RAFFLES JUNIOR COLLEGE
PRELIMINARY EXAMINATION 2008

Higher 1

CANDIDATE NAME

CLASS

INDEX NUMBER

CHEMISTRY 8872/02

Paper 2

15 September 2008

2 hours

Candidates answer Section A on the Question Paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Write your name, class and index number in the spaces provided on the cover page.
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 paper clips, highlighters, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **two** questions on separate answer paper.

A Data Booklet is provided. Do not write anything on it.
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.

For Examiner's Use	
Section A	/40
B6	/20
B7	/20
B8	/20
Total	/80

This question booklet consists of **12** printed pages.

Section A

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

1 (a) To determine the concentration of lead(II) ions in a sample of lead(II) nitrate solution, 25.0 cm^3 of the solution was added to 40.00 cm^3 of 0.400 mol dm^{-3} hydrochloric acid. Lead(II) chloride was precipitated out and the mixture was filtered. It was found that 25.0 cm^3 of the filtrate required 27.45 cm^3 of 0.150 mol dm^{-3} silver nitrate solution for complete reaction. Calculate the concentration of lead(II) ions in the lead(II) nitrate solution.

[4]

(b) Sodium nitrite, $NaNO_2$, is used as a preservative in meat products such as frankfurters and bologna. In an acidic solution, nitrite ion, NO_2^-, is oxidised to nitrate ion, NO_3^-, when it reacts with the manganate(VII) ion, MnO_4^-. A 1.00 g sample of a water-soluble solid containing $NaNO_2$ was dissolved in dilute H_2SO_4 and titrated with 0.0100 mol dm^{-3} aqueous $KMnO_4$ solution. The titration required 12.15 cm^3 of the $KMnO_4$ solution.

(i) Write an equation for the reaction between MnO_4^- and NO_2^-.

(ii) Calculate the percentage by mass of $NaNO_2$ in the 1.00 g sample.

[4]
[Total: 8]

2 **(a)** The identities of three unknown elements **X**, **Y** and **Z** are rubidium (Rb), strontium (Sr) and caesium (Cs) but not necessarily in that order. The order of the elements in order of increasing first ionisation energy is **X** < **Y** < **Z**.

(i) Suggest the identity of each element **X**, **Y** and **Z**.

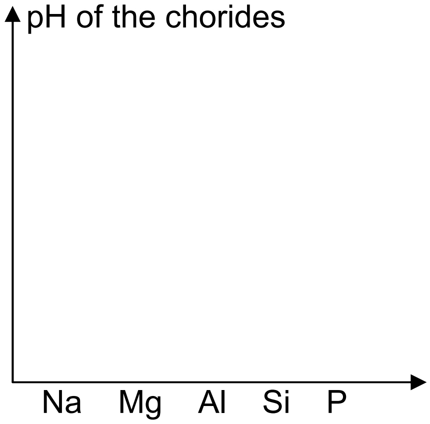
(ii) Explain why the first ionisation energy of element **X** is smaller than the first ionisation energy of element **Y**.

(iii) Explain why the first ionisation energy of element **Y** is smaller than the first ionisation energy of element **Z**.

[5]

(b) The following parts are about the chemistry of Period 3 elements and their compounds.

(i) Complete the sketch for the variation in pH of the aqueous solution of chlorides of the following elements.



(ii) With the aid of relevant equations, briefly explain the shape of your sketch in **(i)**.

(iii) Aluminium oxide is *amphoteric.* Explain what the word in italics means.

[5]
[Total: 10]

3 (a) Define the term *standard enthalpy change of neutralisation.*

[1]

(b) 10.0 cm^3 of 1.00 mol dm^{-3} barium hydroxide was added to 50.0 cm^3 of 0.400 mol dm^{-3} hydrochloric acid. Calculate the temperature change given that the enthalpy change of reaction between aqueous barium hydroxide and hydrochloric acid is –114 kJ mol^{-1} and the amount of heat energy required to raise the temperature of 1 cm^3 of solution by 1 K is 4.20 J.

[3]

(c) Draw an energy profile of the reaction in **(b)**, showing clearly the activation energy and the enthalpy change of the reaction.

[2]

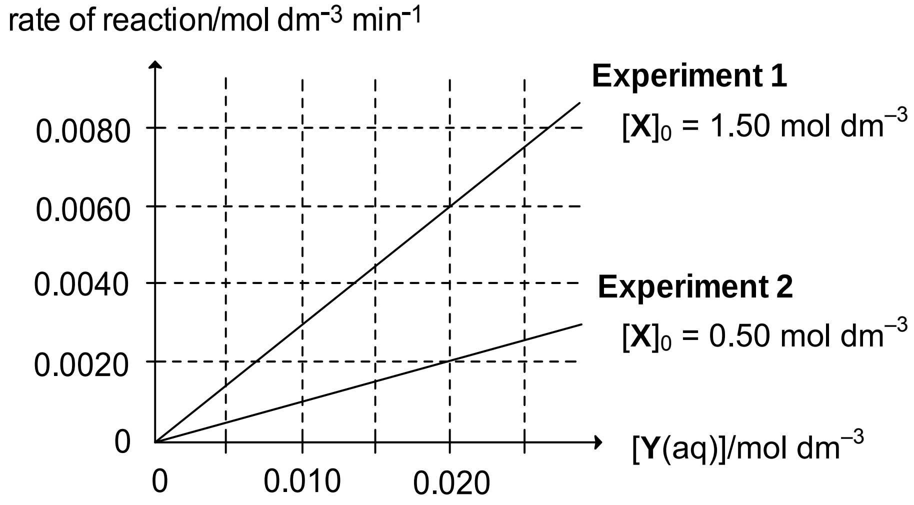
[Total: 6]

4 (a) The reaction between **X** and **Y** can be represented by the following equation:

$$\mathbf{X}(aq) + 2\mathbf{Y}(aq) \longrightarrow \mathbf{Z_1}(aq) + \mathbf{Z_2}(g)$$

To study the kinetics of the above reaction, two experiments were carried out in the presence of excess **X**. The experimental results obtained are graphically represented below.

Note: $[\mathbf{X}]_0$ = initial concentration of **X**(aq)



(i) Explain what is meant by *order of reaction with respect to* ***X***.

(ii) With the aid of the graph, determine the order of reaction with respect to each of the two reactants, **X** and **Y**.

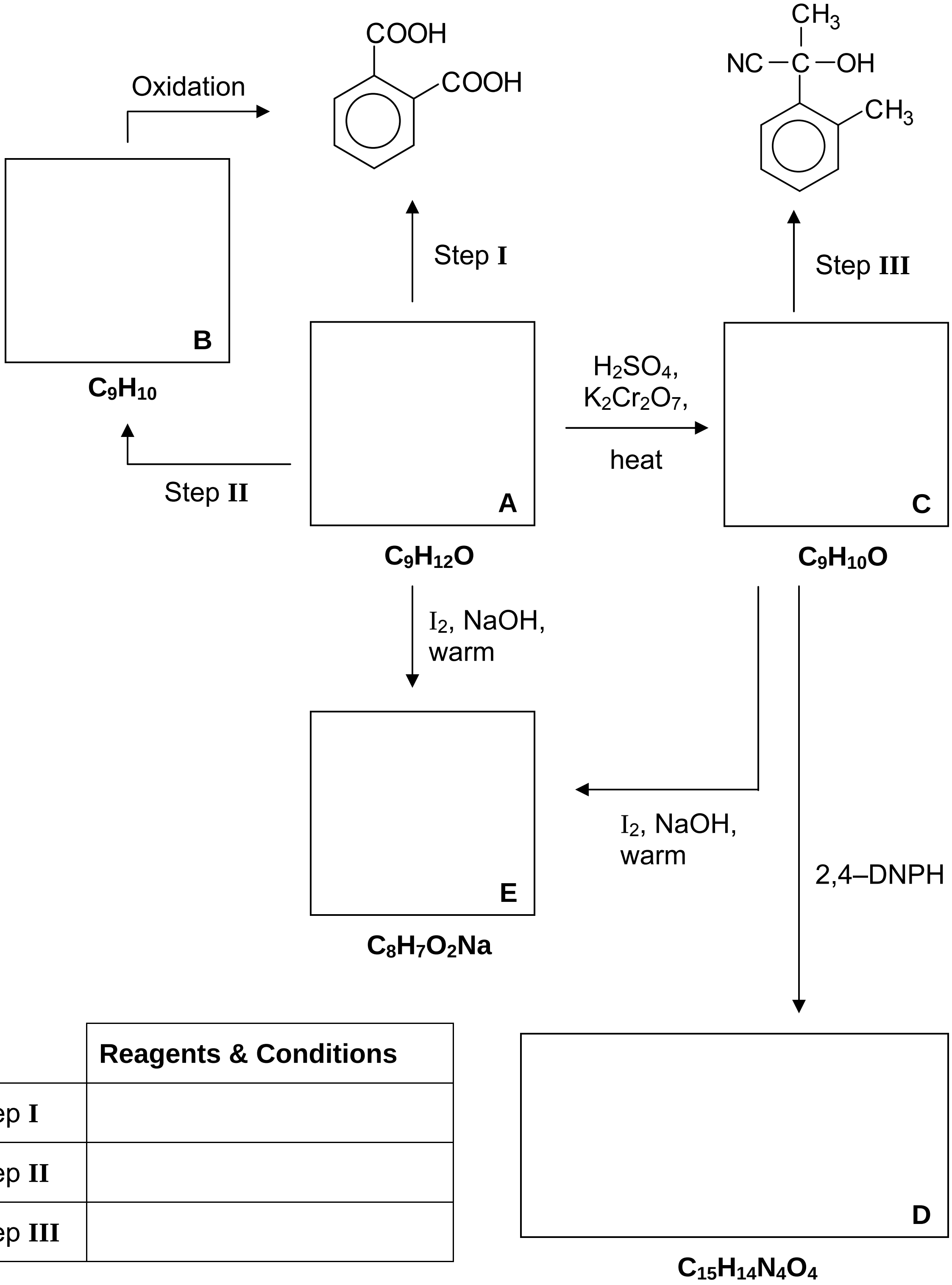
(iii) Hence write down the rate equation for the reaction and state the units for the rate constant k.

[5]

(b) With the aid of a sketch of the *Boltzmann distribution*, state and explain the effect of an increase in temperature on the rate of a chemical reaction.

[3]
[Total: 8]

5 For the reaction scheme below, give the reagents and conditions for steps **I** to **III** in the table provided, and draw the structural formulae of **A** to **E** in the boxes provided



	Reagents & Conditions
Step **I**	
Step **II**	
Step **III**	

[Total: 8]

Section B

Answer **two** of the three questions in this section on separate paper.

6 (a) With the crude oil prices hitting over US\$100 a barrel, many motorists are opting for lower octane rating petrol to make ends meet. The octane rating of a fuel is the knock resistance (anti-knock rating) compared to a mixture of an isomer of octane and heptane. As octane has a total of 18 isomers, It is useful to study how these isomers may be used to derive cheaper but yet acceptable knock resistance fuel.

Isomers of octane may also be distinguished by the number of mono-brominated products formed upon reaction with bromine.

(i) Name the reaction mechanism of the above reaction of octane with bromine. State the reagents and conditions required

(ii) Draw an isomer of octane which reacts with limiting bromine to give

- **(1)** only <u>one</u> mono–brominated product
- **(2)** <u>three</u> mono–brominated products

(iii) State the type of isomerism exhibited by your answers to **(ii)**.

(iv) State which isomer, **(1)** or **(2)**, has a higher boiling point.

[6]

(b) To combat pollution and soaring fuel cost, luxury sports car maker Ferrari is experimenting with ethanol to help produce cars with lower carbon dioxide emissions and improved fuel economy. Titled “Drunk with Power”, this project using ethanol as fuel also claims to bring about an increase in the horsepower of the automobile too!

(i) Draw a dot–and–cross diagram of ethanol and hence suggest a value for the C–O–H bond angle.

(ii) Write an equation that represents the standard enthalpy change of formation of ethanol.

(iii) Using the data given below and relevant bond energy data from the Data Booklet, calculate the standard enthalpy change of formation for ethanol.

ΔH^{o}_{atom} C (s) = +717 kJ mol^{-1}
$\Delta H^{o}_{vaporisation}$ CH_3CH_2OH (l) = +43 kJ mol^{-1}

(iv) Write an equation for the complete combustion of ethanol. Using answer to **(iii)** and the following data, calculate the standard enthalpy change of combustion for ethanol.

$\Delta H^o_f\ CO_2(g) = -394\ \text{kJ mol}^{-1}$
$\Delta H^o_f\ H_2O(l) = -286\ \text{kJ mol}^{-1}$ [8]

(c) Ethanol is often used in the synthesis of many organic compounds, such as ethanal, ethanoic acid and sodium methanoate.

(i) Write an equation for the synthesis of sodium methanoate from ethanol.

(ii) Draw a dot–and–cross diagram of sodium methanoate.

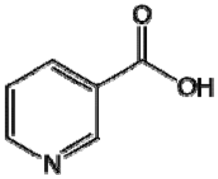
(iii) Rank the following compounds in order of increasing acidity:

ethanol ethanal ethanoic acid

Explain your answer.

[6]
[Total: 20]

7 (a) Niacin, also known as nicotinic acid and vitamin B_3, is an organic compound with the formula $HO_2CC_5H_4N$.



It is used in the treatment of hyperlipidemia because it reduces very-low-density lipoprotein (VLDL), a precursor of low-density lipoprotein (LDL) or "bad" cholesterol. It also *increases* the level of high-density lipoprotein (HDL) or "good" cholesterol in blood, and therefore it is sometimes prescribed for patients with low HDL, who are also at high risk of a heart attack.

(i) Given that nicotinic acid is a monobasic acid and can be denoted as HX. Its $K_a = 1.4\text{x}10^{-5}\ \text{mol dm}^{-3}$. Write an expression for the acid dissociation constant, K_a, and determine the pH of a 0.10 mol dm^{-3} solution of nicotinic acid.

(ii) Explain what is meant by the term buffer solution. With the aid of equations, describe how aqueous nicotinic acid (HX) and sodium nicotinate (NaX) work as a buffer.

(iii) A 0.10 mol dm^{-3} solution of nicotinic acid was titrated against a solution of a strong base. The equivalence point was found to be V cm^3. Sketch the titration curve and indicate in the sketch, the region within which the mixture is acting as a buffer solution. Suggest a suitable indicator used for the titration.

[11]

(b) Niacin was first described by Weidel in 1873 in his studies of nicotine. The original preparation remains useful and it involves the oxidation of nicotine using nitric acid, HNO_3.

(i) Draw a dot and cross diagram to show the bonding in nitric acid. Use your diagram to suggest the shape of nitric acid and the type of hybridisation around nitrogen atom in the molecule.

(ii) Nitric acid is a powerful oxidising agent. It can oxidise a solution of vanadium(III), V^{3+}, to VO^{2+}. Nitrogen dioxide, a pungent smell brown gas, is also produced. Write a balanced chemical equation with state symbols for the above reaction. State the change in oxidation number of vanadium and nitrogen in the reaction.

(iii) Predict whether niacin is soluble in water. Explain with an appropriate diagram.

[9]
[Total: 20]

8 Hydrogen iodide is used in the manufacture of hydriodic acid and in the preparation of organic and inorganic iodides. It is also used as a reducing agent. It can be formed by the reaction between H_2 and I_2 under strongly heated platinised asbestos. It exists as a homogeneous equilibrium system.

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

(a) Calculate the value of K_c at 445 °C, if the equilibrium concentrations in mol dm^{-3} of $H_2(g)$, $I_2(g)$ and HI (g) are 2.06, 13.40 and 36.98 respectively. [1]

(b) The values for the equilibrium constant K_c for the following reactions of the halogens with hydrogen at 1000 °C are shown in the table below.

Reaction	K_c at 1000 °C
$H_2(g) + F_2(g) \rightleftharpoons 2\,HF(g)$	1.0×10^{24}
$H_2(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g)$	2.0×10^{8}
$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$	1.3×10^{1}

(i) By comparing the values of K_c at 445 °C and 1000 °C, deduce whether the reaction between hydrogen and iodine is endothermic or exothermic.

(ii) State and explain the effect of an increase in total pressure of the equilibrium mixture on

(1) the rate of the forward reaction, and

(2) the composition of the equilibrium mixture.

(iii) Using the above values of K_c, comment on the strength of hydrogen–halogen bonds. Explain your answer in terms of bonding.

[8]

(c) HF, HC*l* and HI can react with alkene to form respective halogenoalkanes. The latter have enormous range of uses which include refrigerants; aerosol propellants; fire extinguisher; grease solvents and polymer production such as PVC.

(i) Give the name of the type of the reaction of HI with butene and write an equation for the reaction.

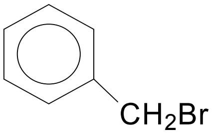
(ii) Iodobutane reacts with excess concentrated ammonia in a sealed tube. Give the name of the type of reaction undergone. State and explain how the rate of this reaction changes when iodobutane is replaced by chlorobutane or fluorobutane.

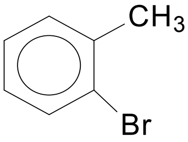
(iii) Draw structural formulae of compounds **P, Q** and **R** in the following scheme.

$$CH_3CH_2I \xrightarrow{\text{NaCN}} \textbf{P} \xrightarrow[\text{heat}]{H^+\text{(aq)/}} \textbf{Q} \xrightarrow[\text{heat}]{\substack{\mathbf{C_2H_5OH/} \\ \textbf{conc } \mathbf{H_2SO_4}}} \textbf{R}\ C_5H_{10}O_2$$

(iv) Suggest reagents and conditions for the elimination of hydrogen iodide from 2-iodobutane.

(v) Outline a simple chemical test to distinguish the following compounds, clearly stating your observations.





[11]

[Total: 20]

End of Paper

RJC H1 Chemistry Prelim 2008 Paper 2 Suggested Answers

Section A

1 (a) $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

Amt of Cl^- left in 25.0 cm^3 of filtrate = Amt of Ag^+ added
= $(27.45 \times 10^{-3})(0.15)$
= 4.118×10^{-3} mol

Amt of Cl^- left in original sample = $(4.118 \times 10^{-3})(65/25)$
= 0.01071 mol

Amt of Cl^- that has reacted = $(40/1000)(0.400) - 0.01071$
= 5.295×10^{-3} mol

$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$

Amt of Pb^{2+} = $(½)(5.295 \times 10^{-3})$
= 2.647×10^{-3} mol

Concentration of Pb^{2+} in sample = $(2.647 \times 10^{-3})/0.025$
= 0.106 mol dm^{-3}

(b) (i) $6H^+(aq) + 5NO_2^-(aq) + 2MnO_4^-(aq) \rightarrow 5NO_3^-(aq) + 2Mn^{2+}(aq) + 3H_2O(l)$

(ii) Amt of $KMnO_4$ required = $(0.0100)(12.15 \times 10^{-3})$
= 1.215×10^{-4} mol

Amt of HNO_2 present = $(1.215 \times 10^{-4})(5/2)$
= 3.038×10^{-4} mol

Molar mass of $NaNO_2$ = 23.0 + 14.0 + 2(16.0)
= 69.0 g mol^{-1}

Mass of $NaNO_2$ present = $(69.0)(3.038 \times 10^{-4})$
= 2.096×10^{-2} g

Percentage of $NaNO_2$ = $(2.096 \times 10^{-2}/1.00) \times 100\%$
= 2.10 %

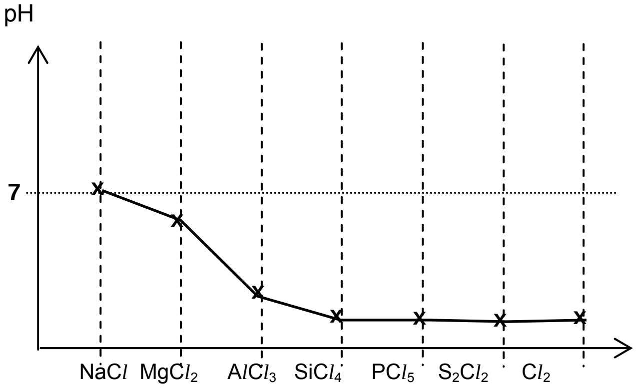
2 (a) (i) **X** = Cs, **Y** = Rb, **Z** = Sr

(ii) The valence electrons of element **X** experiences greater nuclear charge and greater shielding effect than the valence electrons of element **Y** due to more inner filled principal quantum shells.

However, the effect of increased shielding outweighs the effect of increased nuclear charge . Thus, the valence electrons of **X** are less tightly held by the nucleus than those of **Y**. Less energy is then required to remove an electron from **X**.

(iii) The valence electrons of **Y** experiences a lower nuclear charge than that of **Z**. However, both experience approximately the same shielding effect as valence electrons are found in the same principal quantum shell. Hence, effective nuclear charge experienced by valence electrons of **Y** is less than that of **Z** **,** thus, they are less tightly held by the nucleus . Less energy is then required to remove an electron from **Y**.

(c) (i)



(ii) $NaCl$ solid dissolves forming aquated ions e.g. $Na^+(aq)$, $Cl^-(aq)$

$NaCl\ (s) \rightarrow Na^+(aq) + Cl^-(aq)$ pH = 7

$MgCl_2$ dissolves with slight hydrolysis (due to high charge density of Mg^{2+})

$MgCl_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}\ (aq) + 2Cl^-\ (aq)$ pH = 6.5

$[Mg(H_2O)_6]^{2+}\ (aq) \rightleftharpoons [Mg(H_2O)_5(OH)]^+\ (aq) + H^+(aq)$

$AlCl_3$. dissolves with appreciable salt hydrolysis as Al^{3+} ion has **high charge density or**, **high polarising power**, it draws electrons away from its surrounding water molecules and weakens the O–H bond.

$AlCl_3(s) + 6H_2O \rightarrow [Al\ (H_2O)_6]^{3+}\ (aq) + 3Cl^-\ (aq)$ pH = 3

$[Al\ (H_2O)_6]^{3+}\ (aq) \rightleftharpoons [Al\ (H_2O)_5(OH)]^{2+}\ (aq) + H^+(aq)$

$SiCl_4$ and PCl_3/ PCl_5 all react with H_2O to form HCl (thus giving rise to acidic solutions)

$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$ OR
$PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HCl(aq)$ OR
$PCl_5(l) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$

6 equations each ½ mark or mention the following each ½ mark

- NaC*l* dissolves to give Na$^+$(aq),C*l*$^-$(aq) pH=7
- MgCl_2 dissolves with slight hydrolysis, pH=6.5
- A*l*C*l* $_3$. dissolves with appreciable hydrolysis
- Al^{3+} ion has **high charge density or**, **high polarizing power**, it draws electrons away from its surrounding water molecules and weakens the O–H bond.
- SiCl_4 and PCl_3/ PCl_5 all react with H_2O to form HC*l*
- pH of the chlorides decreases from Na to P

[Total 3]

(iii) Al_2O_3 is *amphoteric* means it shows both basic and acidic properties or it can react with both acid and base to give salt and water.

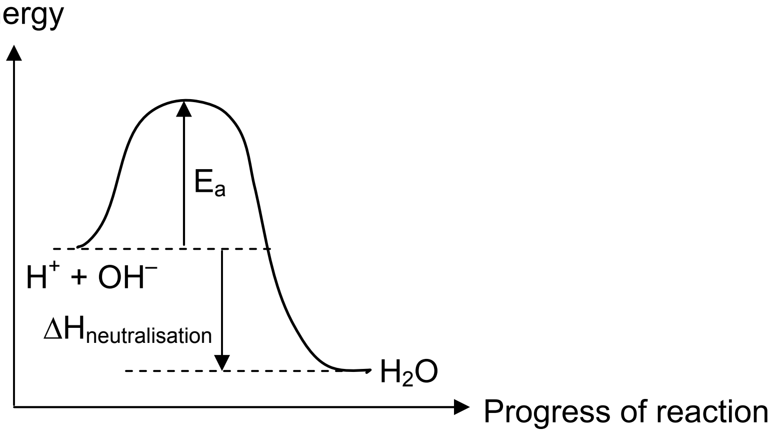
3 (a) The amount of energy evolved when 1 mole of water forms from the neutralisation of strong acid and strong base under standard conditions.

(b) Amount of barium hydroxide = (1.00)(10.0/1000) = 0.0100 mol
Amount of hydrochloric acid = (0.400)(50.0/1000) = 0.0200 mol
$Ba(OH)_2(aq) + 2HCl\ (aq) \rightarrow BaCl_2(s) + 2H_2O(l)$

Heat evolved = (114000)(0.0200)
= 2280 J
= (50.0 + 10.0)(4.20)ΔT
ΔT = 9.05 K

The temperature rose by 9.05 K.

(c)



4 **(a)** **(i)** The term ‘order of reaction with respect to **X**’ refers to the power to which the concentration of **X** is raised in the experimentally determined rate equation.

(ii) Consider either experiment 1 or experiment 2.
The graph obtained is a straight line having a positive gradient and passing through the origin. This implies that the rate is directly proportional to [Y]. Hence order of reaction with respect to Y is 1. ,

Consider the two rates of reaction when [Y] = 0.020 mol dm^{-3}.
For expt. 1 where $[X]_0$ = 1.50 mol dm^{-3},
rate = 0.0060 mol dm^{-3} min^{-1}.

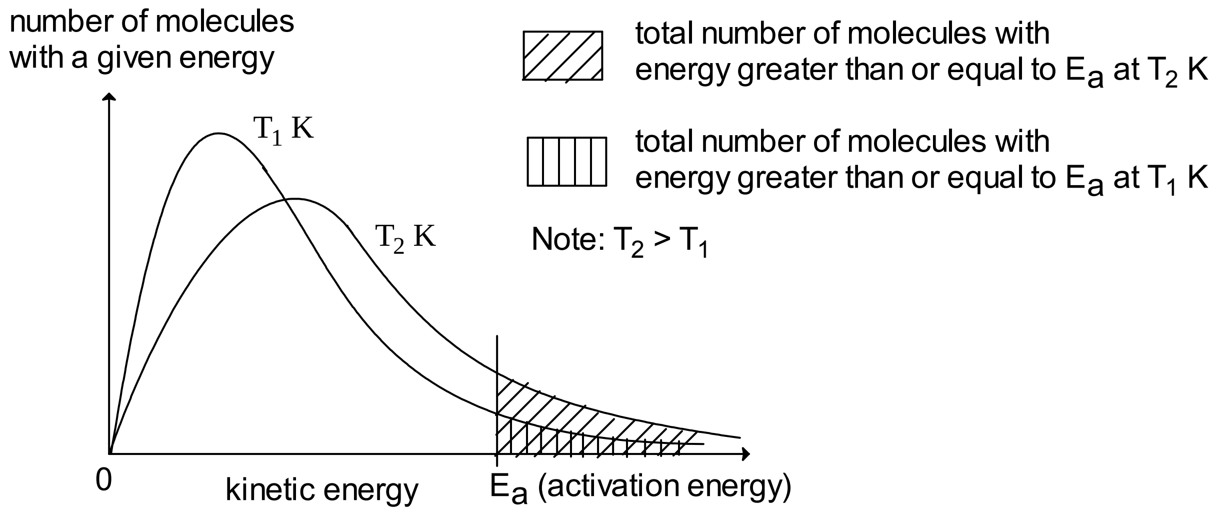
For expt. 2 where $[X]_0$ = 0.50 mol dm^{-3},
rate = 0.0020 mol dm^{-3} min^{-1}.

Hence when [X] is tripled, rate is corresponding tripled.
This implies that rate is directly proportional to [X].
Therefore order of reaction with respect to X is 1. ,

(iii) rate = k [X][Y]
units for rate constant, k: mol^{-1} dm^{3} min^{-1}

(b)

The distribution of molecular energies at two different temperatures.



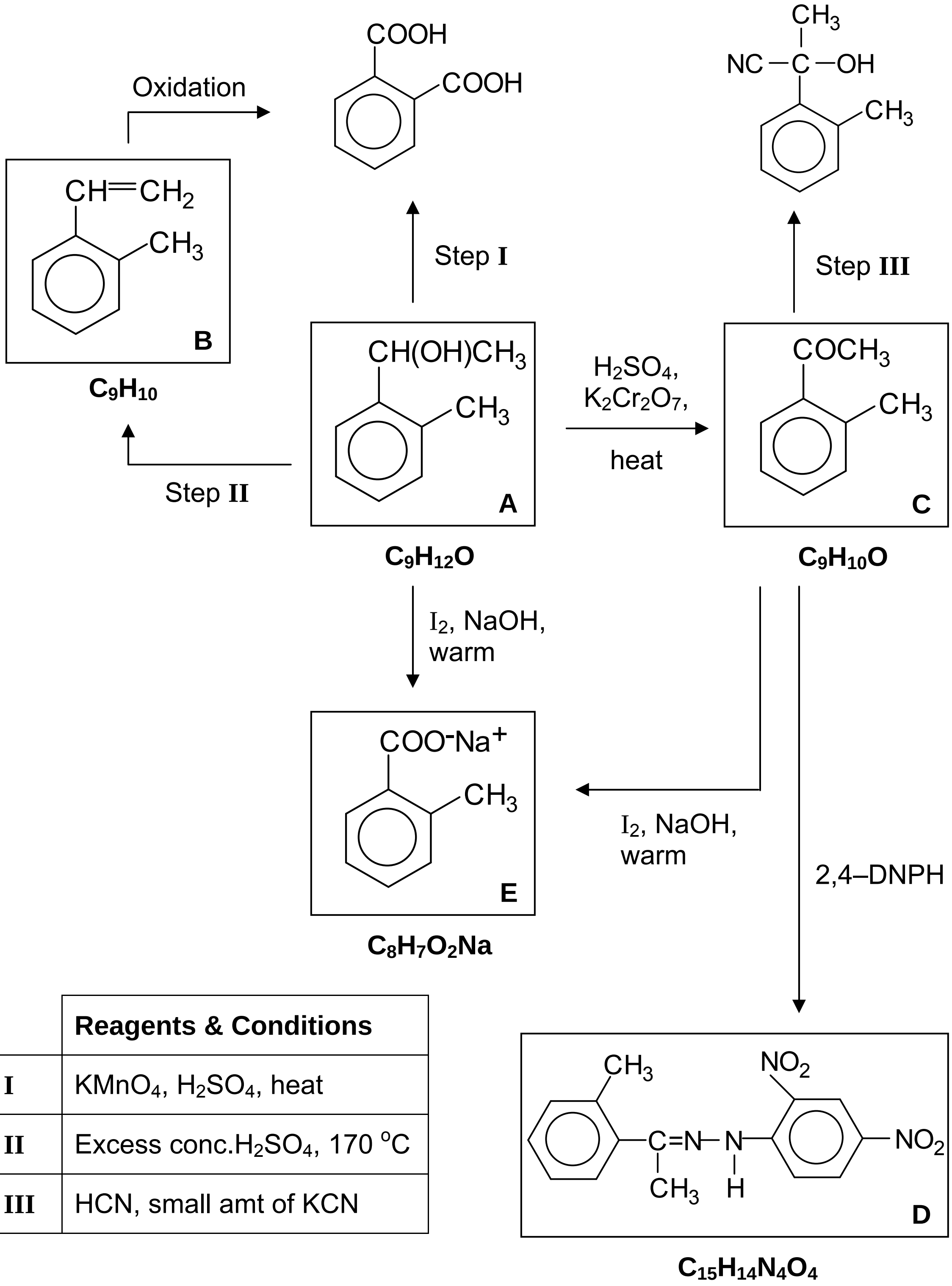
When temperature is increased, the average kinetic energy of the reacting particles is increased such that the number of reacting particles with energy greater than or equal to the activation energy (E_a) is increased significantly. ,

This can be seen from the significantly larger shaded area at T_2 K in the Boltzmann distribution curve shown above.

Consequently, the total number of effective collisions per unit time increases accordingly and hence the reaction rate increases. ,

An increase in temperature also leads to a larger rate constant and hence an increase in the reaction rate.

5

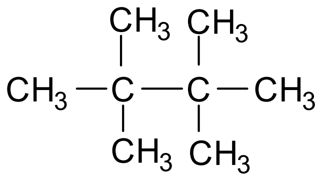


	Reagents & Conditions
Step **I**	$KMnO_4$, H_2SO_4, heat
Step **II**	Excess conc.H_2SO_4, 170 °C
Step **III**	HCN, small amt of KCN

Section B

6 **(a)** **(i)** Free radical substitution
uv light/sunlight, limiting bromine ,

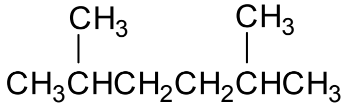
(ii) **(1)**



$CH_3C(CH_3)_2C(CH_3)_2CH_3$

2,2,3,3–Tetramethylbutane

(2)



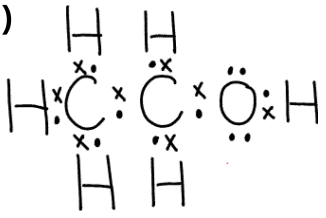
$CH_3CH(CH_3)CH_2CH_2CH(CH_3)CH_3$

2,5–Dimethylhexane

(iii) Structural isomerism.

(iv) Isomer **(2)** has a higher boiling point.

(b) **(i)**



Around O atom,
4 regions of electron density
Electron-pair geometry is tetrahedral
2 bond pairs, 2 lone pairs
Bond angle resembles that of H_2O, i.e. 105°

(ii) $2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3CH_2OH(l)$

(iii) $\Delta H_f[CH_3CH_2OH(l)] = 2\Delta H^o_{atom}[C(s)] + 3BE(H–H) + \frac{1}{2}BE(O{=}O) – BE(C–C) – BE(C–O) – BE(O–H) – 5BE(C–H) – \Delta H^o_{vap}[CH_3CH_2OH(l)]$

$= 2(717) + 3(436) + \frac{1}{2}(496) – (350) – 360 – 460 – 5(410) – 43$

$= –273 \text{ kJ mol}^{–1}$,

(iv) $CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

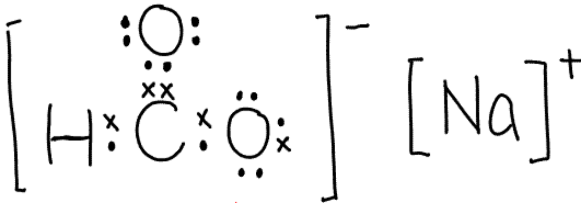
$\Delta H_c[CH_3CH_2OH(l)] = 2\Delta H_f[CO_2(g)] + 3\Delta H_f[H_2O(l)] – \Delta H_f[CH_3CH_2OH(l)]$

$= 2(–394) + 3(–286) – (–273)$

$= – 1373 \text{ kJ mol}^{–1}$

(c) **(i)** $CH_3CH_2OH + 4I_2 + 6NaOH \rightarrow HCOO^-Na^+ + CHI_3 + 5NaI + 5H_2O$

(ii)



(iii) In order of increasing acidity,

ethanal < ethanol < ethanoic acid

Ethanal is a neutral compound and is not acidic
Acidity of organic compounds depends on the stability of conjugate base when compound is hydrolysed in water.
OR
Let HX be the organic acid,

$$HX \rightleftharpoons X^- + H^+$$

Upon dissociation of ethanol in water, the ethoxide ion, $CH_3CH_2O^-$, is destabilised by the electron donating ethyl group which intensifies the negative charge on the O atom.

Upon dissociation of ethanoic acid in water, the ethanoate ion, CH_3COO^-, is resonance stabilised (2 equivalent resonance structures). Hence it is more stable than the ethoxide ion and thus ethanoic acid is a stronger acid than ethanol as position of equilibrium lies more to the right to generate more H^+ ions.

7 (a) (i) $HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$

$$K_a = \frac{[H^+(aq)][X^-(aq)]}{[HX(aq)]} = 1.4 \times 10^{-5}\ mol dm^{-3}$$

	$HX(aq) \rightleftharpoons$	$H^+(aq)$	$X^-(aq)$
Initial conc./mol dm^{-3}	0.10	0	0
Equil. conc./mol dm^{-3}	0.10 – x	x	x

$\therefore K_a = x^2/(0.10 - x) = 1.4 \times 10^{-5}$ assume $0.10 - x \approx 0.1$
$\Rightarrow x^2 = 1.4 \times 10^{-6}$
$x = 1.18 \times 10^{-3}$ mol dm^{-3}

Therefore $[H^+] = 1.18 \times 10^{-3}$ mol dm^{-3}

$pH = -\log [H^+] = 2.928 = 2.93$

(ii) A buffer solution is usually a mixture of weak acid (nicotinic acid) and its salt (sodium nicotinate) or a weak base and its salt which is <u>able to resist pH changes when a little acid or base is added to it.</u>

$HX(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + X^-(aq)$

$NaX(aq) \rightarrow Na^+(aq) + X^-(aq)$ **both equations**

OR

NaX dissociates completely to give a large concentration of X^-. By common ion effect, the presence of X^- suppresses the ionisation of HX. Hence, there is a **large reservoir of both HX and X^- ions.**

With addition of H^+,

$$H^+ + X^- \rightarrow HX$$

H^+ removed, hence, constant pH.

With addition of OH^-,

$$OH^- + HX \rightarrow H_2O + X^-$$

OH^- removed, hence, constant pH**.**

Alternatively,

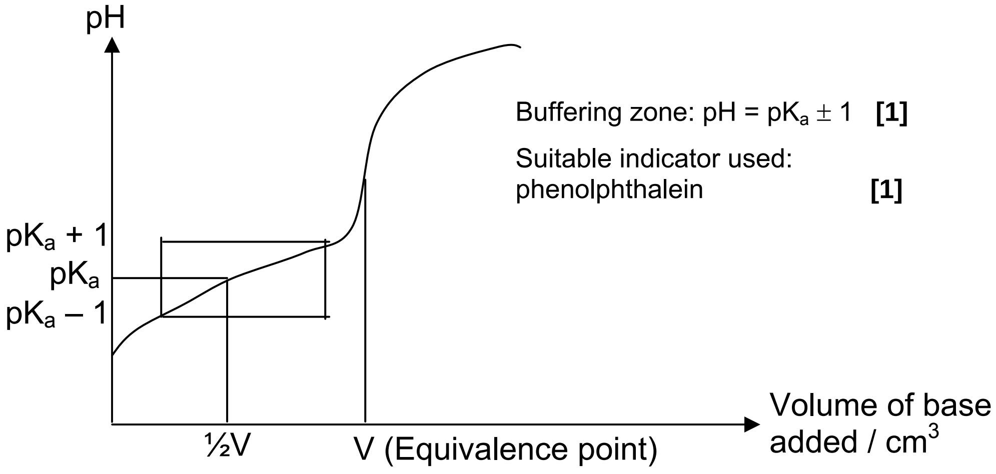
$$HX(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + X^-(aq)$$

A large reservoir of HX and X^- are required in order to have an effective buffer.

When $H_3O^+(aq)$ is added, $[H_3O^+]$ increases. According to Le Chatelier's Principle, the above equilibrium position would shift left, hence decreasing the increased $[H_3O^+]$.

When $OH^-(aq)$ is added, $H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$, therefore $[H_3O^+]$ decreases. According to Le Chatelier's Principle, the above equilibrium position would shift right and thus maintaining a constant $[H_3O^+]$.

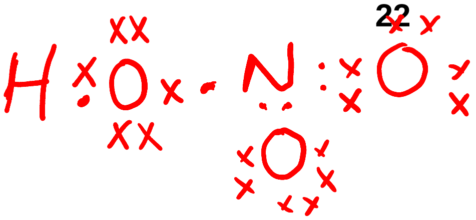
(iii)



Buffering zone: pH = $pK_a \pm 1$ **[1]**

Suitable indicator used: phenolphthalein **[1]**

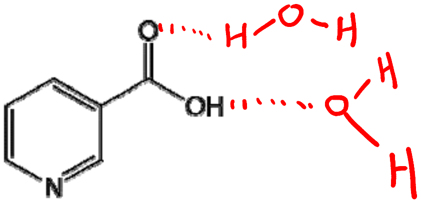
(b) (i)



Shape of HNO_3 : trigonal planar around N atom
Type of hybridization: sp^2

(ii) $2V^{3+}(aq) + 2HNO_3(aq) \rightarrow 2VO^{2+}(aq) + 2NO_2(g) + 2H^+(aq)$ **[2]**
Change in O.N. of V = +3 in V^{3+} to +4 in VO^{2+}
Change in O.N. of N = +5 in HNO_3 to +4 in NO_2

(iii) Niacin is soluble in water . H bonding between the –COOH group and the water molecule



8 (a)

$$K_c = \frac{[HI]^2}{[H_2][I_2]} \qquad \Rightarrow K_c = \frac{36.98^2}{2.06 \times 13.40} = 49.5$$

(b) (i) **K_c** at **1000 °C < K_c** at **445 °C**

⇒ at a **higher temperature,** there is a **smaller proportion** of HI at equilibrium

⇒ **backward reaction** is **favoured to absorb the heat .**

⇒ forward reaction is **exothermic.**

(ii) **(1)** The rate of forward reaction increases , increase in pressure brought molecules closer together and collide more frequently .

(2) The composition of the equilibrium mixture remains unchanged. Both forward and backward reactions produce the **same number** of gaseous molecules, hence an increase or decrease in pressure will not favour or affect either reaction .

(iii) K_c indicates the extent of formation of HX . Since K_c of HF > HC*l* > HI, the tendency for HX to form is HF > HC*l* > HI and thus the strength of HX bond is in the order: HF > HC*l* > HI. . As **size of the halogen increases** from Fluorine to Iodine, there would be **less effective orbital overlapping** between the 1s orbital of H and the p orbital of the halogen; the **difference in electronegativity between H and X also decreases** from F to I, hence the covalent bond strength between hydrogen and halogen decreases from F to I.

(c) (i) Electrophilic addition

$CH_3CH_2CH{=}CH_2 + HI \rightarrow CH_3CH_2CHICH_3$

(ii) Nucleophilic substitution

$CH_3(CH_2)_2CH_2–F < CH_3(CH_2)_2CH_2–Cl < CH_3(CH_2)_2CH_2–Br < CH_3(CH_2)_2CH_2–I$

Reaction involves breaking C–X bond.

Strength of C–X bond is dependent on difference in electronegativity between C and X.

Decreasing bond polarity from F to I results in decreasing bond strength.

Strength of C–X bond is also dependent on effectiveness of overlap between valence orbital of C and X

Since valence orbital of X is more diffuse from F to I , effectiveness of overlap decreases from C–F to C– I, resulting in decreasing bond strength from F to I.

Since bond strength decreases from C–F to C– I, reactivity with ammonia increases from $CH_3(CH_2)_2CH_2–F$ to $CH_3(CH_2)_2CH_2–I$.

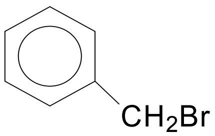
(iii) **P:** CH_3CH_2CN

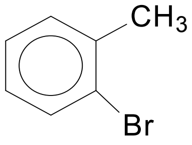
Q: CH_3CH_2COOH

R: $CH_3CH_2COOCH_2CH_3$ ($C_5H_{10}O_2$)

(iv) Ethanolic KOH/NaOH, heat or reflux

(v)

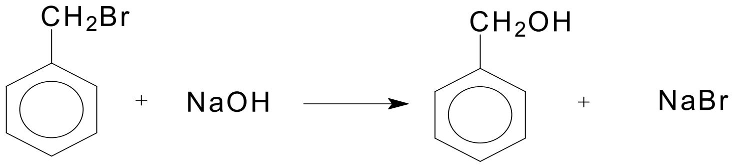




Warm both compounds **C** and **D** with <u>aqueous NaOH or KOH, cool, acidify with nitric acid and then add aqueous $AgNO_3$.</u>

Cream ppt is observed for benzyl bromide.

Clear solution for 2-bromo methylbenzene].



$$Ag^+ + Br^- \longrightarrow AgBr\,(s)$$