## 2011 H1 MYE Section A Marker's Remarks

- 1 Elements **D** and **E** are period 3 elements.
  - (a) D is a white solid with melting point of 317 K. When exposed to air, it reacts spontaneously, producing a white powder of empirical formula D<sub>2</sub>O<sub>5</sub>. D<sub>2</sub>O<sub>5</sub> readily undergoes neutralisation with aqueous NaOH to form salt and water.
    - (i) From the observations, deduce an identity of **D**. Include equations, with state symbols, for any reactions that has occurred.

Low melting point hence **D** must be of simple molecular structure: sulfur or phosphorus.

The oxide of **D** is a <u>white powder with empirical formula  $D_2O_5$  hence must</u> <u>be phosphorus</u> as sulfur is yellow and its oxide does not have empirical formula of  $D_2O_5$ .

 $P_4$  (s) + 5  $O_2$  (g) →  $P_4O_{10}$  (s)  $P_4O_{10}$ (s) +12 NaOH(aq) → 4 Na<sub>3</sub>PO<sub>4</sub>(aq) + 6 H<sub>2</sub>O( $\hbar$ )

(ii) Suggest and account for a pH value for the resultant solution when the oxide of **D** dissolves in water.

**P**<sub>4</sub>**O**<sub>10</sub>(s) + 6H<sub>2</sub>O( $\hbar$ ) → 4 H<sub>3</sub>PO<sub>4</sub>(aq) Resulting pH: <u>2</u> or <u>3</u>

[6]

[2]

(b) The successive ionisation energies of element E is shown below. [2]

<b>`</b>		3				<b>b</b> 4		
	1st	2 <sup>nd</sup>	3rd	4th	5th	6th	7 <sup>th</sup>	8 <sup>th</sup>
I.E. kJmol <sup>-1</sup>	999	2265	3331	5071	7008	8487	27107	31719

(i) Deduce the group number in which **E** belongs.

Group VI

(ii) Write down the electronic configuration of **E** in the +4 oxidation state.

 $1s^2 2s^2 2p^6 3s^2$ 

(c) Compare the 1<sup>st</sup> ionisation energy of **E** with the element just before it. Explain.

E will have a <u>lower 1<sup>st</sup> I.E.</u> compared to the element just before it. Due to <u>inter-electronic repulsion</u> between the pair of electrons sharing the same orbital, thus <u>lesser amount of energy</u> is required to remove an electron from Element **E**.

- 2 Manganese dioxide, MnO<sub>2</sub> is a strong oxidising agent and it is also commonly used as a catalyst.
  - (a) On the grid below, sketch and label the energy distribution of gas molecules in the presence of a catalyst. Your sketch should clearly illustrate the effect of catalyst on rate of reaction.



(b) The lattice energy of MnO<sub>2</sub> can be calculated based on the energy cycle shown below.



G: <u>O(g)</u>

- 1  $\Delta H_{f}$
- 2 <u>1<sup>st</sup> ionisation of Mn</u>
- 3 <u>2<sup>nd</sup> ionisation</u> of Mn
- 4 <u>lattice energy</u> of MnO<sub>2</sub>

[3]

- (c) Potassium manganate (VII), KMnO<sub>4</sub>, can be manufactured from MnO<sub>2</sub>. During the process, MnO<sub>2</sub> is reacted with concentrated KOH to produce potassium manganate (VI), K<sub>2</sub>MnO<sub>4</sub>. When a solution of K<sub>2</sub>MnO<sub>4</sub> is acidified, a *disproportionation* reaction occurs. This produces a dark brown MnO<sub>2</sub> precipitate and a solution of KMnO<sub>4</sub>.
  - (i) With reference to oxidation states of manganese, explain what is meant by *disproportionation* and suggest an equation for this reaction.

*Disproportionation* is a reaction where <u>reduction and oxidation</u> of the <u>same</u> <u>element</u> occurs <u>simultaneously</u>.

Mn changes its oxidation state from +5 to +4 and +7

 $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$ 

(ii) In alkaline solution, KMnO<sub>4</sub> reacts with sodium sulfite, Na<sub>2</sub>SO<sub>3</sub> in a 1:1 ratio. Suggest the final oxidation state of manganese.
[Given: SO<sub>3</sub><sup>2-</sup> + 2OH<sup>-</sup> → SO<sub>4</sub><sup>2-</sup> + H<sub>2</sub>O + 2e]

Since  $MnO_4^- \equiv SO_3^{2^-}$ , The number of electrons transferred = 2

The final oxidation state of Mn = 7-2 = +5

[5] Total: [10] 3 H is a halogenoalkane with molecular formula C<sub>4</sub>H<sub>9</sub>C*l*. When reacted with hot ethanolic NaOH, the product, J is found to display geometrical isomerism. When refluxed with aqueous NaOH, compound K is formed.

**K** undergoes oxidation when reacted with two different sets of reagents and conditions. When **K** is oxidised using the first set of reagents and conditions, followed by acidification, propanoic acid is formed. However, when **K** is oxidised using the second set of reagents and conditions, another product **L** is formed. **L** reacts with 2,4-DNPH but not with Tollens' reagent.

(a) Using the information given above, deduce the structures of compounds H, J, K and L and draw the structural formulae of the molecules in the relevant boxes provided in the flowchart.





With reference to structure and bonding, explain why this is so.

Compound K has a <u>simple molecular structure</u> with <u>intermolecular hydrogen</u> <u>bonds</u> while compound L has a simple molecular structure with <u>intermolecular van</u> <u>der Waals' forces of attraction</u>. <u>More energy</u> is needed to break the <u>stronger</u> hydrogen bonds between molecules of K compared to the <u>weaker</u> van der Waals' forces of attraction between molecules of L. Hence, K has a higher boiling point than L.

> [2] Total: [10]

4 Halogenoalkanes, RX, are important intermediates used to produce many organic compounds. They may be converted into Grignard reagents by reacting them with magnesium in dry ether:

$$RX + Mg \xrightarrow{Dry ether} R \xrightarrow{--} Mg \xrightarrow{--} X$$
  
Grignard reagent

where R is an alkyl group and **X** is chlorine, bromine or iodine.

(i) With relevant data from data booklet, explain why the reactivity between halogenoalkanes and Mg is in the following order:
iodoalkane > bromoalkane > chloroalkane

C-C*l* bond: 340 kJ mol<sup>-1</sup> C-Br bond: 280 kJ mol<sup>-1</sup> C-I bond: 240 kJ mol<sup>-1</sup> Strength of C-X bond: C-C*l*> C-Br > C- I Ease of breakage of the bond: C- I > C-Br > C-C*l* Therefore reactivity: iodoalkane > bromoalkane > chloroalkane

On reaction with carbonyl compounds, RMg**X** forms various classes of alcohols. The reaction below shows an example of the formation of a secondary alcohol:



(ii) Draw the structure of the organic product formed when the following are reacted:





(iii) Draw the displayed formula of the chloroalkane which can be used to form a Grignard reagent that would react with propanone to give 2-methylpentan-2-ol.

[4]

(b) The following shows a series of reactions that compound **M** can undergo.



N/O:



N/O:



P:



Q:



(ii) State the reagents and conditions for step 1 and 2:

Step 1: Aqueous iodine, NaOH (aq), warm

Step 2: Ethanolic or alcoholic KCN, heat

[6] Total: [10]

(i)

## **Section B Mark Scheme**

Answer **two** questions from this section on separate answer paper.

5

Hydroxy acids are compounds that consist of a carboxylic acid with a hydroxyl group on the adjacent carbon. A typical structure of a hydroxy acid is as follows:



Where R is an alkyl group

These compounds are most often used in the cosmetics industry to produce antiwrinkle and anti-ageing products for the skin.

(a) Compound **S** is a hydroxy acid with the molecular formula  $C_xH_yO_3$ .

When 7.5  $\text{cm}^3$  of the liquid **S** was reacted with an excess of sodium metal. 2.4  $\text{cm}^3$  of hydrogen gas was produced.

Another sample of 7.5 cm<sup>3</sup> of the liquid **S** was completely combusted in an excess of oxygen in an enclosed vessel, the volume of gas (measured at r.t.p.) did not change. When the mixture of gas was passed through NaOH (aq), a reduction in gas volume of 7.2 cm<sup>3</sup> (measured at r.t.p.) was observed.

(i) Write a balanced equation for the combustion of **S**.

$$C_{x}H_{y}O_{3} + \left(x + \frac{y}{4} - \frac{3}{2}\right)O_{2} \longrightarrow xCO_{2} + \frac{y}{2}H_{2}O$$

(ii) Use the data given above to calculate values for x and y in the molecular formula of compound **S**.

From the combustion data, since the volume of the gas did not change after the combustion,

[5]

Therefore,

$$\left(x + \frac{y}{4} - \frac{3}{2}\right) = x$$
$$y = \mathbf{\underline{6}}$$

Given that the compound has a carboxylic acid group and hydroxyl group, every mole of the compound will produce one mole of  $H_2(g)$ .

	Therefore	e, x =	: <u>3</u>					
	1	:	3					
	1 x 10⁻⁴	:	3 x ′	10 <sup>-4</sup>				
Amount c	of $C_x H_y O_3$	:	Amo	ount of	CO <sub>2</sub>			
Amount c	of CO <sub>2</sub> pro	duce	d	= 7.2 -	÷ 24 00	0 = 3 x	: 10 <sup>-4</sup> mo	J
Amount c	of H <sub>2</sub> produ	iced		= 2.4 - = Amo	+ 24 00 ount of (	0 = 1 x C <sub>x</sub> H <sub>y</sub> O <sub>3</sub>	10 <sup>-4</sup> mo reacted	lc t

(b) Compound **T** is another hydroxy acid with molecular formula  $C_8H_8O_3$ . It reacts with hot, acidified KMnO<sub>4</sub> to produce **U** and carbon dioxide gas.

When **T** is refluxed with a small amount of concentrated sulfuric acid, a molecule, **V** is produced.

**V** has 3 six-membered rings and does not react with sodium metal or sodium carbonate. **V** has a molecular formula of  $C_{16}H_{12}O_4$ .

Deduce the structural formulae of **T**, **U** and **V**, giving reasons for your answer.

[6]

T has <u>comparable number</u> of carbon and hydrogen atoms, and <u>more than 6</u> <u>carbon atoms</u>.

→T has a <u>benzene ring</u>.

**T** undergoes **<u>oxidation</u>** with hot, acidified KMnO<sub>4</sub>.

→ T must be a primary or secondary alcohol or R group with benzylic H

V does not undergo <u>neutralisation</u> with sodium metal or sodium carbonate. Hence, it <u>does not have a hydroxyl or carboxylic acid group</u>.

T undergoes <u>nucleophilic subsitution/esterification</u> to form V which is an <u>ester</u>.

Since V has 3 six-membered rings, T reacted with another molecule of itself.



T is

(c) Hydroxy acids can undergo nucleophilic substitution reaction with another organic molecule to produce an ester. An example of such a reaction is shown below:

 $CH_3CH(OH)COOH(l) + CH_3CH_2OH(l) \longrightarrow CH_3CH(OH)COOCH_2CH_3(l) + H_2O(l)$ 

When 23.0 g of CH<sub>3</sub>CH<sub>2</sub>OH was heated with 40.0 g of CH<sub>3</sub>CH(OH)COOH in a vessel of V dm<sup>3</sup> and allowed to reach equilibrium again, it was found that 25% of CH<sub>3</sub>CH<sub>2</sub>OH remained in the system.

(i) Define the term *dynamic equilibrium*.

A dynamic equilibrium is one where <u>rate of forward reaction</u> equals to <u>rate of backward reaction</u> for a <u>reversible</u> reaction.

(ii) Given that the temperature of the system remained unchanged throughout the whole process, calculate the value of K<sub>c</sub>.

$$K_{c} = \frac{[CH_{3}CH(OH)COOCH_{2}CH_{3}][H_{2}O]}{[CH_{3}CH(OH)COOH][CH_{3}CH_{2}OH]}$$

Initial amount of CH<sub>3</sub>CH<sub>2</sub>OH =  $\frac{23.0}{46.0}$  = 0.5000 mol

Initial amount of CH<sub>3</sub>CH(OH)COOH = 
$$\frac{40.0}{90.0}$$
 = 0.4444 mol

	$CH_{3}CH(OH)COOH(l) + CH_{3}CH_{2}OH(l) = CH_{3}CH(OH)COOCH_{2}CH_{3}(l) + H_{2}O(l)$				
Initial amount / mol	0.4444	0.5000	0	0	
Change in amount / mol	-0.3750	-0.3750	+0.3750	+0.3750	
Amount at Eq <sup>m</sup> / mol	0.06940	0.25 × 0.5000 = 0.1250	0.3750	0.3750	

Let the volume of the vessel be V dm<sup>3</sup>.



(iii) Given that the enthalpy change of the above process is positive, suggest with a reason how the position of equilibrium might alter when the temperature is increased.

[6]

By Le Chatelier's Principle, the **position of equilibrium** shifts to the **right** to **absorb** the excess heat, favouring the **endothermic** reaction.

(d) Apart from undergoing esterification with another organic molecule, hydroxy acids can form cyclic esters (lactones) through a process known as lactonisation. In a lactonisation process, there was some contamination resulting in the production of a mixture of two lactones:



Describe chemical test(s) by which the two lactones, W and Y can be distinguished from each other, and describe clearly what will be observed for each of the lactones.

[3] [Total: 20]

	Reagents and Conditions		
Step I	HC <i>l</i> (aq) / NaOH(aq), heat		
Step II	alkaline $I_2(aq) / I_2(aq)$ with aq NaOH, warm		

Alternative Test: NaOH(aq), I<sub>2</sub>(aq) and heat

If the sample is Lactone **F**, the <u>brown</u> iodine solution will <u>decolourise</u>, and <u>yellow</u> <u>ppt</u> of  $CHI_3$  will be formed.

If the sample is Lactone E, the <u>brown</u> iodine solution <u>will not decolourise</u>, and <u>no</u> <u>yellow ppt</u> of  $CHI_3$  will be formed.

- **6** Ammonia, NH<sub>3</sub>, is one of the most highly produced inorganic chemicals. It can be used in fertilisers, cleaning products, colour dyes and even in the making of explosives.
  - (a) Ammonia is synthesised from its elements in the Haber process.
    - (i) Given that the reaction is exothermic and incomplete, write an equation for the Haber process.

 $N_2(g) + 3H_2(g) \xrightarrow{\sim} 2NH_3(g)$ 

(ii) State the three conditions necessary for the efficient working of a Haber process

Temperature: **450** °C Pressure: **250 atm** Catalyst: Finely divided **iron** 

(iii) Explain why the temperature you have quoted in (a)(ii) is used.

At low temperature, by Le Chatelier's Principle, the position of equilibrium shifts to the <u>right</u> to <u>release heat</u>, favouring the <u>exothermic</u> reaction. Hence, <u>high</u> yield of ammonia is obtained.

However, **too low a temperature will cause the reaction to be too slow which makes the process uneconomical**. Thus a moderate temperature of 450°C is adopted and a catalyst is used.

[5]

(b) Ammonia is given off from urine. And the nitrogen containing substance in urine is urea, CO(NH<sub>2</sub>)<sub>2</sub>.

 $H_2O(l) + CO(NH_2)_2 (aq) \rightarrow CO_2 (aq) + 2NH_3 (aq)$ 

Compound	ΔH <sup>θ</sup> / kJ mol⁻¹
H <sub>2</sub> O ( <i>l</i> )	- 287.0
CO(NH <sub>2</sub> ) <sub>2</sub> (aq)	- 320.5
CO <sub>2</sub> (aq)	- 414.5
NH <sub>3</sub> (aq)	- 81.0

Use the data given below to calculate the standard enthalpy change for the hydrolysis of urea. [2]

$$\Delta H_{rxn} = \sum \Delta H_{f}^{\theta}(pdt) - \sum \Delta H_{f}^{\theta}(rxt)$$
  
= (- 414.5 + 2(- 81.0)) - (- 287.0 + (- 320.5))  
= 31.0 kJ mol<sup>-1</sup>

(c) The labels of two monoacidic bases, aqueous sodium hydroxide, NaOH, and aqueous ammonia,  $NH_3$ , have fallen off in the laboratory.

In order to determine the identity of these chemicals, a student conducted calorimetric experiments to determine the standard enthalpy change of neutralisation with hydrochloric acid with each of these chemicals.

(i) Define what is meant by the standard enthalpy change of neutralisation.

Standard enthalpy change of neutralisation  $(\Delta H_n^{\theta})$  is the <u>energy evolved</u> when <u>one mole of water</u> is formed from the <u>neutralisation</u> between acid and alkali under <u>standard conditions</u>.

(ii) Explain why the student is able to distinguish NaOH (aq) from NH<sub>3</sub> (aq) from the calorimetric experiments? Assume that both experiments were conducted under similar experimental conditions.

The enthalpy change of neutralisation involving HC/ and  $\text{NH}_3$  is  $\underline{\text{less}}$  exothermic .

 $NH_3$  is a weak base and NaOH is a strong base.

Some of the energy evolved from the neutralisation process is used to <u>further dissociate the weak base</u> completely / to cause <u>ionisation of the</u> <u>undissociated weak base</u>.

(iii) When 40 cm<sup>3</sup> of 3.0 mol dm<sup>-3</sup> hydrochloric acid, was added to 60 cm<sup>3</sup> of 1.4 mol dm<sup>-3</sup> of one of the monoacidic base in a polystyrene cup. The maximum temperature rise was recorded as 10.5 °C. Given that the specific heat capacity of the solution = 4.2 J g<sup>-1</sup> K<sup>-1</sup> and the process is 100% efficient, calculate the standard enthalpy change of neutralisation for the reaction.

Amount of  $HCI = 40/1000 \times 3 = 0.1200 \text{ mol}$ 

Amount of base = 60/1000 x 1.4 = 0.08400 mol

Base is the limiting reagent.

Amount of  $H_2O = 0.08400$  mol

$$Q = mc\Delta T$$
  
= 100 x 4.2 x 10.5  
= 4410 J  
$$\Delta H_n^{\theta} = -\frac{Q}{n_{H_2O}}$$
  
= -4410 / 0.084  
= -52500 J mol<sup>-1</sup>  
= -52.5 kJ mol<sup>-1</sup>

[6]

- (d) Phosphine,  $PH_3$  has a similar structure to  $NH_3$ .
  - (i) By considering the VSEPR theory, comment on the relative bond angle of  $PH_3$  and  $NH_3$ .

<u>N is more electronegative</u> than P, the electron density of its <u>bonding</u> <u>pairs</u> will be held <u>closer</u> to N than P.

The closer the bonding electrons are to the central atom, the **greater the repulsion** on each other.

or

Resulting in greater bonding pair - bonding pair repulsions in  $\text{NH}_3$  than in  $\text{PH}_3$ 

Hence, **bond angle**: ∠H-P-H (<107°) < ∠H-N-H (107°)

(ii)  $PH_3$  has a boiling point of -87.7 °C while  $NH_3$  has a boiling point of -33.34 °C. Explain for the observation in terms of bonding.

<u>More energy</u> is needed to overcome the <u>stronger intermolecular</u> <u>hydrogen bonds</u> in ammonia compared to the <u>weaker intermolecular van</u> <u>der Waals' forces of attraction</u> in phosphine.

[4]

(e) In organic chemistry, ammonia can act as a nucleophile in substitution reactions to form amines. The following is a proposed synthesis of an amine.



In step I,  $AlCl_3$  is involved in the following manner:



(i) Draw the dot and cross diagram for  $[A/Cl_4]^-$ .



(ii) Using your knowledge in periodicity and with the aid of equations, suggest why  $A/Cl_3$  cannot be in aqueous state for it to function in **step I**.

A/C/<sub>3</sub> first dissolves to form A/<sup>3+</sup> and C/ aqueous ions: A/C/<sub>3</sub> (s) + 6 H<sub>2</sub>O (/)  $\rightarrow$  [A/(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> (aq) +3 C/ (aq)

The  $AI^{3+}$  ions undergo hydrolysis with water molecules:  $[AI(H_2O)_6]^{3+}(aq) \rightarrow [AI(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$ 

(iii) Suggest why the amine cannot be obtained using the above synthesis

The electron donating R group is 2,4-directing.



$$=$$
 20.0 cm<sup>3</sup>

(iii) Given the pH range of some acid-base indicators in the table below, select the most suitable indicator for this titration and explain your choice.

Indicator	pH range at which colour change occurs			
Methyl violet	0.5 – 1.5			
Bromocresol blue	3.8 – 5.5			
Alizarin yellow	10.1 – 12.0			

<u>Alizarin yellow</u>. pH transition range of Alizarin yellow lies within the <u>rapid pH</u> <u>change over the equivalence point</u> (iv) An equal volume of CH<sub>3</sub>COOH and CH<sub>3</sub>COO<sup>-</sup>Na<sup>+</sup> was mixed together. Explain, with the aid of equations, how this mixture can resist changes in pH when small amounts of acid or base is added to it.

When small amount of H<sup>+</sup> is added,  $CH_3COO^-(aq) + H^+(aq) \rightarrow CH_3COOH(aq)$ The added H<sup>+</sup> is removed as  $CH_3COOH$ . Hence pH <u>remains fairly constant</u>

When a small amount of base, OH<sup>-</sup> is added:  $CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(I)$ The added OH<sup>-</sup> is removed as  $CH_3COO^-(aq) + H_2O(I)$ . Hence pH <u>remains fairly constant</u>

(v) Suggest, with reasoning, whether you would expect the same volume of carbon dioxide gas to be evolved in each case when equal volumes of the CH<sub>3</sub>COOH and hydrochloric acid of the same concentration are separately reacted with an excess of sodium carbonate.

 $CH_{3}COOH (aq) \iff H^{+}(aq) + CH_{3}COO^{-} (aq) ---- (1)$  $HC/ (aq) \rightarrow H^{+}(aq) + C/ (aq)$ 

Reaction of H<sup>+</sup> with Na<sub>2</sub>CO<sub>3</sub>: 2H<sup>+</sup> (aq) + CO<sub>3</sub><sup>2-</sup>  $\rightarrow$ CO<sub>2</sub> (g) + H<sub>2</sub>O(I)

By Le Chatelier's Principle, <u>equilibrium position in (1)</u> will <u>shift right to increase</u> [H<sup>+</sup>], hence reaction will eventually go to completion

Amount of acid eventually used in each case will be the **same** So **volume of CO**<sub>2</sub> gas evolved in each case will be the **same** 

## (vi) Compare the acidities of ethanol, ethanoic acid and chloroethanoic acid. Explain your answer.

[14]

Order of increasing acidity: ethanol < ethanoic acid < chloroethanoic acid



 $CH_3CO_2H$  and  $CH_2C/COOH$  are <u>more acidic</u> than  $CH_3CH_2OH$  as the carboxylate ion is stabilised by <u>charge delocalisation</u>.

OR

Alkoxide ion is **<u>not</u> stabilised** by charge delocalisation

OR

Presence of **electron-donating alkyl** group **intensifies** the negative charge on the **alkoxide** ion. **Destabilises** the alkoxide ion.

## Lone pair of electrons on oxygen interacts with the C=O group.

This <u>disperses the negative charge</u> on the <u>two</u> oxygen on the carboxylate ion and stabilises it to a greater extent. The loss of  $H^+$  is greatly promoted.

Presence of <u>electron-withdrawing Cl group</u> in CH<sub>2</sub>ClCOOH <u>Dispersion of negative charge on carboxylate ion</u>

Increase in stability of carboxylate ion

**(b)** Peroxodisulfate ions,  $S_2O_8^{2^2}$ , can oxidise iodide ions, I<sup>-</sup> as shown in the equation:

$$S_2O_8^{2^-}(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2SO_4^{2^-}(aq) \qquad \Delta H < 0$$

The kinetics of this reaction can be investigated experimentally by varying the concentration of the two reactants involved and determining the time taken for the brown iodine colour to first appear. The data below was obtained.

Expt	[S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ] / mol dm <sup>-3</sup>	[I <sup>−</sup> ] / mol dm <sup>-3</sup>	Relative rate / s <sup>-1</sup>
1	0.1	0.2	1
			32
2	0.2	0.2	1
			16
3	0.3	0.3	9
			64

(i) Deduce the order of reaction with respect to  $S_2O_8^{2-}$  and  $\Gamma$ . Explain your reasoning.

Comparing experiments <u>1 and 2</u>, when [I<sup>-</sup>] is <u>kept constant</u>, while  $[S_2O_8^{2^-}]$  <u>doubles</u>, the rate also <u>doubles</u>. Therefore, the reaction is <u>first order</u> w.r.t.  $S_2O_8^{2^-}$ .

Let rate =  $k[S_2O_8^{2^-}][\Gamma]^x$  $\frac{rate_3}{rate_2} = \frac{k(0.3)(0.3)^x}{k(0.2)(0.2)^x}$   $\frac{9/64}{1/6} = (1.5)(1.5)^x$  x = 1  $\therefore \text{ Order of reaction w.r.t } \Gamma \text{ is } 1$ 

Eg:

Comparing expt 1 and 3,

When  $[S_2O_3^{2^-}]$  increases by 3 times, rate will also increase by 3 times as order of reaction wrt to  $S_2O_3^{2^-}$  is 1.

However, rate actually increases by 4.5 times.

Thus, it can be deduced that the rate further increases by 1.5 times when [I] increases by 1.5 times too.

Therefore order of reaction wrt to  $[I^-]$  is one.

(ii) Write the rate equation for this reaction.

rate = 
$$k[S_2O_8^{2^-}][I^-]$$

(iii) Suggest a reason why the reaction is slow.

The reaction involved <u>two anions</u> / <u>negatively charged particles</u> which will <u>repel</u> each other resulting in the slow reaction.

(iv) Define rate constant, k, and state the effect on k when temperature is lowered.

k is the **proportionality constant** of the rate equation. It **decreases** when T is lowered.

> [6] [Total: 20]