^2 2p^4$

The electron removed from $\mathbf{Q}^+$ is an unpaired electron in 2p orbitals whereas the electron removed from $\mathbf{R}^+$ is from a paired electron in 2p orbitals which experiences inter–electronic repulsion. Lesser energy is hence required to remove the electron from $\mathbf{R}^+$. [1]

(b) (i)



[1]

H_2O molecules can form hydrogen bonding within themselves, whereas there are only permanent dipole–permanent dipole interactions within H_2S molecules. More energy is required to break the stronger hydrogen bonding between the water molecules, thus a higher boiling point. [1]

(ii) O is more electronegative than S. Thus, the two bond pairs in H_2O are closer to the central atom than in H_2S. Hence bp–bp repulsion in H_2O is greater, leading to a larger bond angle. [1]
(accept greater electron density; larger angle to minimise repulsion)

(c) **(i)** Na_2O_2: **–1**
Na_2CO_3: **–2**
O_2: **0** [1]

(ii) Disproportionation reaction [1]

(iii) [1]

Sodium peroxide (has a giant ionic lattice structure), where Na^+ and O_2^{2-} ions are held together by strong electrostatic forces of attraction. [1]

In solid state, the ions are fixed in the lattice. Hence there are no mobile charge carriers and Na_2O_2 is an insulator. [1]

(d) $2Na_2O_2(s) + 2CO_2(g) \longrightarrow 2Na_2CO_3(s) + O_2(g)$

$n(NaOH) = \frac{23}{1000} \times 0.50 = 1.15 \times 10^{-2}$ mol

$n(NaOH) = n(HCl)$ left in 10.0 cm^3 = 1.15 x 10^{-2} mol

$n(HCl)$ left in 50.0 cm^3 = 5.75 x 10^{-2} mol [1]

$n(HCl)$ added = $\frac{50}{1000} \times 1.50 = 7.50 \times 10^{-2}$ mol

$n(HCl)$ reacted = 7.50 x 10^{-2} – 5.75 x 10^{-2}
= 1.75 x 10^{-2} mol [1] ecf

$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$

$\frac{n(Na_2CO_3)}{n(HCl)} = \frac{1}{2}$

$n(Na_2CO_3)$ formed = 1.75 x 10^{-2} / 2 = 8.75 x 10^{-3} mol

$\frac{n(Na_2CO_3)}{n(Na_2O_2)} = \frac{1}{1}$

Mass of Na_2O_2 = 8.75 x 10^{-3} x (23.0 x 2 + 16.0 x 2) = **0.683 g** [1] ecf

CATHOLIC JUNIOR COLLEGE
JC1 PROMOTIONAL EXAMINATIONS
Higher 2

CHEMISTRY

9647

Paper 1 Multiple Choice

Tuesday 09 October 2012
30 mins

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not use staples, paper clips, highlighters, glue or correction fluid.
Write and/or shade your name, NRIC / FIN number and HT group on the Multiple Choice Answer Sheet in the spaces provided.

There are **twenty** questions in this paper. Answer **all** questions. For each question, there are four possible answers, **A, B, C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Multiple Choice Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.

The Multiple Choice Answer Sheet will be collected at the end of 30 minutes.

This document consists of **8** printed pages and **0** blank page.

[Turn over

Section A

For each question there are ***four*** possible answers, ***A, B, C and D***. Choose the one you consider to be ***correct*** and record your choice in soft pencil on the ***separate answer sheet*** provided.

1 Which of the following has the same number of atoms as that in 140 g of gallium, Ga?

A Oxygen atoms in 90.8 g of $Ca(NO_3)_2$.
B Hydrogen atoms in 1 mol of $Zn_4Si_2O_7(OH)_2$.
C Helium atoms in 19.9 dm^3 of He gas at rtp.
D Carbon atoms in 36 dm^3 of 0.023 mol dm^{-3} of CH_3COOH.

2 Two identical Br^- solutions were titrated separately with acidified $Cr_2O_7^{2-}$ and acidified MnO_4^- solution of the same concentration.

$$Br_2 + 2\ e^- \rightleftharpoons 2\ Br^-$$
$$Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \rightleftharpoons 2\ Cr^{3+} + 7\ H_2O$$
$$MnO_4^- + 8\ H^+ + 5\ e^- \rightleftharpoons Mn^{2+} + 4\ H_2O$$

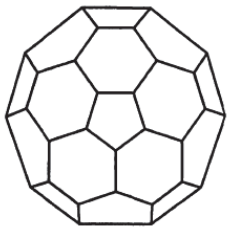
Which of the following describes the volume of $Cr_2O_7^{2-}$ and of MnO_4^- solution required in the titrations to completely react with Br^-?

A The volume of $Cr_2O_7^{2-}$ needed is 0.45 times that of MnO_4^- needed.
B The volume of $Cr_2O_7^{2-}$ needed is 0.83 times that of MnO_4^- needed.
C The volume of $Cr_2O_7^{2-}$ needed is 1.50 times that of MnO_4^- needed.
D The volume of $Cr_2O_7^{2-}$ needed is 2.50 times that of MnO_4^- needed.

3 Which of the following species does ***not*** have a half-filled or fully-filled 3d subshell?

A Cr **B** Mn^{2+} **C** Zn **D** Cu^{2+}

4 Buckminsterfullerene, C_{60}, is a spherical molecule which resembles a soccer ball made up of carbon atoms.



Buckminsterfullerene

The bonding in buckminsterfullerene is similar to that in **graphite**.

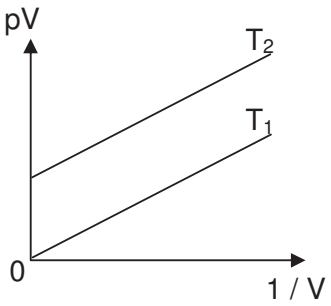
Which of the following best describes the property of a buckminsterfullerene molecule?

A It will have a higher melting point compared to diamond.
B It will be harder than diamond.
C It will possess delocalised electrons.
D It will be soluble in polar solvents such as water.

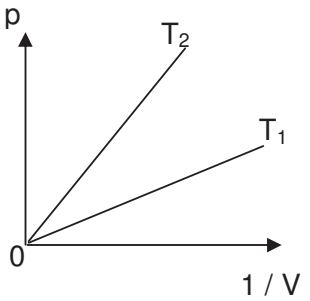
[Turn over

5 Which of the following graphs shows the behaviour of a fixed mass of an ideal gas at two constant temperatures, T_1 and T_2 (where $T_2 > T_1$)?

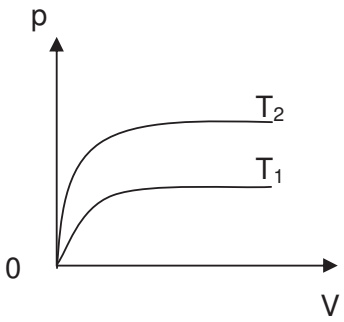
A



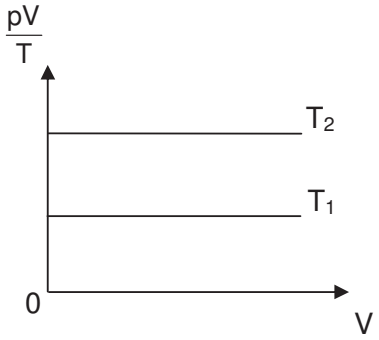
C



B



D



6 Consider the reaction:

$Fe_2O_3(s) + 3\ H_2(g) \longrightarrow 2\ Fe(s) + 3\ H_2O(g)$ $\quad \Delta H^{\ominus} = +96\ kJ\ mol^{-1}$; $\Delta S^{\ominus} = +138\ J\ mol^{-1}\ K^{-1}$.

Which of the following statements is true for the above reaction?

A The reactants are in a more disorderly state than the products.
B The reaction is spontaneous under standard conditions.
C As the reaction proceeds, the temperature will increase.
D As the temperature increases, the reaction becomes more spontaneous.

7 Given the lattice energy of AlF_3 is –6220 kJ mol^{-1}, the enthalpy change of solution of AlF_3 is +51 kJ mol^{-1} and the hydration energies of the ions involved are:

	Al^{3+}	F^-
Hydration energy / kJ mol^{-1}	–4750	*x*

What is the value of *x*, in kJ mol^{-1}?

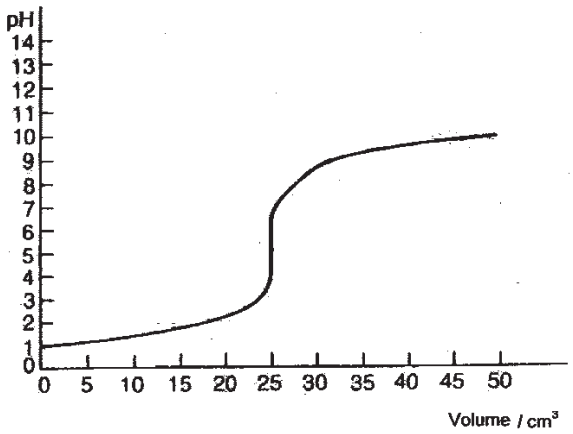
A -473 **B** -710 **C** -1419 **D** -1521

[Turn over

8 Which statement is correct about a reaction for which the equilibrium constant is ***independent*** of temperature?

A The rates for the forward and reverse reactions do not vary with temperature.
B The activation energies for both forward and reverse reactions are zero.
C The enthalpy change is zero.
D There are equal numbers of moles of reactants and products.

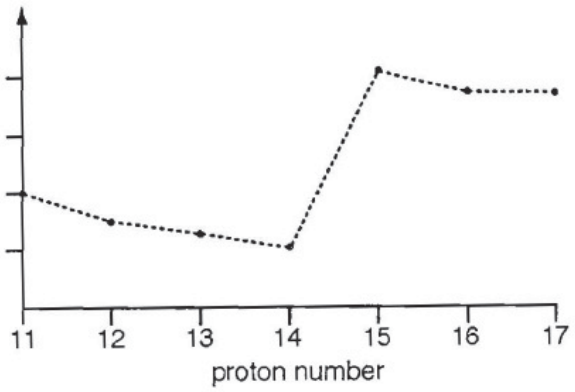
9 In an acid-base titration, a 0.10 mol dm^{-3} solution of a base is added to 25 cm^3 of a 0.10 mol dm^{-3} solution of an acid. The pH value of the solution is plotted against the volume, V, of base added as shown in the diagram.



Which of the following is an indicator that could be used for the above titration?

A litmus
B universal indicator
C phenolphthalein
D methyl orange

10 The graph below shows how a property of the elements from Period 3 varies with proton number.

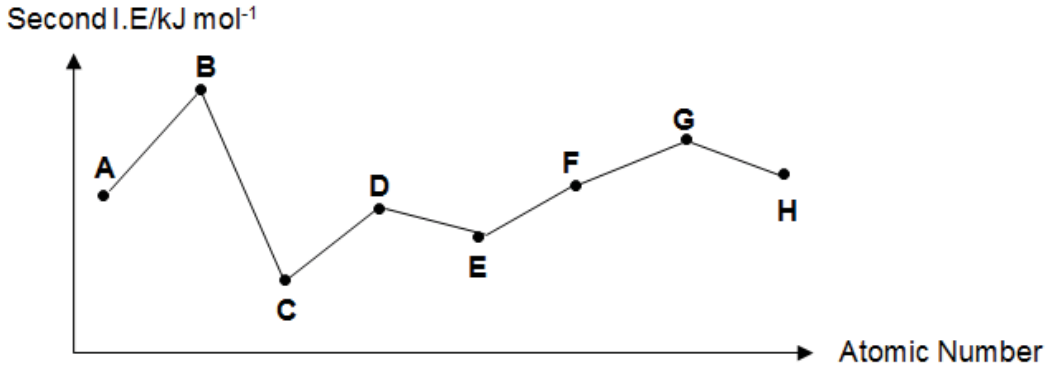


What is the property?

A first ionisation energy
B electronegativity
C melting point
D ionic radius

[Turn over

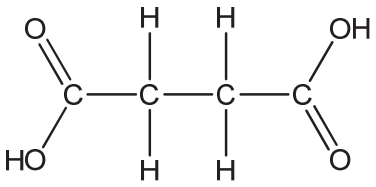
11 The following graph shows the **second** ionisation energies of eight consecutive elements, **A** to **H** which have atomic numbers between 3 to 20 in the Periodic Table.



Which one of the following statements about the oxides of the elements is correct?

A **B** forms a liquid oxide that forms a neutral solution when dissolved in water.
B **D** forms an oxide which can react with both NaOH(aq) and H_2SO_4(aq).
C **E** forms an oxide which is soluble in water to give a solution of pH 9.
D **F** forms an oxide which reacts with water to give a green solution with universal indicator.

12 Malic acid is commonly found in fruits such as green apple and is used as an additive for "super sour" candy. It has the following structure:



What type of hybridisation is shown by the carbon atoms in the molecule?

A sp^3 only
B sp^2 and sp^3
C sp, sp^2 and sp^3
D sp^2 only

13 Cars are usually fitted with catalytic converters in the exhaust system to remove pollutant gases present in the exhaust gases.

Which of the following is **not** a reaction that occurs in the catalytic converter?

A $2\ CO + O_2 \rightarrow 2\ CO_2$
B $2\ NO + 2\ CO \rightarrow N_2 + 2\ CO_2$
C $2\ CO_2 + N_2 \rightarrow 2\ CO + 2\ NO$
D hydrocarbons $+ O_2 \rightarrow CO_2 + H_2O$

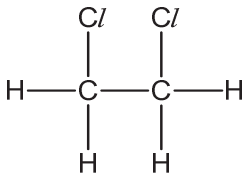
[Turn over

14 Which of the following is a possible electrophile?

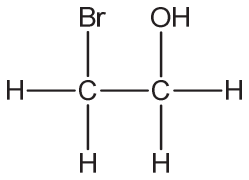
A Cl^+ **B** NH_3 **C** NO_2 **D** Na^+

15 Which of the following is **not** a product formed when ethene ($H_2C=CH_2$) reacts with Br_2 in NaCl(aq)?

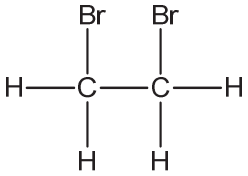
A



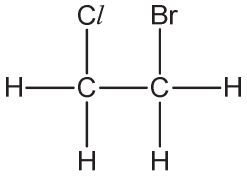
C



B



D

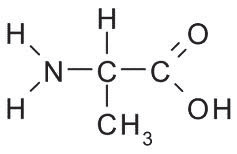
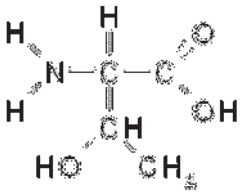
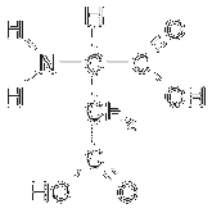


For each of the following questions, one or more of the three numbered statements ***1 to 3*** may be correct. Decide whether each of the statements is or is not correct. The responses ***A to D*** should be selected on the basis of:

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

16 An amino acid has four elements in its molecule. The approximate composition, by mass is C: 40%, H: 8%.

Which of the following could be this molecule?

1	2	3
		
Alanine	Threonine	Aspartic Acid

[Turn over

The responses ***A to D*** should be selected on the basis of:

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

17 $NH_3(g)$ dissociates at 500 K into its elements according to the following equilibrium:

$$2\ NH_3(g) \rightleftharpoons N_2(g) + 3\ H_2(g) \qquad \Delta H = +38\ kJ\ mol^{-1}$$

Given that K_p for the reaction at 500 K is $3.11 \times 10^7\ Pa^2$, which of the following statements is true?

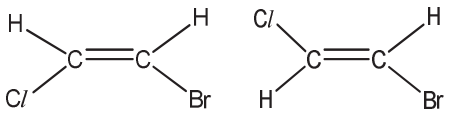
1 K_p decreases when more $N_2(g)$ is added to the equilibrium mixture.
2 K_p increases when the temperature is increased to 600 K.
3 Addition of a catalyst will not have any effect on the value of K_p.

18 Which of the following properties of the oxides across Period 3 elements from Na to S are true?

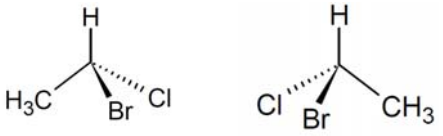
1 The covalent character increases.
2 The oxides of the elements changes from basic to acidic.
3 The oxides formed are increasingly soluble in water across Period 3.

19 Which of the following pairs are stereoisomers of each other?

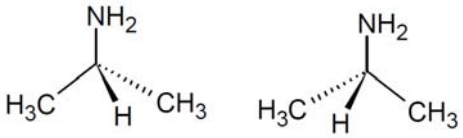
1



2



3

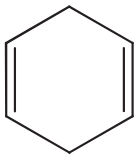


[Turn over

The responses ***A to D*** should be selected on the basis of:

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

20 Dienes are hydrocarbons that contain two C=C double bonds. An example of a diene is cyclohexa-1,4-diene with the following structure.



Which of the following deductions can be made about the organic product formed when cyclohexa-1,4-diene reacts with hot acidified $KMnO_4$?

1 Only one product is formed.
2 The product possesses hydrogen bonding.
3 The product is optically active.

End Of Paper

CATHOLIC JUNIOR COLLEGE
JC1 PROMOTIONAL EXAMINATIONS
Higher 2

CHEMISTRY

Paper 1 Multiple Choice

9647
Tuesday 09 October 2012
30 mins

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not use staples, paper clips, highlighters, glue or correction fluid.
Write and/or shade your name, NRIC / FIN number and HT group on the Multiple Choice Answer Sheet in the spaces provided.

There are **twenty** questions in this paper. Answer **all** questions. For each question, there are four possible answers, **A, B, C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Multiple Choice Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.

The Multiple Choice Answer Sheet will be collected at the end of 30 minutes.

WORKED SOLUTIONS

This document consists of **8** printed pages and **0** blank page.

[Turn over

Section A

For each question there are ***four*** possible answers, ***A, B, C and D***. Choose the one you consider to be ***correct*** and record your choice in soft pencil on the ***separate answer sheet*** provided.

1 Which of the following has the same number of atoms as that in 140 g of gallium, Ga?

A Oxygen atoms in 90.8 g of $Ca(NO_3)_2$.
B Hydrogen atoms in 1 mol of $Zn_4Si_2O_7(OH)_2$.
C Helium atoms in 19.9 dm^3 of He gas at rtp.
D Carbon atoms in 36 dm^3 of 0.023 mol dm^{-3} of CH_3COOH.

Worked solution:

No. of mol of Ga = 140 / 69.7 = 2
No. of Ga atoms = 2 x 6.02 x 10^{23} = 1.20 x 10^{24}

A No. of mol of $Ca(NO_3)_2$ = 90.8 / [40.1 + 2(14 + 3 x 16)] = 0.553
$Ca(NO_3)_2 \equiv 6$ O
No. of mol of O atoms = 0.553 x 6 = 3.32
No. of O atoms = 3.32 x 6.02 x 10^{23} = 2.00 x 10^{24}

B $Zn_4Si_2O_7(OH)_2 \equiv 2$ H
No. of mol of H atoms = 2
No. of H atoms = 2 x 6.02 x 10^{23} = **1.20 x 10^{24}**

C No. of mol of He = 19.9 / 24 = 0.829
No. of He atoms = 0.829 x 6.02 x 10^{23} = 4.99 x 10^{23}

D No. of mol of CH_3COOH = 36 x 0.023 = 0.828
$CH_3COOH \equiv 2$ C
No. of mol of C atoms = 0.828 x 2 = 1.656
No. of C atoms = 1.656 x 6.02 x 10^{23} = 9.97 x 10^{23}

2 Two identical Br^- solutions were titrated separately with acidified $Cr_2O_7^{2-}$ and acidified MnO_4^- solution of the same concentration.

$$Br_2 + 2\,e^- \rightleftharpoons 2\,Br^-$$
$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightleftharpoons 2\,Cr^{3+} + 7\,H_2O$$
$$MnO_4^- + 8\,H^+ + 5\,e^- \rightleftharpoons Mn^{2+} + 4\,H_2O$$

Which of the following describes the volume of $Cr_2O_7^{2-}$ and of MnO_4^- solution required in the titrations to completely react with Br^-?

A The volume of $Cr_2O_7^{2-}$ needed is 0.45 times that of MnO_4^- needed.
B The volume of $Cr_2O_7^{2-}$ needed is 0.83 times that of MnO_4^- needed.
C The volume of $Cr_2O_7^{2-}$ needed is 1.50 times that of MnO_4^- needed.
D The volume of $Cr_2O_7^{2-}$ needed is 2.50 times that of MnO_4^- needed.

[Turn over

Worked solution:

$2\ Br^- \rightleftharpoons Br_2 + 2\ e^-$

$Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \rightleftharpoons 2\ Cr^{3+} + 7\ H_2O$

$\therefore 6\ Br^- \equiv 1\ Cr_2O_7^{2-}$

$Br_2 + 2\ e^- \rightleftharpoons 2\ Br^-$

$MnO_4^- + 8\ H^+ + 5\ e^- \rightleftharpoons Mn^{2+} + 4\ H_2O$

$\therefore 10\ Br^- \equiv 2\ MnO_4^-$

Hence, $5\ Cr_2O_7^{2-} \equiv 30\ Br^- \equiv 6\ MnO_4^-$
So, Volume of $Cr_2O_7^{2-} = 0.83$ (Volume of MnO_4^-)

3 Which of the following species does ***not*** have a half-filled or fully-filled 3d subshell?

A Cr **B** Mn^{2+} **C** Zn **D** Cu^{2+}

Worked solution:

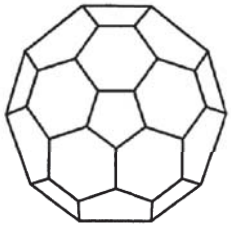
A Cr: [Ar] $3d^5\ 4s^1$ (half filled)

B Mn^{2+}: [Ar] $3d^5$ (half filled)

C Zn: [Ar] $3d^{10}\ 4s^2$ (fully filled)

D Cu^{2+}: [Ar] $3d^9$

4 Buckminsterfullerene, C_{60}, is a spherical molecule which resembles a soccer ball made up of carbon atoms.



Buckminsterfullerene

The bonding in buckminsterfullerene is similar to that in **graphite**.

Which of the following best describes the property of a buckminsterfullerene molecule?

A It will have a higher melting point compared to diamond.
B It will be harder than diamond.
C It will possess delocalised electrons.
D It will be soluble in polar solvents such as water.

[Turn over

Worked solution:

A The melting point of diamond is higher than that in graphite as there is more extensive covalent bonding between carbon atoms. Similarly, diamond will also have higher melting point than buckminsterfullerene.

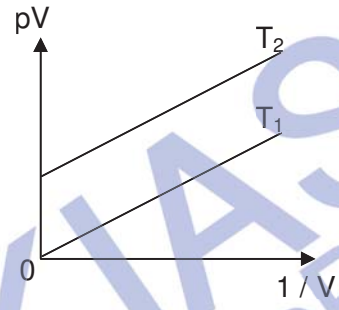
B The discrete buckminsterfullerene molecules are joint together by weak van der Waal's forces of attraction and therefore able to glide pass each other, therefore making it less hard than diamond.

C Each carbon in graphite is bonded to 3 other carbons therefore the last valence electron is delocalised along each layer. Since the bonding of buckminsterfullerene is similar to that of graphite, there will also be delocalised electrons since each carbon in buckminsterfullerene is also bonded to only 3 other carbons.

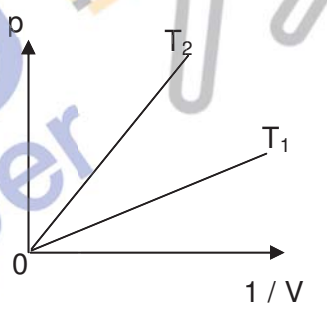
D The buckminsterfullerene molecule is a non-polar molecule and therefore it will not be able to dissolve in polar solvents such as water.

5 Which of the following graphs shows the behaviour of a fixed mass of an ideal gas at two constant temperatures, T_1 and T_2 (where $T_2 > T_1$)?

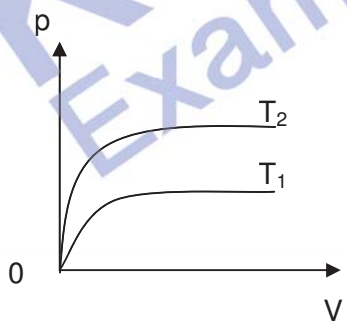
A



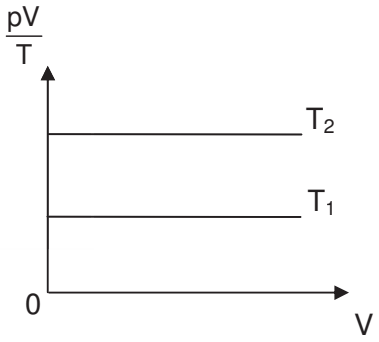
C



B



D



Worked solution:

A pV = constant. Hence, T_1 and T_2 should be a horizontal straight line.

B $p \alpha \left(\frac{1}{V}\right)$. Hence, T_1 and T_2 should be a exponential curve.

C $p \alpha T \left(\frac{1}{V}\right)$. Hence, T_1 and T_2 should lines passing through the origins with different gradient.

D $\frac{pV}{T}$ = constant. Hence, T_1 and T_2 should be a horizontal straight line but the value of the constant for T_1 should be higher.

over

6 Consider the reaction:

$Fe_2O_3(s) + 3\ H_2(g) \longrightarrow 2\ Fe(s) + 3\ H_2O(g)$ $\Delta H^{\ominus} = +96\ kJ\ mol^{-1}$; $\Delta S^{\ominus} = +138\ J\ mol^{-1}\ K^{-1}$.

Which of the following statements is true for the above reaction?

A The reactants are in a more disorderly state than the products.
B The reaction is spontaneous under standard conditions.
C As the reaction proceeds, the temperature will increase.
D As the temperature increases, the reaction becomes more spontaneous.

Worked solution:

A **False.** Increase in no. of particles leads to more ways of arranging particles & distributing energy, hence an increase in disorder upon reaction.

B **False.** $\Delta G = \Delta H - T\Delta S$
At stp, $\Delta G = 96 - 273(138/1000) = 58.3\ kJ\ mol^{-1}$
Since $\Delta G > 0$, reaction is not spontaneous at stp.

C **False.** Forward reaction is endothermic, hence as reaction proceeds, energy is taken in from the surroundings, temperature will decrease.

D **True.** $\Delta G = \Delta H - T\Delta S$
$\Delta G = (+) - T(+)$
As temperature increase, $- T\Delta S$ increase and becomes more negative, and correspondingly ΔG becomes more negative, hence reaction becomes more spontaneous.

7 Given the lattice energy of AlF_3 is $-6220\ kJ\ mol^{-1}$, the enthalpy change of solution of AlF_3 is $+51\ kJ\ mol^{-1}$ and the hydration energies of the ions involved are:

	Al^{3+}	F^-
Hydration energy / kJ mol^{-1}	–4750	*x*

What is the value of *x*, in kJ mol^{-1}?

A -473 **B** -710 **C** -1419 **D** -1521

Worked solution:

$\Delta H_{sol} = -LE + \Sigma\Delta H_{hyd}$
$+51 = -(-6220) + [-4750 + 3x]$
$x = -473\ kJ\ mol^{-1}$ **(A)**

[Turn over

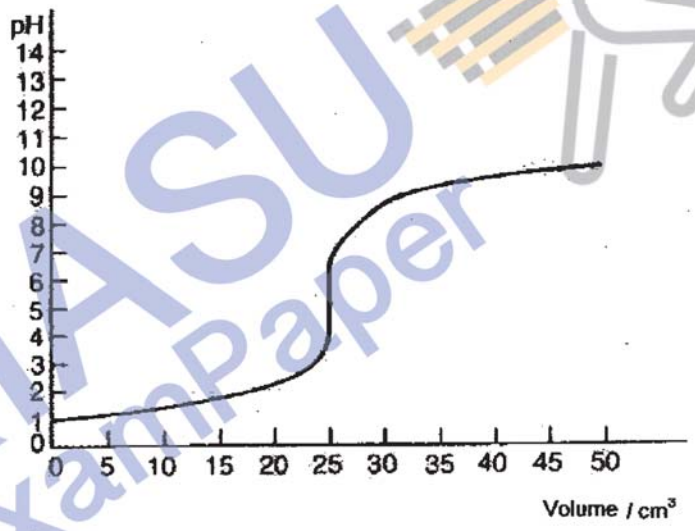
8 Which statement is correct about a reaction for which the equilibrium constant is ***independent*** of temperature?

A The rates for the forward and reverse reactions do not vary with temperature.
B The activation energies for both forward and reverse reactions are zero.
C The enthalpy change is zero.
D There are equal numbers of moles of reactants and products.

Worked solution:

If $\Delta H > 0$, equilibrium constant increases with increasing temperature.
If $\Delta H < 0$, equilibrium constant decreases with increasing temperature.
If $\Delta H = 0$, changing temperature ***does not*** shift equilibrium position to the left or right and the equilibrium concentrations of the products and reactants do not change and equilibrium constant remains the same.

9 In an acid-base titration, a 0.10 mol dm^{-3} solution of a base is added to 25 cm^3 of a 0.10 mol dm^{-3} solution of an acid. The pH value of the solution is plotted against the volume, V, of base added as shown in the diagram.



Which of the following is an indicator that could be used for the above titration?

A litmus
B universal indicator
C phenolphthalein
D methyl orange

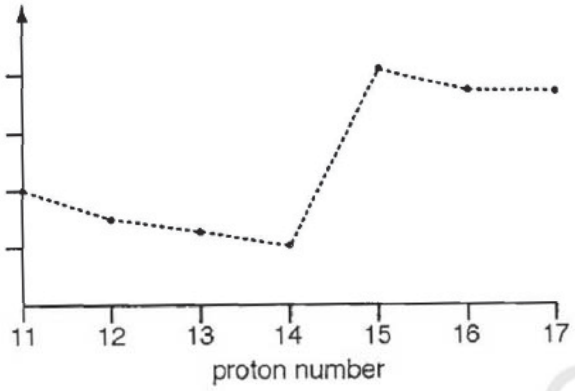
Worked solution:

At equivalence point, pH of salt solution < 7.

This indicates that this is a strong acid-weak base titration. Hence indicator to be used is methyl orange.

[Turn over

10 The graph below shows how a property of the elements from Period 3 varies with proton number.

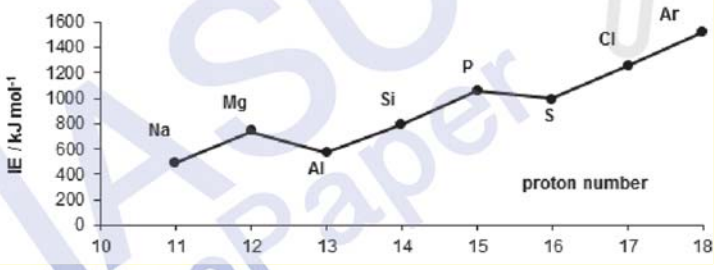


What is the property?

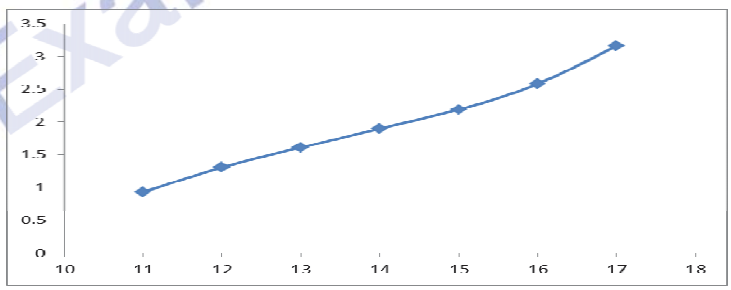
A first ionisation energy
B electronegativity
C melting point
D ionic radius

Worked solution:

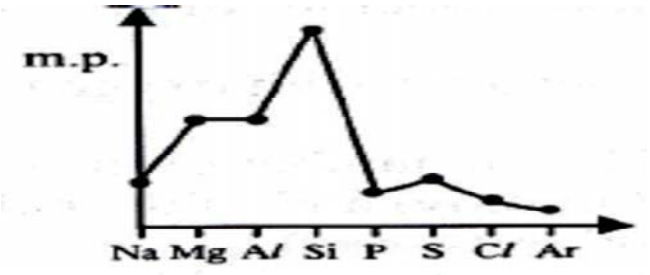
A



B

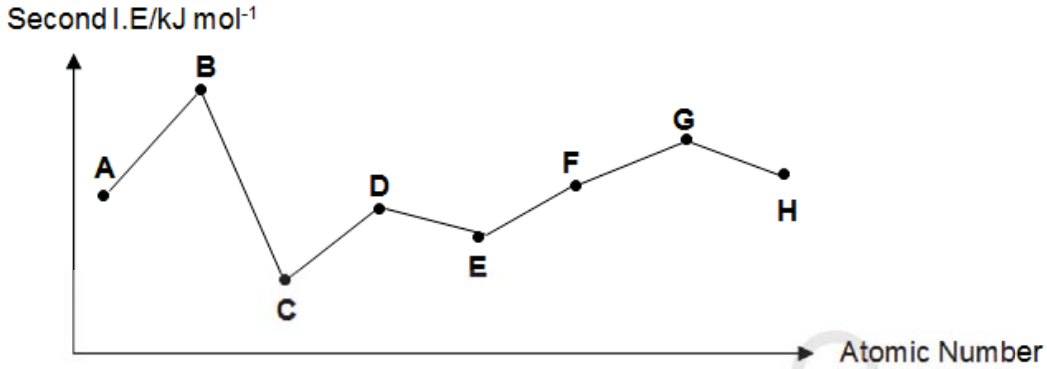


C



over

11 The following graph shows the **second** ionisation energies of eight consecutive elements, **A** to **H** which have atomic numbers between 3 to 20 in the Periodic Table.



Which one of the following statements about the oxides of the elements is correct?

A **B** forms a liquid oxide that forms a neutral solution when dissolved in water.
B **D** forms an oxide which can react with both NaOH(aq) and H_2SO_4(aq).
C **E** forms an oxide which is soluble in water to give a solution of pH 9.
D **F** forms an oxide which reacts with water to give a green solution with universal indicator.

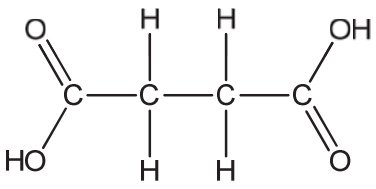
Worked solution:

From the graph, element **B** is from Group I since it has the highest second I.E.

Element	A	B	C	D	E	F	G	H
Group	0	I	II	III	IV	V	VI	VII
Oxide	--	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_6	SO_2	--
Nature of oxide	--	Basic	Basic	Amphoteric	Acidic (insoluble in water)	Acidic	Acidic	--

Therefore only **B** is true.

12 Malic acid is commonly found in fruits such as green apple and is used as an additive for "super sour" candy. It has the following structure:

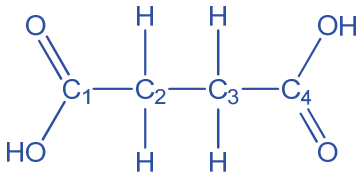


What type of hybridisation is shown by the carbon atoms in the molecule?

A sp^3 only
B sp^2 and sp^3
C sp, sp^2 and sp^3
D sp^2 only

[Turn over

Worked solution:



The respective hybridisation is: C_1: sp^2 C_3: sp^3
C_2: sp^3 C_4: sp^2

13 Cars are usually fitted with catalytic converters in the exhaust system to remove pollutant gases present in the exhaust gases.

Which of the following is **not** a reaction that occurs in the catalytic converter?

A $2\ CO + O_2 \rightarrow 2\ CO_2$
B $2\ NO + 2\ CO \rightarrow N_2 + 2\ CO_2$
C $2\ CO_2 + N_2 \rightarrow 2\ CO + 2\ NO$
D hydrocarbons $+ O_2 \rightarrow CO_2 + H_2O$

Worked solution:

The catalytic converter removes CO, NO_x and unburnt hydrocarbons by converting these gases into the less harmful CO_2, N_2 and H_2O.

Option **C** is incorrect because the polluting gases CO and NO are produced instead.

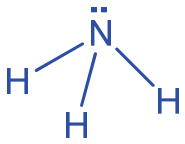
14 Which of the following is a possible electrophile?

A Cl^+ **B** NH_3 **C** NO_2 **D** Na^+

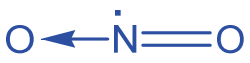
Worked solution:

An electrophile is a species that can accept electrons since it is electron-deficient.

A Cl^+ electrophile
B



nucleophile

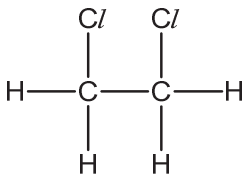
C  free radical

D Na^+ has an octet configuration and is not electron-deficient.

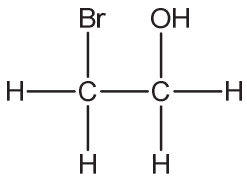
n over

15 Which of the following is **not** a product formed when ethene ($H_2C=CH_2$) reacts with Br_2 in NaC*l*(aq)?

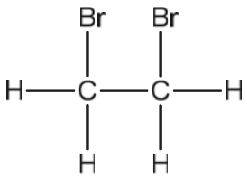
A



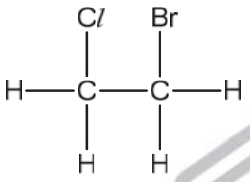
C



B

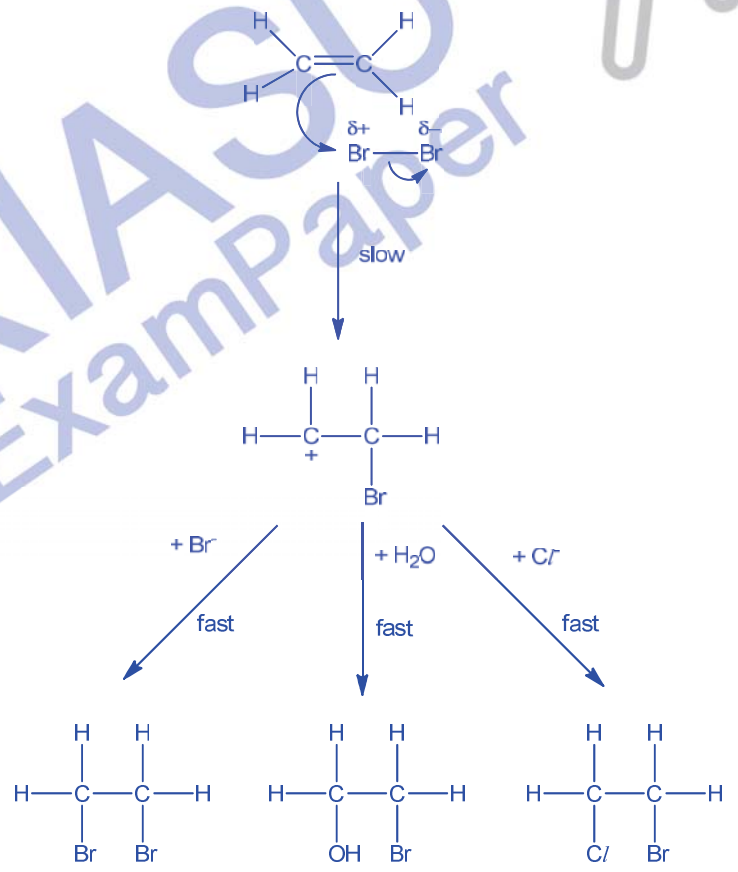


D



Worked solution:

The nucleophiles that can react with the carbocation are :Br^-, H_2O: and :Cl^-.



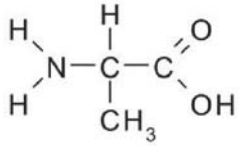
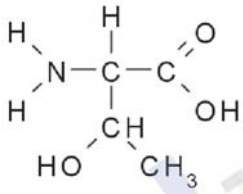
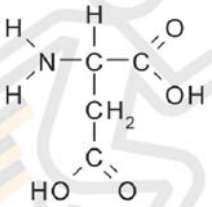
[Turn over

For each of the following questions, one or more of the three numbered statements ***1 to 3*** may be correct. Decide whether each of the statements is or is not correct. The responses ***A to D*** should be selected on the basis of:

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

16 An amino acid has four elements in its molecule. The approximate composition, by mass is C: 40%, H: 8%.

Which of the following could be this molecule?

1	2	3
 Alanine	 Threonine	 Aspartic Acid

Worked solution:

1 Molecular formula is $C_3H_7NO_2$.
% by mass of carbon = 36 / 89 x 100 = 40.4 %
% by mass of hydrogen = 7 / 89 x 100 = 7.87 %

2 Molecular formula is $C_4H_9NO_3$.
% by mass of carbon = 48 / 119 x 100 = 40.3 %
% by mass of hydrogen = 9 / 119 x 100 = 7.56 %

3 Molecular formula is $C_4H_7NO_4$.
% by mass of carbon = 48 / 133 x 100 = 36.1 %
% by mass of hydrogen = 7 / 133 x 100 = 5.26 %

17 $NH_3(g)$ dissociates at 500 K into its elements according to the following equilibrium:

$$2\ NH_3(g) \rightleftharpoons N_2(g) + 3\ H_2(g) \qquad \Delta H = +38\ kJ\ mol^{-1}$$

Given that K_p for the reaction at 500 K is $3.11 \times 10^7\ Pa^2$, which of the following statements is true?

1 K_p decreases when more $N_2(g)$ is added to the equilibrium mixture.
2 K_p increases when the temperature is increased to 600 K.
3 Addition of a catalyst will not have any effect on the value of K_p.

[Turn over

Worked solution:

K_p only changes with changes in temperatures so the statement is incorrect.
Since the forward reaction is endothermic, increase in temperature from 500 K to 600 K, shifts the equilibrium position to the right, so the K_p increases. Correct statement.
A catalyst does not change the K_p value so this statement is correct.

18 Which of the following properties of the oxides across Period 3 elements from Na to S are true?

1 The covalent character increases.
2 The oxides of the elements changes from basic to acidic.
3 The oxides formed are increasingly soluble in water across Period 3.

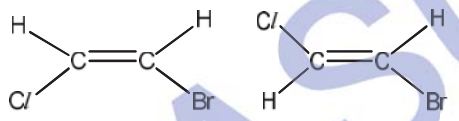
Worked solution:

Answers: **1** and **2** only (**B**)

Al_2O_3 and SiO_2 are insoluble in water.

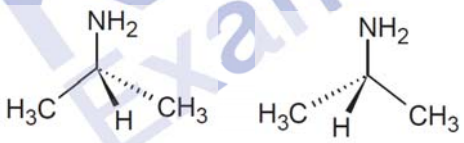
19 Which of the following pairs are stereoisomers of each other?

1



2

3



Worked solution:

.

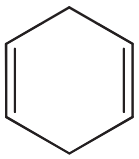
1 There is C=C double bond with two different substituents attached to each doubly bonded C atom. Hence, there is geometric isomerism.

2 There is a chiral carbon atom present; hence there is optical isomerism.

3 There is no chiral carbon; hence no optical isomerism.

[Turn over

20 Dienes are hydrocarbons that contain two C=C double bonds. An example of a diene is cyclohexa-1,4-diene with the following structure.



Which of the following deductions can be made about the organic product formed when cyclohexa-1,4-diene reacts with hot acidified $KMnO_4$?

1 Only one product is formed.
2 The product possesses hydrogen bonding.
3 The product is optically active.

Worked solution:

When cyclohexa-1,4-diene reacts with hot and concentrated $KMnO_4$, oxidative cleavage of the C=C double bond occurs.

End Of Paper

[Turn over

H

CATHOLIC JUNIOR COLLEGE
JC1 PROMOTIONAL EXAMINATIONS
Higher 2

CANDIDATE NAME	
CLASS	**1T**

CHEMISTRY

9647

Paper 2 Section B Structured Questions
Section C Free Response Questions

Tuesday 09 October 2012
2 hours

Additional Materials: Data Booklet
Writing Papers

READ THESE INSTRUCTIONS FIRST

Write your HT group and name in the boxes above.
Write in dark blue or black pen on 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.
Give non-exact numerical answers correct to 3 significant figures unless a different level of accuracy is specified in the question.

You are advised to show all working in calculations.
You may use a calculator.
A Data Booklet is provided.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
Section A	/20
Q1	/10
Q2	/10
Q3	/10
Q4	/10
Section B	/40
Section C	/40
TOTAL	/100

QUESTION PAPER

This document consists of **12** printed pages and **0** blank page.

[Turn over

Section B

Answer ***all*** questions in this section. Write your answers in the spaces provided.

You are advised to spend **not** more than one hour on this section.

1

(a) The air inhaled by a human becomes saturated with water vapour as it enters the lungs. The saturated vapour pressure of water, which is the pressure exerted by water vapour in air, at 37 ^{o}C is 6.26 kPa.

(i) Given that the temperature and pressure in the lungs is 37 °C and 101 kPa respectively, find the total pressure exerted by the gases in the inhaled air (not including water vapour) in kPa.

(ii) Given that air in the atmosphere contains approximately 0.4 ppt by volume of CO_2 (1 ppt = 1 volume of CO_2 in 1000 volumes of air), calculate the pressure exerted by carbon dioxide in the inhaled air in kPa.

[2]

(b) An average adult exhales about 500 cm^3 of air per breath at rest. The exhaled air contains 4 % of CO_2 by volume.

(i) Calculate the volume of CO_2 per breath of air exhaled by an average adult at rest.

[Turn over

(ii) Hence, calculate the amount, in moles, of CO_2 produced by the adult in one breath at 37 ^oC and 1 atm.

(iii) State a possible assumption made about CO_2 and suggest whether this assumption is valid.

……

……

……

(iv) In order to measure the rate of respiration, a person exhales into a respirometer in which the exhaled air is bubbled at 37 ^oC and 1 atm through 200 cm^3 of 1.00 mol dm^{-3} of calcium hydroxide to obtain a white precipitate. The equation for this reaction is

$$CO_2(g) + Ca(OH)_2(aq) \rightarrow CaCO_3(s) + H_2O(l)$$

The white precipitate was filtered, washed and dried before reaction with 150 cm^3 of 0.200 mol dm^{-3} of hydrochloric acid. The resultant solution was transferred into a volumetric flask and made up to 250 cm^3 with de-ionised water.

A 25.0 cm^3 aliquot of this diluted solution required 6.0 cm^3 of a 0.200 mol dm^{-3} solution of sodium hydroxide for complete neutralisation.

Calculate the amount of HC*l* that reacted with the white precipitate.

(v) Hence, calculate the amount, in moles, of CO_2 present in the exhaled air.

(vi) Using your answer in **(b)(v)**, calculate the number of times the person exhaled into the respirator.

[8]

[Total: 10]

2 Phosphorus was the 13th element to be discovered. For this reason, and also due to its use in explosives, poisons and nerve agents, it is sometimes referred to as "the Devil's element".

(a) **(i)** Write the chemical equation, with state symbols, to represent the first ionisation energy of phosphorus, P.

……

(ii) Explain why the first ionisation energy of phosphorus, P, is higher than that of both silicon, Si, and sulfur, S, with the use of relevant electronic configurations.

……

……

……

……

……

[4]

[Turn over

(b) Phosphorus pentachloride, PCl_5, is a colourless, water-sensitive solid, although commercial samples can be yellowish and contaminated with hydrogen chloride, HCl.

Write an equation to show why PCl_5 is water-sensitive and easily contaminated with HCl.

……...

[1]

(c) Solid PCl_5 exists as two ions, PCl_4^+ and PCl_6^-, while solid PBr_5 exists as ions, but in this case as PBr_4^+ and Br^-. Suggest a reason for this difference in the ions formed.

……

……

[2]

(d) An important starting material for the manufacture of polyphosphazenes is the cyclic molecule $(NPCl_2)_3$. The molecule has a symmetrical six-membered ring of alternating N and P atoms, with Cl atoms bound to P atoms only. The nitrogen-phosphorus bond energy in the compound is larger than that expected for an N—P single bond.

(i) Draw a likely structure for the molecule.

(ii) State the total number of lone pairs of electrons on the ring atoms.

……

[3]

[Total: 10]

[Turn over

3 Hexamethylenetetramine is a heterocyclic organic compound with the formula $(CH_2)_6N_4$. This white crystalline compound is highly soluble in water and polar organic solvents. It is a primary component of solid fuel tablets used by campers for heating rations.

(a) Upon complete combustion, hexamethylenetetramine, $(CH_2)_6N_4$ forms gaseous nitrogen pentoxide, N_2O_5, carbon dioxide and water.

(i) Write a balanced chemical equation to show the complete combustion of hexamethylenetetramine.

……...

(ii) Use the thermochemical data below to calculate the enthalpy change of combustion of hexamethylenetetramine.

Enthalpy change of formation of hexamethylenetetramine	+ 400 kJ mol^{-1}
Enthalpy change of formation of nitrogen pentoxide	+ 11 kJ mol^{-1}
Enthalpy change of formation of carbon dioxide	- 394 kJ mol^{-1}
Enthalpy change of formation of water	- 243 kJ mol^{-1}

(iii) 100 g of water was heated in a camping stove by burning a sample of hexamethylenetetramine, $(CH_2)_6N_4$. The temperature rise of the water recorded was 40 ℃. Using your answer to **(ii)**, calculate the mass of hexamethylenetetramine burnt, assuming that 70% of the heat evolved is absorbed by the water. (specific heat capacity of water = 4.20 J K^{-1} mol^{-1})

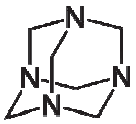
[5]

[Turn over

(b) Solid hexamethylenetetramine, $(CH_2)_6N_4$, can be prepared by the reaction of gaseous formaldehyde, CH_2O, with gaseous ammonia.

(i) The skeletal formulae of formaldehyde and hexamethylenetetramine are shown below.

formaldehyde



hexamethylenetetramine

The reaction between formaldehyde and ammonia yields hexamethylenetetramine and water.

I Write a balanced equation for the above reaction.

……

II Using appropriate values from the *Data Booklet*, calculate the enthalpy change for the above reaction.

(ii) Predict and explain the sign of the entropy change for the above reaction, with clear reference to the number of ways of arrangement of particles before and after reaction.

……

……

……

……

[5]

[Total: 10]

[Turn over

4

(a) In the gaseous state, NO_2, which is used in the preparation of nitric (V) acid, can dimerise as given in the equation.

$$2\ NO_2(g) \rightleftharpoons N_2O_4(g)$$

When 1 mol of NO_2 is placed in a 2 dm^3 vessel at room temperature, it is found that the equilibrium mixture contains 0.3 mol of N_2O_4.

(i) Write an expression for the equilibrium constant, K_c for the dimerisation of NO_2.

……

(ii) Calculate a value of K_c for the reaction, giving its units, showing clearly the workings.

(iii) The NO_2 molecule has an ***unpaired*** electron on the nitrogen atom but the N_2O_4 molecule does not. Using the information,

I name the type of species that has an unpaired electron, such as NO_2.

……

II suggest a full structural/displayed formula for N_2O_4, clearly showing the types of bonds present.

[Turn over

III hence, explain whether the dimerisation of NO_2 is endothermic or exothermic.

……

……

(iv) Explain, with reasons, whether the dimerisation of NO_2 is favoured by

I high or low pressure,

……

……

II high or low temperature.

……

……

[8]

(b) At 448 ^{o}C the equilibrium constant K_c for the reaction,

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

is 50.5. Predict in which direction the reaction will proceed to reach equilibrium at 448 ^{o}C if 2.0×10^{-2} mol of HI, 1.0×10^{-2} mol of H_2 and 3.0×10^{-2} mol of I_2 in a 2 dm^3 container, were present at the start.

[2]

[Total: 10]

[Turn over

Section C

Answer ***all*** questions in this section. Write your answers on the writing paper provided.
Answer each question on a new page.

You are advised to spend **not** more than one hour on this section.

5 This question is about chlorine and its compounds.

(a) Chlorine and fluorine are halogens in Group VII of Periodic Table, chlorine being a bigger atom than fluorine.

(i) Explain why the melting point of $AlCl_3$ is 192 °C, but that of AlF_3 is 1291 °C, with reference to structure and bonding of the two substances.

(ii) Explain why phosphorus forms a pentachloride, PCl_5, but nitrogen does not form a pentachloride NCl_5.

[5]

(b) Hydrochloric acid, HCl, has numerous applications in industry, from the production of plastics to food additives to cleaning stains. About 20 million tonnes of hydrochloric acid are produced annually.

(i) HCl is a strong acid and fully ionises in water. Draw a diagram showing the attractions formed when HCl is dissolved in water. Label clearly the attractions present.

(ii) Calculate the pH of a 30.0 cm^3 solution of 0.10 mol dm^{-3} HCl.

[3]

(c) Chloric (I) acid, HClO, is a weak acid, and its salts, chlorate (I), ClO^- are used as bleaching agents, deodorants and disinfectants.

(i) Draw the dot-and-cross diagram for a HClO molecule and hence state its shape and bond angle, given that oxygen is the central atom.

(ii) Calculate the pH of the solution formed by adding 10.0 cm^3 of 0.10 mol dm^{-3} NaOH to 20.0 cm^3 of 0.10 mol dm^{-3} chloric (I) acid, HClO.

[K_a of HClO = 4.00×10^{-8} mol dm^{-3}]

(iii) Calculate the concentrations of HClO and ClO^- upon the addition of another 0.2 cm^3 of NaOH to the solution above. Hence, show that the change in pH of the solution is approximately 0.02 units.

(iv) Explain why the pH change in **(c)(ii)** is small upon the addition of a small amount of NaOH, illustrating your answer with an appropriate equation.

[9]

(d) Mercury (I) chloride, Hg_2Cl_2, contains the Hg_2^{2+} ion. The K_{sp} of Hg_2Cl_2 is 1.43×10^{-18} mol^3 dm^{-9}.

(i) Write the K_{sp} expression for Hg_2Cl_2. Hence, calculate its solubility in water.

(ii) Explain how the addition of dilute HCl will affect the solubility of Hg_2Cl_2.

[3]

[Total: 20]

[Turn over

6 This question is about the reactions of halogens with organic compounds.

(a) CFCs or chlorofluorocarbons such as dichlorodifluoromethane, CF_2Cl_2, can be synthesised from methane. CFCs have been widely used as refrigerants, aerosol propellants and solvents. However, they have been gradually phased out under the Montreal Protocol and have been replaced with products such as HFCs or hydrofluorocarbons which do not deplete the ozone layer like CFCs.

The first step in production of CF_2Cl_2, is to react methane with chlorine to form chloromethane.

(i) Write a balanced equation for the reaction between methane and chlorine.

(ii) State the condition necessary for the reaction between methane and chlorine.

(iii) State and describe the mechanism that occurs between methane and chlorine.

(iv) Hence explain why ethane can sometimes be found in small quantities in the reaction mixture.

CFCs are harmful as they undergo homolytic fission to produce free radicals which then break down the ozone.

(v) Write an equation to show how radicals are produced from CF_2Cl_2.

(vi) Hence, by quoting relevant bond energies values data from the *Data Booklet*, explain why HFCs such as CH_2F_2 do not deplete the ozone layer.

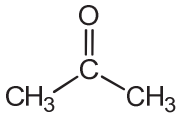
[10]

(b) 0.01 moles of liquid hydrocarbon **X** was burnt completely in an excess of oxygen in an enclosed vessel. After combustion, the resultant gases were passed through an excess of NaOH, a reduction in gas volume of 1.44 dm^3 was observed at r.t.p. 0.01 mole of liquid **X** also reacts completely with 1.6 g of Br_2 in the dark.

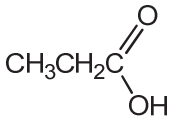
(i) Using the information above, deduce that the molecular formula of **X** is C_6H_{12}, and state the type of functional group it contains.

(ii) Suggest a structure for compound **A**, which has the same molecular formula as **X**, but does not decolourise bromine in the dark.

X, C_6H_{12} reacts with hot acidified concentrated $KMnO_4$ to produce propanone, CH_3COCH_3, and propanoic acid, $CH_3CH_2CO_2H$. **X** also reacts with HBr to give **Y**, which has a chiral carbon.



propanone



propanoic acid

(iii) Use this information to draw the structural formulae of **X** and **Y**.

(iv) State and explain the type of isomerism that **Y** exhibits.

(v) Hence, explain why the solution containing **Y** will not rotate plane polarised light.

[8]

[Turn over

(c) Predict the products formed when propene reacts with

(i) cold dilute $KMnO_4$

(ii) steam, concentrated H_3PO_4, 300 ^oC, 70 atm

[2]

[Total: 20]

End of Paper

H

CATHOLIC JUNIOR COLLEGE
JC1 PROMOTIONAL EXAMINATIONS
Higher 2

CANDIDATE NAME	
CLASS	**1T**

CHEMISTRY

9647

Paper 2 Section B Structured Questions
Section C Free Response Questions

Tuesday 09 October 2012
2 hours

Additional Materials: Data Booklet
Writing Papers

READ THESE INSTRUCTIONS FIRST

Write your HT group and name in the boxes above.
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For Examiner's Use	
Section A	/20
Q1	/10
Q2	/10
Q3	/10
Q4	/10
Section B	/40
Section C	/40
TOTAL	/100

SOLUTIONS

This document consists of **12** printed pages and **0** blank page.

[Turn over

Section B

Answer ***all*** questions in this section. Write your answers in the spaces provided.

You are advised to spend **not** more than one hour on this section.

1

(a) The air inhaled by a human becomes saturated with water vapour as it enters the lungs. The saturated vapour pressure of water, which is the pressure exerted by water vapour in air, at 37 °C is 6.26 kPa.

(i) Given that the temperature and pressure in the lungs is 37 °C and 101 kPa respectively, find the total pressure exerted by the gases in the inhaled air (not including water vapour) in kPa.

Dalton's law states that
$P_{total} = P_{water} + P_{other\ gases}$
Total pressure exerted by gases from atmosphere = 101 – 6.26= **94.7 kPa**

(ii) Given that air in the atmosphere contains approximately 0.4 ppt by volume of CO_2 (1 ppt = 1 volume of CO_2 in 1000 volumes of air), calculate the pressure exerted by carbon dioxide in the inhaled air in kPa.

At the same pressure, volume is proportional to number of moles (Avogadro's law). Hence, volume fraction = mole fraction

P_{CO_2} = 0.4 / 1000 x 94.7
= **0.0379 kPa**

[2]

(b) An average adult exhales about 500 cm^3 of air per breath at rest. The exhaled air contains 4 % of CO_2 by volume.

(i) Calculate the volume of CO_2 per breath of air exhaled by an average adult at rest.

Volume of CO_2 produced by adult = 4/100 x 500
= **20.0 cm^3**

(ii) Hence, calculate the amount, in moles, of CO_2 produced by the adult in one breath at 37 °C and 1 atm.

PV = nRT

No. of moles of CO_2 produced = $\frac{1.01 \times 10^5 \times 20.0 \times 10^{-6}}{8.31 \times 310}$

= **7.84×10^{-4} mol**

(iii) State a possible assumption made about CO_2 and suggest whether this assumption is valid.

The gas is behaving ideally/ideal gas/negligible intermolecular forces of attraction. This assumption is invalid because of the siginificant intermolecular forces of attraction in CO_2 due to the low temperature of 37°C.

OR

Negligible volume of particles compared to space it occupies/volume of container. It is valid as there is low pressure of 1 atm

OR

Same volume of CO_2 exhaled at each breath. It is invalid as person's metabolic rate may change.

OR

CO_2 does not dissolve in water vapour. It is valid as CO_2 is mildly soluble in water.

(iv) In order to measure the rate of respiration, a person exhales into a respirometer in which the exhaled air is bubbled at 37 °C and 1 atm through 200 cm^3 of 1.00 mol dm^{-3} of calcium hydroxide to obtain a white precipitate. The equation for this reaction is

$$CO_2(g) + Ca(OH)_2(aq) \rightarrow CaCO_3(s) + H_2O(l)$$

The white precipitate was filtered, washed and dried before reaction with 150 cm^3 of 0.200 mol dm^{-3} of hydrochloric acid. The resultant solution was transferred into a volumetric flask and made up to 250 cm^3 with de-ionised water.

A 25.0 cm^3 aliquot of this diluted solution required 6.0 cm^3 of a 0.200 mol dm^{-3} solution of sodium hydroxide for complete neutralisation.

Calculate the amount of HC*l* that reacted with the white precipitate.

HC*l* ≡ NaOH
Amt of HC*l* in 25cm^3 aliquot = Amt of NaOH reacted
= 6/1000 x 0.2
= 0.00120mol

Amt of HC*l* in 250cm^3 = 0.0120mol
Amt of HC*l* used = 150/1000 x 0.2 = 003 mol
Amt of HC*l* reacted with white precipitate = 0.03 – 0.012
= 0.018 mol

[Turn over

(v) Hence, calculate the amount, in moles, of CO_2 present in the exhaled air.

$CO_2(g) + Ca(OH)_2(aq) \rightarrow CaCO_3(s) + H_2O(l)$
$CaCO_3(s) + 2\ HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

$2\ HCl \equiv CaCO_3 \equiv CO_2$ present in exhaled air
Amt of CO_2 present in exhaled air = ½ x 0.018
= 0.009 mol

(vi) Using your answer in **(b)(v)**, calculate the number of times the person exhaled into the respirator.

Total amount of "breaths" = 0.009 / 0.000784 = 11.5
Hence, no of breath = 12

[8]

[Total: 10]

2 Phosphorus was the 13th element to be discovered. For this reason, and also due to its use in explosives, poisons and nerve agents, it is sometimes referred to as "the Devil's element".

(a) (i) Write the chemical equation, with state symbols, to represent the first ionisation energy of phosphorus, P.

$P(g) \rightarrow P^+(g) + e^-$

(ii) Explain why the first ionisation energy of phosphorus, P, is higher than that of both silicon, Si, and sulfur, S, with the use of relevant electronic configurations.

1st ionisation energy of P is higher than Si because P has a **higher nuclear charge and smaller atomic size** than Si but **similar shielding effect**. Hence, it is more difficult to remove an electron from P(g) atom.
P: [Ne] $3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$
S: [Ne] $3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1$

The 1st ionisation energy of P is higher than that of S due to **inter-electronic repulsion effect present in the paired 3p orbital in the S(g) atom**. Hence, it is easier to remove an electron from S atom than P atom.

[4]

[Turn over

(b) Phosphorus pentachloride, PCl_5, is a colourless, water-sensitive solid, although commercial samples can be yellowish and contaminated with hydrogen chloride, HCl.

Write an equation to show why PCl_5 is water-sensitive and easily contaminated with HCl.

$PCl_5(s) + 4\ H_2O(l) \rightarrow H_3PO_4(aq) + 5\ HCl(g)$
OR $PCl_5(s) + H_2O(l) \rightarrow POCl_3(aq) + 2\ HCl(g)$ (limited water)

PCl_5 is hydrolysed exothermically/ vigorously with water to form $HCl(g)$.

[1]

(c) Solid PCl_5 exists as two ions, PCl_4^+ and PCl_6^-, while solid PBr_5 exists as ions, but in this case as PBr_4^+ and Br^-. Suggest a reason for this difference in the ions formed.

Br atom is larger than Cl atom. Hence, it is **spatially/sterically impossible** to fit 6 Br atoms around P to form PBr_6^-. The release of Br^- from PBr_5 results in a sterically more favourable PBr_4^+ rather than PBr_5.

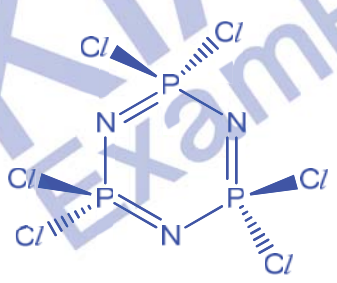
OR

Br^- ion is larger than Cl^- ion, hence it is **more stable** and less likely to form PBr_6^-.

[2]

(d) An important starting material for the manufacture of polyphosphazenes is the cyclic molecule $(NPCl_2)_3$. The molecule has a symmetrical six-membered ring of alternating N and P atoms, with Cl atoms bound to P atoms only. The nitrogen-phosphorus bond energy in the compound is larger than that expected for an N—P single bond.

(i) Draw a likely structure for the molecule.



(ii) State the total number of lone pairs of electrons on the ring atoms.

3 (all on N)

[3]

[Total: 10]

[Turn over

3 Hexamethylenetetramine is a heterocyclic organic compound with the formula $(CH_2)_6N_4$. This white crystalline compound is highly soluble in water and polar organic solvents. It is a primary component of solid fuel tablets used by campers for heating rations.

(a) Upon complete combustion, hexamethylenetetramine, $(CH_2)_6N_4$ forms gaseous nitrogen pentoxide, N_2O_5, carbon dioxide and water.

(i) Write a balanced chemical equation to show the complete combustion of hexamethylenetetramine.

$(CH_2)_6N_4(s) + 14\ O_2(g) \rightarrow 6\ CO_2(g) + 2\ N_2O_5(g) + 6\ H_2O(l)$

(ii) Use the thermochemical data below to calculate the enthalpy change of combustion of hexamethylenetetramine.

Enthalpy change of formation of hexamethylenetetramine	+ 400 kJ mol^{-1}
Enthalpy change of formation of nitrogen pentoxide	+ 11 kJ mol^{-1}
Enthalpy change of formation of carbon dioxide	- 394 kJ mol^{-1}
Enthalpy change of formation of water	- 243 kJ mol^{-1}

$\Delta H_{c\ (CH_2)_6N_4} = \Sigma\Delta H_{f\ products} - \Sigma\Delta H_{f\ reactants}$
$= [6(-394) + 2(11) + 6(-243)] - [400]$
$= -4200\ kJ\ mol^{-1}$

(iii) 100 g of water was heated in a camping stove by burning a sample of hexamethylenetetramine, $(CH_2)_6N_4$. The temperature rise of the water recorded was 40 °C. Using your answer to **(ii)**, calculate the mass of hexamethylenetetramine burnt, assuming that 70% of the heat evolved is absorbed by the water. (specific heat capacity of water = 4.20 J K^{-1} g^{-1})

Energy used to heat 100 g of water
$= 100 \times 4.2 \times (40)$
$= 1.68 \times 10^4$ J

Since 30 % of heat is lost to surroundings,
Actual heat energy evolved from combustion of $(CH_2)_6N_4$

$$= 1.68 \times 10^4 \times \frac{100}{70}$$
$$= 2.40 \times 10^4 \text{ J}$$

From **(ii)** $\Delta H_{c\ (CH_2)_6N_4} = -4200\ kJ\ mol^{-1}$
$4200 = (24.0) / (mass_{(CH_2)_6N_4} / 140)$
$mass_{(CH_2)_6N_4} = 0.800$ g

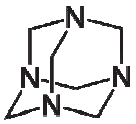
[5]

[Turn over

(b) Solid hexamethylenetetramine, $(CH_2)_6N_4$, can be prepared by the reaction of gaseous formaldehyde, CH_2O, with gaseous ammonia.

(i) The skeletal formulae of formaldehyde and hexamethylenetetramine are shown below.

formaldehyde



hexamethylenetetramine

The reaction between formaldehyde and ammonia yields hexamethylenetetramine and water.

I Write a balanced equation for the above reaction.

$6\ CH_2O(g) + 4\ NH_3(g) \rightarrow (CH_2)_6N_4(s) + 6\ H_2O(l)$

II Using appropriate values from the *Data Booklet*, calculate the enthalpy change for the above reaction.

Bonds broken		**Bonds formed**	
12 C-H bonds	12(410)	12 C-H bonds	12(410)
6 C=O bonds	6(740)	12 C-N bonds	12(305)
12 N-H bonds	12(390)	12 O-H bonds	12(460)

$\Delta H_r = +[(12(410)+6(740)+12(390)] - [(12(410)+12(305)+12(460)]$

$\Delta H_r = -60\ kJ\ mol^{-1}$

(ii) Predict and explain the sign of the entropy change for the above reaction, with clear reference to the number of ways of arrangement of particles before and after reaction.

Negative entropy change due to a decrease in disorder as a result of a change in phase from gas to solid & liquid/decrease in number of gas particles , resulting in fewer ways of arranging the particles .

[5]

[Total: 10]

[Turn over

4

(a) In the gaseous state, NO_2, which is used in the preparation of nitric (V) acid, can dimerise as given in the equation.

$$2\ NO_2(g) \rightleftharpoons N_2O_4(g)$$

When 1 mol of NO_2 is placed in a 2 dm^3 vessel at room temperature, it is found that the equilibrium mixture contains 0.3 mol of N_2O_4.

(i) Write an expression for the equilibrium constant, K_c for the dimerisation of NO_2.

$$K_c = \frac{[N_2O_4]}{[NO_2]^2}$$

(ii) Calculate a value of K_c for the reaction, giving its units, showing clearly the workings.

	$2\ NO_2(g)$	$\rightleftharpoons$	$N_2O_4(g)$	
Initial amt / mol:	1		0	
Equil amt / mol:	$1 - 2x$		x	$(x = 0.3)$
Equil conc / mol dm^{-3}:	$\frac{1 - 2(0.3)}{2}$		$\frac{0.3}{2}$	
	$= 0.2$		0.15	

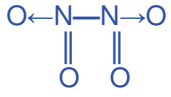
$$K_c = \frac{0.15}{(0.2)^2} = 3.75\ mol^{-1}\ dm^3$$

(iii) The NO_2 molecule has an ***unpaired*** electron on the nitrogen atom but the N_2O_4 molecule does not. Using the information,

I name the type of species that has an unpaired electron, such as NO_2.

Free radical

II suggest a full structural/displayed formula for N_2O_4, clearly showing the types of bonds present.



III hence, explain whether the dimerisation of NO_2 is endothermic or exothermic.

Exothermic since it involves N—N ***bond formation***.

[Turn over

(iv) Explain, with reasons, whether the dimerisation of NO_2 is favoured by

I high or low pressure,

High pressure as equilibrium position shifts to the right to a direction which results in the decrease in the number of moles of gas so as to reduce the pressure.

II high or low temperature.

Low temperature as the equilibrium position shifts to the right as the forward reaction is exothermic which results in the increase in temperature.

[8]

(b) At 448 °C the equilibrium constant K_c for the reaction,

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

is 50.5. Predict in which direction the reaction will proceed to reach equilibrium at 448 °C if 2.0×10^{-2} mol of HI, 1.0×10^{-2} mol of H_2 and 3.0×10^{-2} mol of I_2 in a 2 dm^3 container, were present at the start.

$$\frac{[HI]^2}{[H_2]\,[I_2]} = \frac{(2.0 \times 10^{-2} / 2)^2}{(1.0 \times 10^{-2} / 2)\,(3.0 \times 10^{-2} / 2)}$$

$$= 1.33$$

Since the quotient above is 1.33 which is < K_c (50.5), the [HI] must increase and the $[H_2]$ and $[I_2]$ must decrease to reach equilibrium; the reaction will proceed from left to right as it moves towards equilibrium.

[2]

[Total: 10]

[Turn over

Section C

Answer ***all*** questions in this section. Write your answers on the writing paper provided.
Answer each question on a new page.

You are advised to spend **not** more than one hour on this section.

5 This question is about chlorine and its compounds.

(a) Chlorine and fluorine are halogens in Group VII of Periodic Table, chlorine being a bigger atom than fluorine.

(i) Explain why the melting point of $AlCl_3$ is 192 °C, but that of AlF_3 is 1291 °C, with reference to structure and bonding of the two substances.

While the structure in $AlCl_3$ is simple molecular/covalent, the structure in AlF_3 is giant ionic. Hence more energy is required to overcome the stronger ionic bonds/electrostatic forces between Al^{3+} and F^- ions in AlF_3 than the weaker van der Waals forces in $AlCl_3$, hence the higher melting point of AlF_3.

(ii) Explain why phosphorus forms a pentachloride, PCl_5, but nitrogen does not form a pentachloride NCl_5.

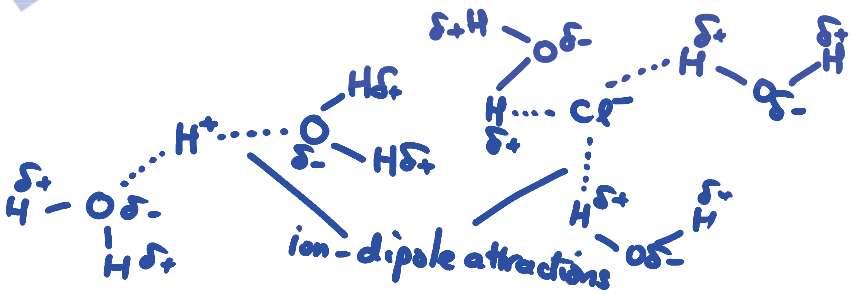
Phosphorus is in Period 3, it is able to expand its octet due to the availability of low lying empty d-orbitals.

Nitrogen is in Period 2. It is unable to expand its octet.

[5]

(b) Hydrochloric acid, HCl, has numerous applications in industry, from the production of plastics to food additives to cleaning stains. About 20 million tonnes of hydrochloric acid are produced annually.

(i) HCl is a strong acid and fully ionises in water. Draw a diagram showing the attractions formed when HCl is dissolved in water. Label clearly the attractions present.



[Turn over

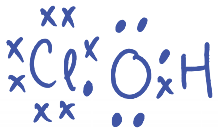
(ii) Calculate the pH of a 30.0 cm^3 solution of 0.10 mol dm^{-3} HC*l*.

pH = - lg 0.10 = 1.00

[3]

(c) Chloric (I) acid, HC*l*O, is a weak acid, and its salts, chlorate (I), C*l*O$^-$ are used as bleaching agents, deodorants and disinfectants.

(i) Draw the dot-and-cross diagram for a HC*l*O molecule and hence state its shape and bond angle, given that oxygen is the central atom.



Shape: Bent Bond angle: 105°

(ii) Calculate the pH of the solution formed by adding 10.0 cm^3 of 0.10 mol dm^{-3} NaOH to 20.0 cm^3 of 0.10 mol dm^{-3} chloric (I) acid, HC*l*O.

[K_a of HC*l*O = 4.00 × 10^{-8} mol dm^{-3}]

[HC*l*O] = [C*l*O$^-$]

pH = pK_a
= - lg (4.00×10^{-8})
= 7.40

(iii) Calculate the concentrations of HC*l*O and C*l*O$^-$ upon the addition of another 0.2 cm^3 of NaOH to the solution above. Hence, show that the change in pH of the solution is approximately 0.02 units.

Moles of HC*l*O left = $\frac{9.8}{1000} \times 0.10 = 9.80 \times 10^{-4}$ mol

Moles of C*l*O$^-$ formed = $\frac{10.2}{1000} \times 0.10 = 1.02 \times 10^{-3}$ mol

[HC*l*O] = $\frac{9.80 \times 10^{-4}}{\frac{10.2+20}{1000}}$ = 0.03245 mol dm^{-3}

[C*l*O$^-$] = $\frac{1.02 \times 10^{-3}}{\frac{10.2+20}{1000}}$ = 0.03378 mol dm^{-3}

pH = $pK_a + \lg \frac{[ClO^-]}{[HClO]}$

Change in pH = $\lg \frac{[ClO^-]}{[HClO]}$
= $\lg \frac{0.03378}{0.03245}$
= 0.0174
= 0.02 units

[Turn over

(iv) Explain why the pH change in **(c)(ii)** is small upon the addition of a small amount of NaOH, illustrating your answer with an appropriate equation.

The solution in (c)(ii) is a buffer solution.

When small amount of NaOH is added (0.2 cm^3),

$HClO + OH^- \rightarrow ClO^- + H_2O$

The large reservoir of HClO removes OH^- by reacting with it, hence the pH is almost unchanged.

[9]

(d) Mercury (I) chloride, Hg_2Cl_2, contains the Hg_2^{2+} ion. The K_{sp} of Hg_2Cl_2 is 1.43×10^{-18} $mol^3\ dm^{-9}$.

(i) Write the K_{sp} expression for Hg_2Cl_2. Hence, calculate its solubility in water.

Let the solubility of Hg_2Cl_2 be x mol dm^{-3}.

$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2\ Cl^-(aq)$
x 2x

$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = 1.43 \times 10^{-18}$
$(x)(2x)^2 = 1.43 \times 10^{-18}$
$4x^3 = 1.43 \times 10^{-18}$
$x = 7.10 \times 10^{-7}$ mol dm^{-3}

(ii) Explain how the addition of dilute HCl will affect the solubility of Hg_2Cl_2.

Cl^-, being a common ion will increase the concentration of Cl^- in the solution. Hence, position of equilibrium will shift to the left/common ion effect and solubility of Hg_2Cl_2 will decrease .

[3]

[Total: 20]

[Turn over

6 This question is about the reactions of halogens with organic compounds.

(a) CFCs or chlorofluorocarbons such as dichlorodifluoromethane, CF_2Cl_2, can be synthesised from methane. CFCs have been widely used as refrigerants, aerosol propellants and solvents. However, they have been gradually phased out under the Montreal Protocol and have been replaced with products such as HFCs or hydrofluorocarbons which do not deplete the ozone layer like CFCs.

The first step in production of CF_2Cl_2, is to react methane with chlorine to form chloromethane.

(i) Write a balanced equation for the reaction between methane and chlorine.

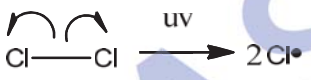
$Cl_2 + CH_4 \rightarrow CH_3Cl + HCl$

(ii) State the condition necessary for the reaction between methane and chlorine.

uv light or sunlight or 400 °C

(iii) State and describe the mechanism that occurs between methane and chlorine.

Free Radical Substitution
Initiation:



Propagation:
$CH_4 + Cl\bullet \rightarrow \bullet CH_3 + HCl$
$\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$

Termination:
$2\ \bullet CH_3 \rightarrow CH_3\text{-}CH_3$
$Cl\bullet + \bullet CH_3 \rightarrow CH_3Cl$
$2\ Cl\bullet \rightarrow Cl_2$

(iv) Hence explain why ethane can sometimes be found in small quantities in the reaction mixture.

Ethane is formed when 2 methyl radicals combine in the termination step.

CFCs are harmful as they undergo homolytic fission to produce free radicals which then break down the ozone.

(v) Write an equation to show how radicals are produced from CF_2Cl_2.

$CF_2Cl_2 \rightarrow \bullet CF_2Cl + Cl\bullet$

[Turn over

(vi) Hence, by quoting relevant bond energies values data from the *Data Booklet*, explain why HFCs such as CH_2F_2 do not deplete the ozone layer.

Bond energy of C-C*l* bond = 340 kJ mol^{-1}
Bond energy of C-H bond = 410 kJ mol^{-1}
The weak C-C*l* bonds break easily compared to C-H to generate C*l*• radicals which breaks down the ozone.

[10]

(b) 0.01 moles of liquid hydrocarbon **X** was burnt completely in an excess of oxygen in an enclosed vessel. After combustion, the resultant gases were passed through an excess of NaOH, a reduction in gas volume of 1.44 dm^3 was observed at r.t.p. 0.01 mole of liquid **X** also reacts completely with 1.6 g of Br_2 in the dark.

(i) Using the information above, deduce that the molecular formula of **X** is C_6H_{12}, and state the type of functional group it contains.

$C_xH_y(l) + (x+\frac{y}{4})\ O_2(g) \rightarrow x\ CO_2(g) + \frac{y}{2} H_2O(l)$

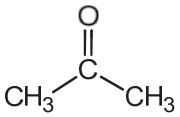
No. of moles of CO_2 formed = 1.44 / 24 = 0.06 mol
$C_xH_y : CO_2 = 1 : 6$ No. of moles of Br_2 = 1.6/(79.9 x 2) = 0.01 mol
Since no. of moles of Br_2 = no. of moles of X → only 1 C=C present in X

Hence the molecular formula of the compound is C_6H_{12}.

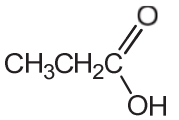
It contains an alkene.

(ii) Suggest a structure for compound **A**, which has the same molecular formula as **X**, but does not decolourise bromine in the dark.

X, C_6H_{12} reacts with hot acidified concentrated $KMnO_4$ to produce propanone, CH_3COCH_3, and propanoic acid, $CH_3CH_2CO_2H$. **X** also reacts with HBr to give **Y**, which has a chiral carbon.

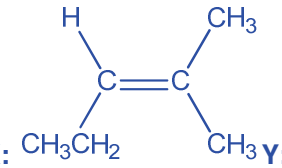


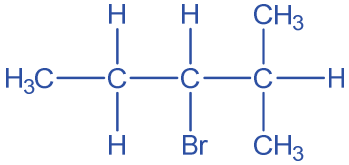
propanone



propanoic acid

(iii) Use this information to draw the structural formulae of **X** and **Y**.

X:


Y:


(iv) State and explain the type of isomerism that **Y** exhibits.

Y exhibits optical isomerism . The isomers are non-superimposable mirror images of each other and have no plane of symmetry .

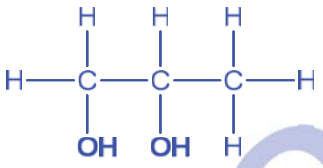
(v) Hence, explain why the solution containing **Y** will not rotate plane polarised light.

Solution is a racemic mixture/contains both enantiomers in equimolar amount.

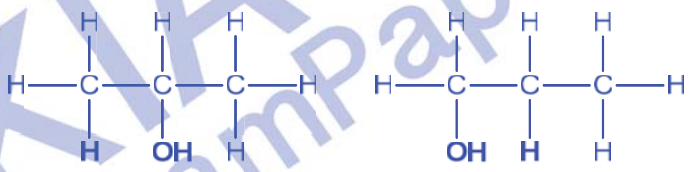
[8]

(c) Predict the products formed when propene reacts with

(i) cold dilute $KMnO_4$



(ii) steam, concentrated H_3PO_4, 300 ^oC, 70 atm



[2]

[Total: 20]

End of Paper

Name:		Index Number:		Class:	

DUNMAN HIGH SCHOOL
Promotional Examination
Year 5

H2 CHEMISTRY
Paper 1 Multiple Choice

9647/01
21 September2012
30 minutes

Additional Materials: Optical Mark Sheet
Data Booklet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this question paper.

2 There are **twenty** questions in this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Optical Mark Sheet.

3 Each correct answer will score one mark. A mark will not be deducted for wrong answer.

4 Any rough working should be done in this booklet.

5 You may use a calculator.

This question paper consists of **9** printed pages and **1** blank page

[Turn over

Section A

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

1 10 cm^3 of a gaseous alcohol, C_xH_yOH, is sparked with 95 cm^3 of oxygen (in excess). The residual gases are then cooled to r.t.p and the volume determined to be 75 cm^3. After passing the gases through aqueous potassium hydroxide, the bottle of KOH(aq) increased by 0.0733 g. What is molecular formula of the alcohol?

A C_3H_5OH **B** C_3H_7OH **C** C_4H_7OH **D** C_4H_9OH

2 A student has mixed up the data containing first ionisation energies of the following Period 5 elements: Rb, In, Sb and Te.

What is the identity of element **Z**?

	W	**X**	**Y**	**Z**
First I.E./ kJ mol^{-1}	403	558	834	896

A Rb **B** In **C** Te **D** Sb

3 Which statement describes a phenomenon that **cannot** be explained by hydrogen bonding?

A Water at 4 °C has a higher density than ice at 0 °C.

B Fluoromethane has a higher melting point than chloromethane.

C Ammonia has greater solubility in methanol than phosphine (PH_3) gas.

D Hydrogen fluoride gas exhibits greater deviation from ideality compared to hydrogen chloride gas.

4 Which of the following pairs do **not** have similar molecular shapes?

A NO_2, HCN **C** SO_4^{2-}, PO_4^{3-}

B SO_3, BH_3 **D** PCl_6^-, IOF_5

5 Two pressure vessels are connected to each other, regulated by a pressure valve. At 25 °C, the 80 dm^3vessel is filled with nitrogen at a pressure of 8 MPa and the 40 dm^3 vessel is filled with hydrogen at 6 MPa. The gases are then allowed to mix at a temperature of 500 °C. What is the resultant pressure of the system?
(1 MPa refers to 1 x 10^6 Pa)

A 14MPa **C** 19 MPa

B 16 MPa **D** 36 MPa

6 It is known that $Ba(OH)_2$ is **more** soluble in water than $Ca(OH)_2$.

In the table below, which of the following correctly represents the sign of energychanges?

	$\Delta H_{hyd}(Ba^{2+})$– $\Delta H_{hyd}(Ca^{2+})$	$\Delta H_{soln}(Ba(OH)_2)$– $\Delta H_{soln}(Ca(OH)_2)$	$\Delta H_{latt}(Ba(OH)_2)$– $\Delta H_{latt}(Ca(OH)_2)$
A	+	–	–
B	+	–	+
C	+	+	–
D	+	+	+

7 43.6g of potassium sulfate (K_2SO_4) is dissolved in 1.0 kg of water at 40 °C.

Type of energy change	Magnitude/ $kJmol^{-1}$
Lattice energy of K_2SO_4	1935
Enthalpy change of hydration of K^+ ion	322
Enthalpy change ofhydration of SO_4^{2-}ion	1137

Given the above data and assuming that the specific heat capacity of solution is 4.2 $Jg^{-1}K^{-1}$, what is the final temperature of the solution?

A 3°C **B** 31°C **C** 49°C **D** 77°C

8 The enthalpy changes for two gas–phase reaction at constant pressure are shown below.

$$CH_3–CH_3 \rightarrow H\bullet + CH_3–CH_2\bullet \qquad \Delta H^{\theta} = +414 \text{ kJ mol}^{-1}$$
$$CH_3–CH_2\bullet \rightarrow H\bullet + CH_2=CH_2 \qquad \Delta H^{\theta} = +172 \text{ kJ mol}^{-1}$$

What is the enthalpy change for the following reaction?

$$2CH_3–CH_2\bullet \rightarrow CH_2=CH_2 + CH_3–CH_3$$

A –242 kJ mol^{-1} **C** –586 kJ mol^{-1}

B +242 kJ mol^{-1} **D** +586 kJ mol^{-1}

9 The numerical values of the solubility products at 25 °C for AgC*l* and AgI are 1.6 x 10^{-10} and 8.0 x 10^{-17} respectively.

What is the equilibrium constant for the reaction below?

$$AgCl(s) + I^-(aq) \rightleftharpoons AgI(s) + Cl^-(aq)$$

A 1.3 x 10^{-26} **C** 2.0 x 10^{6}

B 5.0 x 10^{-7} **D** 1.3 x 10^{16}

10 How much water should be added to increase the pH of 10 cm^3 of 0.1 moldm^{-3} of hydrochloric acid by 2 units?

A 90 cm^3 **C** 990 cm^3

B 900 cm^3 **D** 999 cm^3

11 A solid compound **Q** is dissolved readily in water giving a weakly acidic solution. However, **Q** is recovered unchanged on evaporation of water. Which one of the following could be **Q**?

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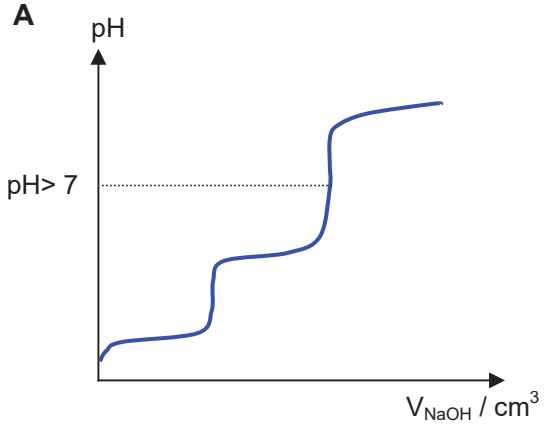
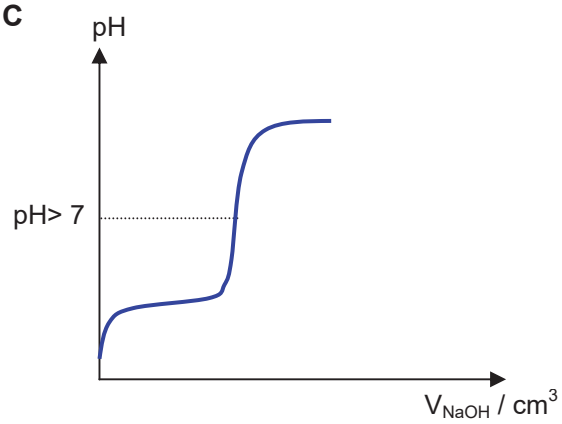
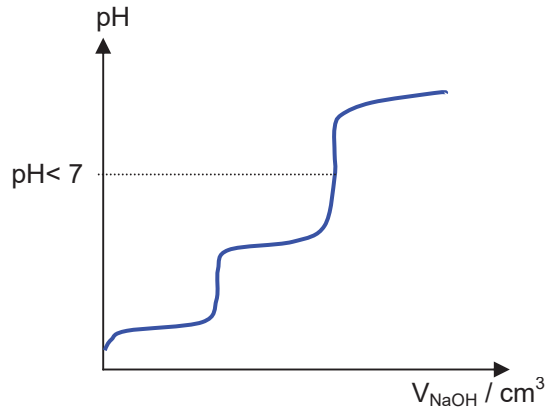
A



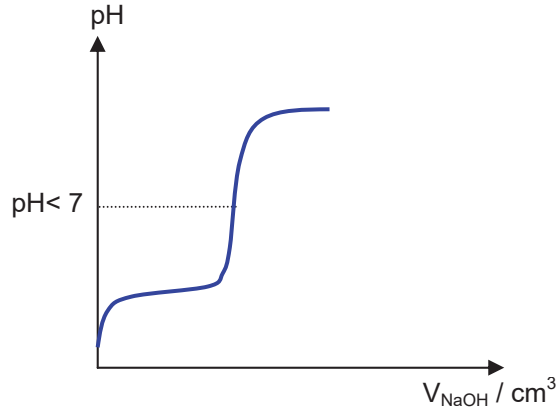
C



B



D



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A 5.8 x 10^{-28} mol^5dm^{-15}

B 1.7 x 10^{-42} mol^5dm^{-15}

C 1.5 x 10^{-44} mol^5dm^{-15}

D 6.8 x 10^{-45} mol^5dm^{-15}

14 Toluene is a clear, water–insoluble liquid with the typical smell of paint thinners. It boils at 111 °C at 1 atm.

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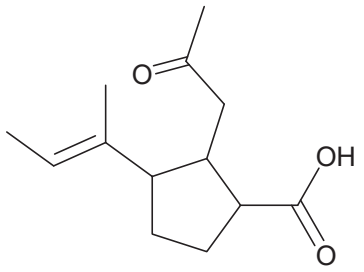

Derivative of kainic acid

A 4 **B** 8 **C** 16 **D** 32

Section B

For each question in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements which you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

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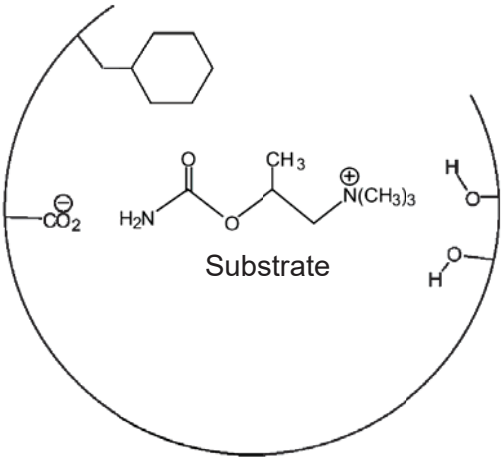

Active site of enzyme

Which of the following interactions could be formed between the active site of the enzyme and the substrate shown above?

1 Electrostatic attraction

2 Hydrogen bonding

3 van der Waals attraction

The responses **A** to **D** should be selected on the basis of

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At a pressure of 2atm and 0°C,1 mole of gas **A** occupies a volume of 11.5 dm^3, 1 mole of gas **B** occupies a volume of 8 dm^3 and 1 mole of gas **C** occupies 6 dm^3.

Which of the following statements are correct?

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18 Which of these are possible products formed from the reaction between but–2–ene and bromine dissolved in sodium chloride solution?

1 2,3–dichlorobutane

2 2,3–dibromobutane

3 2–bromo–3–chlorobutane

19 Which of the following properties are exactly the same for the two enantiomers of 2–chloropropanoic acid, $CH_3CH(Cl)CO_2H$?

1 ΔH_f^{θ}

2 pK_a

3 Boiling points

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

20 Which one of the following alcohols in dehydration yields more than one different alkene?

1 $CH_3CH(OH)CH_2CH_3$

2 $CH_3CH_2CH_2C(OH)(CH_3)_2$

3 $CH_3CH(CH_3)CH_2CH_2OH$

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Name:	Mark Scheme	Index Number:		Class:	

DUNMAN HIGH SCHOOL
Promotional Examination
Year 5

H2 CHEMISTRY
Paper 1 Multiple Choice

9647/01
21 September2012
30 minutes

Additional Materials: Optical Mark Sheet
Data Booklet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this question paper.

2 There are **twenty** questions in this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Optical Mark Sheet.

3 Each correct answer will score one mark. A mark will not be deducted for wrong answer.

4 Any rough working should be done in this booklet.

5 You may use a calculator.

This question paper consists of **9** printed pages and **1** blank page

[Turn over

Section A

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

1 10 cm^3 of a gaseous alcohol, C_xH_yOH, is sparked with 95 cm^3 of oxygen (in excess). The residual gases are then cooled to r.t.p and the volume determined to be 75 cm^3. After passing the gases through aqueous potassium hydroxide, the bottle of KOH(aq) increased by 0.0733 g. What is molecular formula of the alcohol?

A C_3H_5OH **B** C_3H_7OH **C** C_4H_7OH **D** C_4H_9OH

2 A student has mixed up the data containing first ionisation energies of the following Period 5 elements: Rb, In, Sb and Te.

What is the identity of element **Z**?

Ionisation Energy (I.E.) /$kJmol^{-1}$	**W**	**X**	**Y**	**Z**
First I.E.	403	558	834	896

A Rb **B** In **C** Te **D** Sb

3 Which statement describes a phenomenon that **cannot** be explained by hydrogen bonding?

A Water at 4 °C has a higher density than ice at 0 °C.

B Fluoromethane has a higher melting point than chloromethane.

C Ammonia has greater solubility in methanol than phosphine (PH_3) gas.

D Hydrogen fluoride gas exhibits greater deviation from ideality compared to hydrogen chloride gas.

4 Which of the following pairs do **not** have similar molecular shapes?

A NO_2, HCN **C** SO_4^{2-}, PO_4^{3-}

B SO_3, BH_3 **D** PCl_6^-, IOF_5

5 Two pressure vessels are connected to each other, regulated by a pressure valve. At 25 °C, the 80 dm^3vessel is filled with nitrogen at a pressure of 8 MPa and the 40 dm^3 vessel is filled with hydrogen at 6 MPa. The gases are then allowed to mix at a temperature of 500 °C. What is the resultant pressure of the system?
(1 MPa refers to 1 X 10^6 Pa)

A 14MPa **C** 19 MPa

B 16 MPa **D** 36 MPa

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In the table below, which of the following correctly represents the sign of energychanges?

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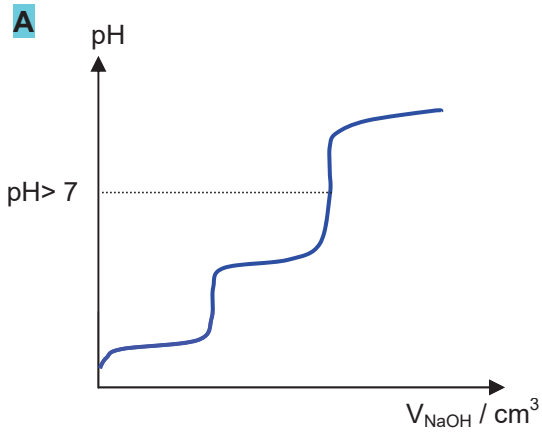

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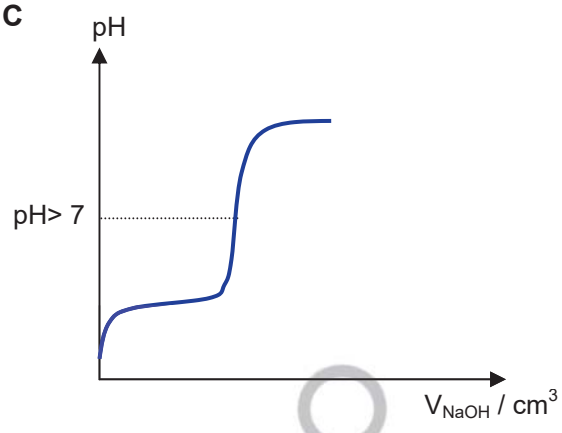
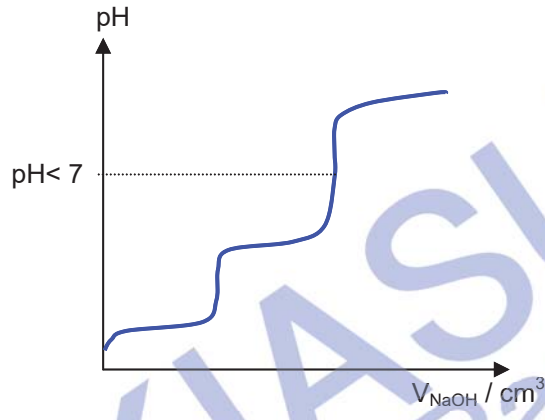
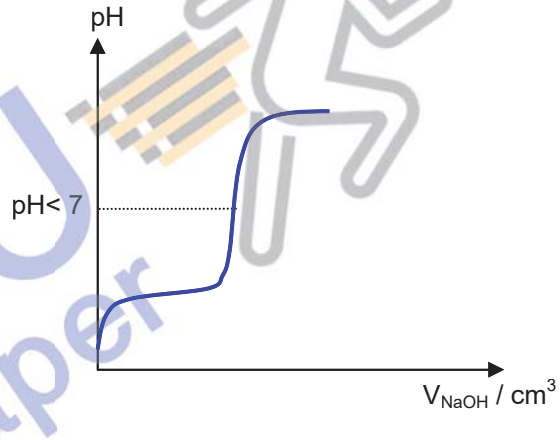


B



D



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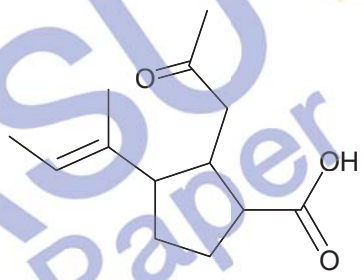

Derivative of kainic acid

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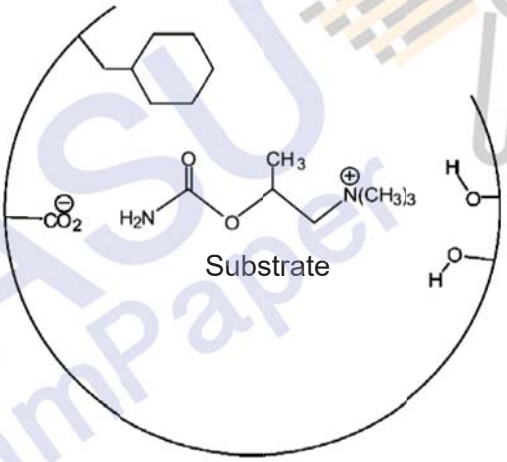

Active site of enzyme

Which of the following interactions could be formed between the active site of the enzyme and the substrate shown above?

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2 Hydrogen bonding

3 van der Waals' attraction

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3 Boiling points

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3 $CH_3CH(CH_3)CH_2CH_2OH$

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Name:		Index Number:		Class:	

DUNMAN HIGH SCHOOL
Promotional Examination
Year 5

H2 CHEMISTRY
Paper 2 Structured and Free Response

Additional Materials: Data Booklet

9647/02
21 September 2012
2 hours 10 minutes

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this question paper and on all writing paper used.
2 Write in dark blue or black pen on both sides of the paper.
3 You may use a soft pencil for any diagrams, graphs or rough working.
4 Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer***all***questions in section A and B.

SECTION A – STRUCTURED QUESTIONS [40 MARKS]

5 Write your answers in the spaces provided on the question paper.
6 You are advised to spend a maximum of 70 minutes on Section A.

SECTION B – FREE–RESPONSE QUESTIONS [40 MARKS]

7 Write your answers on the separate answer paper provided.
8 Start each question on a fresh sheet of paper.
9 You are advised to show all workings in calculations.
10 You are reminded of the need for good English and clear presentation in your answers.
11 At the end of the examination, fasten all your answer papers securely together with the**Cover Sheet**on top.
12 You are advised to spend a maximum of 60 minutes on Section B.

The total marks for this paper is 80 marks.

FOR EXAMINER'S USE

Question No.	1	2	3	4	Total	%
Marks	/10	/10	/11	/9	/[40]	

This question paper consists of **15** printed pages and **1** blank page.

[Turn over

Section A

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

1 Planning

Hess' Law allows us to calculate the enthalpy change of some reactions which cannot be found directly or are not feasible. For example, the $\Delta H^{\ominus}_r$ for the conversion of solid anhydrous copper(II) sulfate to solid hydrated copper(II) sulfate, as shown by the equation below.

$$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4 \bullet 5H_2O(s) \qquad \Delta H^{\ominus}_r < 0$$

This enthalpy change cannot be measured directly as hydrated copper(II) sulfate can only be formed from crystallisation, not by directly adding water to anhydrous copper(II) sulfate.

In order to make use of Hess' Law, the enthalpy change of solution of anhydrous and hydrated copper(II) sulfate are first calculated from different experiments.

$$CuSO_4(s) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq) \qquad \Delta H^{\ominus}_{soln1} < 0$$
$$CuSO_4 \cdot 5H_2O(s) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq) + 5H_2O(l) \qquad \Delta H^{\ominus}_{soln2} > 0$$

You are to plan an experiment to calculate $\Delta H^{\ominus}_{soln1}$, using common laboratory apparatus such as 50 cm^3 measuring cylinder, 1 ºC thermometer, a polystyrene cup, stopwatch and electronic balance.The following information may be useful.

- The specific heat capacity of water is 4.18 J K^{-1} g^{-1}.
- The estimated value for $\Delta H^{\ominus}_{soln1}$ is –47 kJ mol^{-1}.
- For safety reasons, temperature of liquids should not exceed 40 ºC.
- You are recommended to use between 25 – 50 cm^3 of water.

(a) Describe a procedure to find the enthalpy change of solution of anhydrous copper(II) sulfate, $\Delta H^{\ominus}_{soln1}$. Your plan should include plotting of a suitable graph to correct for surrounding heat transfer and the use of appropriate apparatus, masses and volumes of reagents. [*Mr: $CuSO_4$= 159.6; $CuSO_4 \cdot 5H_2O$ = 249.6*]

[4]

(b) Draw tables with appropriate headings to record appropriate measurements from your procedure

[1]

(c) Sketch the graph that you expect to obtain in the experiment. Indicate clearly the axes and the initial and final temperatures that you would read. Show how you would use the values from your procedure and the graph to calculate $\Delta H^{\ominus}_{soln1}$.

[2]

(d) Draw an energy cycle and show how $\Delta H^{\ominus}_{r}$ can be calculated from $\Delta H^{\ominus}_{soln1}$ and $\Delta H^{\ominus}_{soln2}$ using Hess' law.

[1]

[Turn over

(e) Another experiment in which hydrated copper(II) sulfate is added to water is performed to determine $\Delta H^{\ominus}_{soln2}$. The following data is recorded.

Initial temperature / ºC	30.0
Final temperature / ºC	29.5
Change in temperature / ºC	0.5

With reference to the magnitude of the temperature change, state one possible significant source of error and a method of improvement.

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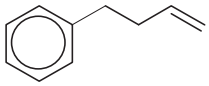
[2]

[Total: 10]

2 **(a)** 4–phenylbut–1–ene is a useful molecule often employed by organist chemists during synthesis.



4–phenylbut–1–ene

4–phenylbut–1–ene can be converted to its isomer 4–phenylbut–2–ene in two steps as shown below. Suggest how this can be done by drawing the intermediate product**A** in the box below and hence stating the reagents and conditions for **Step 1** and **Step 2**.

4–phenylbut–1–ene 4–phenylbut–2–ene

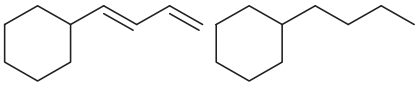
Step 1: .....

A :

Step 2: .....

[3]

(b) The following molecules, **B** and **C** are analogs of 4–phenylbut–2–ene. Suggest a suitable chemical test to distinguish **B** and **C**. For each test, state the relevant reagents and conditions, and describe the observations.



B **C**

.....

.....

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.....

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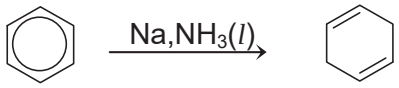
.....

.....

[2]

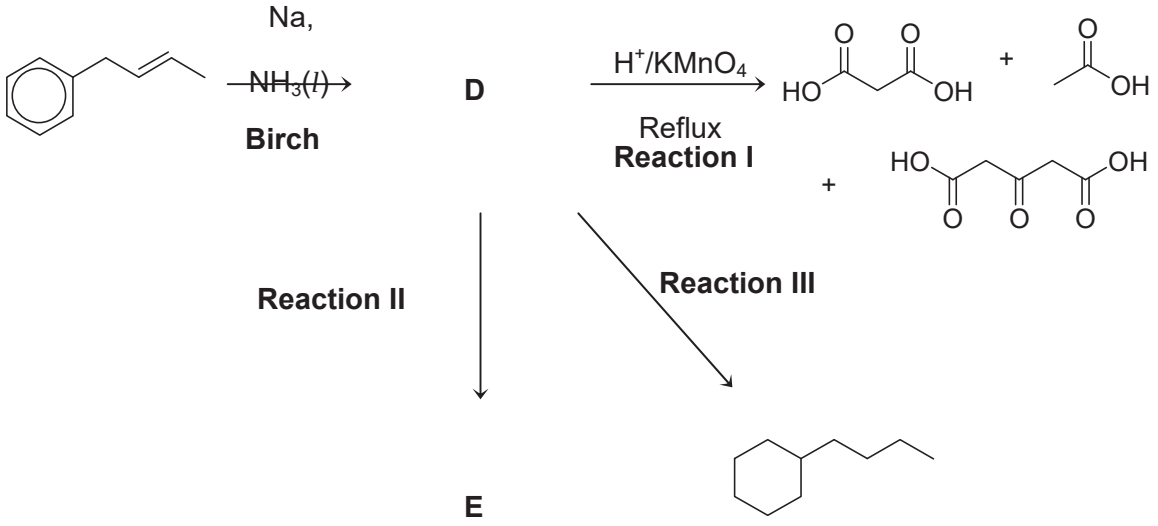
(c) The Birch reduction reduces the benzene ring to a 1,4–cyclohexadiene. The reagent used is sodium dissolved in liquid ammonia. The reduction of benzene is shown in the equation below.



Benzene 1,4–cyclohexadiene

4–phenylbut–2–ene can be converted to **D** via the Birch reduction. **D** is a 1,4–cyclohexadiene that is bonded to an alkyl chain. **D** can be strongly oxidised to give three organic molecules as shown in **Reaction I**.

Deduce the structure of **D** and complete the reaction scheme below by drawing the structure of**E**, the product for **Reaction II** and stating the reagents and conditions for **Reaction III**.



D	E

Reagents and conditions for **Reaction III**: .....

[3]

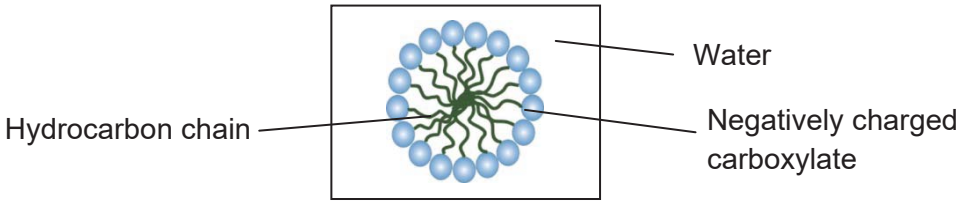
(d) 4–phenylbut–2–ene can be oxidised to benzoic acid, C_6H_5COOH, which is an effective food preservative. However, due to its low solubility, it is often used together with its sodium salt, sodium benzoate, $C_6H_5COO^-Na^+$. At pH 5 or lower, it can inhibit the growth of microorganisms that cause food spoilage.

In a laboratory, a food chemist mixes 12.2 g of benzoic acid with 18.3 g of sodium benzoate in 500 cm^3 of water. Given that the K_a of benzoic acid is 6.17×10^{-5} mol dm^{-3}, deduce if mixture can be used as a food preservative, showing your calculations.

[2]

[Total: 10]

3 Sodium stearate, $C_{18}H_{35}O_2Na$, is a major component of many different types of soaps. In its saturated solution, its concentration is 0.015 mol dm^{-3}. In aqueous solution, the $C_{18}H_{35}O_2^-$ anion form *micelles*, a special structure in which the hydrocarbon chains of many anions cluster together, leaving the negatively charged carboxylate on the surface. During cleaning, oil and dirt can be trapped within the hydrocarbon chains of the *micelle* and is thus easily removed.



A micelle in aqueous solution

(a) (i) Write an expression for the solubility product, K_{sp}, of sodium stearate and calculate its value, including its units.

(ii) The last stage in the manufacture of soaps involves adding sodium chloride to the reaction mixture in order to precipitate the soap. By writing relevant equation(s), explain why soap precipitates when sodium chloride is added.

[5]

(b) (i) The enthalpy change of solution of sodium stearate is –12 kJ mol^{-1}. Given that $\Delta G^{\ominus}_{soln}$ is +47.5 kJ mol^{-1}, calculate $\Delta S^{\ominus}_{soln}$ and hence suggest an explanation for the sign of $\Delta S^{\ominus}_{soln}$.

[Turn over

(ii) How will the spontaneityfor the dissolving of sodium stearate change with temperature? Explain your answer with reference to $\Delta G^{\ominus}_{soln}$.

.....

.....

.....

.....

[4]

(c) Potassium stearate is also a component of soap.

Compare the relative magnitudes of the lattice energies of sodium stearate and potassium stearate.

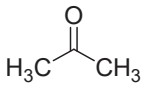
.....

.....

[2]

[Total:11]

4 Calcium ethanoate, $(CH_3COO^-)_2Ca^{2+}$, decomposes upon heating to form propanone and an inorganic compound **F**.

$(CH_3COO^-)_2Ca^{2+} \rightarrow$  + **F**

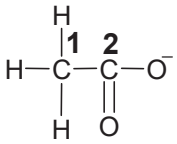
Calcium ethanoate Propanone

(a) In the space below, draw and label an energy level diagram to illustrate the electronic configuration of Ca, using arrows to represent electrons.

Energy

[2]

(b) **(i)** The diagram below shows the Lewis structure of the ethanoate anion, with the two carbon atoms separately labelled as **1** and **2**. With reference to the valence shell electron pair repulsion (VSEPR) theory, state the shape with respect to each carbon atom.



Shape around carbon atom **1**: .....

Shape around carbon atom **2**: .....

(ii) Identify and describe the hybridisation of carbon atom**2**.

.....

.....

.....

.....

.....

.....

.....

.....

[4]

(c) **(i)** State the cation present in **F**.

.....

(ii) To a 0.69 g sample of **F**, 25.0 cm^3 of 1.0 mol dm^{-3} hydrochloric acid was added. The remaining solution was diluted to 100.0 cm^3. A 20.0 cm^3 aliquot required 22.55 cm^3 of 0.1 mol dm^{-3} sodium hydroxide for neutralisation. Calculate the relative molecular mass of **F** assuming two moles of hydrochloric acid reacts with one mole of **F**.

(iii) Hence or otherwise, deduce the identity of **F**.

.....

[3]

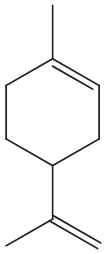
[Total: 9]

Section B

Answer **all**questions.

1 Food additives are substances added to food to enhance its tastes and appearance. Some additives occur naturally while others are synthetically made.

The oil of orange is an essential oil derived from the rind of oranges and some other citrus fruits. This essential oil comprises mainly of a colourless liquid, limonene ($C_{10}H_{16}$).



limonene

Limonene can exist as two isomers with different characteristics. One isomer has a piney, turpentine–like smell while the other has a pleasing citrus orange scent.

(a) **(i)** Identify the type of isomerism that is present in limonene.

(ii) Draw the structural formula to illustrate the type of isomerism in **(i)**.

[2]

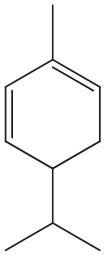
(b) Besides being used in a flavour and fragrance additive, limonene is a biodegradable solvent which can be used remove grease from machine parts. Explain, in terms of structure and bonding, how limonene can be used to remove grease effectively.

[2]

(c) Limonene is able to undergo addition reaction with diatomic molecules such as bromine gas. Describe the reaction mechanism that limonene undergo with bromine gas.

[3]

(d) Limonene is a structural isomer of α–phellendrene.

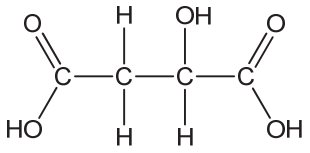


α–phellendrene

Two unlabelled bottles containing limonene and α–phellendrene were found in the laboratory. Describe a suitable chemical reaction to distinguish between limonene and α–phellendrene. State clearly the observations and one relevant equation.

[3]

(e) Another naturally occurring food additive, malic acid is present as one of the many organic acids found in wines.



malic acid

Malic acid is a dibasic acid which can be represented by H_2A. The acid dissociation constants for malic acid are given below:

Step 1: $H_2A + H_2O \rightleftharpoons HA^- + H_3O^+ K_{a1} = 3.98 \times 10^{-4} moldm^{-3}$
Step 2: $HA^- + H_2O \rightleftharpoons A^{2-} + H_3O^+ K_{a2} = 6.31 \times 10^{-6} moldm^{-3}$

Suggest an explanation for the difference in the acid dissociation constants, K_{a1} and K_{a2}, for malic acid.

[2]

(f) Many wines undergo a process called 'malo–lactic fermentation' to convert the sharp tasting malic acid to a milder lactic acid to enhance the quality of wines.

Lactic acid is a monobasic acid that has the following composition by mass: C: 40.0%; H: 6.7%; O: 53.3%.

A particular brand of wine containing lactic acid has a pH of 3.00. The concentration of lactic acid in the wine can be determined by titration with sodium hydroxide.

A 15.30 cm^3 sample of this wine containing 0.010 g of lactic acid is found to require 22.20 cm^3 of $5 \times 10^{-3} moldm^{-3}$ sodium hydroxide for neutralisation. Lactic acid is assumed to be the only acid that contributes to the acidity of this wine.

(i) Calculate the concentration of lactic acid in $moldm^{-3}$ and hence explain whether lactic acid is a strong or weak acid.

(ii) Calculate the acid dissociation constant, K_a of lactic acid.

(iii) Calculate the M_r of lactic acid and hence its molecular formula.

(iv) Sketch the pH curve when 35.00 cm^3 of $5 \times 10^{-3} moldm^{-3}$ sodium hydroxide is added to the 15.30 cm^3 sample of wine containing lactic acid.

[8]

[Total: 20]

2 The Group VII elements (halogens) play an important part in the development of chemistry.

(a) Chlorine, one of the most important halogens, has its uses in the manufacture of many products in everyday life.

Sodium hypochlorite, NaC*l*O, is an active ingredient in many household liquid bleaches. NaC*l*O is manufactured when chlorine gas dissolves in cold aqueous sodium hydroxide. Chlorine gas undergoes a disproportionation reaction into Cl^- and ClO^-.

(i) By using the reaction of chlorine gas in cold aqueous sodium hydroxide, explain what is meant by 'disproportionation reaction'.

(ii) Write a balanced equation for the reaction between chlorine gas and cold aqueous sodium hydroxide.

(iii) The percentage of hypochlorite ion, ClO^- in household liquid bleach can be determined by iodometric titration.

A 25.0 cm^3 sample of household liquid bleach is made up to a total volume of 250 cm^3 in a volumetric flask. Iodine is produced when an excess of potassium iodide was added to 20.0 cm^3 aliquot of this solution in acidic medium. The iodine produced in the 20.0 cm^3 solution required 25.30 cm^3 of 0.0240 $moldm^{-3}$ sodium thiosulfate for complete reaction.

Calculate the concentration of hypochlorite ions in the household liquid bleach.

[5]

(b) **(i)** Halogens are very reactive and can form many compounds with metals. The halogens react vigorously with aluminium to form aluminium halides. The melting points of aluminium chloride and aluminium fluoride are shown below.

Aluminium chloride, A*l*Cl_3	Aluminium fluoride, A*l*F_3
192°C	1291 °C

With reference to the structure and bonding, suggest an explanation for the difference in melting points for aluminium chloride and aluminium fluoride.

(ii) A 0.500 g sample of aluminium chloride was heated to 200 °C at a pressure of 1.00 x 10^5 Pa. The volume of its vapour was found to be 73.6 cm^3.

Calculate the relative molecular mass of the vapour at this temperature and, hence draw the structure of aluminium chloride vapour showing clearly the bonds and relevant bond angles around each atom.

(iii) Using the following data, and relevant data from the *Data Booklet*, construct an energy level diagram to calculate the enthalpy change of formation of aluminium fluoride.

	$\Delta H^{\ominus}$ / kJ mol^{-1}
Lattice energy of aluminium fluoride	–6246
Electron affinity of fluorine	–328
Enthalpy change of atomisation of aluminium	+ 330

[11]

(c) 2–methylbutane is relatively unreactive as it does not react with acids, bases or strong oxidising agents. However, under suitable conditions, 2–methylbutane is able to react with chlorine gas to produce useful chlorinated organic compounds.

(i) Name the mechanism of the reaction between chlorine and 2–methylbutane.

(ii) When 2–methylbutane reacts with chlorine gas, isomers of mono–substituted 2–methylbutane are produced. Draw the displayed formulae of the isomers and suggest in which ratio they might be formed.

[4]

[Total: 20]

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Name:	Mark Scheme	Index Number:		Class:	

DUNMAN HIGH SCHOOL
Promotional Examination
Year 5

H2 CHEMISTRY

9647/02

Paper 2 Structured and Free Response

21 September 2012
2 hours 10 minutes

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this question paper and on all writing paper used.

2 Write in dark blue or black pen on both sides of the paper.

3 You may use a soft pencil for any diagrams, graphs or rough working.

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

Answer ***all*** questions in section A and B.

SECTION A – STRUCTURED QUESTIONS [40 MARKS]

5 Write your answers in the spaces provided on the question paper.

6 You are advised to spend a maximum of 70 minutes on Section A.

SECTION B – FREE–RESPONSE QUESTIONS [40 MARKS]

7 Write your answers on the separate answer paper provided.

8 Start each question on a fresh sheet of paper.

9 You are advised to show all workings in calculations.

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

11 At the end of the examination, fasten all your answer papers securely together with the **Cover Sheet** on top.

12 You are advised to spend a maximum of 60 minutes on Section B.

The total marks for this paper is 80 marks.

FOR EXAMINER'S USE

Question No.	1	2	3	4	Total	%
Marks	/10	/10	/11	/9	/[40]	

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

1 Planning

Hess' Law allows us to calculate the enthalpy change of some reactions which cannot be found directly or are not feasible. For example, the $\Delta H^{\ominus}_r$ for the conversion of solid anhydrous copper(II) sulfate to solid hydrated copper(II) sulfate, as shown by the equation below.

$$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_2O(s) \qquad \Delta H^{\ominus}_r < 0$$

This enthalpy change cannot be measured directly as hydrated copper(II) sulfate can only be formed from crystallisation, not by directly adding water to anhydrous copper(II) sulfate.

In order to make use of Hess' Law, the enthalpy change of solution of anhydrous and hydrated copper(II) sulfate are first calculated from different experiments.

$$CuSO_4(s) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq) \qquad \Delta H^{\ominus}_{soln1} < 0$$
$$CuSO_4{\cdot}5H_2O(s) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq) + 5H_2O(l) \qquad \Delta H^{\ominus}_{soln2} > 0$$

You are to plan an experiment to calculate $\Delta H^{\ominus}_{soln1}$, using common laboratory apparatus such as 50 cm^3 measuring cylinder, 1 ºC thermometer, a polystyrene cup, stopwatch and electronic balance. The following information may be useful.

- The specific heat capacity of water is 4.18 J g^{-1} K^{-1}.
- The estimated value for $\Delta H^{\ominus}_{soln1}$ is –47 kJ mol^{-1}.
- For safety reasons, temperature of liquids should not exceed 40 ºC.
- You are recommended to use between 25 – 50 cm^3 of water.

(a) Describe a procedure to find the enthalpy change of solution of anhydrous copper(II) sulfate, $\Delta H^{\ominus}_{soln1}$. Your plan should include plotting of a suitable graph to correct for surrounding heat transfer and the use of appropriate apparatus, masses and volumes of reagents.

Mr: $CuSO_4 = 159.6$; $CuSO_4{\cdot}5H_2O = 249.6$

1. **Weigh** an **empty** and **dry** **weighing bottle** using an **electronic balance**.

✓ (1) correct apparatus used for weighing; can accept small beaker in place of weighing bottle.

2. **Weigh 5 g** of anhydrous copper (II) sulfate in the weighing bottle.
3. Using a **50 cm^3 measuring cylinder**, measure **50 cm^3** of **distilled/deionised water** and pour it into a **polystyrene cup**.

✓(2 and 3) accept 0.35 g – 10.7 g of solid and 25 – 50 cm^3 of water. However, **range of $[CuSO_4]$ must be between 14.2 g dm^{-3} to 213 g dm^{-3}**.

*(Setter's assumption: min ΔT of 1 ^oC and max ΔT of 15 ^oC; **Range of $[CuSO_4]$ must be between 14.2 g dm^{-3} to 213 g dm^{-3}**.)*

Note: Any value lower than this range will have ΔT < 1 ^oC (too small) while value higher than this range will have ΔT > 15 ^oC (too large as it does not follow data).

4. **Stir** gently with the thermometer and **record the temperature** of the solution **every 30 seconds for 2.5 minutes**.

✓(4) accept any indication to take temperature at regular intervals of less than 1 min. [0.5] awarded if student mentions the recording or initial temperature only.

5. At **exactly 3.0 minutes**, **add** the anhydrous copper (II) sulfate **from the weighing bottle** to the distilled/deionised water in the polystyrene cup. **Do not read the temperature at this time**.

✓(5) time for addition should correspond to point 4. Final sentence must be included.

6. **Stir** the mixture thoroughly, and continue to **record the temperature** every **30 seconds from 3.5 minutes to 9.0 minutes.**

✓ (6) interval should correspond to point 4. Interval and time period should provide a minimum of 4 readings. [0.5] awarded for incorrect time interval mentioned with clear start and end times.

7. **Weigh** the weighing bottle **again**. [0.5]

8. Plot a **cooling correction curve** to correct for heat loss or **Extrapolate the decrease in temperature to obtain the maximum temperature** reached. [0.5]

Any correct description to obtain the maximum temperature or the correct name of graph will be awarded [0.5].

✓ = 1 marking point = 1 mark

Total of 5 marking points (1m each) and 2 minor points (0.5 as indicated), maximum 4 marks.

Note that the description of apparatus should include volume with appropriate number of significant figures ie 50 cm^3 measuring cylinder (and not 50.0).

[4]

(b) Draw tables with appropriate headings to record appropriate measurements from your procedure

Mass of empty weighing bottle / g Mass of anhydrous $CuSO_4$ and weighing bottle / g Mass of weighing bottle after using anhydrous $CuSO_4$ / g	
Mass of anhydrous $CuSO_4$ / g	

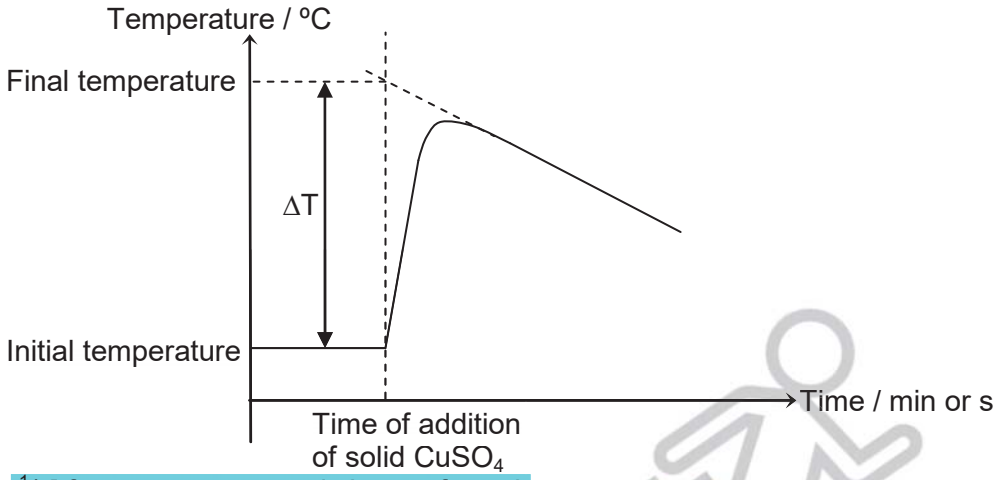
(ecf awarded for mass table according to procedures)

Time (min or s)	Temperature (°C)

(No marks awarded if table indicates record of T_{max}; table for temperature must show no temperature taken when solid was added.)

[$^1/_2$] for every correct table [1]

(c) Sketch graph that you expect to obtain in the experiment. Indicate clearly the axes and the initial and final temperatures that you would read. Show how you would use the values from your procedure and the graph to calculate $\Delta H^{\ominus}_{soln1}$.



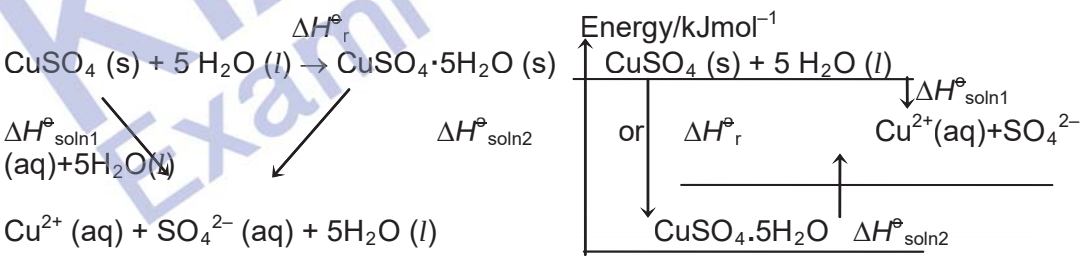
[$^1/_2$] for correct axes and shape of graph
[$^1/_2$] for correct extrapolation, $T_{initial}$ and T_{final}

$$\text{Heat evolved} = \frac{50 \times 4.18\,(\text{Final Temp} - \text{Initial Temp})}{1000}\ \text{kJ}\quad [^1/_2]$$

$$\Delta H^{\ominus}_{soln1} = \frac{50 \times 4.18\,(\text{Final Temp} - \text{Initial Temp}) \div 1000}{5 / 159.6}\ \text{kJ mol}^{-1}\quad [^1/_2]$$

[2]

(d) Draw an energy cycle and show how $\Delta H^{\ominus}_{r}$ can be calculated from $\Delta H^{\ominus}_{soln1}$ and $\Delta H^{\ominus}_{soln2}$ using Hess' law.



Correct energy cycle or energy level diagram [$^1/_2$]

Using Hess' law,
$\Delta H^{\ominus}_{r} = \Delta H^{\ominus}_{soln1} - \Delta H^{\ominus}_{soln2}$ [$^1/_2$]

[1]

(e) Another experiment in which hydrated copper(II) sulfate is added to water is performed to determine $\Delta H^{\ominus}_{soln2}$. The following data is recorded.

Initial temperature / ºC	30.0
Final temperature / ºC	29.5

Change in temperature / ºC	0.5

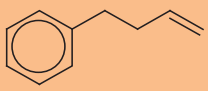
With reference to the magnitude of the temperature change, state one possible significant source of error and a method of improvement.

Source of error	Method of improvement
The 1° thermometer may **not be sensitive** and **accurate enough** to read such a small temperature change, as the temperature change recorded (0.5°C) is only **half a division**. $\%\ error = \frac{0.5}{0.5} \times 100\% \approx 100\ \%$ This results in a **very large percentage error**.	Use a thermometer that is **more sensitive** and has **smaller divisions** to provide for more accurate readings. For example, **thermocouple** or thermometer with **0.1 ºC divisions**. $\%\ error = \frac{0.05}{0.5} \times 100\% \approx 10\ \%$ This greatly **reduces** the percentage error. or Use a **larger mass of hydrated copper(II) sulfate** or a **smaller volume of water**. This will **increase the heat absorbed** by the reaction, **increasing the temperature change**, and thus **reduce the percentage error**.
Since the reaction is endothermic, some **heat could have been gained** from the surroundings, resulting in a **temperature decrease that is smaller than the actual value**.	The **polystyrene cup could be placed in a 250 cm^3 beaker** to provide a **layer of air for insulation**, **allowing the actual value** of the temperature decrease **to be recorded.** or A **lid** could also be used to **prevent transfer of heat from the surroundings into the reaction**, **allowing the actual value** of the temperature decrease **to be recorded**.

Any logical error [1]; any logical corresponding improvement [1]

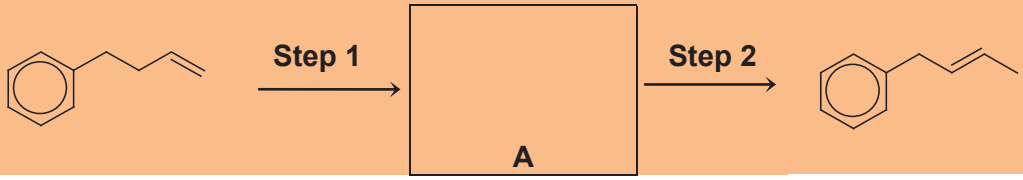
[2]

2 (a) 4–phenylbut–1–ene is a useful molecule often employed by organist chemists during synthesis.

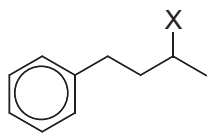
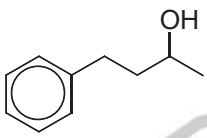


4–phenylbut–1–ene

4–phenylbut–1–ene can be converted to its isomer 4–phenylbut–2–ene in two steps. Suggest how this can be done by drawing the intermediate product **A** in the box below and hence stating the reagents and conditions for **Step 1** and **Step 2**.



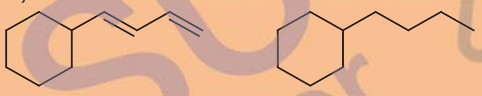
Step 1: HX or cold conc H_2SO_4 followed by H_2O, heat or H_3PO_4, H_2O, 300°C, 70 atm [1]
Step 2: alcoholic NaOH, reflux or excess conc H_2SO_4, 170 ºC [1]

Intermediate product, A:  or  [1]

Steps must match intermediate product in order to obtain full marks. In case of mis–match, award marks to matching steps only.

[3]

(b) The following molecules, **B** and **C** are analogs of 4–phenylbut–2–ene. Suggest chemical test reactions to distinguish **B** and **C**. For each test, state the relevant reagents and conditions, and describe the observations.



B **C**

Add **bromine in CCl_4 / Br_2 (aq)** to separate samples of **B** and **C** at room temperature, in the **absence of UV light**. [1] **B will decolourise the reddish–brown bromine** [$^1/_2$] while **C will not decolourise reddish–brown bromine**. [$^1/_2$]

or

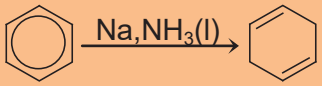
Add **cold, dilute, alkaline $KMnO_4$** to separate samples of **B** and **C**. [1] **B will decolourise the purple $KMnO_4$** [$^1/_2$] while **C will not decolourise the purple $KMnO_4$**. [$^1/_2$]

or

Add **acidified $KMnO_4$** to separate samples of **B** and **C** and **heat**. [1] **B will decolourise the purple $KMnO_4$** with the **efferverscene of CO_2(g)** which forms white precipitate with calcium hydroxide. [$^1/_2$] **C will not decolourise the purple $KMnO_4$** and **will not form efferverscene**. [$^1/_2$]

[2]

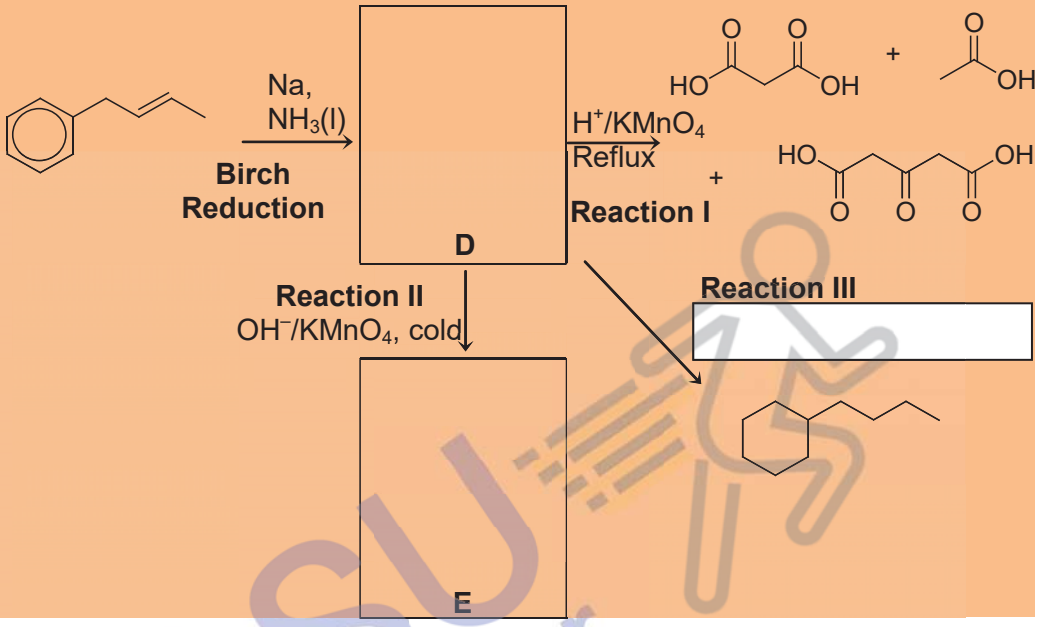
(c) The Birch reduction reduces the benzene ring to a 1,4–cyclohexadiene. The reagent used is sodium dissolved in liquid ammonia. The reduction of benzene is shown in the equation below.



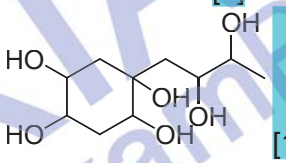
Benzene 1,4–cyclohexadiene

4–phenylbut–2–ene can be converted to **D** via the Birch reduction. **D** is a 1,4–cyclohexadiene that is bonded to an alkyl chain. **D** can be strongly oxidised to give three organic molecules as shown in **Reaction I**.

Deduce the structure of **D** and complete the reaction scheme below by drawing the structure of **E**, the product for **Reaction II** and stating the reagents and conditions for **Reaction III**.



D: [1]



E: [1]

Reaction II: H_2/Ni, reflux[1]

(e.c.f. can be awarded for **E** according to the structure of **D**; no marks for **E** if **D** is not drawn.)

[3]

(d) 4–phenylbut–2–ene can be oxidised to benzoic acid, C_6H_5COOH, which is an effective food preservative. However, due to its low solubility, it is often used together with its sodium salt, sodium benzoate, $C_6H_5COO^-Na^+$. At pH 5 or lower, it can inhibit the growth of microorganisms that cause food spoilage.

In a laboratory, a food chemist mixes 12.2 g of benzoic acid with 18.3 g of sodium benzoate in 500 cm^3 of water. Given that the K_a of benzoic acid is 6.17 x 10^{-5} mol dm^{-3}, deduce if mixture can be used as a food preservative, showing your calculations.

Number of moles of sodium benzoate = $\frac{18.3}{12.0\times7+5.0+32.0+23.0}$ = **0.127 mol**

Number of moles of benzoic acid = $\frac{12.2}{12.0\times7+6.0+32.0}$ = **0.100 mol** [$^1/_2$]

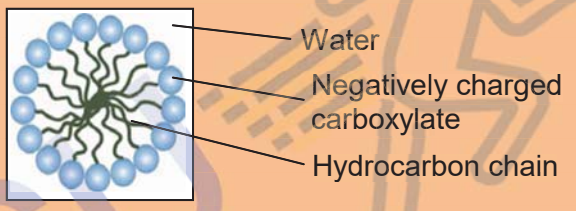
$$\text{pH} = pK_a + \log_{10}\frac{[C_6H_5COO^-]}{[C_6H_5COOH]}$$ [½] (Also accept $\frac{[\text{salt}]}{[\text{acid}]}$ or $\frac{[\text{conj base}]}{[\text{acid}]}$)

$$= -\log_{10}(6.17 \times 10^{-5}) + \log_{10}\frac{0.127/0.500}{0.100/0.500} = \mathbf{4.31}$$ [½]

Yes, the mixture can be used as a food preservative. [½]
(e.c.f can be awarded if pH above 5 is obtained; no marks awarded if only 'yes' or 'no' is stated without any calculation).

[2]

3 Sodium stearate, $C_{18}H_{35}O_2Na$, is a major component of many different types of soap. At 25 °C, the solubility of sodium stearate is 0.015 mol dm^{-3}. In aqueous solution, the $C_{18}H_{35}O_2^-$ anion form *micelles*, a special structure in which the hydrocarbon chains of many anions cluster together, leaving the negatively charged carboxylate on the surface. During cleaning, oil and dirt can be trapped within the hydrocarbon chains of the *micelle* and is thus easily removed.



A micelle in aqueous solution

(a) (i) Write an expression for the solubility product, K_{sp}, of sodium stearate and calculate its value, including its units.

$C_{18}H_{35}O_2Na(s) \rightleftharpoons C_{18}H_{35}O_2^-(aq) + Na^+(aq)$

$K_{sp} = [C_{18}H_{35}O_2^-][Na^+]$ [½]

$= (0.015)^2 = 2.25 \times 10^{-4}$ mol^{2}dm^{-6} [1] for ans and [½] for units

(Marker can decide to reallocate the 2 marks within this question part.)

(ii) The last stage in the manufacture of soaps involves adding sodium chloride to the reaction mixture in order to precipitate the soap. By writing relevant equation(s), explain why soap precipitates when sodium chloride is added.

$C_{18}H_{35}O_2Na(s) \rightleftharpoons C_{18}H_{35}O_2^-(aq) + Na^+(aq)$ — (1)

$NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$ — (2)

[1] for any relevant equation that aids explanation

When NaCl is added, this introduces the **common ion Na^+**, and **increases $[Na^+]$**. [½]

AND

By **Le Chatelier's Principle**, the **equilibrium in (1) will shift left** to **reduce $[Na^+]$**. [1] Hence, **solubility of $C_{18}H_{35}O_2Na$ will be reduced**, causing soap to be precipitated. [½]

OR

When **ionic product ($[C_{18}H_{35}O_2^-][Na^+]$) exceeds its K_{sp}**, this causes soap to be precipitated. [1½]

[5]

(b) (i) The enthalpy change of solution of sodium stearate is –12 kJ mol^{-1}. Given that $\Delta G^{\ominus}_{soln}$ is +47.5 kJ mol^{-1}, calculate $\Delta S^{\ominus}_{soln}$ and hence suggest an explanation for the sign of $\Delta S^{\ominus}_{soln}$.

$\Delta G^{\ominus}_{soln} = \Delta H_{soln}^{\theta} - T\Delta S_{soln}^{\theta}$ [$^1/_2$]

$+47.5 = -12.0 - (298)\ \Delta S_{soln}^{\theta}$

ΔS_{soln}^{θ} = **– 0.200 kJ mol^{-1} K^{-1}** (3s.f.) [$^1/_2$]

When the **less mobile micelles are formed** in solution, the **number of free mobile solvated ions decreases**. [$^1/_2$] This causes the degree of disorder/randomness in the system to decrease. [$^1/_2$ only given if previous part point is present] Therefore, entropy decreases ($\Delta S^{\ominus}_{soln} < 0$).

(ii) How will the spontaneity for the dissolving of sodium stearate change with temperature? Explain your answer with reference to $\Delta G^{\ominus}_{soln}$.

As temperature increases, the **magnitude of TΔS increases**. [1] As $\Delta S<0$, **ΔG will become more positive (less negative)**, thus the **reaction will become less spontaneous**. [1]

or

As temperature decreases, the **magnitude of TΔS decreases**. [1] As $\Delta S<0$, **ΔG will become less positive (more negative)**, thus the **reaction will become more spontaneous**. [1]

[4]

(c) Potassium stearate is also a component of soap.

Compare the relative magnitudes of the lattice energies of sodium stearate and potassium stearate.

Charge of cation: $Na^+ = K^+$

Size of cation: $Na^+ < K^+$ [$^1/_2$]

Since magnitude of lattice energy $\propto \left|\frac{q_+ q_-}{r_+ + r_-}\right|$ [$^1/_2$]

Magnitude of lattice energy: sodium stearate > potassium stearate [1]

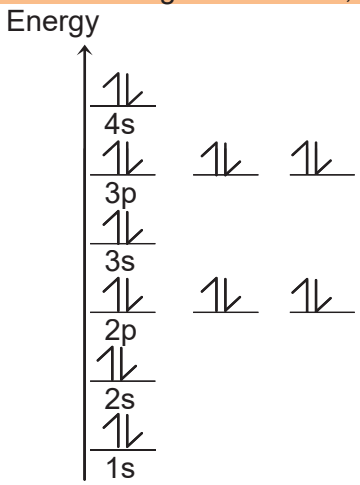
[2]

4 Calcium ethanoate, $(CH_3COO^-)_2Ca^{2+}$, decomposes upon heating to form propanone and an inorganic compound **F**.

$$(CH_3COO^-)_2Ca^{2+} \rightarrow \underset{\text{Propanone}}{H_3C-C(=O)-CH_3} + \mathbf{F}$$

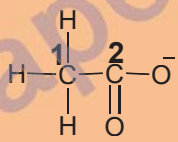
Calcium ethanoate

(a) In the space below, draw and label an energy level diagram to illustrate the electronic configuration of Ca, using arrows to represent electrons.



[2]

(b) **(i)** The diagram below shows the structure of the ethanoate anion, with the two carbon atoms separately labelled as **1** and **2**. With reference to the valence shell electron pair repulsion (VSEPR) theory, state the shape with respect to each carbon atom **1** and **2**.



Carbon **1**: Tetrahedral [$^1/_2$], Carbon **2**: Trigonal planar [$^1/_2$]

(ii) Identify and describe the hybridisation of carbon **2**.

Carbon **2** is **sp^2 hybridised** [1] as it forms **three sigma bonds** and **one pi bond**. [$^1/_2$] **One 2s orbital and two 2p orbitals are hybridised** [$^1/_2$] to give a set of **three equivalent sp^2 hybrid orbitals of equal energy**. [$^1/_2$] The **third 2p orbital remains unhybridised**. [$^1/_2$]

[4]

(c) **(i)** State the cation present in **F**.

Ca^{2+} [$^1/_2$]

(ii) To a 0.69 g sample of **F**, 25.0 cm^3 of 1.0 mol dm^{-3} hydrochloric acid was added. The remaining solution was diluted to 100.0 cm^3. A 20.0 cm^3 aliquot required 22.55 cm^3 of 0.1 mol dm^{-3} sodium hydroxide for neutralisation. Calculate the relative molecular mass of **F** assuming two moles of hydrochloric acid reacts with one mole of **F**.

$$\text{No. of moles of NaOH required} = \frac{22.55}{1000} \times 0.1 = 0.002255 \text{ mol}$$

No. of moles of HC*l* remaining in 20.0 cm^3 = **0.002255 mol** [$^1/_2$]

No. of moles of HC*l* remaining in 100.0 cm^3 = $0.002255 \times \frac{100.0}{20.0}$

= 0.01127 mol

No. of moles of HC*l* reacted = $\frac{25.0}{1000} \times 1.0 - 0.01127$ = **0.01372 mol** [$^1/_2$]

2 HC*l* ≡ **F**

No. of moles of **F** = $\frac{0.01372}{2}$ =**0.006862** [$^1/_2$]

Relative molecular mass of **F** = $\frac{0.69}{0.006862}$ =**100.6** [$^1/_2$]

(iii) Hence or otherwise, deduce the identity of **F**.

$CaCO_3$ [$^1/_2$]

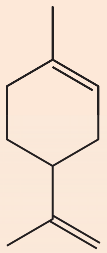
[3]

Section B

Answer ***all*** questions.

1 Food additives are substances added to food to enhance its tastes and appearance. Some additives occur naturally while others are synthetically made.

The oil of orange is an essential oil derived from the rind of oranges and some other citrus fruits. This essential oil comprises mainly of a colourless liquid, limonene ($C_{10}H_{16}$).



limonene

Limonene can exist as two isomers with different characteristics. One isomer has a piney, turpentine–like smell while the other has a pleasing citrus orange scent.

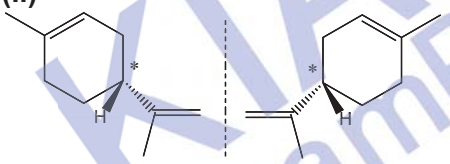
(a) **(i)** Identify the type of isomerism that is present in limonene.

(ii) Draw the structural formula to illustrate the type of isomerism in **(i)**.

[2]

(i) Optical isomerism [1]

(ii)



[1] for correctly drawn isomers in 3D form **and** dotted line for mirror plane
Not necessary to label chiral carbon with *.

(b) Besides being used in a flavour and fragrance additive, limonene is a biodegradable solvent which can be used remove grease from machine parts. Explain, in terms of structure and bonding, how limonene can be used to remove grease effectively.

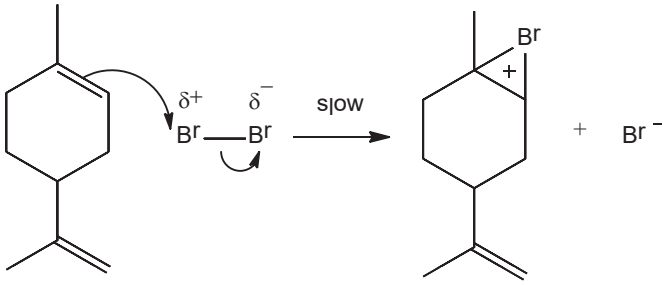
[2]

Limonene has a simple molecular structure [$^1/_2$] and is able to form favourable van der Waals forces (or temporary dipole–dipole interaction) [$^1/_2$] between limonene and grease molecules. [$^1/_2$] The energy released from this interaction is able to detach the grease molecules from the machine parts. [$^1/_2$]

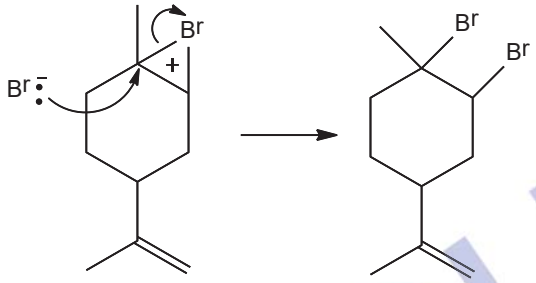
(c) Limonene is able to undergo addition reaction with diatomic molecules such as bromine gas. Describe the reaction mechanism that limonene undergo with bromine gas.

[3]

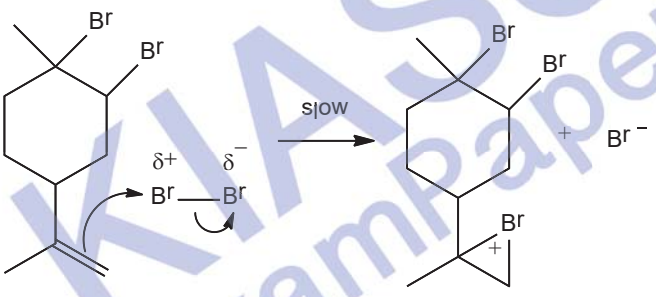
Step 1



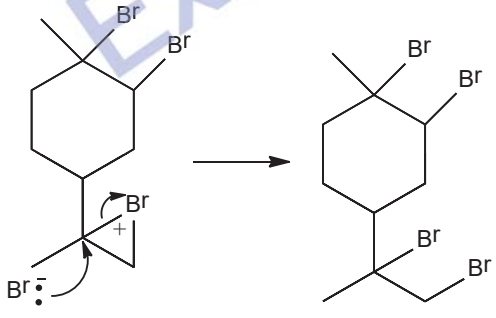
Step 2



Step 3

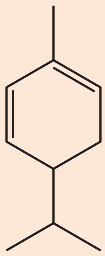


Step 4



[1] for each step with correct species (correct structures, bonds, partial charges on Br_2, positive & negative charges in intermediate species). Award only [1] if the electrophilic addition is only shown at one of the C=C bonds.
[1] for correctly shown curly arrows.
Do not penalise if mechanism is written in 2 steps. (i.e. simultaneous electrophilic addition)
Ignore if the electrophilic attack in on the less stable carbocation.

(d) Limonene is a structural isomer of α–phellendrene.



α–phellendrene

Two unlabelled bottles containing limonene and α–phellendrene are found in the laboratory. Describe a suitable chemical reaction to distinguish between limonene and α–phellendrene. State clearly the observations and one relevant equation.

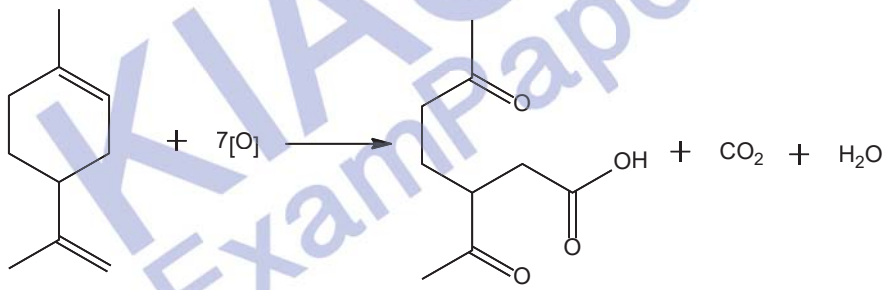
[3]

Test: Add $KMnO_4$ in dilute H_2SO_4 to both samples and heat. [1]

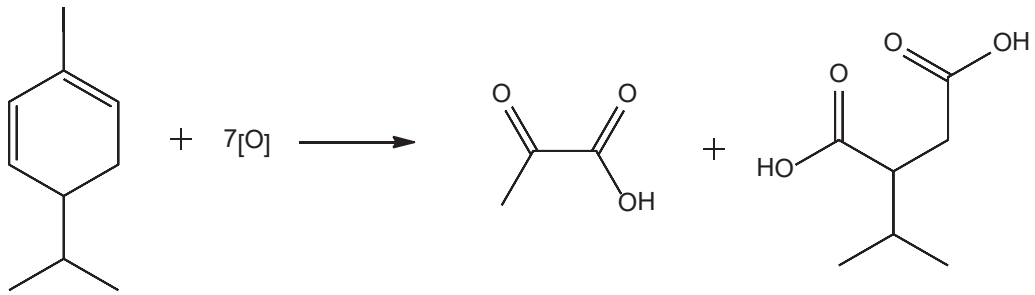
Observations:
For limonene: Purple $KMnO_4$ decolourises. CO_2 gas evolved. [$^1/_2$]
Chemical test for CO_2 is not required.

For α–phellendrene: Purple $KMnO_4$ decolourises. No effervescence (or no CO_2 gas) observed. [$^1/_2$]

Equation: [1]

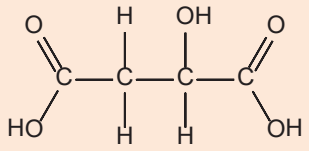


or



Marks will be awarded for any one relevant equation. (Equation for the formation of $CaCO_3$ can also be accepted if it is written.)

(e) Another naturally occurring food additive, malic acid is present as one of the many organic acids found in wines.



malic acid

Malic acid is a dibasic acid which can be represented by H_2A. The acid dissociation constants for malic acid are given below:

Step 1: $H_2A + H_2O \rightleftharpoons HA^- + H_3O^+$ $K_{a1} = 3.98 \times 10^{-4}$ mol dm^{-3}
Step 2: $HA^- + H_2O \rightleftharpoons A^{2-} + H_3O^+$ $K_{a2} = 6.31 \times 10^{-6}$ mol dm^{-3}

Suggest an explanation for the difference in the acid dissociation constants, K_{a1} and K_{a2}, for malic acid.

[2]

The removal of H^+ from HA^- in step 2 requires more energy due to the presence of electrostatic attraction between HA^- and H^+. [1] Hence, the position of equilibrium for step 2 lies more to the left as compared to step 1 which results in a smaller K_{a2}. [1]

(f) Many wines undergo a process called 'malo–lactic fermentation' to convert the sharp tasting malic acid to a milder lactic acid to enhance the quality of wines.

Lactic acid is a monobasic acid that has the following composition by mass: C: 40.0%; H: 6.7%; O: 53.3%.

A particular brand of wine containing lactic acid has a pH of 3.00. The concentration of lactic acid in the wine can be determined by titration with sodium hydroxide.

A 15.30 cm^3 sample of this wine containing 0.010 g of lactic acid is found to require 22.20 cm^3 of 5×10^{-3} mol dm^{-3} sodium hydroxide for neutralisation. Lactic acid is assumed to be the only acid that contributes to the acidity of this wine.

(i) Calculate the concentration of lactic acid in mol dm^{-3} and hence explain whether lactic acid is a strong or weak acid.

[2]

n(NaOH) in 22.20 cm^3 = $5 \times 10^{-3} \times (22.20 / 1000) = 1.11 \times 10^{-4}$ mol

n(lactic acid) in sample of wine = 1.11×10^{-4} mol

[lactic acid] = $1.11 \times 10^{-4} / 0.01530 = 7.25 \times 10^{-3}$ mol dm^{-3} [$^1/_2$]

Assume that lactic acid is a strong acid, 7.25×10^{-3} mol dm^{-3} of lactic acid will dissociate completely to give 7.25×10^{-3} mol dm^{-3} of H^+.

Given that pH = – log [H^+]
3.00 = – log [H^+]
[H^+] = 1.00×10^{-3} mol dm^{-3}

Since [lactic acid] ≠ [H^+] [1] for any reasonable explanation, lactic acid is a weak acid. [$^1/_2$]

(ii) Calculate the acid dissociation constant, K_a of lactic acid.

[1]

$K_a = [H^+]^2 / [\text{lactic acid}]$
$= (1.00 \times 10^{-3})^2 / (7.25 \times 10^{-3} - 1.00 \times 10^{-3})$
$= 1.60 \times 10^{-4}$ mol dm^{-3}
[$^1/_2$] for numerical answer
[$^1/_2$] for correct units

(iii) Calculate the M_r of lactic acid and hence its molecular formula.

[2]

n(NaOH) in 22.20 cm^3 = $5 \times 10^{-3} \times (22.20 / 1000) = 1.11 \times 10^{-4}$ mol

n(lactic acid) in sample of wine = 1.11×10^{-4} mol

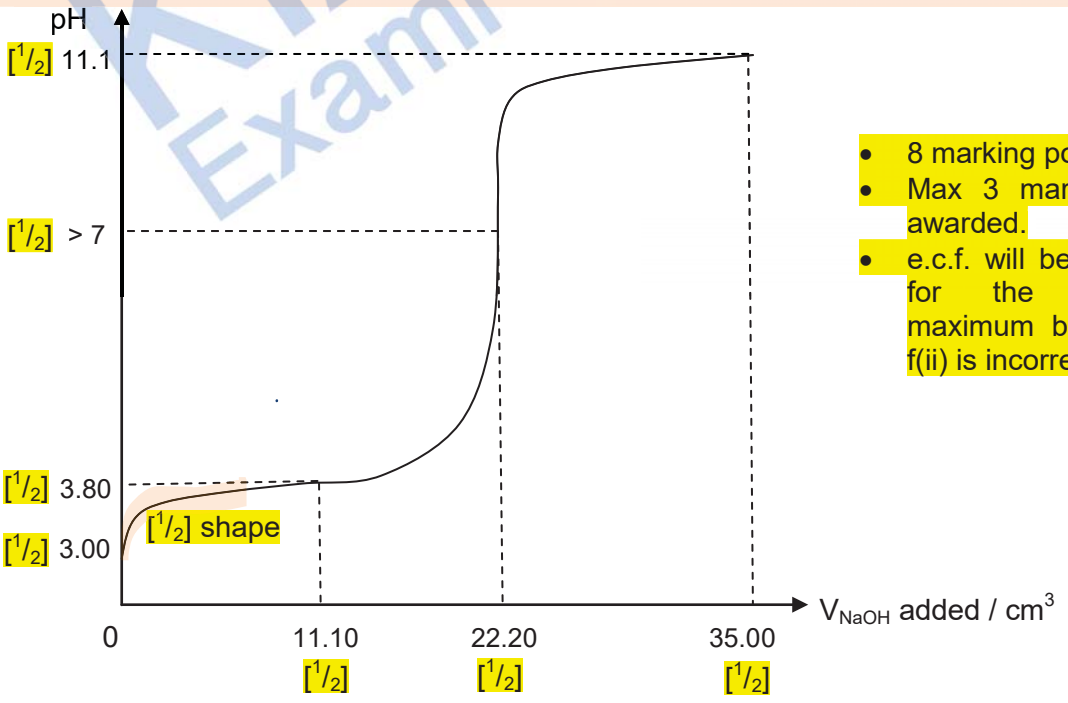
M_r of lactic acid = 0.010 / 0.0111 = 90.1 [$^1/_2$]

	C	H	O
% mass	40.0	6.7	53.3
mole ratio	40.0/12.0 = 3.33	6.7/1.0 = 6.7	53.3/16.0 = 3.33
simplest ratio	1	2	1

Empirical formula = CH_2O
Molecular formula = $C_3H_6O_3$
[1] for any appropriate working to find molecular formula + [$^1/_2$] for correct molecular formula

(iv) Sketch the pH curve when 35.00 cm^3 of 5×10^{-3} mol dm^{-3} sodium hydroxide is added to the 15.30 cm^3 sample of wine containing lactic acid.

[3]



- 8 marking points
- Max 3 marks to be awarded.
- e.c.f. will be awarded for the pH at maximum buffering if f(ii) is incorrect.

[Total: 20]

2 The Group VII elements (halogens) play an important part in the development of chemistry.

(a) Chlorine, one of the most important halogens, has its uses in the manufacture of many products in everyday life.

Sodium hypochlorite, NaC*l*O, is an active ingredient in many household liquid bleaches. NaC*l*O is manufactured when chlorine gas dissolves in cold aqueous sodium hydroxide. Chlorine gas undergoes a disproportionation reaction into C*l*$^-$ and C*l*O$^-$.

(i) By using the reaction of chlorine gas in cold aqueous sodium hydroxide, explain what is meant by 'disproportionation reaction'.

[1]

The oxidation state of same element chlorine in Cl_2 is increased from 0 to +1 in C*l*O$^-$ and reduced from 0 to –1 in C*l*$^-$ simultaneously. [1]

(ii) Write a balanced equation for the reaction between chlorine gas and cold aqueous sodium hydroxide.

[1]

$Cl_2 + 2NaOH \rightarrow NaClO + NaCl + H_2O$
or $Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O$ [1]
(state symbols not required)

(iii) The percentage of hypochlorite ion, C*l*O$^-$ in household liquid bleach can be determined by iodometric titration.

A 25.0 cm^3 sample of household liquid bleach is made up to a total volume of 250 cm^3 in a volumetric flask. Iodine is produced when an excess of potassium iodide was added to 20.0 cm^3 aliquot of this solution in acidic medium. The iodine produced in the 20.0 cm^3 solution required 25.30 cm^3 of 0.0240 mol dm^{-3} sodium thiosulfate for complete reaction.

Calculate the concentration of hypochlorite ions in the household liquid bleach.

[3]

$ClO^- + 2I^- + 2H^+ \rightarrow Cl^- + I_2 + H_2O$
$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

n($S_2O_3^{2-}$) in 25.30 cm^3 = 0.0240 x 0.0253 = 6.072 x 10^{-4} mol [1]

n(C*l*O$^-$) in 20.0 cm^3 = 6.042 / 2 = 3.036 x 10^{-4} mol
n(C*l*O$^-$) in 250 cm^3 = 3.036 x 10^{-4} x (250/20.0) = 3.795 x 10^{-3} mol [1]
method [1] to be awarded for ecf answer in step 1 but next mark will not be awarded.

[C*l*O$^-$] in household bleach = 3.795 x 10^{-3} / 0.0250 = 0.152 mol dm^{-3} [1]

(b) **(i)** Halogens are very reactive and can form many compounds with metals. The halogens react vigorously with aluminium to form aluminium halides. The melting points of aluminium chloride and aluminium fluoride are shown below.

Aluminium chloride, A*l*C*l*$_3$	Aluminium fluoride, A*l*F$_3$
192 °C	1291 °C

With reference to the structure and bonding, suggest an explanation for the difference in melting points for aluminium chloride and aluminium fluoride.

[3]

$AlCl_3$ has a simple molecular structure [$^1/_2$] with weak van der Waals forces (or weak intermolecular temporary dipole–dipole interaction) between the molecules [$^1/_2$]. AlF_3 has a giant ionic lattice structure [$^1/_2$] with strong electrostatic attraction between oppositely charged ions [$^1/_2$]. Less energy is required to overcome the weaker van der Waals forces (or temporary dipole–dipole interaction) than the stronger electrostatic forces of attraction between oppositely charged ions. [1]

(ii) A 0.500 g sample of aluminium chloride was heated to 200 °C at a pressure of 1.00 x 10^5 Pa. The volume of its vapour was found to be 73.6 cm^3.

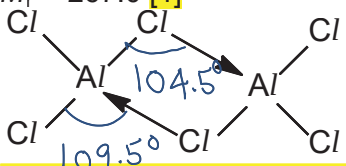
Calculate the relative molecular mass of the vapour at this temperature and, hence draw the structure of aluminium chloride vapour showing clearly the bonds and relevant bond angles around each atom.

[4]

$pV = nRT$

$(1.00 \times 10^5)(73.6 \times 10^{-6}) = (0.500 / M_r) \times 8.31 \times 473$ [1] correct substitution

$M_r = 267.0$ [1]

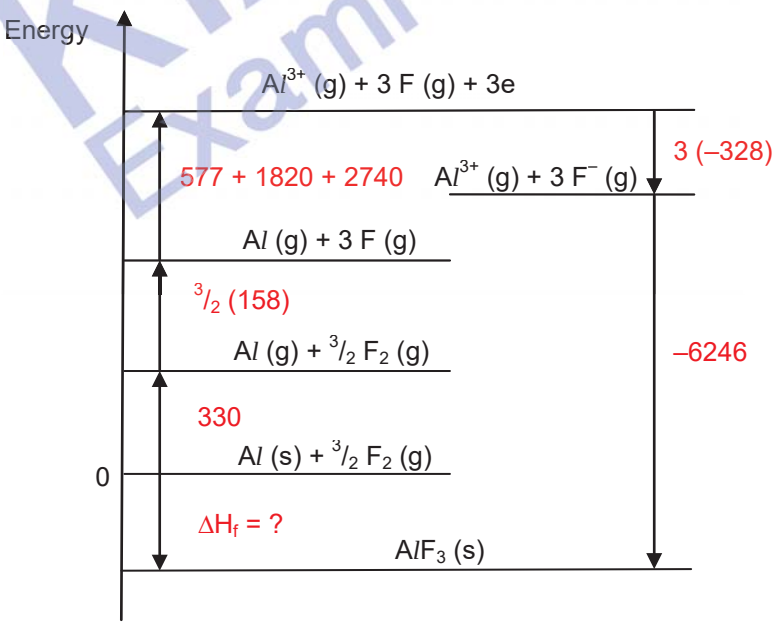


[1] structure (dative bonds must be shown correctly, [1] bond angles

(iii) Using the following data, and relevant data from the *Data Booklet*, construct an energy level diagram to calculate the enthalpy change of formation of aluminium fluoride.

	$\Delta H^\ominus$ / kJ mol^{-1}
Lattice energy of aluminium fluoride	– 6246
Electron affinity of fluorine	– 328
Enthalpy change of atomisation of aluminium	+ 330

[4]



Max [2]. Award [$^1/_2$] for each area (i.e. state symbols, relative energy level with relevant species, correct axis with unit for energy and zero energy level, direction of arrows, correct enthaply)

$\Delta H_f^{\ominus} = 330 + {}^{3}/_{2}(158) + 577 + 1820 + 2740 + 3(-328) - 6246$

[1] for correct application of Hess' law based on diagram above. Ignore wrong values here as it will be penalised in diagram and final answer.

$= -1526$ kJ mol^{-1} [$^{1}/_{2}$] for correct numerical value and [$^{1}/_{2}$] for units

(c) 2–methylbutane is relatively unreactive as it does not react with acids, bases or strong oxidising agents. However, under suitable conditions, 2–methylbutane is able to react with chlorine gas to produce useful chlorinated organic compounds.

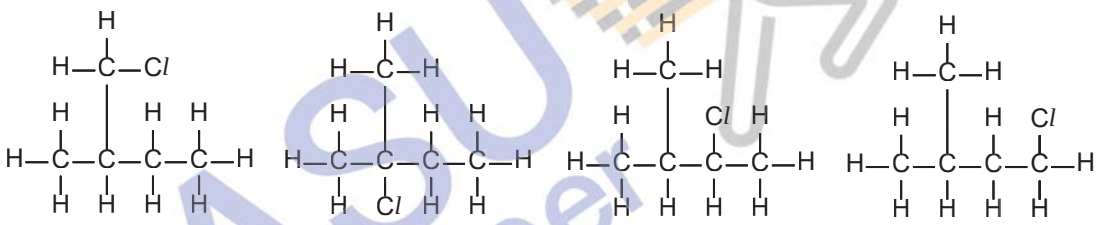
(i) Name the mechanism of the reaction between chlorine and 2–methylbutane.

[1]

Free radical substitution

(ii) When 2–methylbutane reacts with chlorine gas, isomers of mono–substituted 2–methylbutane are produced. Draw the displayed formulae of the isomers and suggest in which ratio they might be formed.

[3]



6 : 1 : 2 : 3

[$^{1}/_{2}$] for each isomer (no marks will be awarded for repeated isomers)
Minus [$^{1}/_{2}$] for not drawing displayed formulae.
[1] for correct ratio based on the 4 isomers.
If only give 3 isomers with correct ratio based on the isomers drawn => award [2]

[Total: 20]

NANYANG JUNIOR COLLEGE
JC 1 PROMOTIONAL EXAMINATION
Higher 2

CHEMISTRY

9647/01

Paper 1 Multiple Choice

5 October 2012

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Write your name, class and tutor's name on the Answer Sheet in the spaces provided unless this has been done for you.

There are **forty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record you choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.

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

Section A

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

1 Bromine gas is toxic. The maximum safe toleration level of bromine gas in air is 0.004 mg dm^{-3}. How many bromine atoms are present in 1 dm^3 of air at this toleration level?

A 1.50×10^{16} **B** 3.00×10^{16}

C 6.00×10^{16} **D** 3.00×10^{19}

Answer: B
Worked solution:
Mr of Br_2 = 159.8

No. of bromine atoms present = $2 \times (\frac{0.004 \times 10^{-3})}{159.8} \times 6.02 \times 10^{23} = 3.00 \times 10^{16}$

2 Group I and Group II ionic hydrides react with water.

$$H^- + H_2O \rightarrow OH^- + H_2$$

In an experiment, 1 g of a sample of an ionic hydride is dissolved in excess H_2O. The resulting solution required 24.0 cm^3 of a 2.0 mol dm^{-3} HCl solution for complete neutralisation.

What is the formula of the hydride?

A CaH_2 **B** LiH

C MgH_2 **D** NaH

Answer: A
Worked solution:
n (HCl) = 2.0 x 0.024 = 0.048 mol
n (OH^-) = n(H^+) = 0.048 mol
Assume group I hydride, n(ionic hydride) = 0.048 mol
Mr (group I hydride) = $\frac{1}{0.048} = 20.8$
Assume group II hydride, n(ionic hydride) = 0.048 / 2 = 0.024
Mr (group II hydride) = $\frac{1}{0.024} = 42.0$
formula of hydride with Mr of 42.0 is CaH_2.

3 Carbon disulfide, CS_2, a volatile flammable liquid used in the manufacture of cellophane, is oxidised on combustion as follows:

$$CS_2(g) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$$

A 20 cm^3 sample of carbon disulfide vapour is ignited with 100 cm^3 of oxygen. The final volume of gas after burning is passed into an excess of aqueous alkali. What percentage of this final volume dissolved in the alkali? (All volumes are measured at the same temperature and pressure, conditions under which CS_2 is a gas.)

A 20% **B** 40% **C** 60% **D** 80%

Answer: C
Worked solution:

	$CS_2(g)$	+	$3O_2(g)$	→	$CO_2(g)$	+ $2SO_2(g)$
initial	20		100		0	0
reacted	-20		-3(20)		+20	+40
final	0		40		20	40

Volume of gases dissolved in alkali = $v(CO_2) + v(SO_2) = 20 + 40 = 60\ cm^3$

% of final volume = $\frac{60}{40+20+40} \times 100\% = 60\%$

4 Which of the following formulae represents a particle with the composition 1 proton, 1 neutron and 2 electrons?
(D represents deuterium, ^2H)

A D **B** D^-

C H^- **D** He

Answer: B
Worked solution:
Particle is negatively charged (1 proton and 2 electrons).
Particle has mass number of 2 (1 proton + 1 neutron)

5 The first seven ionization energies of an element are as follows (in kJ mol^{-1}):

790, 1600, 3200, 4400, 16100, 19800, 23800

The outer electronic configuration of the element is

A ns^1

B ns^2

C $ns^2\ np^2$

D $ns^2\ np^5$

Answer: C
Worked solution:
A big difference between the 4th and 5th IE indicates that the 5th electron is removed from an inner electron shell. The element belongs to Group IV with electronic configuration of ns^2np^2.

6 Which of the following is incorrect for $^{31}P^{3-}$?

A It is more polarizable than N^{3-}.

B It is isoelectronic with argon.

C Its valence p-orbitals are completely filled.

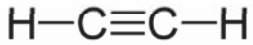
D It is smaller than a phosphorus atom.

Answer: D
Worked solution:
Negatively charged ions are bigger than their atoms due to the removal of electrons from the outer shell.

7 The C_2H_2 molecule is linear. What can be deduced from this about the numbers of σ and π bonds present in the molecule?

	σ	π
A	2	2
B	2	3
C	3	1
D	3	2

Answer: D
Worked solution:



Single bond consist of 1 **σ** bond, triple bond consist of 1 **σ** bond and 2 **π** bonds.

8 Which of the following is the most significant intermolecular force in SO_2?

A ionic bonding

B covalent bonding

C Van der Waals' attractions

D permanent dipole – permanent dipole attractions

Answer: D
Worked solution:
SO_2 is a polar simple molecule (bent-shaped with 1 lone pair of electrons on S atom), thus it experiences pd-pd forces of attraction.

9 The variation in bond angles in the molecules of ammonia and water is due to

A the number of lone electron pairs in the molecule

B a bonding electron pair having greater repulsive force than a lone pair

C a greater repulsion between hydrogen atoms in the longer N-H bond length

D a greater repulsion between the hydrogen atoms in the shorter N-H bond length

Answer: A
Worked solution:
Ammonia has 1 lone pair and 3 bond pairs
Water has 2 lone pairs and 2 bond pairs.

10 For which of the following pairs does the first species have a smaller bond angle?

A CH_4, $SiCl_4$

B PH_4^+, ICl_4^-

C F_2O, H_2O

D SO_3, PH_3

Answer: C
Worked solution:
F is more electronegative than H and thus the bond pair of electrons are drawn further away from the central O atom. Thus the bond pairs of electrons in H_2O experience a greater repulsion, leading to a greater bond angle.

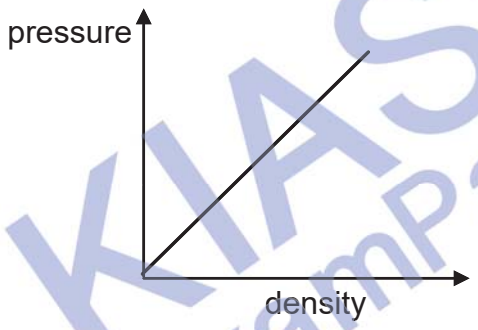
11 SF_4 reacts with $(CH_3)_4NF$ to form $(CH_3)_4N^+SF_5^-$. Which of the following **correctly** describes the shape of the ions in the product?

	Shape of cation (wrt N)	Shape of anion
A	trigonal pyramidal	square planar
B	square planar	trigonal bipyramidal
C	tetrahedral	octahedral
D	tetrahedral	square pyramidal

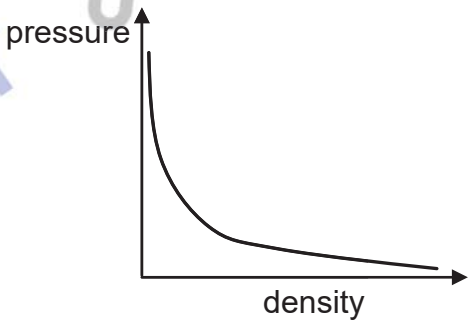
Answer: D
Worked solution:
$(CH_3)_4N^+$ has 4 bond pairs and no lone pairs of electrons, thus it is tetrahedral in shape. SF_5^- has 5 bond pairs and one lone pair of electrons, thus it is square pyramidal in shape.

12 Which of the following diagrams correctly describes the behaviour of a fixed mass of an ideal gas at constant temperature?

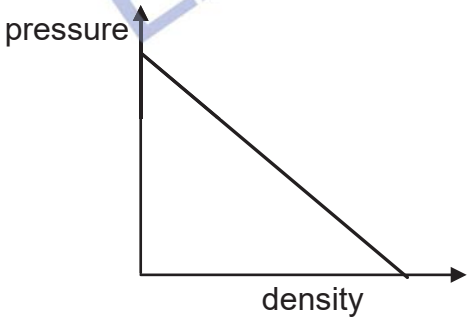
A



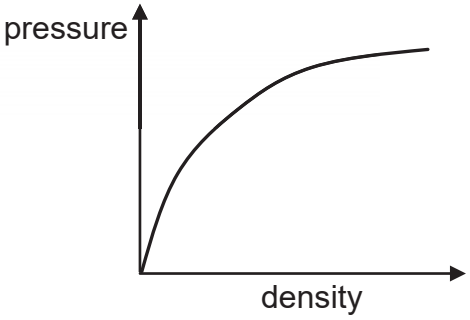
B



C



D



Answer: A
Worked solution:

$PV=nRT \Rightarrow PV = \frac{m}{M}RT \Rightarrow P = \frac{m}{v \times M}RT$

$P = \frac{density}{M}RT$ since M, R and T are constants, P is directly proportional to density.

13 At constant pressure, the following reaction is exothermic.

$$2NO_2\,(g) \rightarrow N_2O_4\,(g)$$

The reaction is

A only spontaneous at low temperatures.

B only spontaneous at high temperatures.

C always spontaneous.

D never spontaneous.

Answer: A
Worked solution:
For the reaction, exothermic, thus ΔH is negative. There are less number of gaseous molecules are produced, thus ΔS is negative. Thus, $-T\Delta S$ is always negative. For a spontaneous reaction ($\Delta G = \Delta H - T\Delta S$, where $\Delta G < 0$) to occur, temperature must be low.

14 For which of the following is the lattice energy likely to have the greatest magnitude?

A lithium fluoride

B lithium iodide

C sodium chloride

D sodium fluoride

Answer: A
Worked solution:
All 4 compounds have the same charges in their cation and anion. However, Lithium fluoride has both the smallest cation and the smallest anion amongst the 4 choices. Recall equation magnitude of LE = $\left|\frac{q^+q^-}{r^+ + r^-}\right|$

15 Phosphine, PH_3, reacts with hydrogen iodide to form phosphonium iodide in the reaction shown.

$$PH_3\,(g) + HI\,(g) \rightarrow PH_4^+I^-\,(s)\ ,\ \Delta H^{\theta} = -101.8\ kJ\ mol^{-1}$$

Given that $\Delta H_f{}^{\theta}$ for PH_3 (g) = +5.4 kJ mol^{-1}, and $\Delta H_f{}^{\theta}$ for HI (g) = +26.5 kJ mol^{-1}, what is the standard enthalpy change of formation of phosphonium iodide?

A $-133.7\ kJ\ mol^{-1}$

B $-69.9\ kJ\ mol^{-1}$

C $+69.9\ kJ\ mol^{-1}$

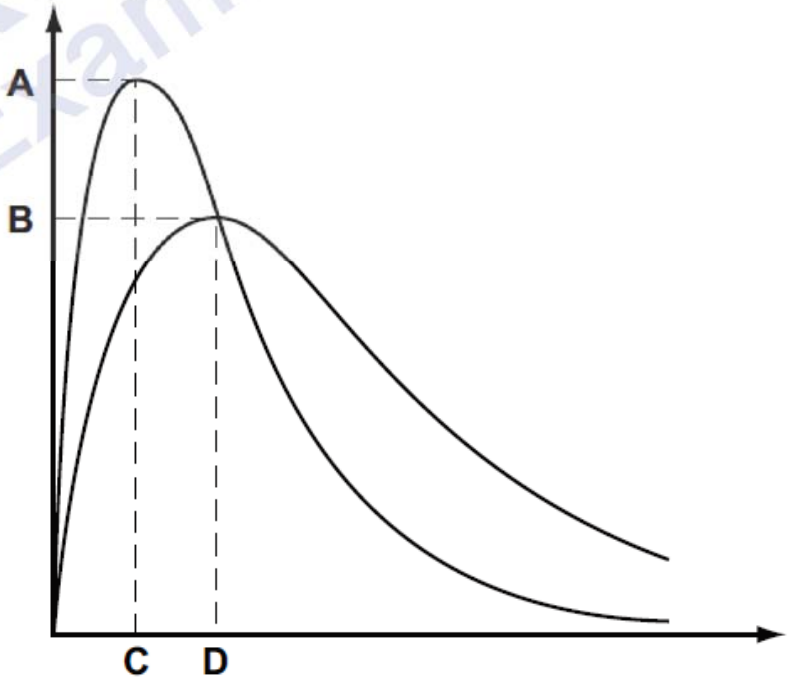
D $+133.7\ kJ\ mol^{-1}$

Answer: B
Worked solution:
$\Delta H_r{}^{\theta}$ = sum of enthalpy of formation of products – sum of enthalpy of formation of reactants.

$-101.8 = x - [5.4 + 26.5]$
$X = -101.8 + 31.9 = -69.9\ kJ\ mol^{-1}$

16 The diagram shows the Maxwell-Boltzmann energy distribution curves for molecules of a sample of a gas at two different temperatures.

Which letter on the axes represents the most probable energy of the molecules at the lower temperature?



Answer: C
Worked solution:
For a Maxwell-Boltzmann energy diagram, x-axis represents energy and y-axis represents number of molecules.

17 The rate equation for the reaction

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

is rate = $k[S_2O_8^{2-}(aq)][I^-(aq)]$, where k is the rate constant.

Which of the following conclusions can be drawn from this information?

A The value of k depends on the concentrations of $S_2O_8^{2-}$ and I^-.

B The value of k depends on the rate of the reaction.

C The value of k is dependent only on changes in temperature.

D The rate of reaction is dependent on concentrations of $S_2O_8^{2-}$ and I^-.

Answer: D
Worked solution:
Since Rate = $k[S_2O_8^{2-}(aq)][I^-(aq)]$, changes in concentrations of both reactants will affect rate. However k is affected by temperature and catalyst (as well as surface area or structure of the reactants).

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

What would be the age of a rock sample, originally lead-free, in which the molar proportion of uranium to lead is now 1:3?

A 1.5×10^9 years

B 2.25×10^9 years

C 4.5×10^9 years

D 9.0×10^9 years

Answer: D
Worked solution:
A ratio of Uranium-238 : Pb = 1:3 as stated in the question. This shows that only ¼ of Uranium-238 remains. Rock is also originally lead free. Hence 2 × half-lives have passed. Therefore age of rock is $2 \times 4.5 \times 10^9$ years = 9.0×10^9 years.

19 The equilibrium constant, K_c for the following reaction is 57.0 at 700 K.

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$

What is the equilibrium concentration of HI at 700K if the initial amounts of H_2 and I_2 are 0.100 mol and 0.200 mol respectively in a 1 dm^3 vessel?

A 0.285

B 0.457

C 1.07

D 1.14

Answer: B
Worked solution:

	$H_2\,(g)$ +	$I_2\,(g)$	$\rightleftharpoons$	$2HI\,(g)$
Initial	0.1	0.2		0
Change	-x	-x		+2x
Equilibrium	0.1 – x	0.2 – x		2x

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = 57.0$$

$$\frac{(\frac{2x}{V})^2}{(\frac{0.1-x}{V})(\frac{0.2-x}{V})} = 57.0 \Rightarrow x = 0.0941 \text{ or } 0.229$$

$[HI] = 2x = 2\,(0.0941) = 0.188$ mol dm^{-3}
Or $[HI] = 2x = 2\,(0.229) = 0.457$ mol dm^{-3}

20 The following equilibrium is established when vanadium (II) compounds are dissolved in water.

$$V^{2+} + H_2O \rightleftharpoons V^{3+} + \frac{1}{2}H_2 + OH^-$$

How could the composition of the equilibrium mixture be altered to increase the concentration of the V^{3+} ions?

A Adding an acid.

B Adding a dehydrating agent.

C Making the solution more alkaline.

D Adding a reagent that selectively precipitates V^{3+} ions.

Answer: A
Worked solution:

The position of equilibrium will shift to the RHS as there is removal of OH^- by the acid.

21 $1 \times 10^{-3}\ m^3$ of hydrogen iodide was kept at 500K and a pressure of 101 kPa until equilibrium was reached and then suddenly cooled to room temperature. The contents of the vessel were found to require 28.00 cm^3 of 0.1 mol dm^{-3} of sodium thiosulfate for complete reaction with iodine.

What is the equilibrium constant, K_C for the thermal decomposition of hydrogen iodide $2HI\ (g) \rightleftharpoons H_2\ (g) + I_2\ (g)$ at 500K?

A 1.96×10^{-3}

B 3.32×10^{-3}

C 3.74×10^{-3}

D 4.24×10^{-3}

Answer: D

Worked solution:
n (HI) = PV / RT = (101000 x 0.001) / (8.314 x 500) = 0.0243 mol
n ($Na_2S_2O_3$) = (0.1/1000) x 28 = 0.0028 mol
n (I_2) = ½ n($Na_2S_2O_3$) = 0.0014 mol
Equilibrium n (HI) = 0.0243 – 2(0.0014) = 0.0215 mol

$2HI\ (g) \rightleftharpoons H_2\ (g) + I_2\ (g)$

$$Kc = \frac{[H_2][I_2]}{[HI]^2} = \frac{(0.014)^2}{(0.0215)^2} = 4.24 \times 10^{-3}$$

22 For the equilibrium

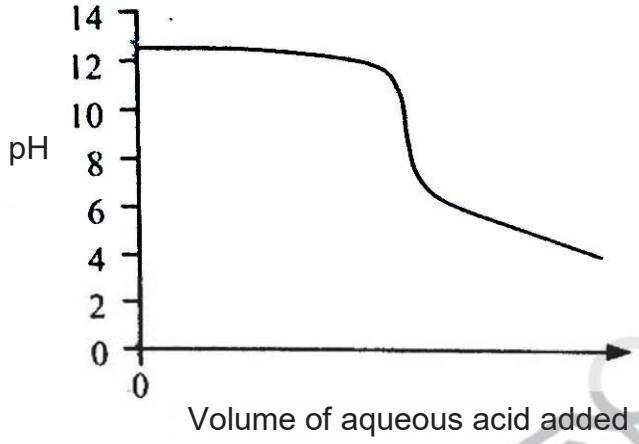
$$H_2SO_4^-\ (aq) + HPO_4^{2-}\ (aq) \rightleftharpoons HSO_4^-\ (aq) + H_2PO_4^-\ (aq)$$

Which one of the following is a conjugate Bronsted-Lowry acid-base pair?

	Base	Conjugate Acid
A	HPO_4^{2-}	$H_2PO_4^-$
B	HPO_4^{2-}	SO_4^{2-}
C	HSO_4^-	$H_2PO_4^-$
D	HSO_4^-	SO_4^{2-}

Answer: A
Worked solution:
Base HPO_4^{2-} accepts protons from HSO_4^- to form its conjugate acid $H_2PO_4^-$.

23 The graph shows a titration curve of an aqueous alkali with an aqueous acid of similar concentration.



What could be the alkali and acid in this titration?

	Alkali	Acid
A	NH_3 (aq)	CH_3CO_2H (aq)
B	NH_3 (aq)	HCl (aq)
C	NaOH (aq)	CH_3CO_2H (aq)
D	NaOH (aq)	HCl (aq)

Answer: C
Worked solution:
Strong base/weak acid titration curve.
The titration curve begins at pH 12.5 (presence of a strong base).
Equivalence point corresponds to a pH > 7 and when excess acid is added, the resulting solution has a pH 4 (presence of a weak acid).

24 An enzyme was found to operate at maximum efficiency in an aqueous solution buffered at pH 5. Which of the following would give the necessary buffer solution when dissolved in 10 dm^3 of water?

A 1 mol of HCl and 1 mol of CH_3CO_2H

B 1 mol of CH_3CO_2H and 1 mol of CH_3CO_2Na

C 1 mol of HCl and 1 mol of CH_3CO_2Na

D 1 mol of $CH_3CO_2NH_4$

Worked solution: B
The buffer solution required is an acidic buffer which is made by mixing a weak acid and the sodium salt of a weak acid.

25 The numerical value of the solubility product of strontium hydroxide, $Sr(OH)_2$, is 3.0×10^{-4}. What mass of $Sr(OH)_2$ is required to prepare a 1 dm^3 of saturated solution?

A 3.0×10^{-4} x 121.6 g

B $\frac{3.0\times10^{-4}}{2}$ x 121.6 g

C $\sqrt{3.0\times10^{-4}}$ x 121.6 g

D $\sqrt[3]{\frac{3.0\times10^{-4}}{4}}$ x 121.6 g

Answer: D
Worked solution:
$Sr(OH)_2\ (s) \rightleftharpoons Sr^{2+}\ (aq) + 2OH^-\ (aq)$ let $[Sr^{2+}]$ = x mol dm^{-3}
$K_{sp} = [Sr^{2+}][OH^-]^2 = 3.0 \times 10^{-4}$

$(x)\ (2x)^2 = 3.0 \times 10^{-4} \Rightarrow x = \sqrt[3]{\frac{3.0\times10^{-4}}{4}}$ mol dm^{-3}

Mass of $Sr(OH)_2 = \sqrt[3]{\frac{3.0\times10^{-4}}{4}}$ x 121.6 g

26 Aluminium hydroxide is a sparingly soluble salt but is often used in tablets taken to relieve the effects of heartburn and stomach ulcers. In aqueous solution, it dissociates according to the following equation:

$Al(OH)_3(s) + aq \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$

If the solubility product, K_{sp} of $Al(OH)_3$ is x, what is the value of $[Al^{3+}(aq)]$ at equilibrium?

A $(x)^{\frac{1}{4}}$

B $(\frac{1}{3}x)^{\frac{1}{4}}$

C $(\frac{1}{9}x)^{\frac{1}{4}}$

D $(\frac{1}{27}x)^{\frac{1}{4}}$

Answer: D
Worked solution:
Let $[Al^{3+}] = y$, $K_{sp} = [Al^{3+}][OH^-]^3 = x$

$$(y)\ (3y)^3 = x \Rightarrow y = (\frac{1}{27}x)^{\frac{1}{4}}$$

27 The numerical values of the solubility product of calcium carbonate and calcium fluoride are 8.7×10^{-9} and 4.0×10^{-11} respectively at 25 °C.

Which of the following statements is true?

A Calcium fluoride has a higher solubility than calcium carbonate.

B Addition of sodium fluoride to a saturated solution of calcium fluoride increases the solubility of calcium fluoride.

C Addition of sodium fluoride to a solution containing calcium fluoride decreases the solubility product of calcium fluoride.

D Addition of calcium nitrate to a solution containing fluoride ions and carbonate ions, both 1 mol dm^{-3}, causes calcium fluoride to precipitate out first.

Answer: A

Worked solution:

Calculate and compare solubilities of $CaCO_3$ and CaF_2 since they are of different formula types.

$K_{sp}\ (CaCO_3) = [Ca^{2+}]\ [CO_3^{2-}] = 8.7 \times 10^{-9} \Rightarrow x^2 = 8.7 \times 10^{-9} \Rightarrow x = 9.33 \times 10^{-5}$

$K_{sp}\ (CaF_2) = [Ca^{2+}]\ [F^-]^2 = 4.0 \times 10^{-11} \Rightarrow 4y^3 = 4.0 \times 10^{-11} \Rightarrow y = 2.15 \times 10^{-4}$

solubility of calcium fluoride is higher than calcium carbonate.

28 Compound S has the following structure:

$(CH_3)_2C{=}CHCH_2CH(OH)CH_2CH{=}C(CH_3)_2$

What is the total number of stereoisomers possible for this molecule?

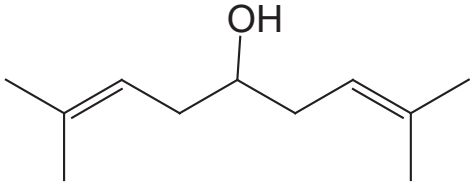
A 0 **B** 1 **C** 2 **D** 3

Answer: A

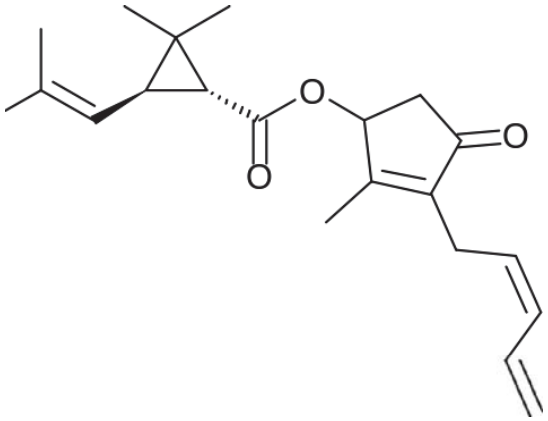
Worked solution:

No chiral centres therefore does not exhibit optical isomerism.

Does not exhibit cis-trans isomerism.



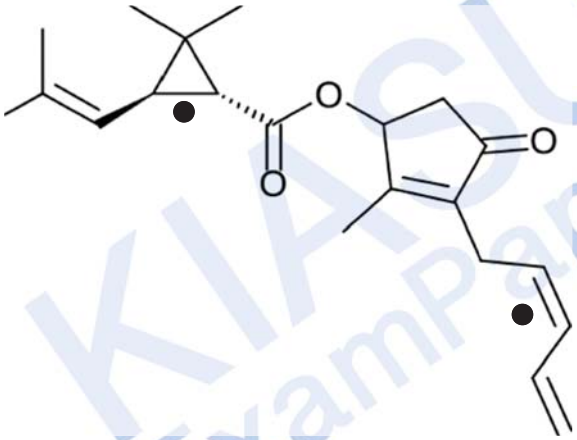
29 Pyrethrin is a natural insecticide made from some chrysanthemum species.



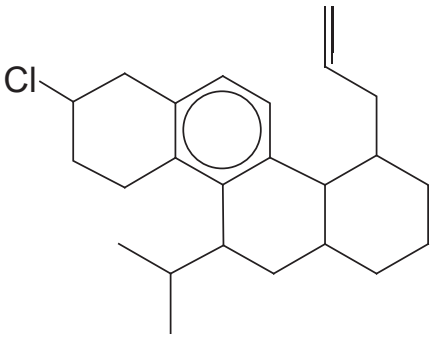
What is the total number of *cis-trans* isomers that are possible for this organic molecule?

A 2 **B** 4 **C** 8 **D** 16

Answer: B
Worked solution:

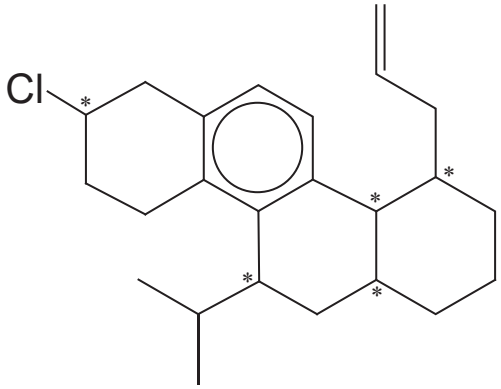


30 How many chiral centres are there in the molecule shown below?



A 4 **B** 5 **C** 6 **D** 7

Answer: B
Worked solution



Section B

For each of the questions in this section one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements which you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

31 Which of the following properties can be explained in terms of hydrogen bonding?

1 Ammonia is very soluble in water.

2 Ice is less dense than water.

3 The relative molecular mass of ethanoic acid is 120 in benzene.

Answer: A
Worked solution:
Hydrogen bonding formed between the lone pair of electrons on N atom in ammonia and the H atom in water.
Water molecules in ice form an open structure with two hydrogen bonds per molecule.
Ethanoic acid dimerises via hydrogen bonding in benzene.

32 For which of the following reactions does the value of ΔH^{θ} represent **both** a standard enthalpy change of combustion **and** a standard enthalpy change of formation?

1 $C(s) + O_2(g) \rightarrow CO_2(g)$

2 $2C(s) + O_2(g) \rightarrow 2CO(g)$

3 $NO(g) + \frac{1}{2} O_2(g) \rightarrow NO_2(g)$

Answer: D
Worked solution:
Only 1 represents both enthalpy of combustion and formation. 2, produces two moles of CO, hence is not the enthalpy of formation of CO. 3 is the enthalpy of combustion of NO. It is not an enthalpy of formation equation because NO is not an element.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

33 Which of the following are always endothermic processes?

1 the hydration of a gaseous cation

2 the dissociation of a diatomic molecule into atoms

3 the sublimation of a solid

Answer: C
Worked solution:
Energy is needed to break up a covalent bond between two atoms in a molecule. Sublimation is the conversion of molecules in a solid into gaseous molecules. That requires energy. Hydration involves forming ion-dipole bonds hence is exothermic.

34 The rate equation for the reaction 2A + B → C + D is given as Rate = k[A][B]. The initial concentration of A = 0.20 mol dm^{-3} and the initial concentration of B = 0.001 mol dm^{-3}.

Which of the following statements regarding the experiments are correct?

1 The half-life for the [B] against time curve is approximately constant.

2 The mechanism for the above reaction involves more than one step.

3 Changing the initial concentration of A to 0.002 mol dm^{-3} will not affect the half-life of B.

Answer: B
Worked solution:
Only statement one and two are correct. The concentration of A is 200 times larger than B, hence a pseudo 1st order kinetics wrt B is created.
Rate = k' [B], where k' = k [A]

Therefore half-life of B will be approximately constant having a value of $t_{½} = \frac{\ln 2}{0.2\ k}$.

And since stoichiometry shows that 2A of reactants are involved, the reaction will have more than one step as the slow step involves only 1A and 1B leaving the other A molecule to be involved in the fast step.
Changing the [A] to 0.002 mol dm^{-3}, removes the pseudo 1st order kinetics and the half-life will not be constant anymore.

35 Consider the equilibrium: $2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g)$ $\Delta H = -197\ kJ\ mol^{-1}$

Which of the following would increase if temperature increases?

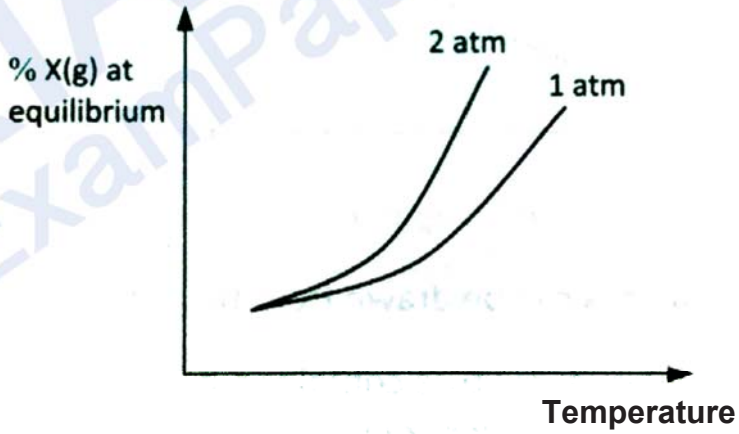
1 Amount of SO_2.

2 Rate of both forward and backward reaction.

3 Equilibrium constant, K_p.

Answer: B
Worked solution:
When temperature increases, equilibrium will shift left to reduce the temperature. Thus, $[SO_2]$ and $[O_2]$ increases. K_p decreases. Both rates of forward and backward reaction increase as temperature increases.

36 The graph below shows how the percentage of reactant X(g) that remained in an equilibrium mixture varies with temperature at pressures of 1 atm and 2 atm.



Which of the following conclusions about the reaction can be drawn from this information?

1 The equation for the above reaction could be $X(g) \rightleftharpoons Y(g) + Z(g)$

2 The reaction is endothermic in the forward reaction.

3 The equilibrium constant K_p decreases as pressure increases.

Answer: D
Worked solution:
As pressure increased from 1 atm to 2 atm, the position of equilibrium shifts left to form more reactant X. By LCP, the no. of moles of gas molecules of reactant must be lower than that of products.
From low to high temperature, the backward reaction is favoured as the % of X at equilibrium increases. Therefore, the forward reaction must be exothermic.
K_p remains constant.

37 Which of the following can affect the magnitude of the solubility product K_{sp}, of silver sulfide, Ag_2S, when it is precipitated by passing H_2S (g) into aqueous silver nitrate?

1 an increase in temperature

2 the addition of silver nitrate solution

3 the presence of an excess acid

Worked solution: D
Ksp is only affected by changes in temperature

38 A metal hydroxide dissolves partially in water as shown

$$M(OH)_2\ (s) + aq \rightleftharpoons M^{2+}\ (aq) + 2OH^-\ (aq) \qquad \Delta H > 0$$

Which of the following are true as temperature increases?

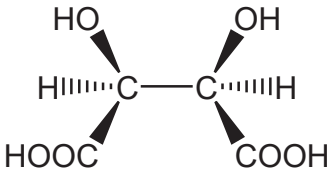
1 Equilibrium is reached at a faster rate

2 $[OH^-]$ increases

3 K_{sp} increases

Answer: A
Worked solution:
The forward reaction is endothermic. When temperature increases, the position of equilibrium shifts right at a faster rate, achieving equilibrium faster. More OH^- ions are produced at higher temperatures. Therefore the K_{sp} is also increased as $K_{sp} = [OH^-][M^{2+}]$

39 The structure below represents meso-tartaric acid.



Which of the following statements explains why this isomer of tartaric acid **does not** exhibit optical activity?

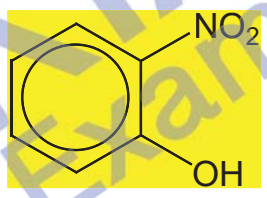
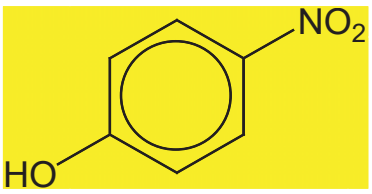
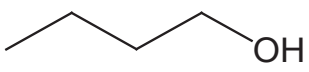
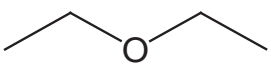
1 The molecule contains a plane of symmetry.

2 The molecule has net dipole moment which cancels out the rotation of plane polarised light.

3 Hydrogen bond formation prevents the molecule from rotating plane-polarised light.

Answer: D
Worked solution:
Even though the compound contains chiral carbon, the plane of symmetry cancel out the rotation of plane polarised light.

40 In which one of the following pairs of compounds is the boiling point of the second compound **B** higher than the first compound **A**?

	A	**B**
1		
2		
3		

Answer: B
Worked solution:
Option 1: Intramolecular H bonding occurs in compound A, it minimises intermolecular H bonding, lowering the boiling point. Compound B has intermolecular H bonding.

Option 2: Both A and B have similar Mr but the surface area for Van der Waals' forces of attraction in A is lower than B. Thus boiling point of B is higher.
Option 3: Compound A has intermolecular hydrogen bonding but compound B has pd-pd forces of attraction. Therefore compound A has a higher boiling point.

2012 NYJC JC1 H2 Chemistry Promo Exam Answer Key

1	B	11	D	21	D	31	A
2	A	12	A	22	A	32	D
3	C	13	A	23	C	33	C
4	B	14	A	24	B	34	B
5	C	15	B	25	D	35	B
6	D	16	C	26	D	36	D
7	D	17	D	27	A	37	D
8	D	18	D	28	A	38	A
9	A	19	B	29	B	39	D
10	C	20	A	30	B	40	B

NANYANG JUNIOR COLLEGE
JC 1 PROMOTIONAL EXAMINATION
Higher 2

CHEMISTRY

9647/01

Paper 1 Multiple Choice

5 October 2012

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Write your name, class and tutor's name on the Answer Sheet in the spaces provided unless this has been done for you.

There are **forty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record you choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.

This document consists of **18** printed pages.

Section A

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

1 Bromine gas is toxic. The maximum safe toleration level of bromine gas in air is 0.004 mg dm^{-3}. How many bromine atoms are present in 1 dm^3 of air at this toleration level?

A 1.50×10^{16} **B** 3.00×10^{16}

C 6.00×10^{16} **D** 3.00×10^{19}

2 Group I and Group II ionic hydrides react with water.

$$H^- + H_2O \rightarrow OH^- + H_2$$

In an experiment, 1 g of a sample of an ionic hydride is dissolved in excess H_2O. The resulting solution required 24.0 cm^3 of a 2.0 mol dm^{-3} HCl solution for complete neutralisation.

What is the formula of the hydride?

A CaH_2 **B** LiH

C MgH_2 **D** NaH

3 Carbon disulfide, CS_2, a volatile flammable liquid used in the manufacture of cellophane, is oxidised on combustion as follows:

$$CS_2\,(g) + 3O_2\,(g) \rightarrow CO_2\,(g) + 2SO_2\,(g)$$

A 20 cm^3 sample of carbon disulfide vapour is ignited with 100 cm^3 of oxygen. The final volume of gas after burning is passed into an excess of aqueous alkali. What percentage of this final volume dissolved in the alkali? (All volumes are measured at the same temperature and pressure, conditions under which CS_2 is a gas.)

A 20% **B** 40% **C** 60% **D** 80%

4 Which of the following formulae represents a particle with the composition 1 proton, 1 neutron and 2 electrons?
(D represents deuterium, ^{2}H)

A D **B** D^-

C H^- **D** He

5 The first seven ionization energies of an element are as follows (in kJ mol^{-1}):

790, 1600, 3200, 4400, 16100, 19800, 23800

The outer electronic configuration of the element is

A ns^1

B ns^2

C $ns^2\,np^2$

D $ns^2\,np^5$

6 Which of the following is incorrect for $^{31}P^{3-}$?

A It is more polarizable than N^{3-}.

B It is isoelectronic with argon.

C Its valence p-orbitals are completely filled.

D It is smaller than a phosphorus atom.

7 The C_2H_2 molecule is linear. What can be deduced from this about the numbers of σ and π bonds present in the molecule?

	σ	π
A	2	2
B	2	3
C	3	1
D	3	2

8 Which of the following is the most significant intermolecular force in SO_2?

A ionic bonding

B covalent bonding

C Van der Waals' attractions

D permanent dipole-permanent dipole attractions

9 The variation in bond angles in the molecules of ammonia and water is due to

A the number of lone electron pairs in the molecule

B a bonding electron pair having greater repulsive force than a lone pair

C a greater repulsion between hydrogen atoms in the longer N-H bond length

D a greater repulsion between the hydrogen atoms in the shorter N-H bond length

10 For which of the following pairs does the first species have a smaller bond angle?

A CH_4, $SiCl_4$

B PH_4^+, ICl_4^-

C F_2O, H_2O

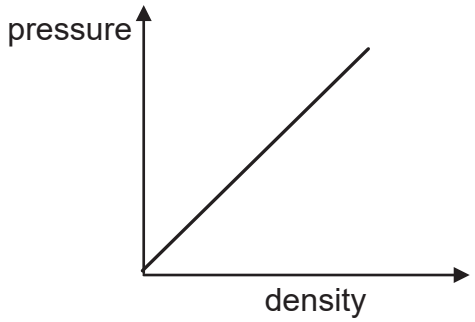
D SO_3, PH_3

11 SF_4 reacts with $(CH_3)_4NF$ to form $(CH_3)_4N^+SF_5^-$. Which of the following **correctly** describes the shape of the ions in the product?

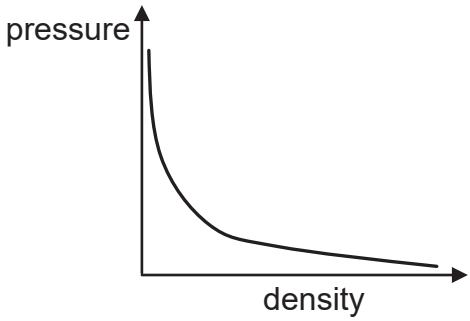
	Shape of cation (wrt N)	**Shape of anion**
A	trigonal pyramidal	square planar
B	square planar	trigonal bipyramidal
C	tetrahedral	octahedral
D	tetrahedral	square pyramidal

12 Which of the following diagrams correctly describes the behaviour of a fixed mass of an ideal gas at constant temperature?

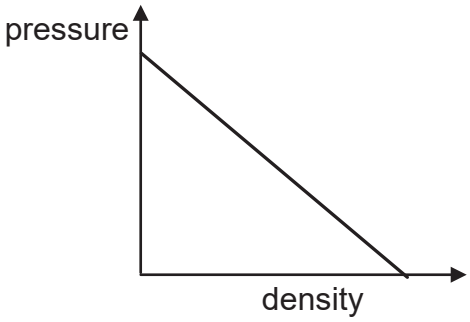
A



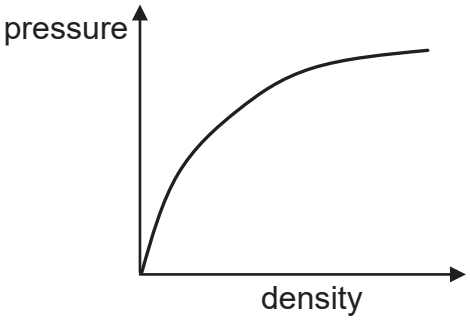
B



C



D



13 At constant pressure, the following reaction is exothermic.

$$2NO_2\,(g) \rightarrow N_2O_4\,(g)$$

The reaction is

A only spontaneous at low temperatures.

B only spontaneous at high temperatures.

C always spontaneous.

D never spontaneous.

14 For which of the following is the lattice energy likely to have the greatest magnitude?

A lithium fluoride

B lithium iodide

C sodium chloride

D sodium fluoride

15 Phosphine, (PH_3), reacts with hydrogen iodide to form phosphonium iodide in the reaction shown.

$$PH_3\,(g) + HI\,(g) \rightarrow PH_4^+I^-\,(s)\ ,\ \Delta H^{\theta} = -101.8\ kJ\ mol^{-1}$$

Given that $\Delta H_f{}^{\theta}$ for PH_3 (g) = +5.4 kJ mol^{-1}, and $\Delta H_f{}^{\theta}$ for HI (g) = +26.5 kJ mol^{-1}, what is the standard enthalpy change of formation of phosphonium iodide?

A $-133.7\ kJ\ mol^{-1}$

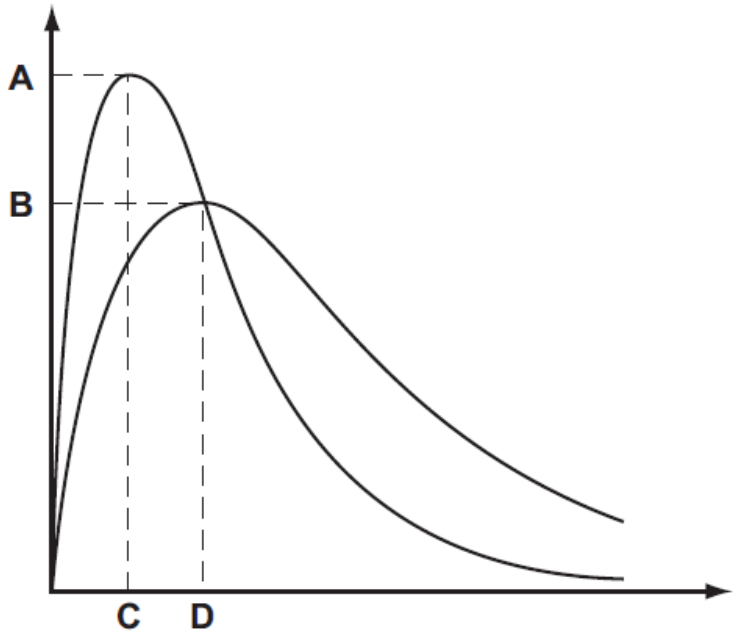
B $-69.9\ kJ\ mol^{-1}$

C $+69.9\ kJ\ mol^{-1}$

D $+133.7\ kJ\ mol^{-1}$

16 The diagram shows the Maxwell-Boltzmann energy distribution curves for molecules of a sample of a gas at two different temperatures.

Which letter on the axes represents the most probable energy of the molecules at the lower temperature?



17 The rate equation for the reaction

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

is rate = $k[S_2O_8^{2-}(aq)][I^-(aq)]$, where k is the rate constant.

Which of the following conclusions can be drawn from this information?

A The value of k depends on the concentrations of $S_2O_8^{2-}$ and I^-.

B The value of k depends on the rate of the reaction.

C The value of k is dependent only on changes in temperature.

D The rate of reaction is dependent on concentrations of $S_2O_8^{2-}$ and I^-.

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

What would be the age of a rock sample, originally lead-free, in which the molar proportion of uranium to lead is now 1:3?

A 1.5×10^9 years

B 2.25×10^9 years

C 4.5×10^9 years

D 9.0×10^9 years

19 The equilibrium constant, K_c for the following reaction is 57.0 at 700 K.

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$

What is the equilibrium concentration of HI at 700K if the initial amounts of H_2 and I_2 are 0.100 mol and 0.200 mol respectively in a 1 dm^3 vessel?

A 0.285

B 0.457

C 1.07

D 1.14

20 The following equilibrium is established when vanadium (II) compounds are dissolved in water.

$$V^{2+} + H_2O \rightleftharpoons V^{3+} + \frac{1}{2}H_2 + OH^-$$

How could the composition of the equilibrium mixture be altered to increase the concentration of the V^{3+} ions?

A Adding an acid.

B Adding a dehydrating agent.

C Making the solution more alkaline.

D Adding a reagent that selectively precipitates V^{3+} ions.

21 1×10^{-3} m^3 of hydrogen iodide was kept at 500K and a pressure of 101 kPa until equilibrium was reached and then suddenly cooled to room temperature. The contents of the vessel were found to require 28.00 cm^3 of 0.1 mol dm^{-3} of sodium thiosulfate for complete reaction with iodine.

What is the equilibrium constant, K_C for the thermal decomposition of hydrogen iodide $2HI\ (g) \rightleftharpoons H_2\ (g) + I_2\ (g)$ at 500K?

A 1.96×10^{-3}

B 3.32×10^{-3}

C 3.74×10^{-3}

D 4.24×10^{-3}

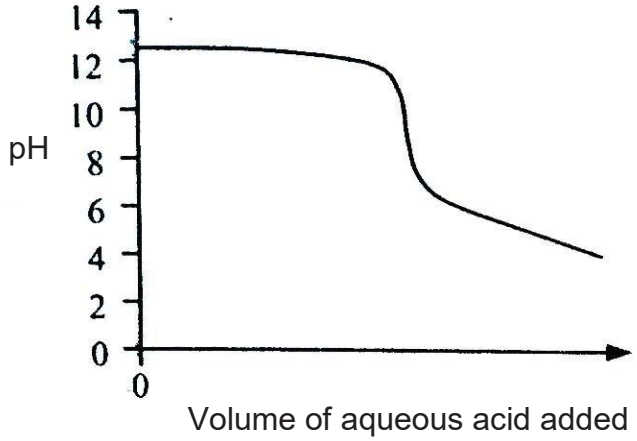
22 For the equilibrium:

$$H_2SO_4^-\ (aq) + HPO_4^{2-}\ (aq) \rightleftharpoons HSO_4^-\ (aq) + H_2PO_4^-\ (aq)$$

Which one of the following is a conjugate Bronsted-Lowry acid-base pair?

	Base	**Conjugate Acid**
A	HPO_4^{2-}	$H_2PO_4^-$
B	HPO_4^{2-}	SO_4^{2-}
C	HSO_4^-	$H_2PO_4^-$
D	HSO_4^-	SO_4^{2-}

23 The graph shows a titration curve of an aqueous alkali with an aqueous acid of similar concentration.



What could be the alkali and acid in this titration?

	Alkali	Acid
A	NH_3 (aq)	CH_3CO_2H (aq)
B	NH_3 (aq)	HCl (aq)
C	NaOH (aq)	CH_3CO_2H (aq)
D	NaOH (aq)	HCl (aq)

24 An enzyme was found to operate at maximum efficiency in an aqueous solution buffered at pH 5. Which of the following would give the necessary buffer solution when dissolved in 10 dm^3 of water?

A 1 mol of HCl and 1 mol of CH_3CO_2H

B 1 mol of CH_3CO_2H and 1 mol of CH_3CO_2Na

C 1 mol of HCl and 1 mol of CH_3CO_2Na

D 1 mol of $CH_3CO_2NH_4$

25 The numerical value of the solubility product of strontium hydroxide, $Sr(OH)_2$, is 3.0 x 10^{-4}. What mass of $Sr(OH)_2$ is required to prepare a 1 dm^3 of saturated solution?

A 3.0×10^{-4} x 121.6 g

B $\frac{3.0 \times 10^{-4}}{2}$ x 121.6 g

C $\sqrt{3.0 \times 10^{-4}}$ x 121.6 g

D $\sqrt[3]{\frac{3.0 \times 10^{-4}}{4}}$ x 121.6 g

26 Aluminium hydroxide is a sparingly soluble salt but is often used in tablets taken to relieve the effects of heartburn and stomach ulcers. In aqueous solution, it dissociates according to the following equation:

$$Al(OH)_3\,(s) + aq \rightleftharpoons Al^{3+}\,(aq) + 3OH^-\,(aq)$$

If the solubility product, K_{sp} of $Al(OH)_3$ is x, what is the value of $[Al^{3+}(aq)]$ at equilibrium?

A $(x)^{\frac{1}{4}}$

B $(\frac{1}{3}x)^{\frac{1}{4}}$

C $(\frac{1}{9}x)^{\frac{1}{4}}$

D $(\frac{1}{27}x)^{\frac{1}{4}}$

27 The numerical values of the solubility product of calcium carbonate and calcium fluoride are 8.7×10^{-9} and 4.0×10^{-11} respectively at 25 °C.
Which of the following statements is true?

A Calcium fluoride has a higher solubility than calcium carbonate.

B Addition of sodium fluoride to a saturated solution of calcium fluoride increases the solubility of calcium fluoride.

C Addition of sodium fluoride to a solution containing calcium fluoride decreases the solubility product of calcium fluoride.

D Addition of calcium nitrate to a solution containing fluoride ions and carbonate ions, both 1 mol dm^{-3}, causes calcium fluoride to precipitate out first.

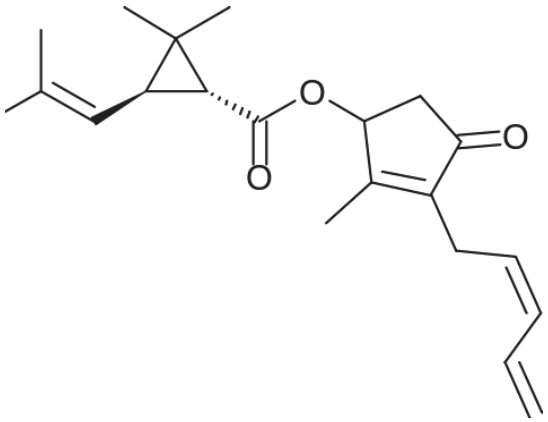
28 Compound S has the following structure:

$$(CH_3)_2C{=}CHCH_2CH(OH)CH_2CH{=}C(CH_3)_2$$

What is the total number of stereoisomers possible for this molecule?

A 0 **B** 1 **C** 2 **D** 3

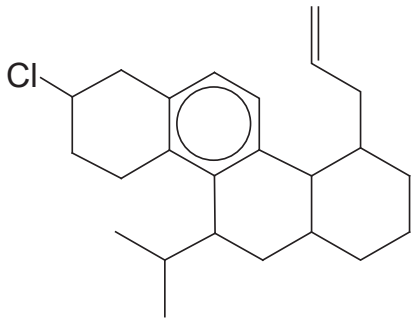
29 Pyrethrin is a natural insecticide made from some chrysanthemum species.



What is the total number of *cis-trans* isomers that are possible for this organic molecule?

A 2 **B** 4 **C** 8 **D** 16

30 How many chiral centres are there in the molecule shown below?



A 4 **B** 5 **C** 6 **D** 7

Section B

For each of the questions in this section one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements which you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

31 Which of the following properties can be explained in terms of hydrogen bonding?

1 Ammonia is very soluble in water.

2 Ice is less dense than water.

3 The relative molecular mass of ethanoic acid is 120 in benzene.

32 For which of the following reactions does the value of ΔH^{θ} represent **both** a standard enthalpy change of combustion **and** a standard enthalpy change of formation?

1 $C\,(s) + O_2\,(g) \rightarrow CO_2\,(g)$

2 $2C\,(s) + O_2\,(g) \rightarrow 2CO\,(g)$

3 $NO\,(g) + \frac{1}{2}\,O_2\,(g) \rightarrow NO_2\,(g)$

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

33 Which of the following are always endothermic processes?

1 the hydration of a gaseous cation

2 the dissociation of a diatomic molecule into atoms

3 the sublimation of a solid

34 The rate equation for the reaction 2A + B → C + D is given as Rate = k[A][B]. The initial concentration of A = 0.20 mol dm^{-3} and the initial concentration of B = 0.001 mol dm^{-3}.

Which of the following statements regarding the experiments are correct?

1 The half-life for the [B] against time curve is approximately constant.

2 The mechanism for the above reaction involves more than one step.

3 Changing the initial concentration of A to 0.002 mol dm^{-3} will not affect the half-life of B.

35 Consider the equilibrium: $2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g)$ $\Delta H = -197$ kJ mol^{-1}

Which of the following would increase if temperature increases?

1 amount of SO_2

2 rate of both forward and backward reaction

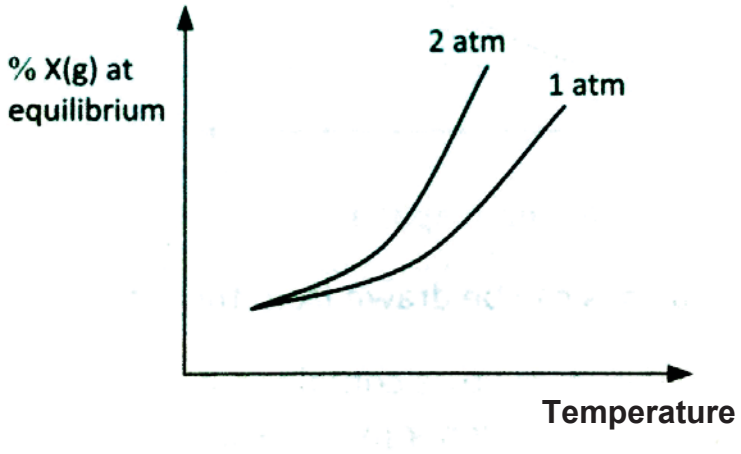
3 equilibrium constant, K_p

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

36 The graph below shows how the percentage of reactant X(g) that remained in an equilibrium mixture varies with temperature at pressures of 1 atm and 2 atm.



Which of the following conclusions about the reaction can be drawn from this information?

1 The equation for the above reaction could be $X(g) \rightleftharpoons Y(g) + Z(g)$

2 The reaction is endothermic in the forward reaction.

3 The equilibrium constant K_p decreases as pressure increases.

37 Which of the following can affect the magnitude of the solubility product K_{sp}, of silver sulfide, Ag_2S, when it is precipitated by passing H_2S (g) into aqueous silver nitrate?

1 an increase in temperature

2 the presence of an excess acid

3 the addition of silver nitrate solution

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

38 A metal hydroxide dissolves partially in water as shown

$$M(OH)_2\,(s) + aq \rightleftharpoons M^{2+}\,(aq) + 2OH^-\,(aq) \qquad \Delta H > 0$$

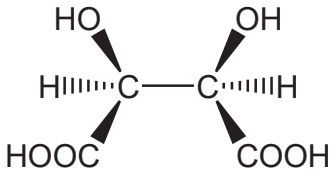
Which of the following are true as temperature increases?

1 equilibrium is reached at a faster rate

2 $[OH^-]$ increases

3 K_{sp} increases

39 The structure below represents meso-tartaric acid.



Which of the following statements explains why this isomer of tartaric acid **does not** exhibit optical activity?

1 The molecule contains a plane of symmetry.

2 The molecule has net dipole moment which cancels out the rotation of plane polarised light.

3 Hydrogen bond formation prevents the molecule from rotating plane-polarised light.

The responses **A** to **D** should be selected on the basis of

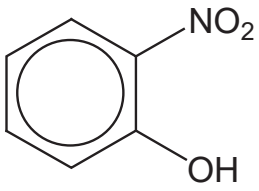
A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

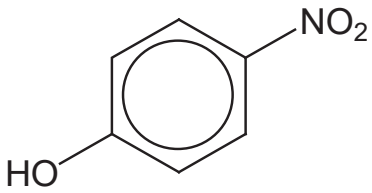
No other combination of statements is used as a correct response.

40 In which one of the following pairs of compounds is the boiling point of the second compound **B** higher than the first compound **A**?

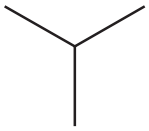
A **B**

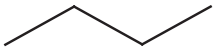
1



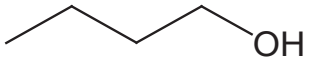


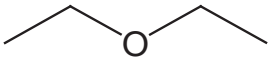
2





3





H

NANYANG JUNIOR COLLEGE
JC 1 PROMOTIONAL EXAMINATION
Higher 2

CANDIDATE NAME **Answers**

CLASS

TUTOR'S NAME

CHEMISTRY

9647/02

Paper 2 Structured

5 October 2012

1 hour 30 minutes

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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Answer **all** questions in the spaces 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	/12
2	/15
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Total	/52

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1 Planning (P)

A student is interested to determine the standard enthalpy change of combustion (ΔH_c) of propanol, C_3H_7OH (l), using common apparatus found in the school laboratory.

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Given that ΔH_c of ethanol, C_2H_5OH (l), is −1371 kJ mol^{-1}, the student first carried out an experiment using ethanol to determine the **heat capacity**, **C**, of his set-up and obtained the following data:

Mass of ethanol and spirit lamp before combustion = 532.68 g

Mass of ethanol and spirit lamp after combustion = 531.30 g

Volume of water = 200 cm^3

Initial temperature of water = 25.0 ^oC

Final temperature of water = 36.3 ^oC

Using the data the student gathered, determine the **heat capacity, C (kJ K^{-1})**, of his set-up.

Ans:

$$\Delta H = \frac{C \times \Delta T}{n_{ethanol}}$$

$$C = \frac{\Delta H \times n_{ethanol}}{\Delta T}$$

$$= \left(\frac{1371 \times \frac{532.68 - 531.3}{46.0}}{(36.3 - 25.0)} \right)$$

$$= 3.640$$

$$= 3.64 \text{ kJ K}^{-1}$$

[2]

(b) Determining ΔH_c of propanol

The student carried out the experiment using the same set-up, this time using propanol as fuel and obtained the following data:

Mass of propanol and spirit lamp before combustion = 538.74 g

Mass of propanol and spirit lamp after combustion = 536.34 g

Volume of water = 200 cm^3

Initial temperature of water = 25.0 ^oC

Final temperature of water = 47.2 ^oC

Use the data above and your answer in **(a)** to determine the enthalpy of combustion of propanol.

Ans:

$$\Delta H = \frac{C \times \Delta T}{n_{ethanol}}$$

$$= \left(\frac{3.640 \times (47.2 - 25.0)}{\frac{538.74 - 536.34}{60.0}} \right)$$

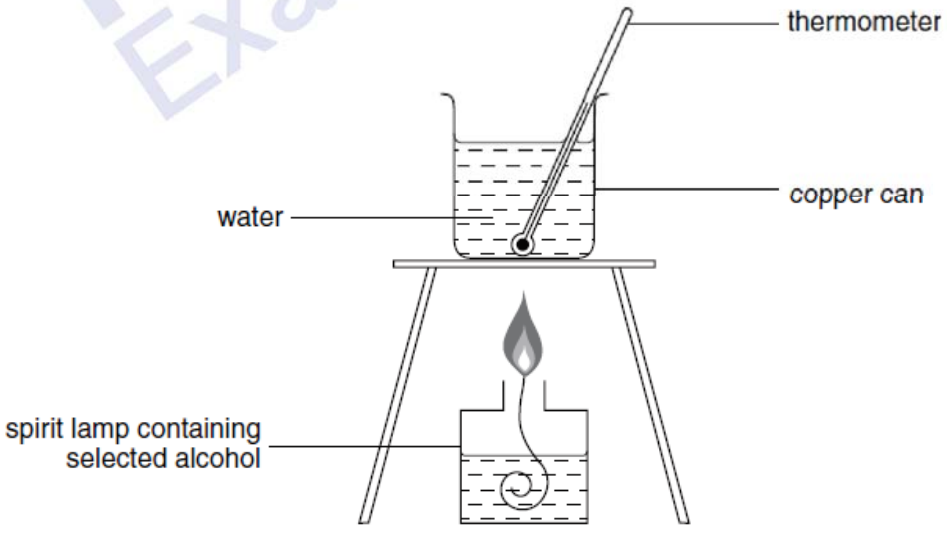
$$= 2020 \text{ kJ mol}^{-1}$$

[2]

(c) Experimental procedures

Draw a labelled diagram to show the set-up the student used to obtain the data for determining ΔH_c of propanol.
Hence, describe the procedure for the experiment.

Ans:



[5]

1. Fill the copper can with 200 cm^3 water and set up the apparatus as in the diagram. Measure and record the initial temperature of the water with a 0.2 °C division thermometer.

2. Weigh and record the initial mass of the entire spirit lamp.

3. Light up the spirit lamp. Stir the contents of the copper can to ensure even mixing until there is a 5 ~ 10 °C rise in temperature. Blow to extinguish the flame and record the maximum temperature.

4. Reweigh the entire spirit lamp

[5]

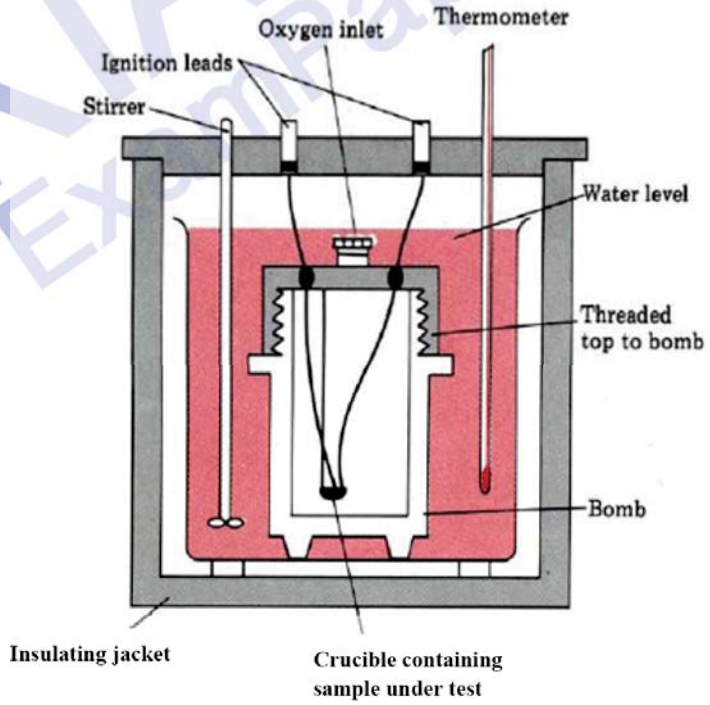
(d) Identify a potential hazard associated with this experiment, and suggest how the hazard can be kept to a minimum.

Any one of the following points:

- Alcohol is volatile and toxic; hence containers of alcohols should be covered when not in use / Proper disposal of alcohols after experiment.
- Alcohol is flammable and may cause a fire if ignited accidentally; hence there should be no naked flames near the chemicals.

[2]

(e) A bomb calorimeter is a type of constant-volume calorimeter that is used to measure accurately the enthalpy of combustion of a particular reaction.



Though highly accurate, the bomb calorimeter is also complex to use and very expensive.

Suggest a reason for the improved accuracy of the Bomb calorimeter compared to the experimental set-up you described in **(c)**.

Any one of the following points:

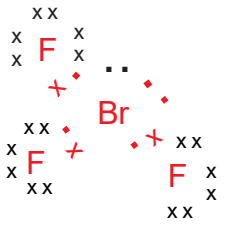
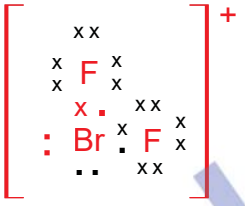
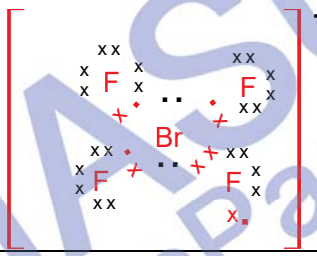
- Air jacket around the calorimeter prevents heat loss to surrounding / acts as insulator.
- Mechanical stirrer helps to ensure heat is evenly distributed in the water; hence temperature measured will be accurate.
- Water completely surrounds the bomb calorimeter to ensure that heat generated will be completely transferred to water.
- Sample is ignited electrically; helps minimize error due to heat loss when naked flame is used / heat contributed by burning of wick.

[1]

[Total: 12]

2 Halogens can react with each other to form interhalogen compounds. These compounds are of special importance as highly reactive intermediates and for providing useful insights into bonding.

(a) (i) Construct dot-and-cross diagrams to illustrate the bonding in **BrF_3**, **BrF_2^+** and **BrF_4^-**. Use the Valence Shell Electron Pair Repulsion theory to predict their shapes.

Species	Dot-and-cross diagram	Shape
BrF_3		T-shaped wrt Br atom: 3 bp, 2 lp
BrF_2^+		Bent wrt Br atom: 2 bp, 2 lp
BrF_4^-		Square planar wrt Br atom: 4 bp, 2 lp

(ii) BrF_3 is a covalent compound which exhibits electrical conductivity in the liquid state at room temperature. By means of writing an equation, suggest an explanation for its electrical conductivity.

BrF_3 ionises in the liquid state to give free mobile ions which can conduct electricity.

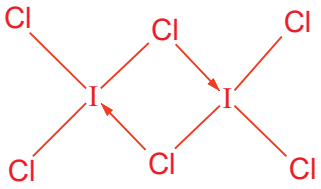
$2BrF_3 \longrightarrow BrF_2^+ + BrF_4^-$

[8]

(b) The compound ICl_3 does not exist but the dimer I_2Cl_6 exists as a yellow solid.

Draw a diagram to illustrate the bonding in the dimer and suggest the bond angle with respect to the iodine atom in the dimer.

Ans:



Bond angle with respect to iodine atom: 109^{o}

[2]

(c) 0.270 g of a metallic salt containing the anion $I_xCl_y^-$ decomposed when heated to form iodine vapour and the metallic chloride. The iodine evolved was bubbled into excess potassium iodide solution.

The dissolved iodine required 21.30 cm^3 of 0.0600 mol dm^{-3} of aqueous sodium thiosulfate for complete reaction. When the residue was dissolved in water, the resultant solution required 6.40 cm^3 of 0.100 mol dm^{-3} aqueous silver nitrate for complete reaction.

(i) Determine the value of ***x*** and ***y*** in $I_xCl_y^-$.

$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$

$n_{S_2O_3^{2-}} = \frac{0.0600}{1000} \times 21.30 = 1.278 \times 10^{-3}$ mol

$n_{I^-} = 1.278X10^{-3}$ mol

$n_{AgNO_3} = \frac{0.100}{1000} \times 6.40 = 6.39X10^{-4}$ mol

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

$n_{Cl^-} = 6.39 \times 10^{-4}$ mol

mole ratio of I^-: Cl^- = **x : y**

$=1.278X10^{-3}$ **:** 6.39×10^{-4}

= **2 : 1**

Hence x = 2 & y = 1

(ii) Hence, determine the identity of the metallic element.

$n_{I_xCl_y^-} = 6.39X10^{-4}$ mol

M_r of the metallic salt = $\frac{0.270}{6.4 \times 10^{-4}} = 421.9$

A_r of metal = 421.9 – (79.9 X 2) – 35.5 = 133

Identity of the metallic element: Caesium / Cs

[5]

[Total: 15]

3 The decomposition of calcium carbonate follows the equation:

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$$

Given that for this reaction, ΔH^{θ} = + 178 kJ mol^{-1} and ΔG^{θ} = + 130 kJ mol^{-1},

(a) (i) Calculate a value for the standard entropy change ΔS^{θ} for the reaction.

Using $\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta}$,
$+130 = (+178) - 298\ (\Delta S^{\theta})$
$\Delta S^{\theta} = +0.161$ kJ mol^{-1} K^{-1}

(ii) Hence, explain the significance of the sign of ΔS^{θ} obtained.

ΔS^{θ}, being positive, means the reaction goes with a decrease in order of the system. This is due to the formation of 1 mole of $CO_2(g)$ in the reaction.

[3]

(b) (i) Calculate the temperature at which the reaction becomes feasible.

Reaction is spontaneous when $\Delta G^{\theta} < 0$
$\Delta H^{\theta} - T\Delta S^{\theta} < 0$
$(+178) - T\,(+0.161) < 0$
$T > 1106$ K
Hence, the reaction becomes spontaneous when temperature is greater than 1106 K.

(ii) State an assumption made in the calculation above.

The assumption is that ΔH^{θ} and ΔS^{θ} do not change with temperature

[3]

[Total: 6]

4 In the vapour phase, methanoic acid associates to form dimers.

$$2HCOOH\ (g) \rightleftharpoons (HCOOH)_2\ (g)$$

At 227 °C and 1.50 x 10^5 Pa, 0.155 g of methanoic acid vapour occupies 69.3 cm^3.

Calculate

(a) (i) the average relative molecular mass of the gaseous mixture

$$pV = nRT$$

$$pV = \frac{m}{M}RT$$

$$M = \frac{(0.155)(8.314)(227+273)}{(1.50\times10^5)(69.3\times10^{-6})}$$

$$= 62.0\ g\ mol^{-1}$$

Mr = 62.0 (1 dpl)

[2]

(ii) α, the degree of association of methanoic acid, defined as the fraction of the methanoic acid that associates, using the formula

$$\alpha = 2\left[\frac{\text{average } M_r - M_r(HCOOH)}{\text{average } M_r}\right]$$

Ans:

$$\alpha = 2\left[\frac{\text{average Mr-Mr(HCOOH)}}{\text{average Mr}}\right]$$

$$= 2\left[\frac{62.0-46.0}{62.0}\right]$$

$$= 0.516$$

[1]

(iii) the partial pressures of HCOOH and $(HCOOH)_2$ at equilibrium.

Let the initial amount of HCOOH be x.

	$2HCOOH\ (g) \rightleftharpoons$	$(HCOOH)_2\ (g)$
Initial / mol	x	0
Change / mol	$-\alpha x$	$+ \frac{1}{2}\alpha x$
Eqm / mol	$x - \alpha x$	$+ \frac{1}{2}\alpha x$

$$n_{TOT} = x - \alpha x + \frac{1}{2}ax = x - \frac{1}{2}ax\ mol$$

$$P_{HCOOH} = \frac{x - \alpha x}{x - \frac{1}{2}\alpha x} \times P_{TOT}$$

$$= \frac{1-\alpha}{1-\frac{1}{2}\alpha} \times 1.50 \times 10^5$$

$$= \frac{1-0.5161}{1-0.2582} \times 1.50 \times 10^5$$

$$= 9.78 \times 10^4 \, Pa$$

$$P_{(HCOOH)_2} = \frac{\frac{1}{2}\alpha x}{x - \frac{1}{2}\alpha x} \times P_{TOT}$$

$$= \frac{\frac{1}{2}\alpha}{1-\frac{1}{2}\alpha} \times 1.50 \times 10^5$$

$$= \frac{0.2582}{1-0.2582} \times 1.50 \times 10^5$$

$$= 5.22 \times 10^4 \, Pa$$

$P_{(HCOOH)_2}$ can also be found by $\left(1.50 \text{ x } 10^5 - 9.78 \text{ x } 10^4\right) = 5.22 \text{ x } 10^4 \text{ Pa}$

[2]

(iv) The value of the equilibrium constant K_p for the dimerisation of methanoic acid at 227 °C.

$$K_p = \frac{P_{(HCOOH)_2}}{(P_{HCOOH})^2} = \frac{5.22 \times 10^4}{(9.78 \times 10^4)^2} = 5.46 \times 10^{-6} \text{ Pa}^{-1}$$

[1]

(b) (i) State and explain whether the forward reaction is endothermic or exothermic.

The forward reaction is exothermic as bond formation is an exothermic process.

(c)

(ii) Predict the effect on the degree of association of methanoic acid in the equilibrium mixture if the temperature is lowered.

By Le Chatelier's Principle, system will react to increase the amount of heat.

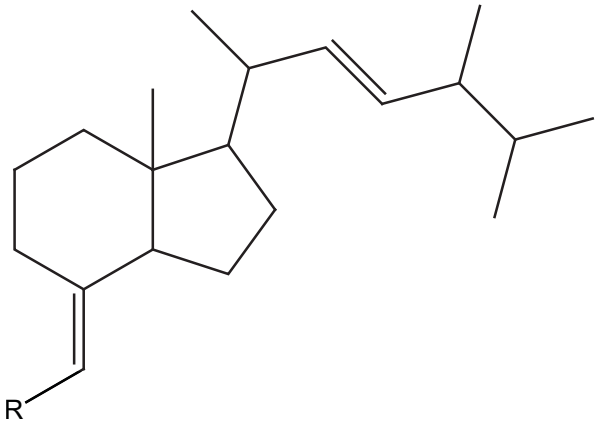
The forward exothermic reaction is favoured / position of equilibrium shifts to the right.

Degree of association will increase.

[3]

[Total: 9]

5 **(a)** Part of the structure of Vitamin D is shown below.

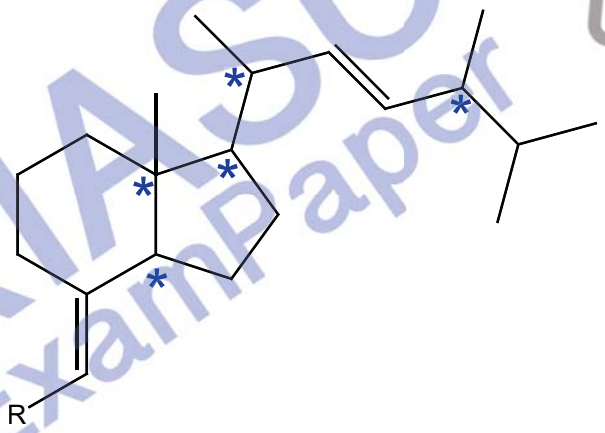


(i) Vitamin D is optically active. Briefly explain what you mean by the term optically active.

The molecule can rotate plane polarized light.

(ii) By means of an asterisk (*), identify the chiral centre(s) in the above structure.

Ans:



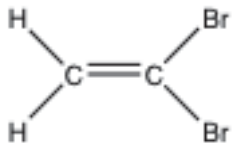
(iii) How many stereoisomers would you expect this form of Vitamin D to have? You can assume that the R group does not have any stereocenters. Show your calculation clearly.

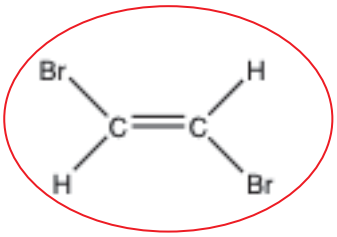
$2^{(5+2)} = 128$

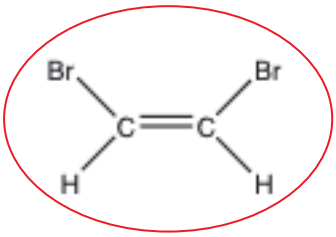
[3]

(b) (i) Draw the displayed formula of all isomers of $C_2H_2Br_2$.

Ans:







(ii) Circle the stereoisomers present in your answer to **(b) (i).**

Circle correctly

(iii) Name the type of stereoisomerism shown and explain the origin of this stereoisomerism.

cis-trans/ geometrical isomerism

due to restricted rotation about the C=C double bond.

(iv) From your answer to **(b)(ii)**, suggest and explain which stereoisomer has a higher boiling point.

The cis isomer is a polar molecule

with permanent dipole – permanent dipole (pd-pd) forces of attraction between molecules

The trans isomer is a non-polar molecule

with weak van der Waals (vdW) forces between molecules.

Strength of pd-pd > vdW

More energy required to overcome, cis isomer has higher boiling point.

[7]

[Total: 10]

[End of Paper]

H

NANYANG JUNIOR COLLEGE
JC 1 PROMOTIONAL EXAMINATION
Higher 2

CANDIDATE NAME

CLASS

TUTOR'S NAME

CHEMISTRY

9647/02

Paper 2 Structured

5 October 2012

1 hour 30 minutes

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[2]

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Use the data above and your answer in **(a)** to determine the enthalpy of combustion of propanol.

[2]

(c) Experimental procedure

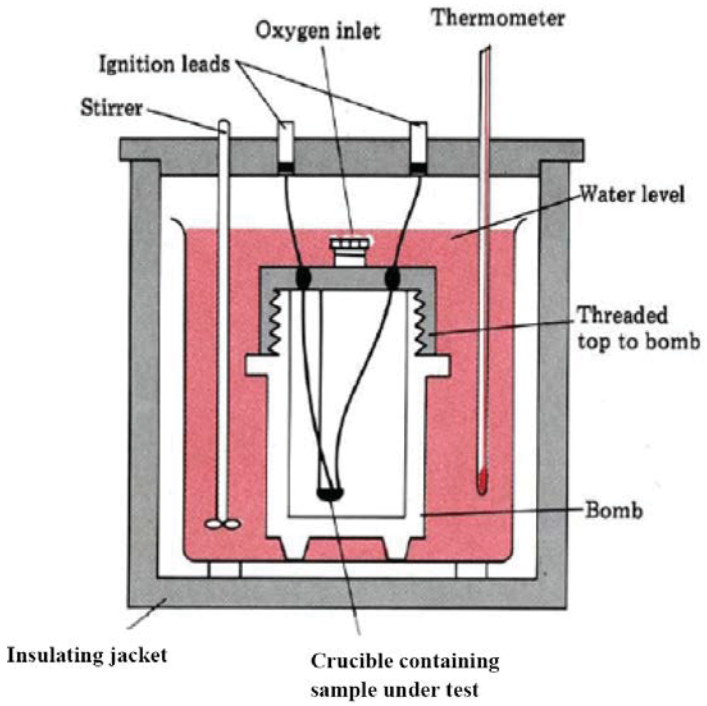
Draw a labelled diagram to show the set-up the student used to obtain the data for determining ΔH_c of propanol.
Hence, describe the procedure for the experiment.

[5]

(d) Identify a potential hazard associated with this experiment and suggest how the hazard can be kept to a minimum.

[2]

(e) A bomb calorimeter is a type of constant-volume calorimeter that is used to measure accurately the enthalpy of combustion of a particular reaction.



Though highly accurate, the bomb calorimeter is also complex to use and very expensive.

Suggest a reason for the improved accuracy of the Bomb calorimeter compared to the experimental set-up you described in **(c)**.

_____

_____

[1]

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(ii) BrF_3 is a covalent compound which exhibits electrical conductivity in the liquid state at room temperature. By means of writing an equation, suggest an explanation for its electrical conductivity.

[8]

(b) The compound ICl_3 does not exist but the dimer I_2Cl_6 exists as a yellow solid.

Draw a diagram to illustrate the bonding in the dimer and suggest the bond angle with respect to the iodine atom in the dimer.

Bond angle with respect to iodine atom :

[2]

(c) 0.270 g of a metallic salt containing the anion $I_xCl_y^-$ decomposed when heated to form iodine vapour and the metallic chloride. The iodine evolved was bubbled into excess potassium iodide solution.

The dissolved iodine required 21.30 cm^3 of 0.0600 mol dm^{-3} of aqueous sodium thiosulfate for complete reaction. When the residue was dissolved in water, the resultant solution required 6.40 cm^3 of 0.100 mol dm^{-3} aqueous silver nitrate for complete reaction.

(i) Determine the value of ***x*** and ***y*** in $I_xCl_y^-$.

(ii) Hence, determine the identity of the metallic element.

[5]

[Total: 15]

3 The decomposition of calcium carbonate follows the equation:

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$$

Given that for this reaction, $\Delta \mathbf{H}^{\theta}$ = + 178 kJ mol^{-1} and $\Delta \mathbf{G}^{\theta}$ = + 130 kJ mol^{-1},

(a) (i) Calculate a value for the standard entropy change $\Delta \mathbf{S}^{\theta}$ for the reaction.

(ii) Hence, explain the significance of the sign of $\Delta \mathbf{S}^{\theta}$ obtained.

[3]

(b) (i) Calculate the temperature at which the reaction becomes feasible.

(ii) State an assumption made in the calculation above.

[3]

[Total: 6]

4 In the vapour phase, methanoic acid associates to form dimers.

$$2HCOOH\ (g) \rightleftharpoons (HCOOH)_2\ (g)$$

At 227 °C and 1.50×10^5 Pa, 0.155 g of methanoic acid vapour occupies 69.3 cm^3.

Calculate

(a) (i) the average relative molecular mass of the gaseous mixture

(ii) α, the degree of association of methanoic acid, defined as the fraction of the methanoic acid that associates, using the formula:

$$\alpha = 2\left[\frac{\text{average } M_r - M_r(HCOOH)}{\text{average } M_r}\right]$$

(iii) the partial pressures of HCOOH and $(HCOOH)_2$ at equilibrium.

(iv) the value of the equilibrium constant K_p for the dimerisation of methanoic acid at 227 °C.

[6]

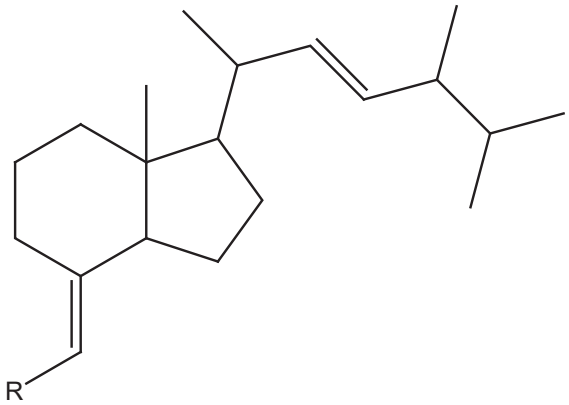
(b) (i) State and explain whether the forward reaction is endothermic or exothermic.

(ii) Predict the effect on the degree of association of methanoic acid in the equilibrium mixture if the temperature is lowered.

[3]

[Total: 9]

5 **(a)** Part of the structure of Vitamin D is shown below.



(i) Vitamin D is optically active. Briefly explain what you understand by the term “optically active”.

(ii) By means of an asterisk (*), identify the chiral centres in the above structure.

(iii) How many stereoisomers would you expect this form of Vitamin D to have? You can assume that the R group does not have any stereocenters. Show your calculation clearly.

[3]

(b) (i) Draw the displayed formula of all isomers of $C_2H_2Br_2$.

(ii) Circle the stereoisomers present in your answer to **(b) (i).**

(iii) Name the type of stereoisomerism shown and explain the origin of this stereoisomerism.

(iv) From your answer to **(b)(ii)**, suggest and explain which stereoisomer has a higher boiling point.

[7]

[Total: 10]

[End of Paper]

NANYANG JUNIOR COLLEGE
JC 1 PROMOTIONAL EXAMINATION
Higher 2

CHEMISTRY

9647/03

Paper 3 Free Response

3 October 2012

1 hour 30 minutes

Answers

Additional Materials: Answer Paper
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 on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

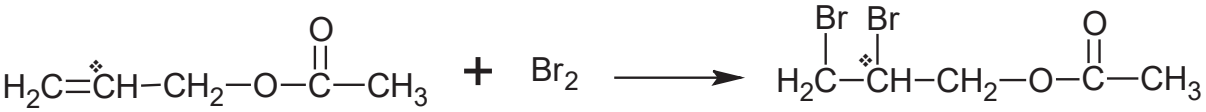
Answer **all** questions.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

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.

This document consists of **13** printed pages

Answer **all** questions on the writing paper provided.

1 In concentrated ethanoic acid, bromine adds to an ester, propenyl ethanoate, $CH_2=CHCH_2OCOCH_3$, slowly enough for the orders of reaction with respect to bromine and ester to be determined in the laboratory.



Experiments were carried out with large excess of ester at room temperature. The change in concentration of bromine was tracked over time by pipetting 25.0 cm^3 samples of the reaction mixture at regular intervals and mixing the samples with an excess of potassium iodide solution. A displacement reaction occurs and iodine and bromide are formed. Iodine is extracted and then titrated with sodium thiosulfate solution, $Na_2S_2O_3$ (aq), of a certain concentration.

The concentration of ester was then varied, keeping the concentration of bromine constant. The following results were obtained:

Time / s	Experiment 1 [ester] = 2.0 mol dm^{-3}	Experiment 2 [ester] = 3.0 mol dm^{-3}
	$V_{S_2O_3^{2-}}$ needed / cm^3	$V_{S_2O_3^{2-}}$ needed / cm^3
0	40.00	40.00
100	28.10	23.80
200	18.00	12.55
300	12.05	7.35
400	9.25	4.85

(a) (i) Suggest how shape and bond angle changes at the labelled carbon ❖**C** in the overall equation above.

It changes from trigonal planar (120°) to tetrahedral (109°).

(ii) Suggest a reason why concentrated ethanoic acid is a suitable solvent for the reactants rather than water.

[4]

Bromine and ester are largely non-polar hence able to form significant van der Waal's interaction with ethanoic acid molecules.

OR

The reactants are not soluble in water as the weak van der Waal's interaction formed between ester/bromine and water molecules are too weak to break the strong hydrogen bonds between water molecules.

(b) (i) Define the term *order of reaction.*

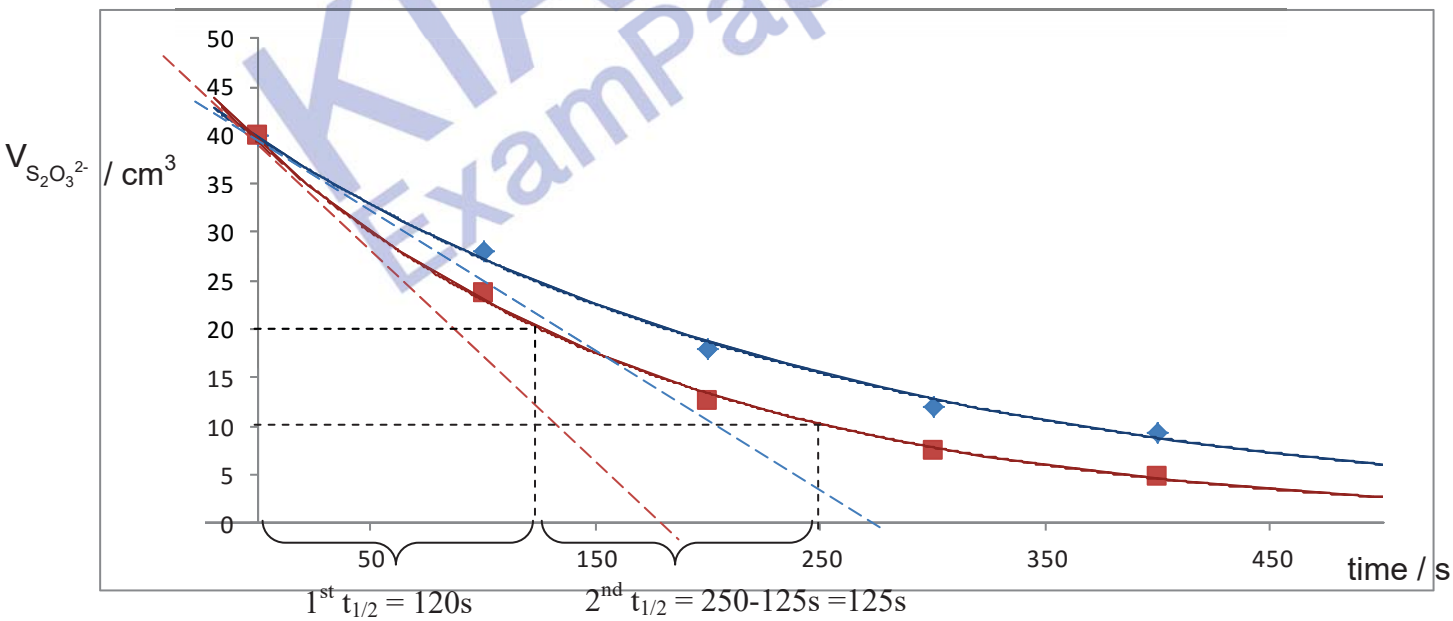
Order of reaction is the power to which the concentration of a reactant is raised in the rate equation.

(ii) Using the same axes, plot graphs of $V_{S_2O_3^{2-}}$ against time for experiments **1** and **2**. Use your graphs to determine the order of reaction with respect to Br_2 and ester, showing your workings clearly. State an assumption made in your calculation.

Assumption: $V_{S_2O_3^{2-}}$ is directly proportional to $[Br_2]$ present.

Graphs should be plotted with the following correctly:

- $V_{S_2O_3^{2-}}$ on y-axis vs time on x-axis
- Units for both axes
- Data points



To determine order of reaction wrt Br_2

- Working in graph (1m)
- Constant half-life + conclude 1st order wrt Br_2 (1m)

From the graph of [ester] = 3.0 mol dm^{-3},
$t_{1/2}$ is a constant at 125s
$\Rightarrow$ Order of reaction wrt Br_2 = 1

OR

From the graph of [ester] = 2.0 mol dm^{-3},
$t_{1/2}$ is a constant at 180s
$\Rightarrow$ Order of reaction wrt Br_2 = 1

To determine order of reaction wrt ester

Tangents drawn in graph

For graph with [ester] = 2.0 mol dm^{-3}

Relative Initial Rate = $\frac{40.0}{270}$

= 0.1481 cm^3 of $S_2O_3^{2-}$ per s

For graph with [ester] = 3.0 mol dm^{-3}

relative initial Rate = $\frac{40.00}{180}$

= 0.2222 cm^3 of $S_2O_3^{2-}$ per s

When [ester] is increased by 1.5 times ($\frac{3.0}{2.0}=1.5$), the rate of reaction also increases by 1.5 times ($\frac{0.2222}{0.1481}\approx 1.5$)

$\Rightarrow$ Order of reaction wrt ester = 1

(iii) Hence, suggest the rate equation and calculate the rate constant k, stating its units.

[11]

rate = k [ester][Br_2]

Using initial rate and [ester] from experiment 1,

$$k = \frac{0.1481\ cm^3 \text{ of } S_2O_3^{2-} \text{ per s}}{(2.0\ moldm^{-3})(40cm^3 \text{ of } S_2O_3^{2-})} \quad (1m)$$

$$= 0.001851\ mol^{-1}\ dm^3\ s^{-1} \quad (1m \text{ for units})$$

Alternatively, students can use pseudo-first order method,

rate = k[ester][Br_2]

rate = k'[Br_2] where k'=k[ester] (constant) (1m)

$k' = \frac{\ln 2}{t_{1/2}}$

from experiment 1: k (2.0) = $\frac{\ln 2}{180}$ = 0.00193$mol^{-1}dm^3s^{-1}$(1m for units)

(c) Suggest an alternative method for studying the kinetics of the reaction.

[1]

Use a colorimeter to track changes in concentration of reddish brown Br_2

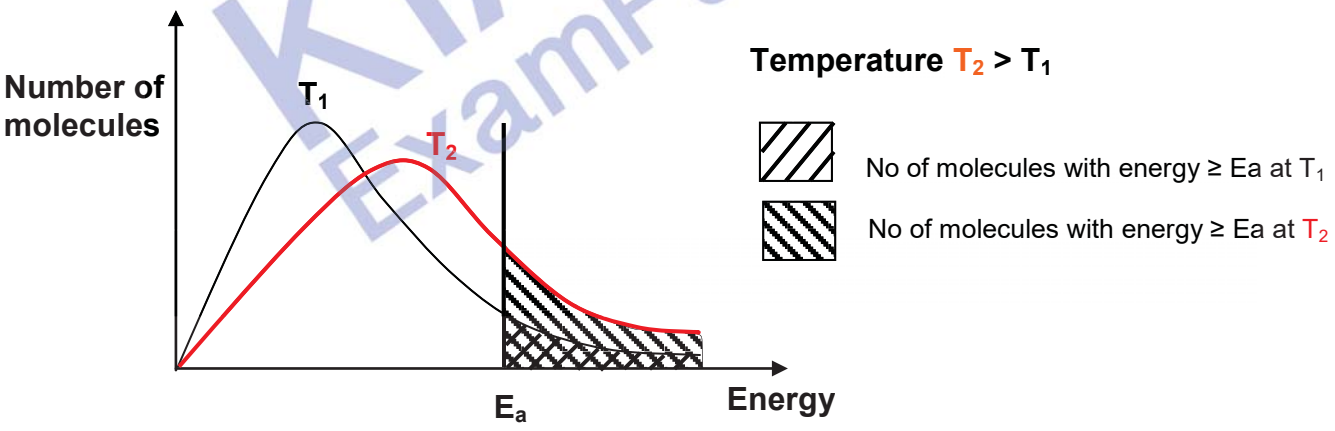
(d) **(i)** Experiments **1** and **2** were conducted at **room temperature**. Experiment **1** was repeated with the same initial concentrations of bromine and ester at **35 °C**. Suggest the volume of sodium thiosulfate needed for titration of the first sample withdrawn at 100 s.

$V_{S_2O_3^{2-}}$ = approximately 14 cm^3 (since rate doubles with a 10 °C rise in temperature).

(ii) With the aid of a suitable diagram, explain in terms of the Collision Theory, why an increase in temperature results in an increase in rate.

[4]

[Total: 20]



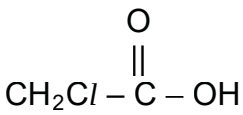
Boltzmann Diagram
- Correct Axes and label Ea
- Two curves and labeled $T_2 > T_1$
- Correct shading and legend

When temperature is increased, average kinetic energy of particles increases. Hence more molecules will have energy larger than Ea / more collisions with energy greater than Ea. Frequency of activated collisions increases and hence rate increases.

2 Drinking water may contain small amounts of contaminants. As overdose of these contaminants may have detrimental effects on health, strict standards for the different contaminants are set. Haloacetic acids are identified as a common water pollutant. These acids are the undesirable by-products formed when water is disinfected using chlorine. Consumption of water containing high levels of haloacetic acid over a long period of time increases the risk of cancer.

Haloacetic acids are carboxylic acids in which a halogen atom takes the place of a hydrogen atom in ethanoic acid.

One of the haloacetic acids is chloroethanoic acid, $CH_2ClCOOH$.



Chloroethanoic acid (K_a = 1.3 x 10^{-3} mol dm^{-3} at 298 K)

(a) (i) Write an expression for the K_a of chloroethanoic acid, $CH_2ClCOOH$.

$$K_a = \frac{[CH_2ClCO_2^-][H^+]}{[CH_2ClCO_2H]}$$

(ii) Hence, determine the concentration of chloroethanoic acid in a sample with pH 2.5.

pH = 2.5

$[H^+] = 10^{-2.5}$ mol dm^{-3}

$$[H^+] = \sqrt{K_a[CH_2ClCO_2H]}$$

$[CH_2ClCO_2H]$ =0.00769 mol dm^{-3}

(iii) The pH of a sample of ethanoic acid is 2.4. The value of K_a for ethanoic acid at 298 K is 1.8 x 10^{-5} mol dm^{-3}.

Using the data provided, compare the relative strengths of chloroethanoic acid and ethanoic acid in terms of their behaviour in water.

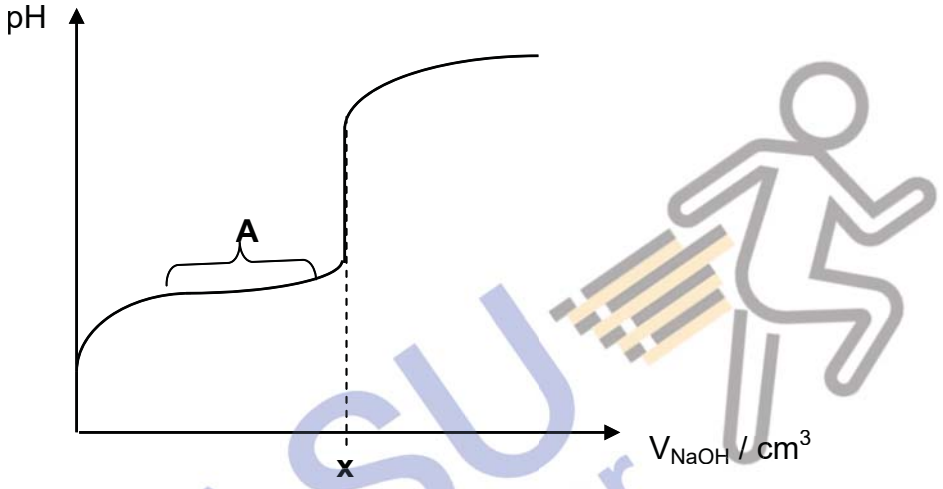
K_a of chloroethanoic acid is larger. Hence, there is greater extent of dissociation in water, making chloroethanoic acid a stronger acid.

(iv) The temperature is increased to 350 K. Predict and explain how the increase in temperature will affect the K_a and pH of the chloroethanoic acid.

[6]

Dissociation is an endothermic process. Increase in temperature will favour the dissociation more, thus, increasing the K_a, hence more H^+ is formed, lowering the pH.

(b) 20.0 cm^3 of 0.01 mol dm^{-3} chloroethanoic acid was titrated against 0.01 mol dm^{-3} sodium hydroxide.



(i) Identify the species present at region **A**. Hence, explain, with the use of relevant equation(s), why the graph remains relatively flat at this region.

$CH_2ClCOOH$, $CH_2ClCOO^-Na^+$

This is the buffer region.

When **small** amount of OH^- is added,

$CH_2ClCOOH + OH^- \rightarrow CH_2ClCOO^- + H_2O$

(ii) State the value of **x** and calculate the corresponding pH at this point.

20.00 cm^3

amount of $CH_2ClCOONa$ = 20.0/1000 x 0.01 = 2 x 10^{-4} mol

$[CH_2ClCOONa]$ = 2 x 10^{-4} x 1000/40.0 = 0.005 mol dm^{-3}

K_b = 10^{-14}/1.3 x 10^{-3} = 7.69 x 10^{-12} mol dm^{-3}

$[OH^-] = \sqrt{7.69\times10^{-12}(0.005)}$ = 1.96 x 10^{-7} mol dm^{-3}

pOH = 6.7, pH = 7.3

(iii) Hence suggest a suitable indicator and the colour change for this titration.

[8]

Phenolphthalein, Colourless to pink

(c) Fluoride is added to drinking water to promote dental health. However, a standard for fluoride ion concentration has to be enforced as drinking excessive fluoride over a long period of time may cause bone disease.

(i) Calcium fluoride, CaF_2, is sparingly soluble in water. The numerical value of the solubility product, K_{sp}, for calcium fluoride in water at 25°C is 1.5×10^{-10}. Calculate the solubility of calcium fluoride at this temperature.

Let solubility of CaF_2 be x mol dm^{-3}.

$K_{sp} = [Ca^{2+}][F^-]^2 = (x)(2x)^2$

$1.5 \times 10^{-10} = 4x^3$

$x = 2.64 \times 10^{-4}$ mol dm^{-3}

(ii) In the United States, the Environmental Protection Agency (EPA) sets a standard for fluoride ions to be 2 mg / L to protect against a condition called dental fluorosis. A sample of heavily polluted water was found to contain 30 mg / L of fluoride.

By means of calculations, predict whether there will be precipitation when 50 cm^3 of 0.100 mol dm^{-3} of calcium nitrate solution is mixed with 50 cm^3 of the sample of fluoride ions in the polluted water. (1 L = 1000 cm^3)

$[F^-] = 30 \times 10^{-3}/19.0 = 0.001579$ mol dm^{-3}

Ionic product $= [Ca^{2+}][F^-]^2 = (0.100/2)(0.001579/2)^2$

$= 3.1 \times 10^{-8}$ mol^3 $dm^{-9} > K_{sp}$

Yes a ppt will form.

(iii) The numerical value of the solubility product of calcium carbonate is 5.0×10^{-9}. A student concluded that since K_{sp} of calcium carbonate is larger than calcium fluoride, the salt is more soluble. Comment on his prediction.

[6]

[Total: 20]

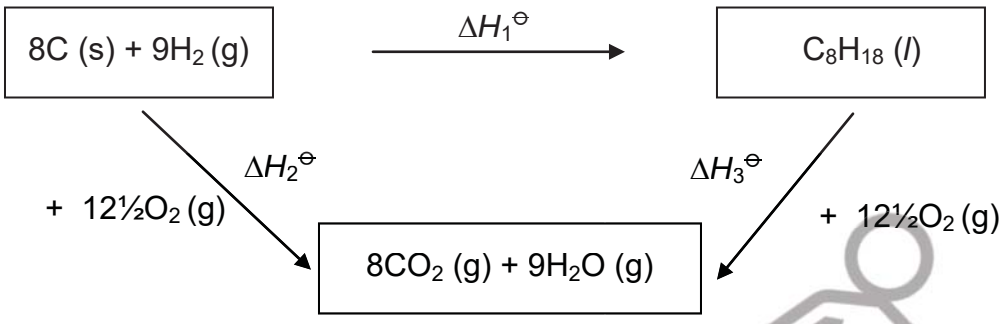
$K_{sp} = [Ca^{2+}][CO_3^{2-}]$

$[Ca^{2+}] = \sqrt{5.0 \times 10^{-9}} = 7.07 \times 10^{-5}$ mol dm^{-3}

since solubility of $CaCO_3$ is smaller than CaF_2, $CaCO_3$ is less soluble.

3 Crude oil is one of the most actively traded commodities and its price is expected to soar as the world economy recovers from the global economic crisis. It is a vital source of hydrocarbons for the manufacture of many useful commercial products as well as the most important source of fuel in the world today. Octane, C_8H_{18}, obtained from distillation of crude oil, is a chief fuel in petrol.

(a) The diagram below shows an energy cycle involving octane.



(i) Name the enthalpy change represented by $\Delta H_1^{\ominus}$.

$\Delta H_1^{\ominus}$ represents the standard enthalpy change of formation of octane.

(ii) Based on the given energy cycle and the following data, calculate the standard enthalpy change of combustion of octane.

$\Delta H_1^{\ominus}$ = –250 kJ mol^{-1}
$\Delta H_c^{\ominus}$ (carbon) = –393 kJ mol^{-1}
$\Delta H_c^{\ominus}$ (hydrogen) = –286 kJ mol^{-1}

[3]

By Hess' Law,

$\Delta H_1^{\ominus} + \Delta H_3^{\ominus} = \Delta H_2^{\ominus}$

standard enthalpy change of combustion of octane, $\Delta H_3^{\ominus}$
$= \Delta H_2^{\ominus} - \Delta H_1^{\ominus}$
$= [8 (-393) + 9(-286)] - (-250)$
$= -5468$ kJ mol^{-1}
$= -5470$ kJ mol^{-1}

(b) Auto-ignition of petrol can cause damage to the internal combustion engines. Branched-chain alkanes are known to be more resistant to auto-ignition than straight-chain alkanes. Petrol blends typically contain mixtures of the straight-chain octane and its branched-chain isomers. The isomers may be distinguished by the number of monochlorinated products formed upon reaction with limited amount of chlorine.

(i) Draw the structural formula of any **one** monochlorinated product obtained in the reaction of straight-chain octane. How many different monochlorinated products can be formed from this reaction? Hence, give the ratio of these monochlorinated products formed.

$CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
|
Cl

(or draw the structure for 2–chloro, or 3–chloro, or 4–chloro–octane)

4 isomers

Proportion will be 6 : 4 : 4 : 4
Or 3 : 2 : 2 : 2
(1–choro: 2–chloro:3–chloro:3–chloro)

(ii) Draw the structural formula of **another isomer of octane** which reacts with chlorine to form only **one** monochlorinated product.

$(CH_3)_3CC(CH_3)_3$

(iii) Explain how you would expect the boiling point of octane to compare with that of the isomer that you have drawn in **(b)(ii)**.

[7]

Boiling point : octane > branched isomer

Greater surface area for intermolecular instantaneous dipole–induced dipole attractions or van der Waals forces between the straight chain/elongated molecules of octane (or less surface area for intermolecular instantaneous dipole–induced dipole attractions or van der Waals forces between the spherically shaped branched chain isomer),
Hence more energy is needed to overcome the stronger instantaneous dipole–induced dipole attractions or van der Waals forces in octane.

(c) Oil spills have recently dominated world news. One of the cleaning methods involves the use of dispersants, which break up the oil into tiny biodegradable droplets.

2-butoxyethanol, $CH_3CH_2CH_2CH_2OCH_2CH_2OH$, is one of the components in a dispersant used in the recent oil spill in the Gulf of Mexico.

(i) Suggest values for the C–O–C and C–O–H bond angles in a molecule of 2-butoxyethanol.

C–O–C : 105°
C–O–H : 105°

(ii) By reference to the type of intermolecular forces, suggest how 2-butoxyethanol interacts with water and oil.

[3]

Hydrogen bonding formed between H_2O molecules and alcohol –OH groups (and/or the ether group, –COC–) allows 2–butoxyethanol molecule to dissolve in water;
van der Waals forces formed between the non–polar hydrocarbon chain of the molecule and oil molecules allow 2–butoxyethanol molecule to dissolve in oil.
(These interactions allow the oil to break up into tiny droplets which are more easily removed.)

(d) Natural gas, the gaseous component of crude oil, is commonly used as an industrial fuel. Natural gas consists mainly of methane. The equation for the combustion of methane is shown below.

$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)$ $\quad \Delta H_c^{\ominus} = -890$ kJ mol^{-1}

(i) A boiler in an industrial process requires 9.0×10^{10} dm^3 of methane, measured at 25 °C and 1 atm, to raise the temperature of water at 20 °C to its boiling point.

Assuming no heat loss, calculate the mass of water in the boiler.

n (CH_4) burnt = $9.0 \times 10^{10}/24 = 3.75 \times 10^9$ mol

Heat produced from burning = $3.75 \times 10^9 \times 890$ kJ

Heat absorbed by water = $3.75 \times 10^9 \times 890 \times 1000 = mc\Delta T$

m (H_2O) = $3.75 \times 10^9 \times 890 \times 1000/(4.18 \times 80)$
$= 9.98 \times 10^{12}$ g

(ii) Use the bond energies given in the *Data Booklet* to calculate another value for the standard enthalpy change of combustion of methane.
[Use a value of 805 kJ mol^{-1} for the bond energy of C=O in CO_2.]

$\Delta H_c^{\ominus}$ = [4(C–H) + 2(O=O)] – [2 (C=O) + 2 x 2 (O–H)]

= (4 x 410) + (2 x 496) – [(2 x 805) + (4 x 460)]

= 2632 – 3450 = – 818 kJ mol^{-1}

(iii) Suggest a reason for the discrepancy between the value you have obtained in **(d)(ii)** and that quoted in **(d)(i)**. What additional quantitative information can be calculated from the difference in these values?

[7]

[Total: 20]

In (d) (i), H_2O is in the liquid state, but in (d)(ii) H_2O is in the gaseous state as bond energy refers to the energy needed to break covalent bonds in gaseous molecules.
Enthalpy change of vapourisation of H_2O can be calculated from the difference in values.

[End of Paper]

NANYANG JUNIOR COLLEGE
JC 1 PROMOTIONAL EXAMINATION
Higher 2

CHEMISTRY

9647/03

Paper 3 Free Response

3 October 2012

1 hour 30 minutes

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

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This document consists of **7** printed pages

Answer **all** questions on the writing paper provided.

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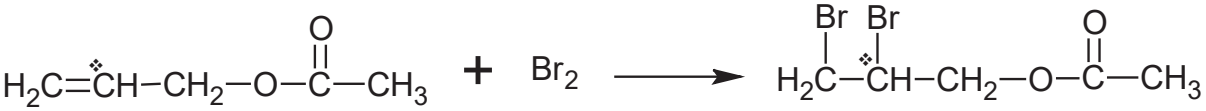


Experiments were carried out with large excess of ester at room temperature. The change in concentration of bromine was tracked over time by pipetting 25.0 cm^3 samples of the reaction mixture at regular intervals and mixing the samples with an excess of potassium iodide solution. A displacement reaction occurs and iodine and bromide are formed. Iodine is extracted and then titrated with sodium thiosulfate solution, $Na_2S_2O_3$ (aq), of a certain concentration.

The concentration of ester was then varied, keeping the concentration of bromine constant. The following results were obtained:

Time / s	**Experiment 1 [ester] = 2.0 mol dm^{-3}**	**Experiment 2 [ester] = 3.0 mol dm^{-3}**
	$V_{S_2O_3^{2-}}$ needed / cm^3	**$V_{S_2O_3^{2-}}$ needed / cm^3**
0	40.00	40.00
100	28.10	23.80
200	18.00	12.55
300	12.05	7.35
400	9.25	4.85

(a) (i) Suggest how shape and bond angle changes at the labelled carbon ❖**C** in the overall equation above.

(ii) Suggest a reason why concentrated ethanoic acid is a suitable solvent for the reactants rather than water.

[4]

(b) **(i)** Define the term *order of reaction.*

(ii) Using the same axes, plot graphs of $V_{S_2O_3^{2-}}$ against time for experiments **1** and **2**. Use your graphs to determine the order of reaction with respect to Br_2 and ester, showing your workings clearly. State an assumption made in your calculation.

(iii) Hence, suggest the rate equation and calculate the rate constant k, stating its units.

[11]

(c) Suggest an alternative method for studying the kinetics of the reaction.

[1]

(d) **(i)** Experiments **1** and **2** were conducted at **room temperature**. Experiment **1** was repeated with the same initial concentrations of bromine and ester at **35 ^{o}C**. Suggest the volume of sodium thiosulfate needed for titration of the first sample withdrawn at 100 s.

(ii) With the aid of a suitable diagram, explain in terms of the Collision Theory, why an increase in temperature results in an increase in rate.

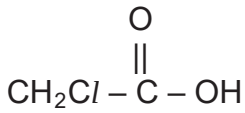
[4]

[Total: 20]

2 Drinking water may contain small amounts of contaminants. As overdose of these contaminants may have detrimental effects on health, strict standards for the different contaminants are set. Haloacetic acids are identified as a common water pollutant. These acids are the undesirable by-products formed when water is disinfected using chlorine. Consumption of water containing high levels of haloacetic acid over a long period of time increases the risk of cancer.

Haloacetic acids are carboxylic acids in which a halogen atom takes the place of a hydrogen atom in ethanoic acid.

One of the haloacetic acids is chloroethanoic acid, $CH_2ClCOOH$.



Chloroethanoic acid (K_a = 1.3 x 10^{-3} mol dm^{-3} at 298 K)

(a) **(i)** Write an expression for the K_a of chloroethanoic acid, $CH_2ClCOOH$.

(ii) Hence, determine the concentration of chloroethanoic acid in a sample with pH 2.5.

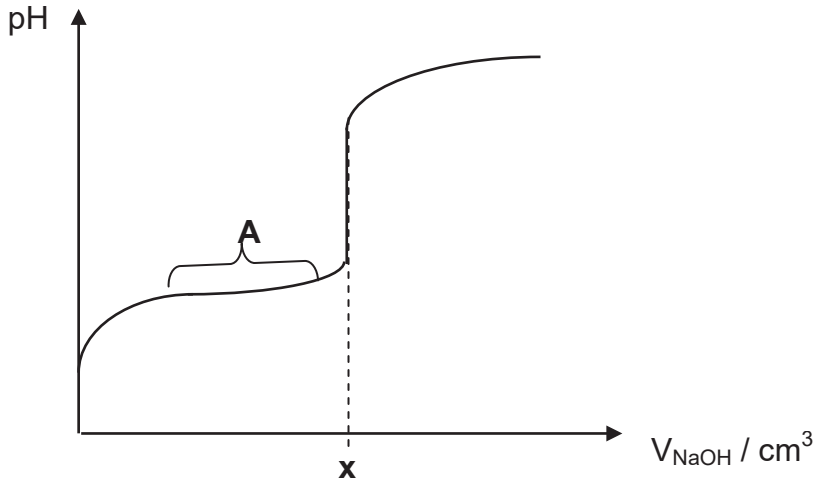
(iii) The pH of a sample of ethanoic acid is 2.4. The value of K_a for ethanoic acid at 298 K is 1.8 x 10^{-5} mol dm^{-3}.

Using the data provided, compare the relative strengths of chloroethanoic acid and ethanoic acid in terms of their behaviour in water.

(iv) The temperature is increased to 350 K. Predict and explain how the increase in temperature will affect the K_a and pH of the chloroethanoic acid.

[6]

(b) 20.0 cm^3 of 0.01 mol dm^{-3} chloroethanoic acid was titrated against 0.01 mol dm^{-3} sodium hydroxide.



(i) Identify the species present at region **A**. Hence, explain, with the use of relevant equation(s), why the graph remains relatively flat at this region.

(ii) State the value of **x** and calculate the corresponding pH at this point.

(iii) Hence suggest a suitable indicator and the colour change for this titration.

[8]

(c) Fluoride is added to drinking water to promote dental health. However, a standard for fluoride ion concentration has to be enforced as drinking excessive fluoride over a long period of time may cause bone disease.

(i) Calcium fluoride, CaF_2, is sparingly soluble in water. The numerical value of the solubility product, K_{sp}, for calcium fluoride in water at 25°C is 1.5 x 10^{-10}. Calculate the solubility of calcium fluoride at this temperature.

(ii) In the United States, the Environmental Protection Agency (EPA) sets a standard for fluoride ions to be 2 mg / L to protect against a condition called dental fluorosis. A sample of heavily polluted water was found to contain 30 mg / L of fluoride.

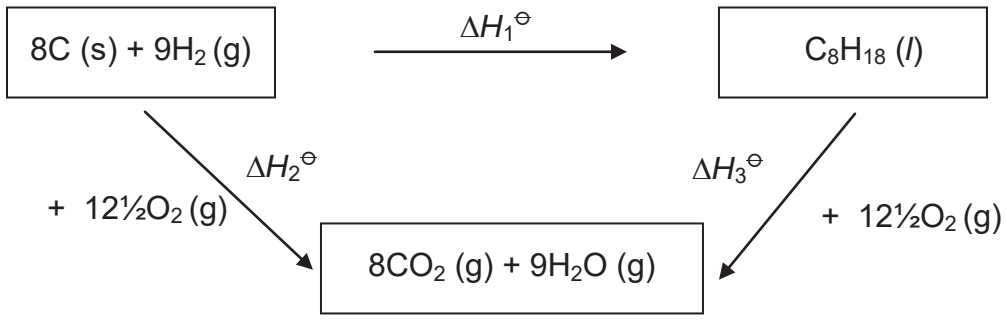
By means of calculations, predict whether there will be precipitation when 50 cm^3 of 0.100 mol dm^{-3} of calcium nitrate solution is mixed with 50 cm^3 of the sample of fluoride ions in the polluted water. (1 L = 1000 cm^3)

(iii) The numerical value of the solubility product of calcium carbonate is 5.0 x 10^{-9}. A student concluded that since K_{sp} of calcium carbonate is larger than calcium fluoride, the salt is more soluble. Comment on his prediction.

[6]
[Total: 20]

3 Crude oil is one of the most actively traded commodities and its price is expected to soar as the world economy recovers from the global economic crisis. It is a vital source of hydrocarbons for the manufacture of many useful commercial products as well as the most important source of fuel in the world today. Octane, C_8H_{18}, obtained from distillation of crude oil, is a chief fuel in petrol.

(a) The diagram below shows an energy cycle involving octane.



(i) Name the enthalpy change represented by $\Delta H_1^{\ominus}$.

(ii) Based on the given energy cycle and the following data, calculate the standard enthalpy change of combustion of octane.

$\Delta H_1^{\ominus}$ = -250 kJ mol^{-1}
$\Delta H_c^{\ominus}$ (carbon) = -393 kJ mol^{-1}
$\Delta H_c^{\ominus}$ (hydrogen) = -286 kJ mol^{-1}

[3]

(b) Auto-ignition of petrol can cause damage to the internal combustion engines. Branched-chain alkanes are known to be more resistant to auto-ignition than straight-chain alkanes. Petrol blends typically contain mixtures of the straight-chain octane and its branched-chain isomers. The isomers may be distinguished by the number of monochlorinated products formed upon reaction with limited amount of chlorine.

(i) Draw the structural formula of any **one** monochlorinated product obtained in the reaction of straight-chain octane. How many different monochlorinated products can be formed from this reaction? Hence, give the ratio of these monochlorinated products formed.

(ii) Draw the structural formula of **another isomer of octane** which reacts with chlorine to form only **one** monochlorinated product.

(iii) Explain how you would expect the boiling point of octane to compare with that of the isomer that you have drawn in **(b)(ii)**.

[7]

(c) Oil spills have recently dominated world news. One of the cleaning methods involves the use of dispersants, which break up the oil into tiny biodegradable droplets.

2-butoxyethanol, $CH_3CH_2CH_2CH_2OCH_2CH_2OH$, is one of the components in a dispersant used in the recent oil spill in the Gulf of Mexico.

(i) Suggest values for the C–O–C and C–O–H bond angles in a molecule of 2-butoxyethanol.

(ii) By reference to the type of intermolecular forces, suggest how 2-butoxyethanol interacts with water and oil.

[3]

(d) Natural gas, the gaseous component of crude oil, is commonly used as an industrial fuel. Natural gas consists mainly of methane. The equation for the combustion of methane is shown below.

$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)$ $\quad \Delta H_c^{\ominus} = -890$ kJ mol^{-1}

(i) A boiler in an industrial process requires 9.0×10^{10} dm^3 of methane, measured at 25 °C and 1 atm, to raise the temperature of water at 20 °C to its boiling point.

Assuming no heat loss, calculate the mass of water in the boiler.

(ii) Use the bond energies given in the *Data Booklet* to calculate another value for the standard enthalpy change of combustion of methane.
[Use a value of 805 kJ mol^{-1} for the bond energy of C=O in CO_2.]

(iii) Suggest a reason for the discrepancy between the value you have obtained in **(d)(ii)** and that quoted in **(d)(i)**. What additional quantitative information can be calculated from the difference in these values?

[7]

[Total: 20]

[End of Paper]

Chemistry Promotional Examinations 2012
Section A

Part 1: *For each question, there are four possible answers,* ***A, B, C*** *and* ***D.*** *Choose the* ***one*** *you consider to be correct.*

1 Alkenes are compounds of carbon and hydrogen. If 0.560 g of an alkene of general formula C_nH_{2n} is burned in excess oxygen, how many moles of H_2O are formed?

A 0.0400 **C** 0.0800

B 0.0600 **D** 0.400

2 Solution **X** contains iron(II) ions. Solution **Y** contains MnO_4^- ions. 25.0 cm^3 of **X** required, in acidic conditions, 20.0 cm^3 of **Y** for complete reaction. What volume of **Y** would be required to oxidise 25.0 cm^3 of **X** in neutral conditions?

The half equations for the reduction of MnO_4^- in acidic and neutral conditions are:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

A $20 \times \frac{1}{5}$ cm^3 **C** $20 \times \frac{5}{4}$ cm^3

B $20 \times \frac{3}{5}$ cm^3 **D** $20 \times \frac{5}{3}$ cm^3

3 In an experiment, 32.50 cm^3 of 0.500 mol dm^{-3} Na_2SO_3 reacted exactly with 100 cm^3 of solution containing 1.39 g of KIO_3.

The half equation for the oxidation of SO_3^{2-} is shown below:

$$SO_3^{2-}(aq) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e$$

What is the final oxidation state of iodine after reaction?

A +1 **B** -1 **C** 0 **D** +5

4 Which of the following species has two unpaired electrons?

A Cr^{3+} **B** Ni^{2+} **C** Ca **D** V

5 Which of the following species is **not** linear in shape?

A XeF_2 **B** CS_2 **C** NH_2^- **D** BCl_2^+

6 One flask contains 1 dm^3 of helium at 2 kPapressure and another flask contains 2 dm^3 of neon at 1 kPa pressure. The two flasks are connected at constant temperature.

The final pressure is

A $1\frac{1}{3}$ kPa **B** $1\frac{1}{2}$ kPa **C** $1\frac{2}{3}$kPa **D** 2 kPa

7 The number of molecules present in a gas with a volume of 2.0 dm^3 at 27°C and at 6.0 x 10^5 Pa is

A $\frac{6.0 \times 10^5 \times 6.02 \times 10^{23} \times 2.0}{8.31 \times 300}$

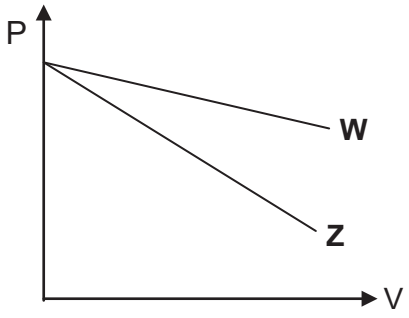
B $\frac{6.0 \times 10^5 \times 6.02 \times 10^{23} \times 2.0 \times 10^{-3}}{8.31 \times 27}$

C $\frac{6.0 \times 10^5 \times 2.0 \times 10^{-3}}{8.31 \times 300}$

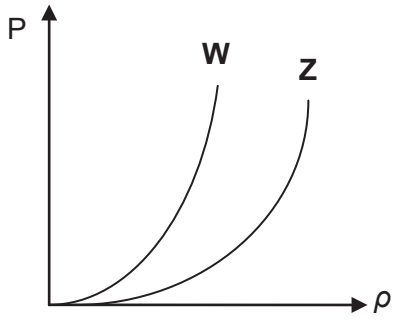
D $\frac{6.0 \times 10^5 \times 6.02 \times 10^{23} \times 2.0 \times 10^{-3}}{8.31 \times 300}$

8 Which graph best represents the behaviour of an ideal gas at constant temperature where the ratio of the number of moles of gas in containers **W** and **Z** are 3:1 respectively? (ρ refers to the density of the gas.)

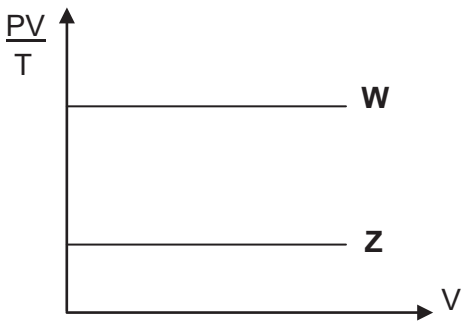
A



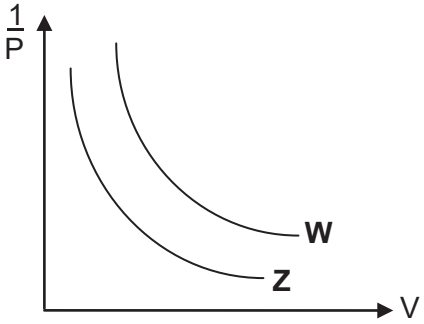
C



B



D



9 The enthalpy changes for two reactions are given by the equations:

$$2Cr(s) + \frac{3}{2}O_2(g) \rightarrow Cr_2O_3(s) \qquad \Delta H = -1130 \text{ kJ}$$

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \qquad \Delta H = -110 \text{ kJ}$$

What is the enthalpy change, in kJ, for the following reaction?

$$3C(s) + Cr_2O_3(s) \rightarrow 2Cr(s) + 3CO(g)$$

A −800 **B** +800 **C** −1460 **D** +1460

10 For which one of the following is the sign of $\Delta S^{\ominus}$ **incorrect**?

	Reactions	$\Delta S^{\ominus}$
A	$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$	positive
B	$HCl(aq) + NaHCO_3(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$	positive
C	$H_2O(l) \rightarrow H_2O(s)$	negative
D	$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$	positive

11 Which of the following statements about the intermediate complex, $[C_6H_6Cl]^+$, formed during the monochlorination of benzene is correct?

A It is planar.

B It contains a chiral centre.

C It contains a sp^3 hybridised carbon atom.

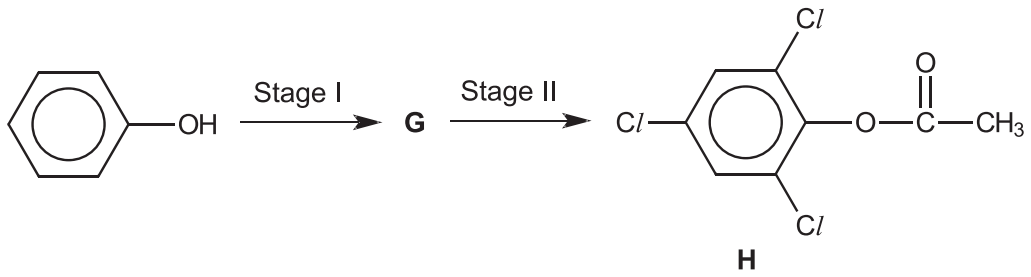
D It can exist in either a *cis* or a *trans* form.

12 Which compound **cannot** be synthesised from propan–1–ol within 2 steps or less?

A 1-bromopropan-2-ol **C** ethanoic acid

B propanone **D** propanoic acid

13 Phenol can be converted to a compound **H**in a two-step synthesis as shown below.



H

Which of the following statements is correctwith regards to the given reaction scheme?

A Stage I may involve the use of Cl_2 in CCl_4.

B Stage I may involve the use of ethanoic acid and concentrated H_2SO_4 as a catalyst.

C Stage II may involve the use of aqueous Cl_2.

D Stage II may involve the use of ethanoyl chloride.

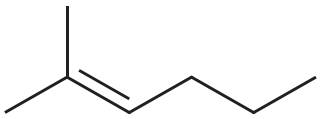
14 Compound **F** has the formula C_7H_{14}.

The reaction of **F** with hot acidified potassium manganate(VII) yields two products, **G** and **H**.

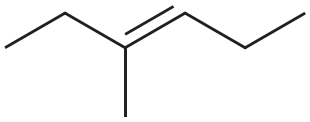
G can be converted to **H** with the use of aqueous alkaline iodine followed by acidification with aqueous sulfuric acid.

Which of the following shows the structure of compound **F**?

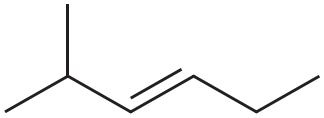
A



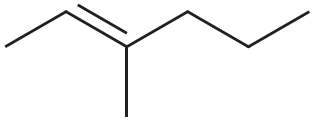
C



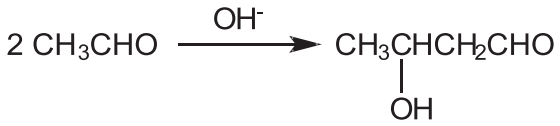
B



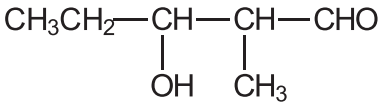
D



15 In the presence of a dilute alkali, some aldehydes and ketones undergo the 'aldol reaction' where they dimerise to form hydroxycarbonyl compound (an aldol). For example, ethanaldimerises in this way to form 3–hydroxybutanal.



Which of the following carbonyl compounds will undergo the aldol reaction to produce the aldol shown below?



A CH_3CH_2CHO **C** CH_3COCH_3

B $CH_3CH_2CH_2CH(CH_3)CHO$ **D** $CH_3CH_2COCH_3$

Part 2: *For each of the questions in this section, one or more of the 3 numbered statements **1** to **3** may be correct.*

Decide whether each of the statements is or is not correct. (You may find it helpful to put a tick against the statements which you consider to be correct.)

*The responses **A** to **D** should be selected on the basis of*

A	B	C	D
1,**2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

16 Which of these statements correctly describe an electron shell with the principal quantum number n = 2?

1 This shell can accommodate a maximum of eight electrons.

2 Electrons occupy the orbitals starting with that of the lowest energy.

3 An orbital in this shell may be spherical or dumb-bell shaped.

17 The bond in the compound **XY** is likely to be ionic rather than covalent if

1 **X** is a large cation

2 **Y** is a small anion

3 **X** has a large positive charge

*The responses **A** to **D** should be selected on the basis of*

A	B	C	D
1,**2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

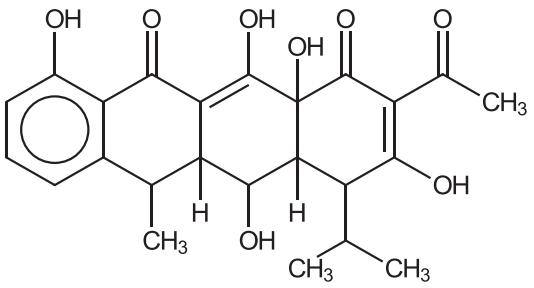
18 Which of the following have the same value as the standard enthalpy change of formation of carbon monoxide?

1 ½ $\Delta H_f^{\ominus}(CO_2)$

2 $\Delta H_f^{\ominus}(CO_2) - \Delta H_c^{\ominus}(CO)$

3 $\Delta H_c^{\ominus}(C) - \Delta H_c^{\ominus}(CO)$

19 **K** is a derivative of the antibiotic doxycycline which is often used in treating acne.



K

Which of the following statements about **K** is correct?

1 **K** turns potassium dichromate green on warming.

2 There are 5 chiral centres in each molecule of **K**.

3 Each mole of **K** produces 5 moles of H_2 when reacted with excess sodium metal.

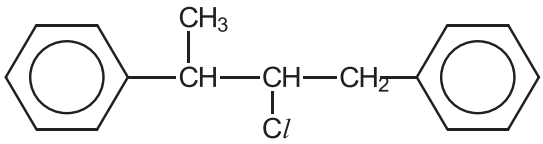
*The responses **A** to **D** should be selected on the basis of*

A	B	C	D
1,**2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

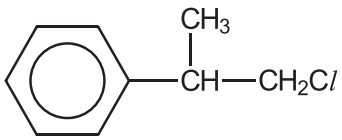
No other combination of statements is used as a correct response.

20 Which of the following compounds **cannot** be formed when ethylbenzene is treated with chlorine in the presence of sunlight?

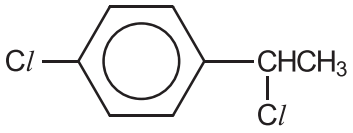
1



2



3



2012H2 Promos MCQ Answers

1	2	3	4	5	6	7	8	9	10
A	D	C	B	C	A	D	B	B	A
11	12	13	14	15	16	17	18	19	20
C	D	B	C	A	A	B	C	D	C

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CANDIDATE NAME							
CIVICS GROUP			/			TUTOR	

CHEMISTRY **9647**

Structured Questions **28th September 2012**

3 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group and name on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
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.

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	
MCQ	/20
1	/12
2	/10
3	/10
4	/10
5	/10
Essay	/40
Total	

This paper consists of **27** printed pages.

For Examiner's Use

1 Planning (P)

FA 1 is a solution containing a mixture of ethanedioic acid, $H_2C_2O_4$ and sodium ethanedioate, $Na_2C_2O_4$. The concentration of the dibasic acid, $H_2C_2O_4$, in **FA 1** is approximately 0.30% by mass. In order to determine the concentration of $Na_2C_2O_4$ in **FA 1**, two titrimetric experiments described below need to be conducted.

(a) **Experiment 1**

A redox titration was performed using potassium manganate(VII) to oxidise the ethanedioate ions, $C_2O_4^{2-}$ in the mixture to carbon dioxide. It was found that 25.0 cm^3 of **FA 1** required 20.00 cm^3 of 0.02 mol dm^{-3} $KMnO_4$ for reaction.

(i) Write a balanced ionic equation for the reaction between MnO_4^- and $C_2O_4^{2-}$.

(ii) Calculate the number of moles of MnO_4^- used to react with 25.0 cm^3 of **FA 1**.

(iii) Hence, calculate the number of moles of $C_2O_4^{2-}$ present in 1 dm^3 of **FA 1**.

[3]

For Examiner's Use

(b) **Experiment 2**

An acid-base titration is to be performed where **FA 1** was titrated against aqueous NaOH.

(i) Write a balanced equation for the reaction between NaOH and the acid in **FA 1**.

(ii) Calculate a suitable concentration for the NaOH solution that would be needed to titrate against 25.0 cm^3 of **FA 1**. Assume that the density of the ethanedioic acid solution is 1.0 g cm^{-3}.

(iii) Assuming that the concentration of NaOH calculated in **(b)(ii)** is available in the laboratory, write a detailed procedure for this titration.

[7]

(iv) Using your answers in **(a)(iii)**, **(b)(ii)** and given that the titre volume in Experiment 2 was **V** cm^3, show how you would determine the concentration in mol dm^{-3} of $Na_2C_2O_4$ in **FA 1**.

For Examiner's Use

[2]

[Total: 12]

For Examiner's Use

2 **(a)** Explain the following:

(i) The first ionisation energy of barium is larger in magnitude than the first ionisation energy of caesium.

(ii) The second ionisation energy of barium is larger in magnitude than the first ionisation energy of barium.

[3]

For Examiner's Use

(b) **(i)** Barium reacts vigorously in cold water.

Write the equation, including state symbols, for the reaction of barium with water.

(ii) 6.00 g of barium is placed in 100 cm^3 of water. The resultant solution is then reacted with 100 cm^3 of 1.2 mol dm^{-3} of HC*l*(aq). Upon mixing, the temperature of the mixture increased by 6.1 ^oC.

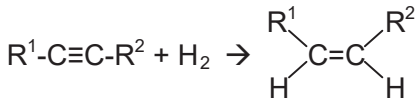
Calculate the enthalpy change for the neutralisation reaction.

(iii) Explain how the enthalpy change of neutralization for the reaction will be different when ethanoic acid is used?

[5]

(c) Alkynes can be converted to alkenes using hydrogen gas and a suitable catalyst.

For Examiner's Use



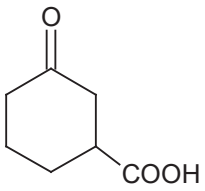
Use suitable bond energy values from the *Data Booklet* to calculate the enthalpy change for the hydrogenation of ethyne, H-C≡C-H to form ethene, C_2H_4.

[2]

[Total: 10]

For Examiner's Use

3 **(a)** The carbon atoms present in the organic compound **A** shown below has undergone orbital hybridisation to give hybrid orbitals of equivalent energy.



Compound **A**

(i) Suggest the type(s) of hybridisation exhibited by the carbon atoms in compound **A**.

(ii) Using hybridisation theory, explain why cyclohexane is not a planar molecule.

[3]

For Examiner's Use

(b) When two ammonia molecules are coupled together by removing a hydrogen atom each, a hydrazine molecule, N_2H_4, is produced. Hydrazine is a colourless, oily liquid which is used in rocket fuels, chemical manufacturing, and as boiler water treatments.

(i) Draw a 'dot-and-cross diagram' to show the electronic structure of a molecule of N_2H_4. By considering the number of bonding and non-bonding electron pairs, suggest and explain the likely shapes and bond angle (with respect to the nitrogen atoms) of this molecule.

(ii) 1 mole of hydrazine reacts with 2 moles of boron trifluoride, BF_3 to form the addition product, $N_2H_4(BF_3)_2$.

State and explain why BF_3 can be bonded to hydrazine and describe the chemical bonds that are formed during the reaction.

(iii) Draw a diagram to illustrate the likely shape and bonding in $N_2H_4(BF_3)_2$, with respect to the nitrogen atoms in the product.

For Examiner's Use

(iv) The boiling points of NH_3 and N_2H_4 are -33 ^oC and 114 ^oC respectively.
Explain the difference in boiling points for the two compounds in terms of their structure and bonding.

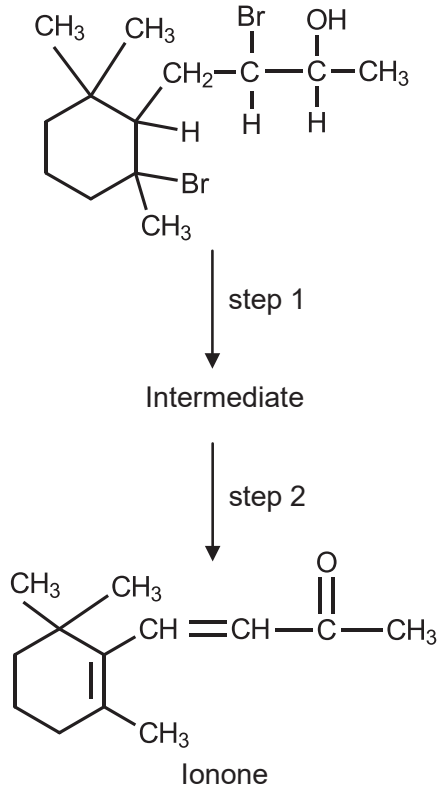
[7]

[Total: 10]

For Examiner's Use

4 Ionone is a sweet-smelling substance found in a variety of essential oils. It is a significant contributor to the aroma of roses, even at low concentration, and is an important fragrance chemical used in perfumery.

(a) Ionone can be prepared in the laboratory according to the following reaction sequence.



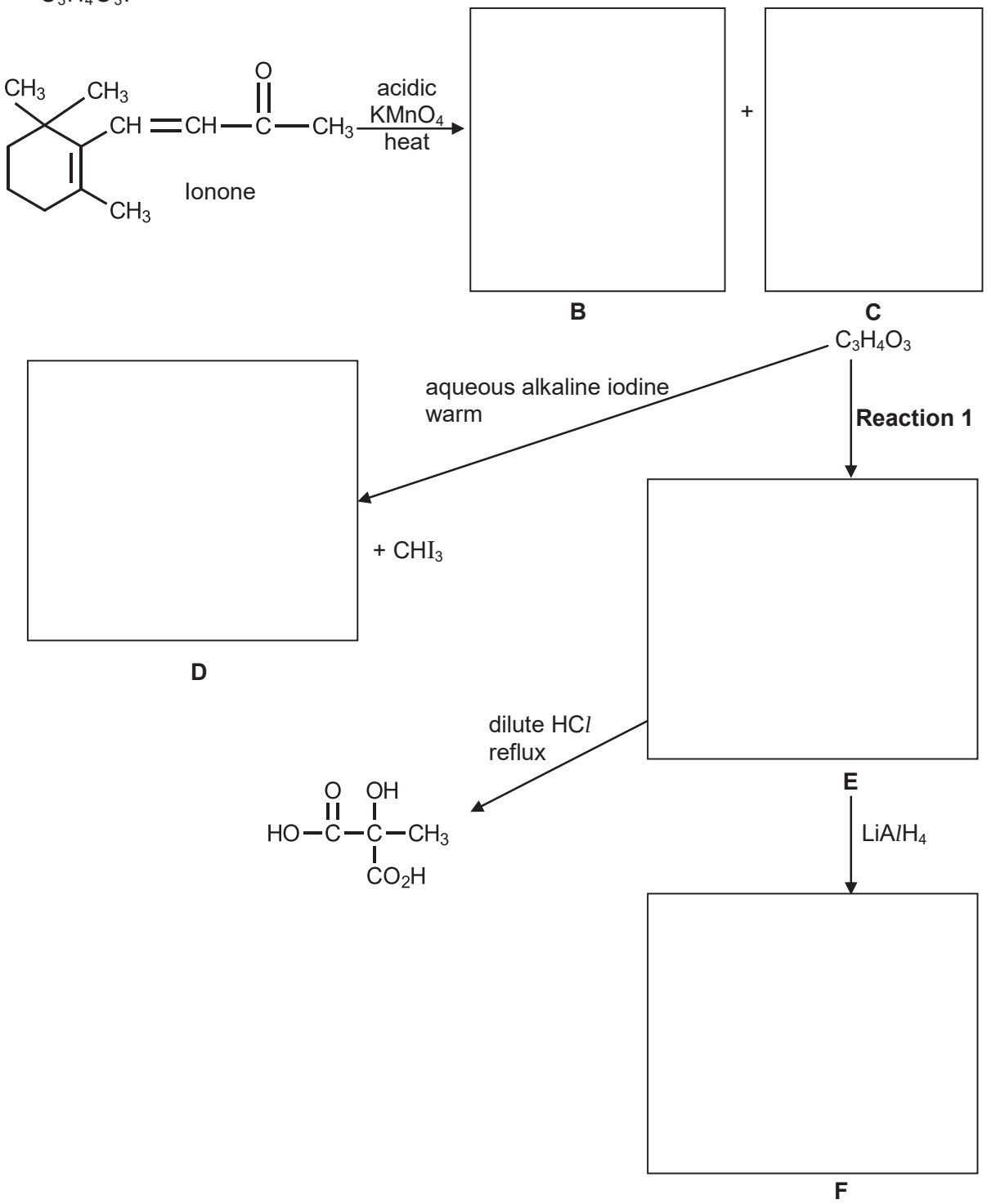
Suggest the reagents and conditions used in steps 1 and 2. [2]

Reagent and condition for step 1: _____

Reagent and condition for step 2: _____

For Examiner's Use

(b) Organic compounds **B** and **C** are formed when ionone is heated with acidic $KMnO_4$. Further reactions are then carried out with compound **C**, which has the molecular formula $C_3H_4O_3$.



(i) Draw the structural formulae of organic products **B** to **F** in the spaces provided in the reaction scheme.

(ii) Name the type of reaction that has taken place in reaction 1. Describe the mechanism for this reaction, including curly arrows showing movement of electrons, and all charges.

For Examiner's Use

Type of reaction: _____

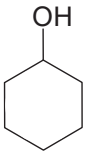
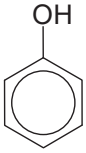
[8]

[Total: 10]

For Examiner's Use

5 This question is about the C_6 alcohols.

(a) Values of the acid dissociation constants, K_a, for some weak acids are given below.

Acid	Formula	K_a / mol dm^{-3}
Cyclohexanol		1.0×10^{-16}
Phenol		1.3×10^{-10}

Explain in terms of their molecular structures why cyclohexanol and phenol have significantly different K_a values.

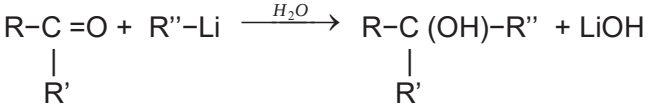
[2]

(b) **(i)** Describe a chemical reaction by which you can distinguish between 2-methylpentan-2-ol and 2-methylpentan-3-ol. State the reagents, conditions and the observations with each compound.

(ii) In the laboratory, hexan-2-ol can be synthesised from hexan-1-ol in **2 steps**. Suggest the sequence of reaction for the conversion, stating clearly the reagents, conditions and the intermediate compounds formed.

[5]

(c) Organometallic compounds, usually a metal attached to an R group, can be used to convert carbonyl compounds to alcohols. An example involving lithium can be seen below:



With the help of the above reaction in a synthesis route, hexan-2-ol can be converted to a C_7 alcohol, 2-methyl-hexan-2-ol, in **2 steps**. Write the reagents and conditions required for the conversion, including the intermediate compounds.

[3]

[Total: 10]

1 Planning (P)

(a) (i) •$2MnO_4^- + 5\ C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

(ii) •Amt MnO_4^- reacted = 20/1000 x 0.02 mol = 4.00×10^{-4} mol

(iii) $2MnO_4^- \cong 5C_2O_4^{2-}$

•Amt $C_2O_4^{2-}$ present in 1 dm^3 FA 1 = 4.00×10^{-4} x 5/2 x 1000/25 = 4.00×10^{-2} mol

(b) (i) •$H_2C_2O_4 + 2NaOH \longrightarrow Na_2C_2O_4 + 2H_2O$

(ii) Conc. of acid = 0.30% by mass

1 dm^3 of FA 1 contains 0.3/100 x 1000 g $H_2C_2O_4$ = 3.00 g $H_2C_2O_4$

•1 dm^3 FA 1 contains 3/90 mol $H_2C_2O_4$ = 3.33×10^{-2} mol $H_2C_2O_4$

25.0 cm^3 FA 1 contains 25/1000 x 3.33×10^{-2} mol $H_2C_2O_4$ = 8.33×10^{-4} mol $H_2C_2O_4$

•Number of moles NaOH needed to react with 25.0 cm^3 FA 1 = 8.33×10^{-4} x 2 mol
= 1.67×10^{-3} mol

•Assume titre volume of 20.00 cm^3 of NaOH.
Concentration of NaOH needed = 1.67×10^{-3} x 1000/20 = 0.0835 mol dm^{-3}

(iii)

1. Pipette 25.0 cm^3 of FA 1 into a 250 ml conical flask.
2. Add 1-2 drops of phenolphthalein as indicator.
3. Titrate with NaOH until the mixture turns from colourless to permanent pink.
4. Repeat the titration until consistent readings are obtained ie titre values differ by ±0.10 cm^3

• Appropriate apparatus & capacity
•Indicator and colour change at end point
•Consistent readings

(iv) Number of moles NaOH used = V/1000 x 0.0835 mol = $8.35V \times 10^{-5}$ mol

•Number of moles $H_2C_2O_4$ in 25.0 cm^3 FA 1 = $8.35V \times 10^{-5}$ / 2 mol
= $4.18V \times 10^{-5}$ mol

Number of moles $C_2O_4^{2-}$ from $H_2C_2O_4$ in 25.0 cm^3 FA 1 = $4.18V \times 10^{-5}$ mol

Number of moles $C_2O_4^{2-}$ from $H_2C_2O_4$ in 1 dm^3 FA 1 = $4.18V \times 10^{-5}$ x 1000/25
= $1.67V \times 10^{-3}$ mol

Number of moles $C_2O_4^{2-}$ from $H_2C_2O_4$ and salt in 1 dm^3 FA 1 = 4.00×10^{-2}mol

Number of moles $C_2O_4^{2-}$ from salt in 1 dm^3 FA 1 = $4.00 \times 10^{-2} - 1.67V \times 10^{-3}$ mol

•Conc $Na_2C_2O_4$ = $4.00 \times 10^{-2} - 1.67V \times 10^{-3}$ mol dm^{-3}

2 (a) (i) ● The first IE of barium is larger in magnitude than the first IE of caesium as barium has greater number of protons (hence a stronger nuclear charge) compared to caesium. Shielding effect remains effectively constant as electrons are on the same quantum shell.
● Hence electrons in barium are closer and held more strongly by the nucleus and more energy is required to remove the electron from barium.

(ii) 1^{st} IE: $Ba \rightarrow Ba^{+} + e^{-}$
2^{nd} IE: $Ba^{+} \rightarrow Ba^{2+} + e^{-}$

● As the electrons are removed from the barium ion, the remaining electrons are fewer and reduction in screening effect and held more strongly by the nucleus which has the same number of protons (nuclear charge remains unchanged) hence more energy is required to remove the next electron to form Ba^{2+}.

(b) (i) ● $Ba(s) + 2H_2O(l) \rightarrow Ba(OH)_2(aq) + H_2(g)$

(ii) $Ba(OH)_2(aq) + 2\,HCl(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$

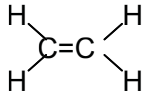
No of moles of HCl = 0.12 mol
No of moles of $Ba(OH)_2$ = 6/137 = 0.0438 mol
● $Ba(OH)_2$ is limiting.

● Heat evolved = $mc\Delta T$ = 200 x 4.18 x 6.1 = 5.10 kJ
(Or q = $mc\Delta T$ = 200 x 4.18 x 6.1 = - 5.10 kJ must have sign)

No of moles of water formed = 0.0438 x 2 = 0.0876 mol

● ΔH = - 5.10 /0.0876 = - 58.2 $kJmol^{-1}$

(iii) ● Ethanoic acid is a weak acid and has a low degree of dissociation in solution. The heat evolved from the neutralisation process is absorbed by the ethanoic acid to further dissociate it to provide H^{+}(aq) ions for the neutralisation with the base. Hence the enthalpy change for the reaction is less exothermic than that of a strong acid being neutralised by a strong base.

(c) $H\text{-}C\equiv C\text{-}H + H\text{-}H \rightarrow$ 

ΔH = Bonds broken – Bonds formed
= 1H-H + C≡C – (C=C + 2C-H)
● = 436 + 840 – (610 + 2(410))
● = - 154 $kJmol^{-1}$

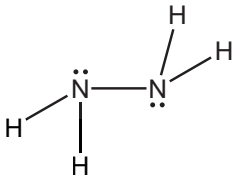
3 (a) (i) ●● sp^2, sp^3

[2]

(ii)

- Every carbon atom in  is bonded to 2 carbon atoms and 2 hydrogen atoms. Hence, these carbon atoms used sp^3 hybrid orbitals for the formation of the 4 sigma bonds. sp^3 hybrid orbitals are arranged in a tetrahedral/non-planar manner. Therefore, cyclohexane cannot be a planar molecule.

(b) (i)



● 4 electron pairs around each N atom
3 bond pairs and 1 lone pair
To maximise stability and minimum repulsion, the arrangement of electron pairs around each nitrogen is tetrahedral
since lone pair-bond pair repulsion is greater than bond pair-bond pair repulsion the shape is trigonal pyramidal at each nitrogen atom.
●Bond angle :107^0

1 mark for dot-cross diagram
1 mark for deducing shape at each nitrogen atom
1 mark for bond angle

(ii)

- **In BF_3, B** has only 6 electrons around it and hence **has an empty orbital** (or is electron deficient). Hence, B can **accept the 1 lone pair of electrons from N in N_2H_4** via **dative bonding** to **attain a stable octet configuration**. Since there are two nitrogen atoms in hydrazine two moles of boron trifluorides can be bonded to 1 molecule of hydrazine

(iii)

Dotted lines and tetrahedral arrangement to be shown for at least one N atom. [5]

(v)

- Both NH_3 and N_2H_4 are discrete molecules with **simple molecular structure**, capable of forming **hydrogen bonding** between their molecules.
- However, **more extensive hydrogen bonding** is formed between N_2H_4 molecules due to **a greater number of lone pairs present on N atoms** (or greater number of H atoms per molecule).

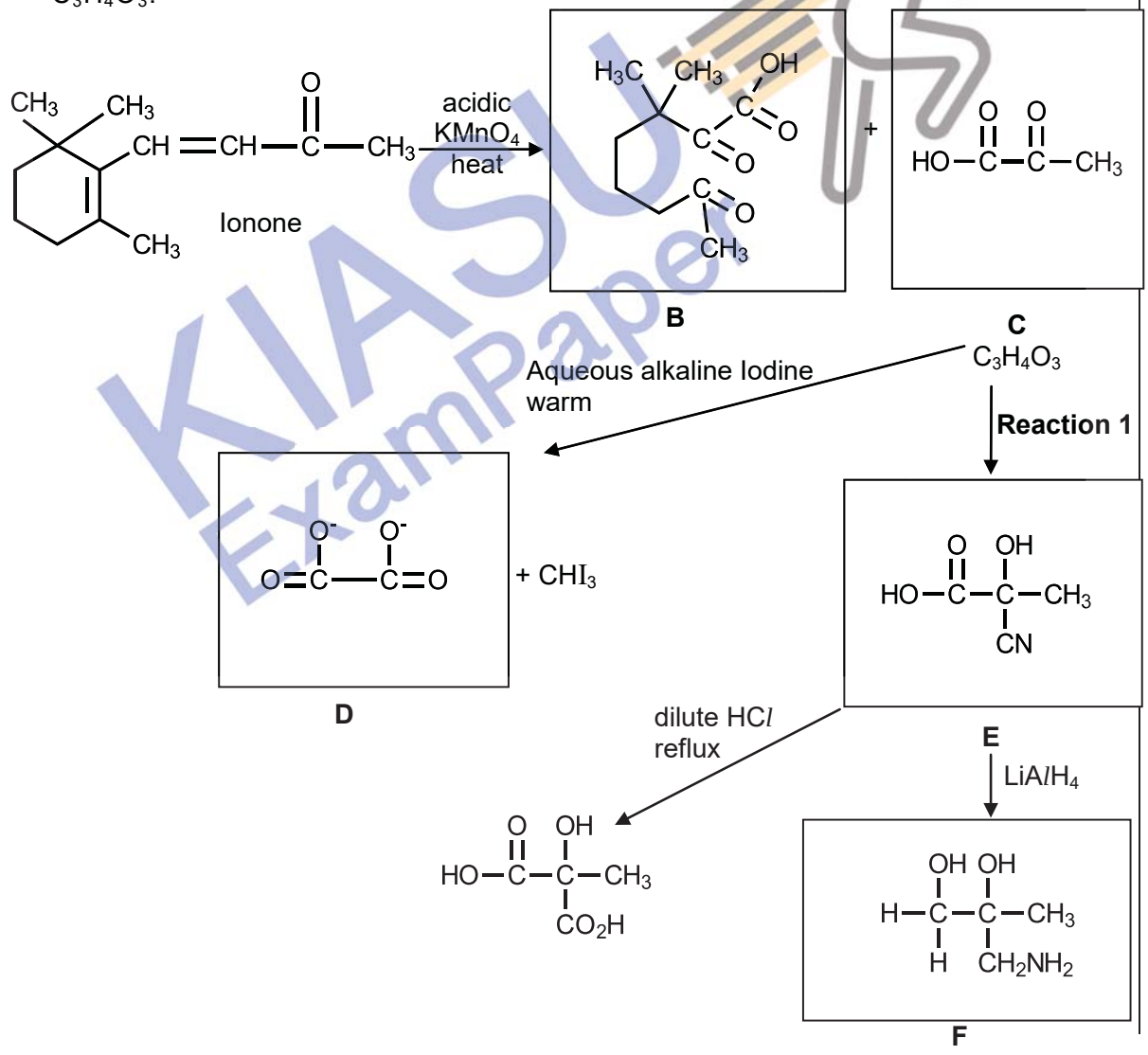
  Hence **more energy is required to break the intermolecular hydrogen bonding** in N_2H_4. Thus N_2H_4 has a higher boiling point than NH_3.

4 (a) Reagent and condition for step 1: **acidic $KMnO_4$ or $K_2Cr_2O_7$, heat**

Reagent and condition for step 2: **alcoholic KOH, reflux**

*** Answers to steps 1 & 2 can be switched, but reject acidic $KMnO_4$ in step 2 as it will oxidise alkene.**

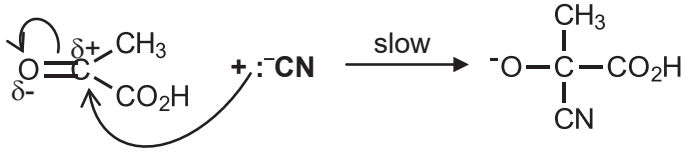
(b) Organic compounds **B** and **C** are formed when ionone is heated with acidic $KMnO_4$. Further reactions are then carried out with compound **C**, which has the molecular formula $C_3H_4O_3$.



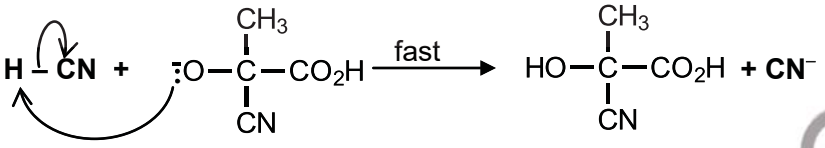
(ii)

- Type of reaction: **nucleophilic addition**

Step 1: Nucleophilic attack of CN^-



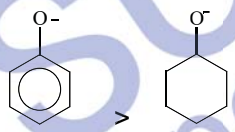
Step 2: Protonation of the negatively charged oxygen atom



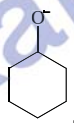
- Equations with correct intermediate
- Partial Charges, lone pair of electrons, slow/fast, arrows to indicate electron flow

[Total: 10]

5 (a) The larger the K_a value, the stronger is the acid.
Strength of acid depends on the stability of the anion when the acid ionises.

Stability of anion is as follows:  >

- For **phenoxide**, the lone pair of electrons on the oxygen atom is delocalised into the benzene ring. The negative charge on the **phenoxide ion** is dispersed, thereby stabilizing the ion. Thus, protons leave the phenol molecules more readily to form the stable phenoxide ion.



- In comparison for , the negative charge is confined to the oxygen atom. Also, the cyclohexyl (alkyl) group in the ion is electron-releasing and it intensifies the negative charge density on the oxygen atom and this destabilizes the anion. The protons do not leave the cyclohexanol molecules readily, thus phenol is more acidic than cyclohexanol.

(b) (i)

- Test: To each compound in separate test tube, add acidified manganate (VII) and heat.
- Observations: For test tube containing 2-methylpentan-3-ol, purple manganate (VII) is decolourised. For test tube containing 2-methylpentan-2-ol, purple colour remains.

OR

- Test: To each compound in separate test tube, add acidified dichromate (VI) and heat.
- Observations: For test tube containing 2-methylpentan-3-ol, the colour of the

solution will turn from orange to green. For test tube containing 2-methylpentan-2-ol, orange colour remains in the solution.

(ii) $CH_3CH_2CH_2CH_2CH_2CH_2OH \longrightarrow CH_3CH_2CH_2CH_2CH(OH)CH_3$

- Excess concentrated H_2SO_4, 180 ^oC
- cold concentrated. H_2SO_4 followed by H_2O, warm at 80 ^oC
- $CH_3CH_2\ CH_2\ CH_2CH{=}CH_2$

2marks for reagents and conditions, 1mark for intermediate.

(c) Organometallic compounds, usually a metal attached to an R group, can be used to convert carbonyl compounds to alcohols. An example involving lithium can be seen below:

$$R{-}C(=O)(R') + R''{-}Li \xrightarrow{H_2O} R{-}C(OH)(R'){-}R'' + LiOH$$

With the help of the above reaction in a synthesis route, hexan-2-ol can be converted to a C_7 alcohol, 2-methyl-hexan-2-ol, in **2 steps**. Write the reagents and conditions required for the conversion, including the intermediate compounds. [3]

$CH_3CH_2\ CH_2\ CH_2CH(OH)CH_3$ —(● Acidified $KMnO_4$, reflux)→ ● $CH_3CH_2CH_2CH_2CH_2COCH_3$

↓

● CH_3 –Li & H_2O

$CH_3CH_2CH_2CH_2C(CH_3)(OH)CH_3$

2 marks for reagents and conditions, 1 mark for intermediate.

[Total: 10]

Section B

Answer **all** questions. Begin each answer on a separate sheet of paper.

1 (a) This question is about organic compounds with molecular formula $C_4H_8O_2$.

One compound with molecular formula $C_4H_8O_2$ is the ester, ethyl ethanoate.

Here are two possible reaction routes for the synthesis of ethyl ethanoate:

Reaction **I** $CH_3CH_2OH(l) + CH_3CO_2H(l) \xrightarrow{\text{heat}} CH_3CO_2CH_2CH_3(l) + H_2O(l)$

Reaction **II** $CH_3CH_2OH(l) + CH_3COCl(l) \rightarrow CH_3CO_2CH_2CH_3(l) + HCl(g)$

(i) State the chemical reagent required for Reaction **I**.

(ii) By means of an energy cycle, determine the ΔH_r^{θ} of Reaction **II**.

Use the following data:

	ΔH_f^{θ} / kJ mol^{-1}
$CH_3CH_2OH(l)$	– 278
$CH_3COCl(l)$	– 275
$CH_3CO_2CH_2CH_3(l)$	– 481
$HCl(g)$	– 92.3

(iii) Predict whether the entropy change, ΔS^{θ}, of Reaction **II** is positive or negative. Explain your prediction.

(iv) Hence explain, in thermodynamic terms, if heat is required for Reaction **II** to be feasible.

[7]

(b) Compounds**A**, **B** and **C** are isomersof ethyl ethanoate, also having the molecular formula $C_4H_8O_2$.

All three compounds **A**, **B** and **C** produce white fumes with solid PCl_5 in the cold.

Compounds **A** and **B**produce an orange precipitate with 2,4-dinitrophenylhydrazine whereas compound **C** does not.

Only compound **A** gives a silver mirror with Tollens' reagent.

When alkaline aqueous iodine is separately warmed with the three compounds, only compounds **A** and **B**produce yellow precipitate.

Compounds **A** and **B**are also optically active. When compound **B** is reacted with $LiAlH_4$ in dry ether, the product formed is optically inactive.

Compound**C**can exhibit *cis-trans* isomerism and when it reacts with hot acidified $KMnO_4$, the only products formed are CO_2 and H_2O.

Deduce the structures of compounds **A**, **B** and **C**, explaining your reasoning.

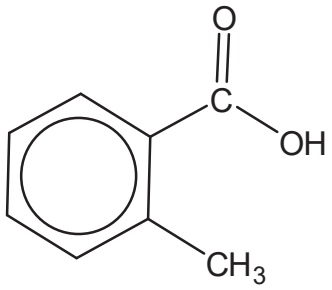
[11]

(c) Compound **D**,$CH(OH)=CHCH(OH)CH_3$, is another isomer which has the molecular formula $C_4H_8O_2$.

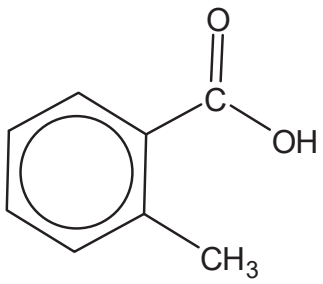
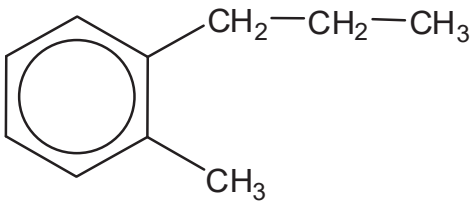
Draw **all** possible stereoisomers of compound **D**. [2]

[Total:20]

2 Compound **E**, 2-methylbenzoic acid, is used as an intermediate for the synthesis of dyes and pesticides.



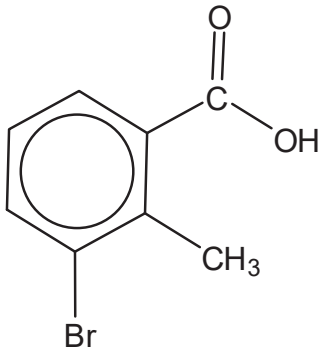
Compound **E**

Compound	M_r	***Boiling Point / °C***
 Compound **E**	136	259
 1-methyl-2-propylbenzene	134	186

(a) Explain the difference in the boiling points of the above compounds. [2]

(b) Explain why compound **E** is miscible with propanone, but is only slightly miscible with water. [3]

(c) Compound **F** can be formed when compound **E** undergoes bromination.



Compound **F**

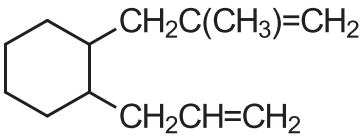
(i) State the reagents and conditions for the reaction.

(ii) Another product, which is the isomer of compound **F,** is also formed in the reaction. Draw the displayed formula of the product.

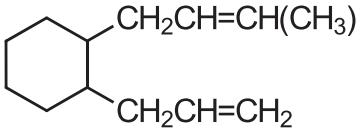
(iii) Name the type of reaction and describe the mechanism for this reaction, including curly arrows showing the movement of electrons, and all charges.

[5]

(d) Compounds **G** and **H** are isomers of each other.



Compound **G**



Compound **H**

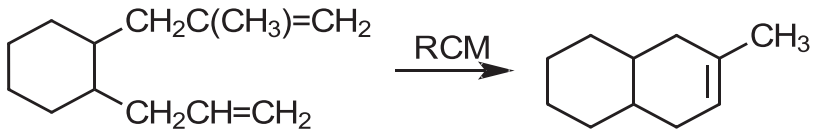
Both compounds react with hot, alkaline $KMnO_4$. Draw the structures of the organic products formed.

[2]

(e) Two students were arguing about the number of geometrical isomers compound **H** exhibits. Alice mentioned in her argument that compound **H**has 4 geometrical isomers. Another student, Ben, argues that there are 8 geometrical isomers. State and explain whether you agree with Alice's or Ben's argument.

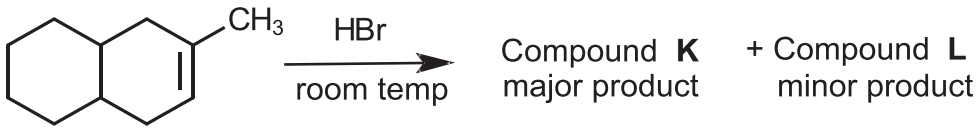
[2]

(f) Ring-Closing Metathesis (RCM) is an efficient and practical method to synthesise cyclic alkenes. Compound **G** undergoes RCM to form compound **J** as shown:



Compound **G** Compound **J**

(i) Upon reacting compound **J** with HBr at room temperature, 2 products are obtained.



Compound **J**

Draw the structures of compounds**K** and **L**.

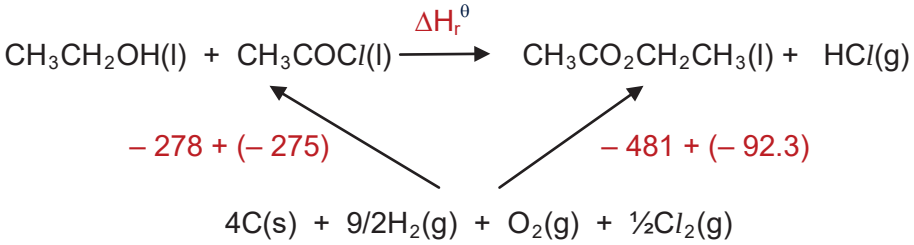
(ii) Suggest a possible reagent and condition to confirm that compound **J** has undergone a complete reaction with HBr.

(iii) Besides HBr, other halogen-containing reagents such as BrC*l* can also react with compound **J**.

Name the type of reaction and describe the mechanism for this reaction, including curly arrows showing the movement of electrons, and all charges.

[6]

[Total:20]

1	(a)	(i)	• Concentrated sulfuric acid.	[1]
		(ii)	•  • By Hess' Law, ΔH_r^θ – 278 – 275 = – 481 – 92.3 • ΔH_r^θ = – 20.3 kJ mol^{-1}	[3]
		(iii)	• Positive. There is an increase in the amount of gas molecules present in the system after the reaction leading to an increase in degree of disorder. There are more ways to arrange the particles in the system and therefore entropy increases.	[1]
		(iv)	• Consider: $\Delta G = \Delta H - T\Delta S$ T is always positive and in this reaction ΔH is negative whereas ΔS is positive. • ΔG would always be negative suggesting that reaction is spontaneous regardless of temperature of reaction and heat is not required.	[2]
	(b)		• Compounds **A, B and C** undergo substitution with PCl$_5$. ➢ All three compounds contain –OH group. (Note: students who wrote that compounds **A**, **B** and **C** are alcohols were NOT awarded the mark – carboxylic acids would have a similar reaction with PCl$_5$.) • Compounds **A** and **B** undergo condensation reaction with 2,4-DNPH whereas compound **C** does not undergo condensation reaction with 2,4-DNPH. ➢ Compounds **A** and **B** are ketone or aldehyde; compound **C** is neither a ketone nor aldehyde. • Only compound **A**undergoesoxidation with Tollens' reagent. ➢ Compound **A** contains aldehyde functional group while compound **B** contains ketone functional group. (Note: student needs to identify compound **A** as aldehyde AND compound **B** as ketone to be awarded the mark.) •• Compounds**A** and **B**react with warm alkaline aqueous iodine whereas compound **C** does not. ➢ Compound **A** has –CH(OH)CH$_3$ group (since the other O atom in compound **A** is found in the aldehyde functional group). ➢ Compound **B** has –CH(OH)CH$_3$ or –COCH$_3$ group.	

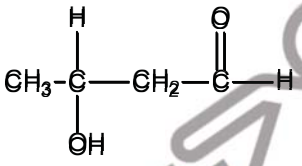
- Compounds **A** and **B** are optically active.
  - ➢ Compounds **A** and **B** have at least one chiral carbon centre and have no plane of symmetry and have non-superimposable mirror images.

- Compound **B** undergoes reduction with $LiAlH_4$ in dry ether to form a product that is optically inactive.
  - ➢ The product from reduction of compound **B** has a plane of symmetry.
  - ➢ The product from reduction of compound **B** is a secondary alcohol.

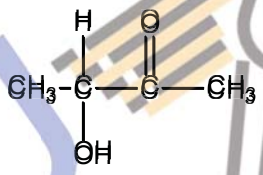
(One additional mark was awarded if student provided the structure of the secondary alcohol formed from reduction of compound **B**, i.e. $CH_3CH(OH)CH(OH)CH_3$)

- Compound **C** can exhibit cis-trans isomerism and undergoes strong oxidation with hot acidified $KMnO_4$ to form only CO_2 and H_2O.
  - ➢ Compound **C** contains C=C bond with 2 different groups on each C in the C=C bond.

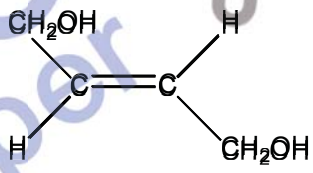
- Compound **A**: $CH_3CH(OH)CH_2CHO$



- Compound **B**: $CH_3CH(OH)COCH_3$



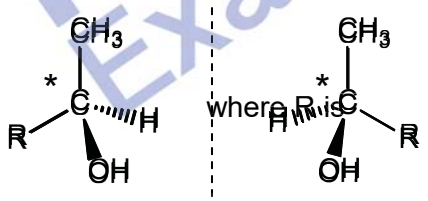
- Compound **C**: $CH_2(OH)CH=CHCH_2OH$

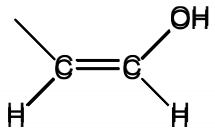


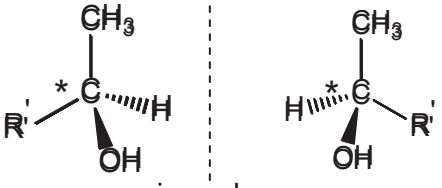
(both cis and trans representations of compound **C**are accepted)

(Note: maximum number of marks award for deduction is 8) [11]

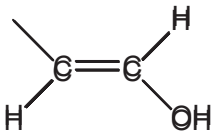
(c)

- 



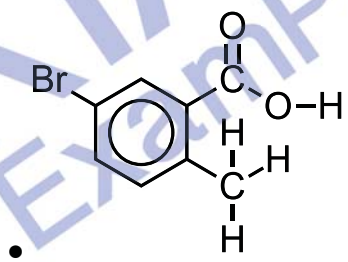
- 

where R' is



[2]

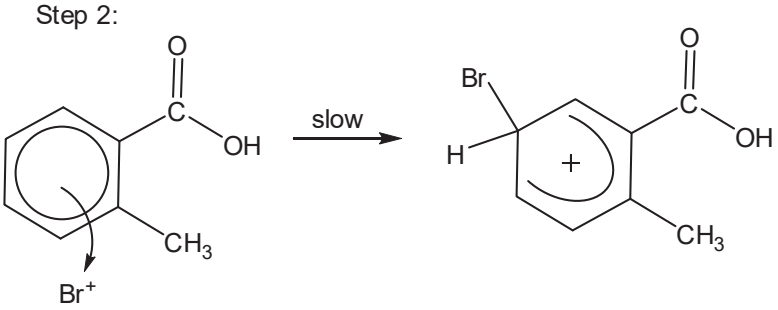
[Total:20]

2	**(a)**	• Both compounds have simple molecular structures. 1-methyl-2-propylbenzenehas van der Waals' forces of attraction between its molecules. Compound **E** has both van der Waals' forces of attraction and hydrogen bonding between its molecules. • Since these molecules have similar M_r, similar electron cloud size, more energy is required to break the hydrogen bonding and van der Waals' forces of attraction between the molecules of compound **E**. Therefore, compound **E** has the highest boiling point.		[2]
	(b)	• Propanone and water have simple molecular structures. Propanone has van der Waals' forces of attraction between its molecules while water has hydrogen bonding between its molecules. *Note: Compound **E**'s structure and bonding need not be mentioned here again, as it has been mentioned in (a).* • As formation of van der Waals' forces of attraction and hydrogen bonding between compound **E** and propanonereleases sufficient energy to break both the van der Waals' forces of attraction between propanone molecules as well as van der Waals' forces of attraction and hydrogen bonding between molecules of compound **E**, compound **E** is miscible with propanone. • As formation of hydrogen bonding between compound **E** and water releases insufficient energy to overcome all the stronger hydrogen bonding between water molecules, as well as van der Waals' forces of attraction and hydrogen bonding between molecules of compound **E**, compound **E** is only slightly miscible in water.		[3]
	(c)	**(i)**	• $Br_2(l)$ in the presence of anhydrous $FeBr_3$ under room conditions	[1]
		(ii)	• 	[1]
		(iii)	• Electrophilic substitution • Slow/fast step, partial charges, lone pair of electron • Curly arrows to indicate electron flow	[3]

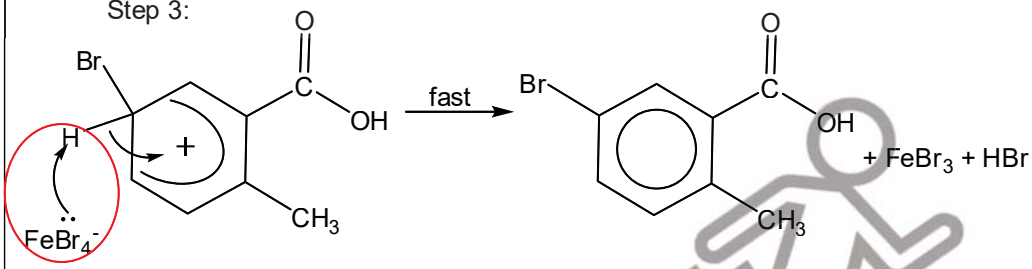
Step 1:

$FeBr_3 + Br\text{-}Br \rightleftharpoons FeBr_4^- + Br^+$

Step 2:



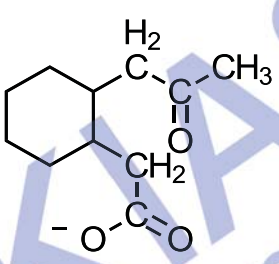
Step 3:

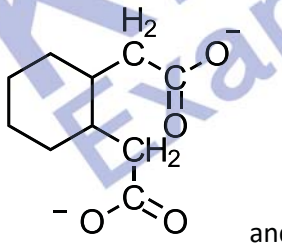


Note: A*l*Br_3 would also be accepted as the catalyst. The circled-arrow is not a marking point.

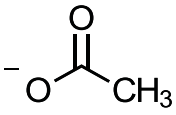
Note: Mechanism for the formation of isomer or compound **F** would be awarded marks.

(d)



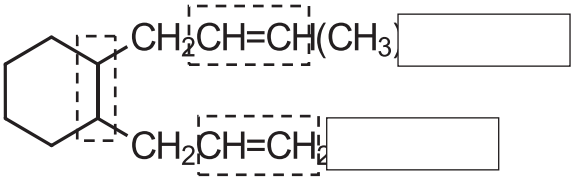


and



[2]

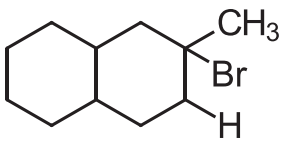
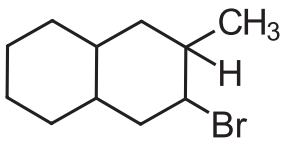
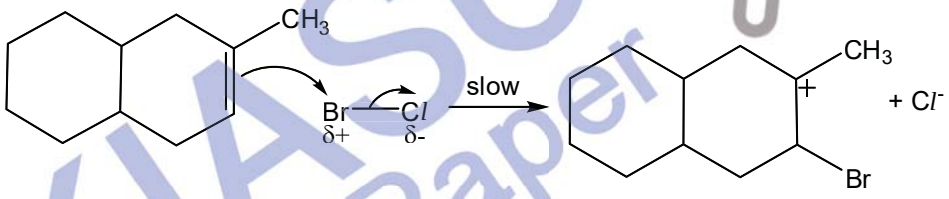
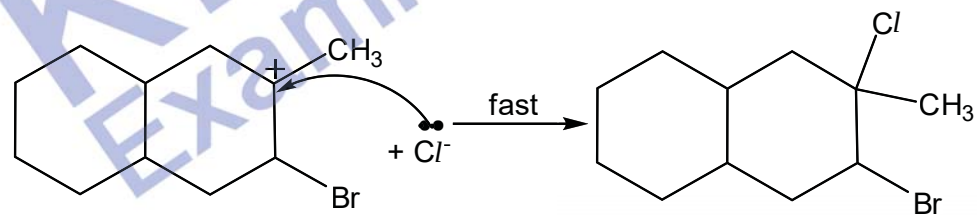
(e)

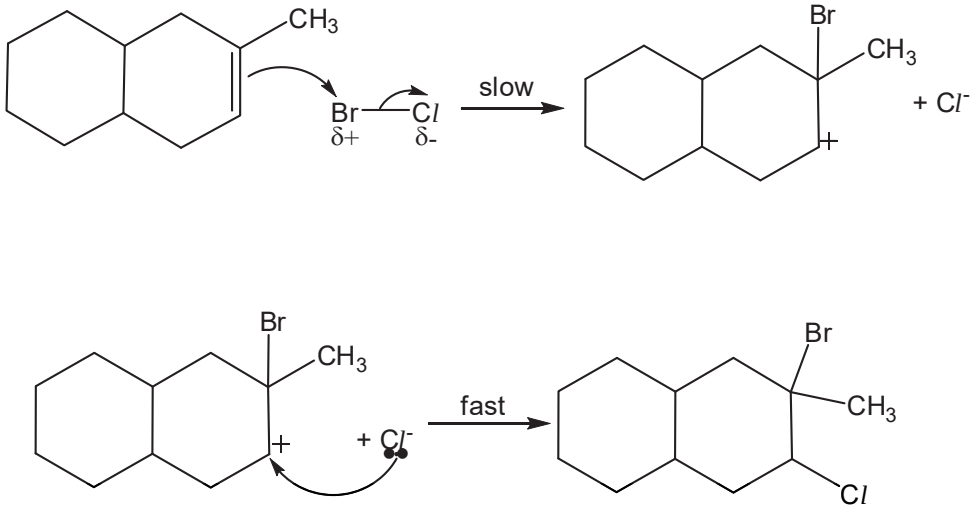


Compound **H**

- I agree with Alice's argument as Compound **H** has 4 geometric isomers.
  Note: No mark for stating Alice is correct without giving any reason, or for supporting it with the wrong reason (such as presence of chiral centres and molecule having no plane of symmetry).
- There is 1 double-bond (C=C) and the cyclohexane ring present in Compound

[2]

			Hwhich exhibits geometric isomerism due to its <u>restricted rotation</u> and that there are <u>2 different substituents attached to each carbon atom</u>in the C=C and the two carbon atoms in cyclohexane.	
	(f)	**(i)**	 Compound **K** Major product  Compound **L** Minor product •Draw the correct product of addition of HBr. •Label which is major or minor / Compound **K** and **L**	[2]
		(ii)	• Br_2 (aq) – bromine water, room temperature Cold, dilute, acidic $KMnO_4$ Acidic $KMnO_4$, heat	[1]
		(iii)	• Electrophilic addition *Either major/minor product drawn will be accepted.* Step 1:  Step 2:  OR	[3]



- 1 mark for balanced equations for both steps, with the correct carbocation
- 1 mark for curly arrows, partial charges, fast and slow steps

[Total:20]