Name:		Class:	

ST ANDREW'S JUNIOR COLLEGE

JC2 Preliminary Examinations
CHEMISTRY
Higher 2 **9746/02**
Paper 2 Structured **26 August 2008**
1 hour 30 minutes

Candidates answer in the space provided on the question paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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
You are reminded of the need for good English and clear presentation in your answers. The number of marks is given in brackets[ ] at the end of each question or part question.

For examiner's use	
Q1	
Q2	
Q3	
Q4	
Q5	
Q6	
Q7	
Q8	
Q9	
Total	

This document consists of **21** printed pages including this page.

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1. **(a)** Draw the dot-and-cross diagram of ClO_4^- and predict the shape of the ion.

[2]

(b) In a particular titration reaction, sodium chlorate(VII), $NaClO_4$, is titrated with an acidified aqueous solution of $\mathbf{M}^{3+}$ ions. Sodium chloride is formed in the process and the oxidation state of **M** changes from +3 to +4.

If 12.50 cm^3 of a 0.0500 mol dm^{-3} aqueous sodium chlorate requires 25.0 cm^3 of $\mathbf{M}^{3+}$ to reach the end point, what is the concentration of the $\mathbf{M}^{3+}$ solution?

[3]

[Total: 5 marks]

[Turn over

2. **(a)** Using the following data, and relevant data from the *Data Booklet*, construct an energy level diagram to calculate the enthalpy change of solution of Na*Cl*.

Enthalpy change of formation of Na*Cl*(s)	-411 kJ mol^{-1}
Enthalpy change of hydration of Na^{+}(g)	-390 kJ mol^{-1}
Enthalpy change of hydration of Cl^{-}(g)	-381 kJ mol^{-1}
Enthalpy change of atomisation of sodium	+108 kJ mol^{-1}
First electron affinity of chlorine	-359 kJ mol^{-1}

[5]

2. **(b)** Calculate the mass of water required to dissolve 11.70 g of NaC*l* if the temperature of the solution decreases from 25.0°C to 22.7°C. [Assume that the heat capacity of all solutions = 4.18 J cm^{-3} K^{-1}]

[2]

[Total: 7 marks]

[Turn over

3. Nitrogen can be recovered from nitrogen monoxide by reacting nitrogen monoxide with hydrogen gas at 700°C:

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

A series of experiments was done to investigate the rate of the above reaction and the results are shown below.

Experiment	**Initial concentration of NO ($mol\ dm^{-3}$)**	**Initial concentration of H_2 ($mol\ dm^{-3}$)**	**Initial rate of reaction ($mol\ dm^{-3}\ s^{-1}$)**
1	0.050	0.001	0.025
2	0.050	0.003	0.075
3	0.100	0.006	0.600

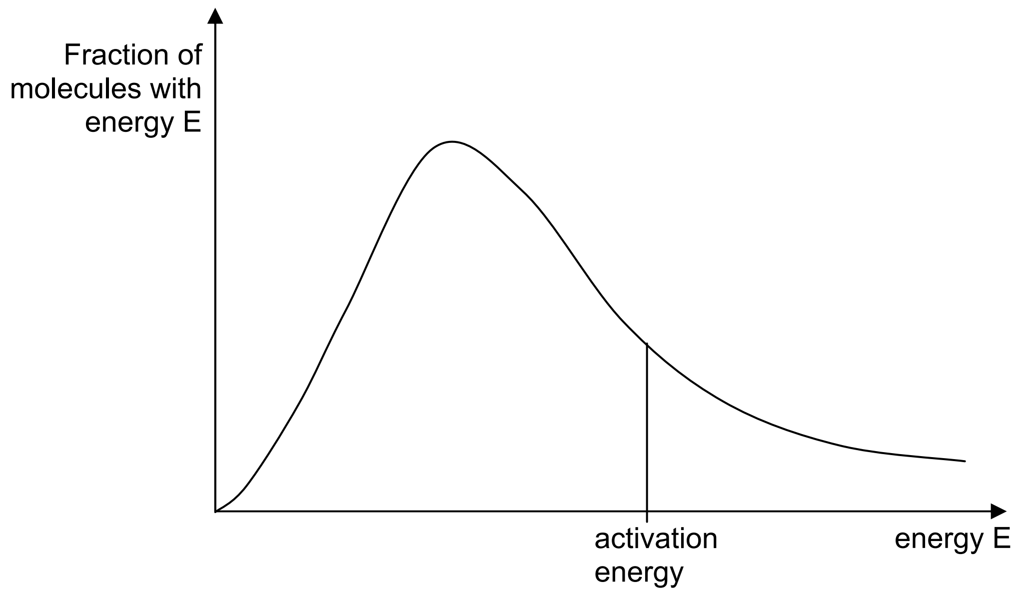
(a) Deduce the order of the reaction with respect to

(i) H_2

(ii) NO

[2]

3. (b) (i) The Boltzmann distribution curve for the reaction at 700°C is shown below. On the same diagram, sketch the Boltzmann distribution curve for the same reaction at 500°C



(ii) By using the concept of collision theory, explain in general terms why temperature affects the rate of a chemical reaction.

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....

....

[3]

[Total: 5 marks]

[Turn over

4. Ammonia gas is produced industrially via Haber Process:

$$N_2(g) \ + \ 3H_2(g) \rightleftharpoons 2NH_3(g)$$

A mixture containing 1.0 mol of $N_2(g)$ and 2.8 mol of $H_2(g)$ was allowed to reach equilibrium in a 2 dm^3 closed reaction vessel. At equilibrium, it was found that 40% of $N_2(g)$ was converted to $NH_3(g)$

(a) Calculate the value of K_C, giving its units.

[4]

4. **(b)** State and explain how the value of K_C would change if 0.1 mol of ammonia gas is removed from the equilibrium mixture.

....

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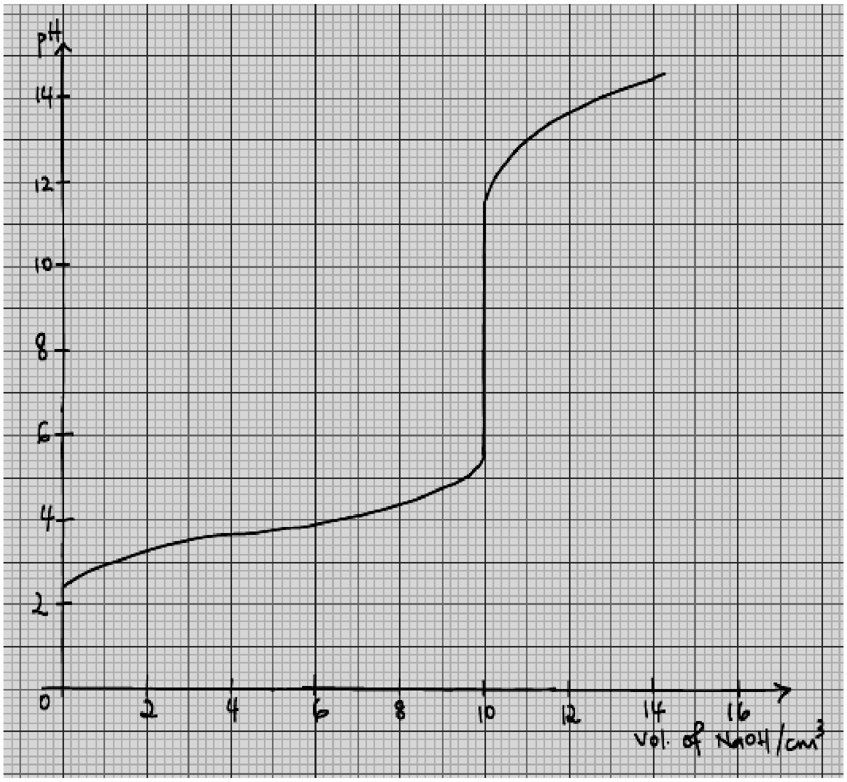
[1]

[Total: 5 marks]

[Turn over

5. An unknown volume of a weak monobasic acid, HA, was titrated against 0.200 mol dm^{-3} aqueous sodium hydroxide and the following curve was obtained.



Using the graph,

(a) determine the acid dissociation constant, K_a, of HA.

[2]

(b) determine the concentration of HA.

[2]

5. (c) hence, determine the volume of HA used in the titration.

[1]

[Total: 5 marks]

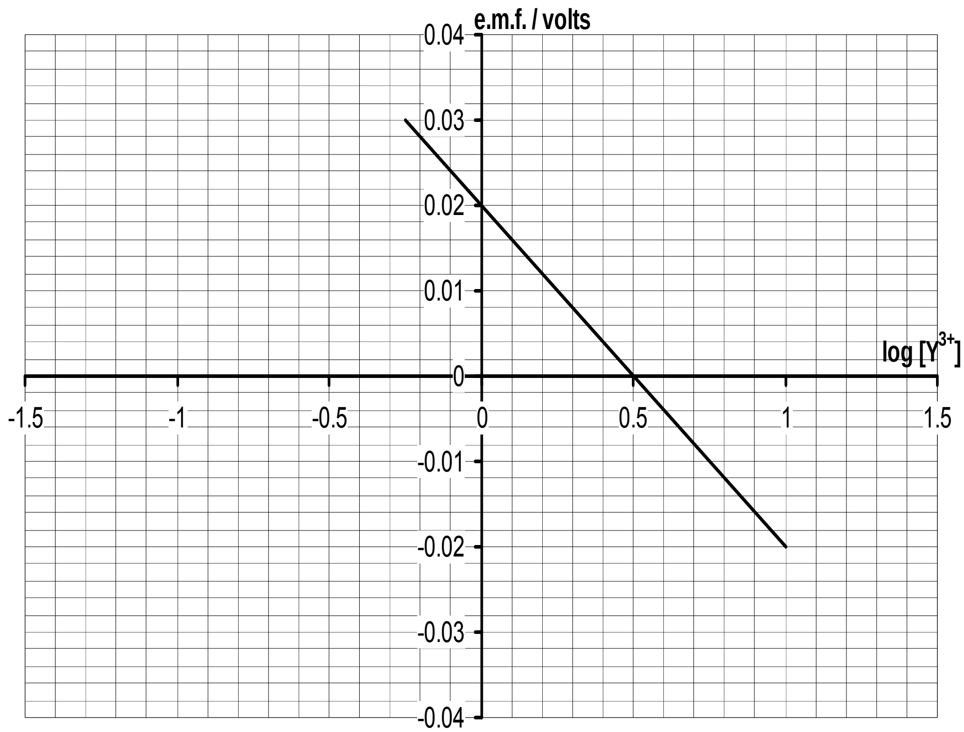
[Turn over

6. *(The use of the Data Booklet is relevant to this question)*

In an experiment to study the reaction

$Sn(s) + 2\mathbf{Y}^{3+}(aq) \rightarrow Sn^{2+}(aq) + 2\mathbf{Y}^{2+}(aq)$

An electrochemical cell was set up using the Sn^{2+}/Sn and $\mathbf{Y}^{3+}/\mathbf{Y}^{2+}$ half-cells at 298K. Throughout the experiment, the Sn^{2+}/Sn half-cell was kept unchanged under standard conditions while solutions containing 1.0 mol dm^{-3} of $\mathbf{Y}^{2+}$ ions but different $\mathbf{Y}^{3+}$ concentrations were used in the other half cell. The e.m.f. of the cell was measured with each change of solution in the $\mathbf{Y}^{3+}/\mathbf{Y}^{2+}$ half-cell and the results are shown in the graph of e.m.f. against log [$\mathbf{Y}^{3+}$] below.



(a) Write a cell diagram for the above cell under standard conditions.

....

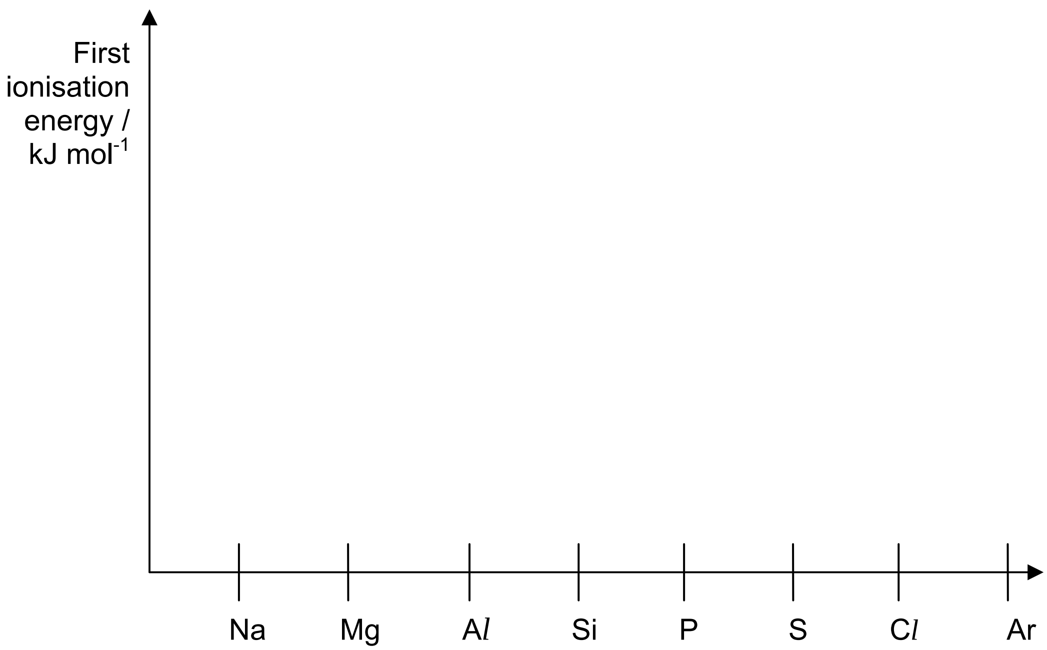
[1]

6. (b) With the aid of the graph, determine the standard electrode potential of the $\mathbf{Y}^{3+}/\mathbf{Y}^{2+}$ half-cell.

[2]

[Total: 3 marks]

7. (a) (i) In the grid below, sketch the trend of the first ionisation energy of the elements in Period 3.



(ii) Account for the general increase in first ionisation energy across Period 3.

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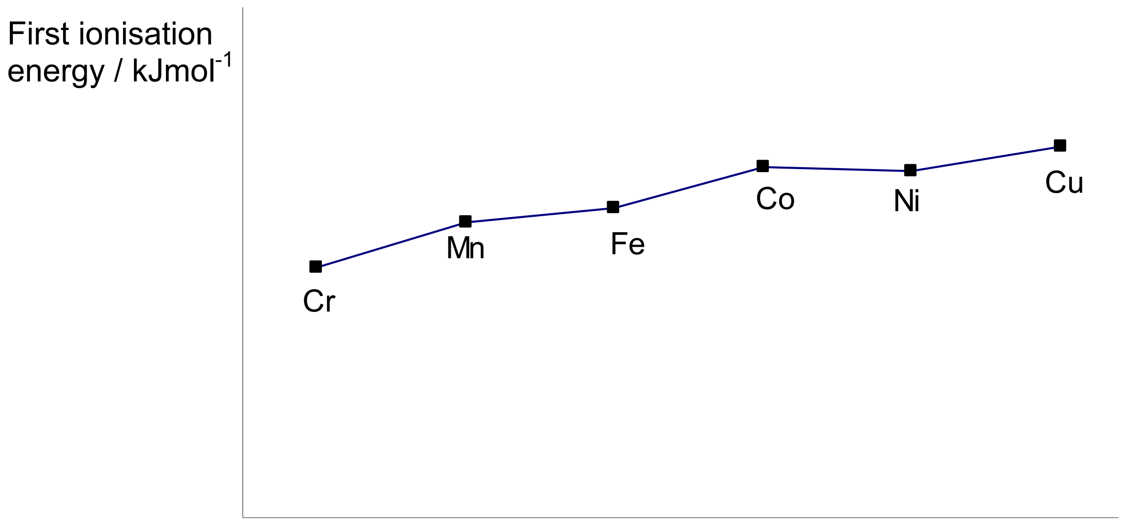
[Turn over

7. (a) (iii) The trend of the first ionisation energy of transition elements from Cr to Cu is shown below. Suggest an explanation for the similarity in their first ionisation energies.



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[5]

7. (b) Hydrogen halides are dissociated at high temperatures according to the following reaction.

$$2HX\ (g) \rightarrow H_2\ (g) + X_2\ (g)$$

The percentage of each hydrogen halide that has undergone dissociation at 2000°C is shown in the table below.

Hydrogen halide	HF	HC*l*	HBr	HI
Percentage dissociation of hydrogen halide	6.1×10^{-5}	3.2×10^{-2}	4.1	36

(i) By making use of relevant data from the *Data Booklet*, explain the trend in the thermal stabilities of the hydrogen halides.

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(ii) Describe and explain the observations when hot, concentrated sulphuric acid is added to HI. Write balanced equations for the reactions that occur.

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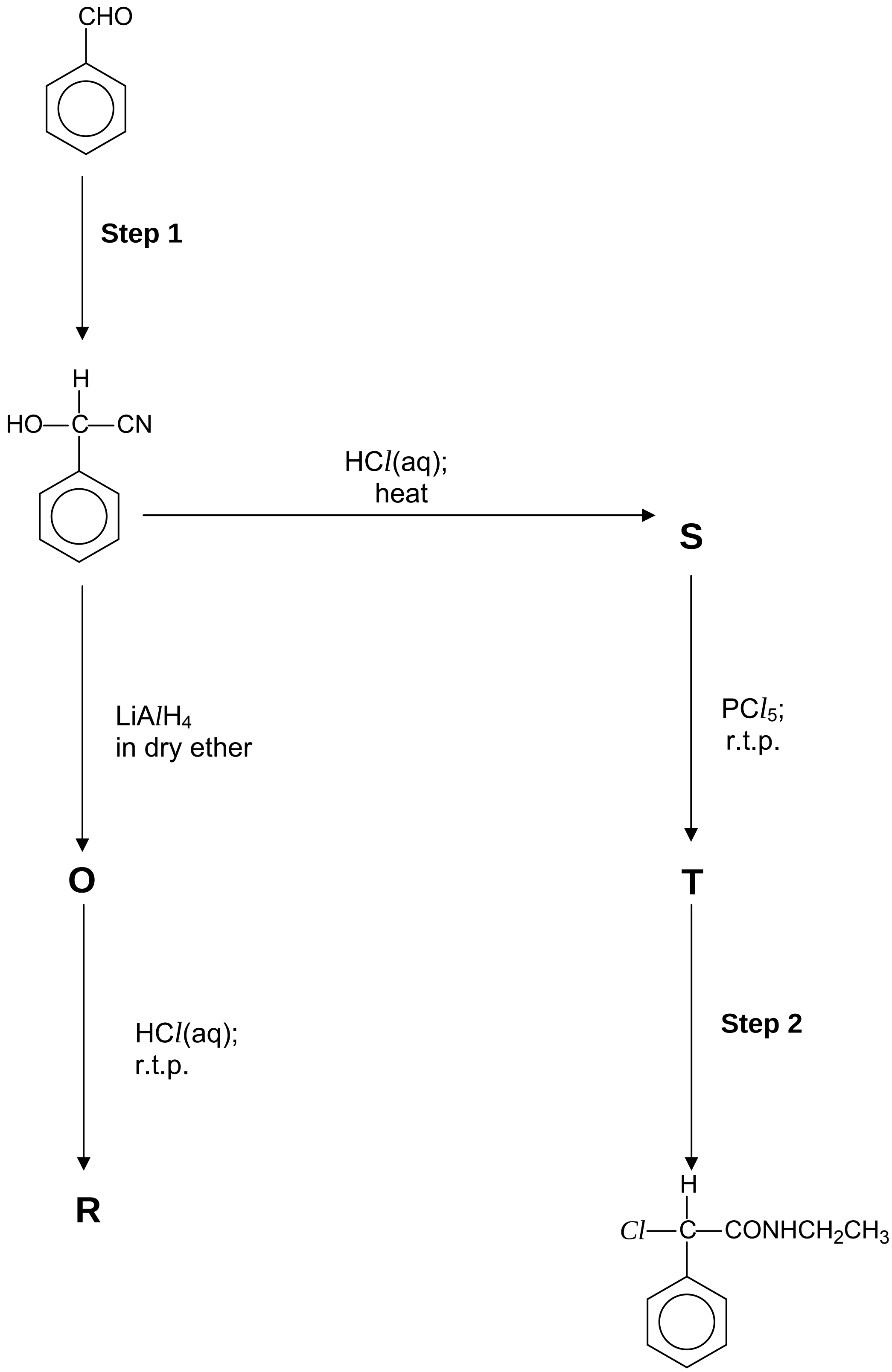
[5]
[Total: 10 marks]

[Turn over

8. Benzaldehyde is an intermediate used to form many compounds. The following shows the outline of the reactions of benzaldehyde.



(a) **(i)** Write the formulae of **Q**, **R**, **S** and **T** in the spaces provided.

Q

R

S

T

(ii) Suggest reagents and conditions for

***Step 1**:*

....

***Step 2**:*

....

[Turn over

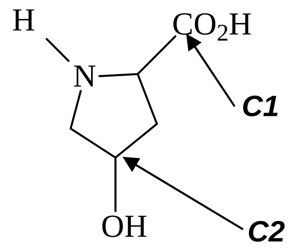
8. (a) (iii) Name and outline the mechanism of ***Step 1.***

Name: ....

Mechanism:

[9]

8. **(b)** 4-Hydroxyproline is a major component of the protein collagen. It plays a key role for the collagen's stability as it permits the sharp twisting of the collagen helix. Its structural formula is shown below:



4-hydroxyproline

(i) What type of hybridisation is present in 4-hydroxyproline at carbon ***C1*** and ***C2***?

C1 *:* ....

C2 : ....

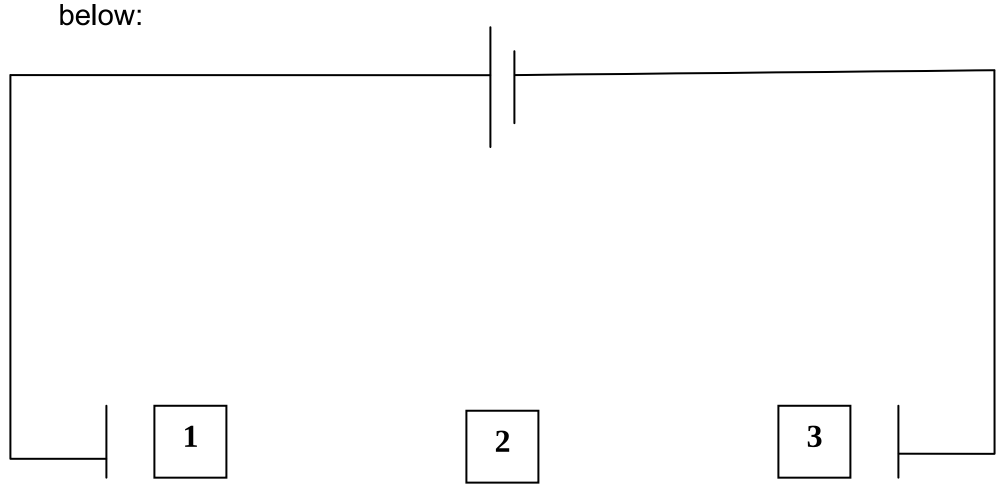
(ii) Sketch the shapes of the hybrid orbitals around carbon ***C2****.*

[Turn over

8. (b) (iii) In the boxes below, draw the structures of 4-hydroxyproline at pH 2 and pH 12.

pH 2	*pH 12*

(iv) Electrophoresis is a technique of identifying amino acids. A solution of 4-hydroxyproline is absorbed into paper and stretched between two electrodes. Positively charged species move towards the cathode, negatively charged species toward the anode. Suggest and explain the position (1,2 or 3) of 4-hydroxyproline in the experimental set-up shown below:



Position: ....

Reason:

....

....

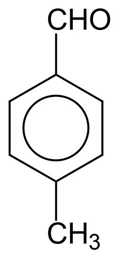
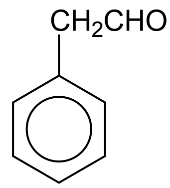
....

[7]

[Total: 16 marks]

9. For each of the following pairs of compounds, suggest ***chemical*** tests by which they can be distinguished from each other. For each pair, state the reagents and conditions as well as the observations.

(a)

	
Reagents and conditions:	
Observations:	

(b)

$H_2C{=}CHCH_2CH(CH_3)OH$	$H_2C{=}CHC(CH_3)_2OH$
Reagents and conditions:	
Observations:	

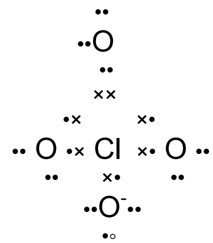
[4]

[Total: 4 marks]

-END OF PAPER-

Solutions

1.



Shape: tetrahedral

(b) $NaClO_4 + 8H^+ + 8e \rightarrow NaCl + 4H_2O$

$M^{3+} \rightarrow M^{4+} + e$

No. of moles of $NaClO_4 = \frac{12.5}{1000} \times 0.0500 = 6.25 \times 10^{-4}$ mol.

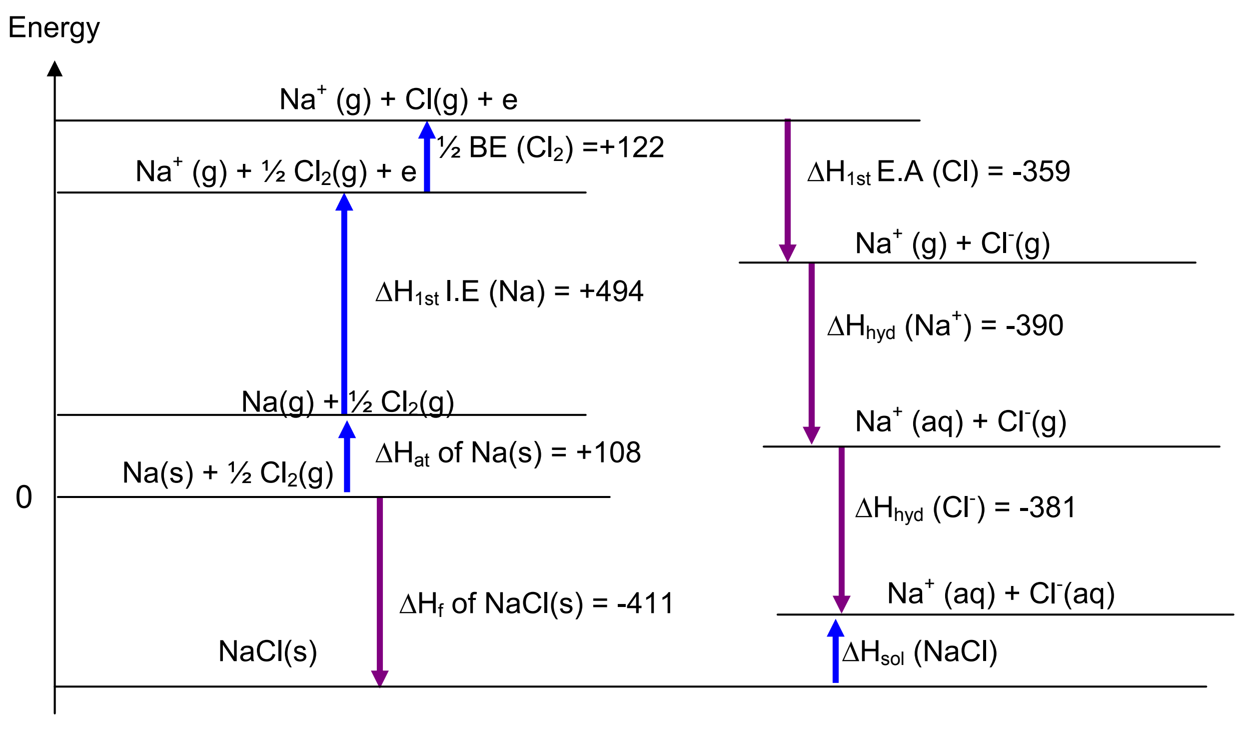
No. of moles of electrons transferred = $6.25 \times 10^{-4} \times 8 = 0.005$ mol.

No. of moles of M^{3+} required = 0.005 mol.

Concentration of $M^{3+} = 0.005 \div \frac{25.0}{1000} = 0.2$ mol dm^{-3}

2.

(a)



ΔH_{sol} (NaCl) + (-411) = +108 + 494 + 122 + (-359) + (-390) + (-381)

ΔH_{sol} (NaCl) = +5 kJ mol^{-1}

(b) Q = mcθ

$$5000 \times \frac{11.70}{23+35.5} = m\,(4.18)\,(25.0-22.7)$$

m = 104 g (to 3 s.f.)

3.(a) (i) Comparing expt 1 and 2, [NO] is constant, [H_2] increased by 3 times, rate increased by 3 times.

Hence 1st order w.r.t. [H_2]

(ii) Comparing expt 2 and 3,

$$\frac{rate_2}{rate_3} = \frac{k(0.003)^1(0.050)^x}{k(0.006)^1(0.100)^x} = \frac{0.075}{0.600}$$

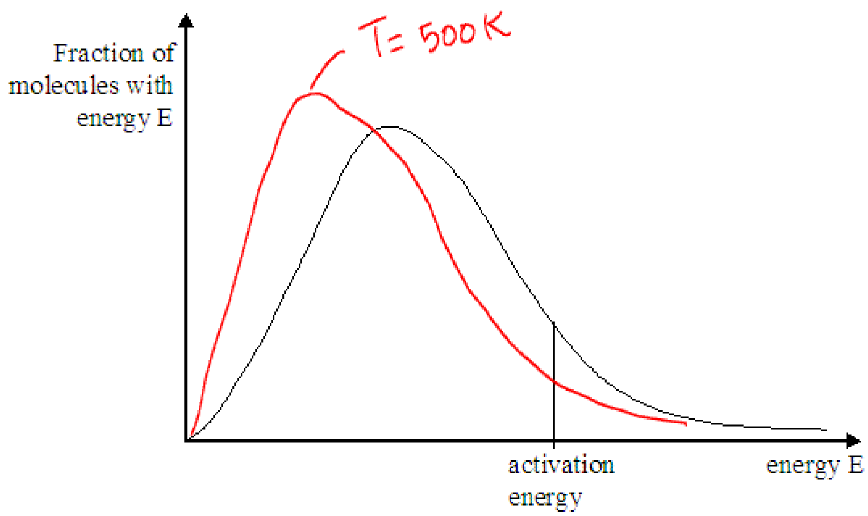
$$0.50^x = 0.25$$

$$x \log 0.50 = \log 0.25$$

$$x = 2$$

order of reaction w.r.t. [NO] = 2

(b) (i)



(ii) When temperature increases, more particles have energy equal to or greater than the activation energy. Effective collisions increase and hence rate increases.

4. (a)

	$N_2(g)$ +	$3H_2(g)$	$2NH_3(g)$
initial no. of mol	1.0	2.8	0
change no. of mol	-0.4	-3(0.4)	+2(0.4)
eqm no. of mol	0.6	1.6	0.8
eqm conc.	0.6/2	1.6/2	0.8/2
	=0.3	=0.8	=0.4

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.4)^2}{(0.3)(0.8)^3} = 1.04\ \text{mol}^{-2}\ \text{dm}^6$$

(b) K_c is unchanged as it is not dependent on conc. It is only dependent on temperature.

5.

(a) pK_a = pH at max buffer = 3.8

$K_a = 10^{-3.8} = 1.58 \times 10^{-4}$ mol dm^{-3}

(b) From graph, pH at vol = 0 is the pH of HA

pH = 2.4

$[H^+] = 10^{-2.4}$

$$[HA] = \frac{[H^+]^2}{K_a} = \frac{(10^{-2.4})^2}{1.58\times10^{-4}} = 0.100\ \text{mol dm}^{-3}$$

(c) HA : NaOH = 1:1

$$\frac{(0.100)V}{(0.200)(10)} = 1$$

V = 20 cm^3

6.

Sn(s) | Sn^{2+}(aq) || Y^{3+}(aq), Y^{2+}(aq) | Pt(s)

For the reaction $Sn(s) + 2Y^{3+}(aq) \rightarrow Sn^{2+}(aq) + 2Y^{2+}(aq)$

Sn is being oxidized and Y^{3+} is being reduced. Hence,

$E_{cell} = E^{\ominus}_{red} + E^{\ominus}_{oxid} = E_r^{\ominus}\ {}_{Y^{3+}/Y^{2+}} + E_o^{\ominus}\ {}_{Sn^{2+}/Sn}$

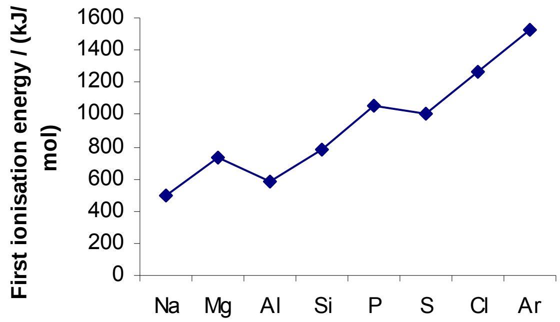
At the standard electrode potential, concentration of Y^{2+} and Y^{3+} = 1.0 mol dm^{-3}

Hence, $\log[Y^{3+}]$ = 0. From graph, e.m.f. of cell = +0.02V

$0.02 = E_r^{\ominus}\ {}_{Y^{3+}/Y^{2+}} + 0.14$

$E_r^{\ominus}\ {}_{Y^{3+}/Y^{2+}} = -0.12V$

7.
a(i)



Total [1m]

a(ii) Across the period, nuclear charge increases because number of protons increases. Successive electrons are added into the same quantum shell, hence screening effect remains almost constant.
The increase in nuclear charge overweighs the screening effect; hence, effective nuclear charge increases. More energy is needed to overcome the stronger attraction between the nucleus and the electrons. Therefore, first ionisation energy increases across the period.

(iii) From Cr to Cu, electrons are added to inner 3d orbitals.
The 3d electrons effectively shield the outer 4s electrons from the increasing nuclear charge, cancelling the effect of the increasing nuclear charge across the period.
Thus effective nuclear charge is almost constant; first ionisation energy almost constant from Cr to Cu.

(b) (i)
From the Data Booklet,

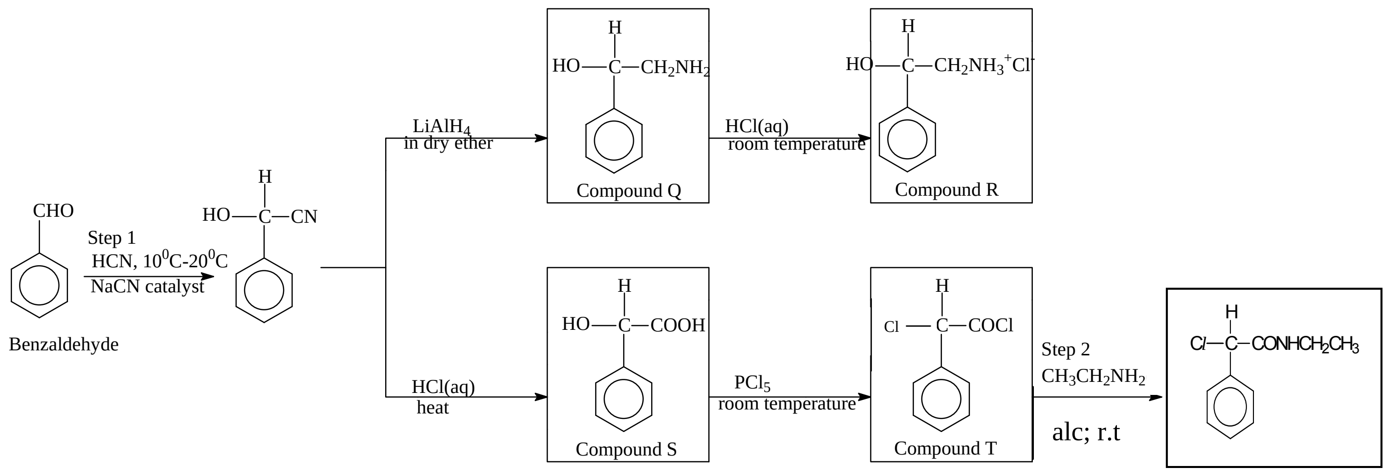
Bond	Bond energy / kJ mol^{-1}
H—F	562
H—Cl	431
H—Br	366
H—I	299

From the values of bond energies, the strength of H-X bond decreases when the group is descended.
This is due to the increasing atomic radii of the halogen atom which leads to poorer orbital overlap between the halogen and hydrogen atoms and increases the bond length.
As a result, it becomes easier to break the H—X bond and decompose the hydrogen halide going down the group.

(ii) Violet fumes or black solids of iodine are seen and a rotten egg smell (H_2S) is detected.
Hydrogen iodide is a strong reducing agent which is able to reduce H_2SO_4 to H_2S

Equations:
$2HI + H_2SO_4 \rightarrow SO_2 + I_2 + 2H_2O$
$8HI + H_2SO_4 \rightarrow H_2S + 4I_2 + 4H_2O$

8. (a) i, ii



iii.

Name: Nucleophilic addition

$HCN \rightleftharpoons H^+ + CN^-$ — ①

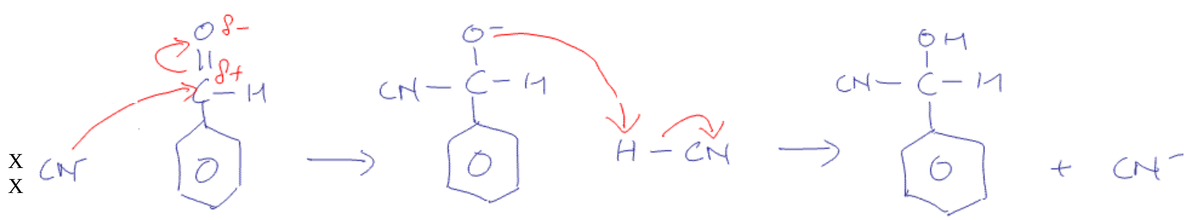
and

$NaCN \rightarrow Na^+ + CN^-$

OR

$NaOH \rightarrow Na^+ + OH^-$

- OH^- removes H^+ of equilibrium in eqn ① and shifts equilibrium to the right.

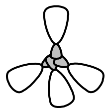


(b) i.

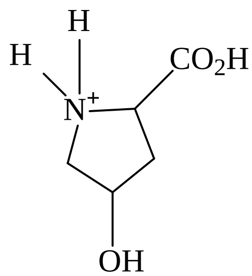
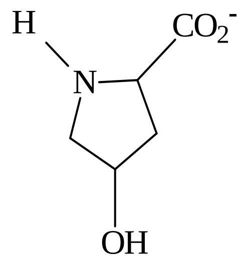
C1 – sp^2 hybridization

C2 – sp^3 hybridization

ii.

C2 - 

iii.

 pH = 2	 pH = 12

(iv) Position: <u>2</u>

Reason: 4-Hydroxyproline has a zwitterionic form which has charge neutrality / has one cation and one anion and has no net charge.

9.

(a) (i)

Reagent and conditions: Fehling's solution (aq. alkaline Cu^{2+} with tartarate ion) and heat[1]
Observations: For X, no reddish brown ppt observed. For Y, reddish brown ppt observed.

(b) (i)
Reagent and conditions: Acidified potassium dichromate and heat.
Observations: For X, orange $Cr_2O_7^{2-}$ solution turns green. For Y, orange $Cr_2O_7^{2-}$ solution does not turn green.
Reagent and conditions: Iodoform test (iodine dissolved in NaOH)
Observations: For X, yellow ppt is observed. For Y, no yellow ppt is observed.