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CHEMISTRY

PHYSICAL CHEMISTRY

Level & Board	CIE (A-LEVEL)
TOPIC:	REACTION KINETICS
PAPER TYPE:	SOLUTION - 1
TOTAL QUESTIONS	10
TOTAL MARKS	101

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REACTIO KINETICS – 1 (SOLUTION)

1)

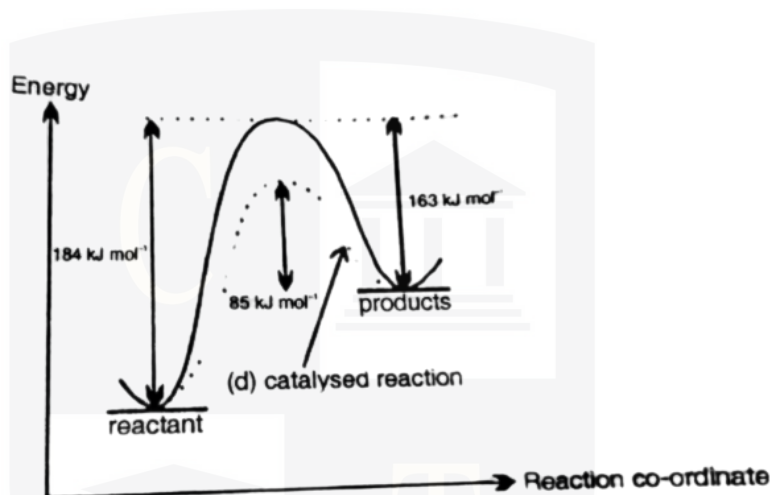
(a) (i) $R = k[\text{HI}]^2$

As the initial $[\text{I}_2]$ doubles from 1.67 to 3.34 to 3.34 mol dm^{-3} , the initial rate in – creases by 4 times from 0.41 to 1.64 $\text{mol dm}^{-3} \text{ s}^{-1}$

(ii) $0.41 = k. (1.67)^2$

$$K = 0.147 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

(b) (i)



(ii) $\Delta H = 184 - 163 = + 21 \text{ KJ mol}^{-1}$

(c) Since the forward reaction is endothermic, increasing the temperature because the equilibrium to shift to the right. According to Le Chatelier's Principle, it shifts right to absorb the excess heat. In addition, the rate of reaction becomes faster since the molecules have greater average kinetic energy to overcome the activation energy.

(d) $E_a = 85 + 21 = 106 \text{ KJ mol}^{-1}$

2)

(a) (i) $R = k[\text{O}_2][\text{NO}]^2$

(ii) in a reaction, $a\text{A} + b\text{B} \rightarrow \text{product}$.

Let the rate equation be $R = k[\text{A}]^m[\text{B}]^n$. Then, k is the rate constant.

m is the order of reaction with respect to A.

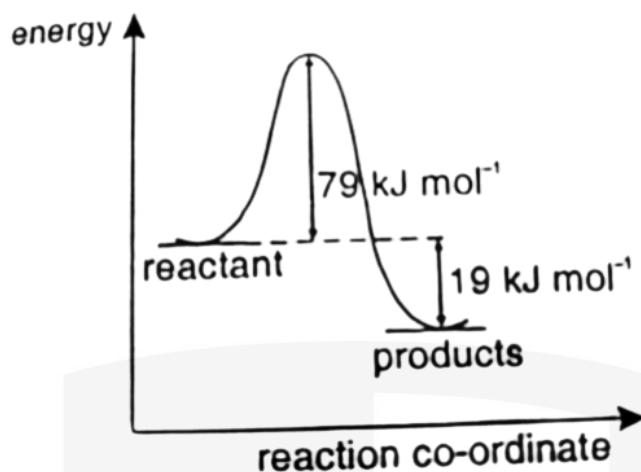
n is the order of reaction with respect to B.

$m + n$ is the overall order of reaction,

in the mechanism of a reaction the slowest elementary step that determines the

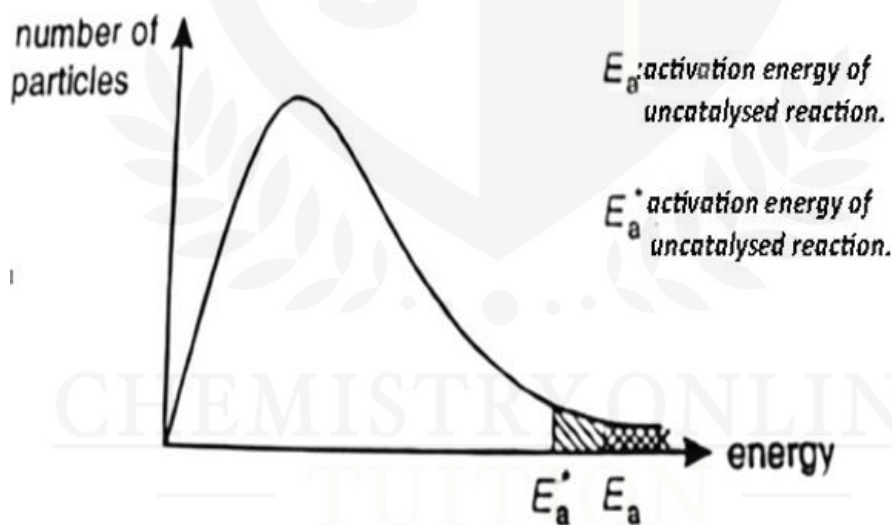
overall rate of reaction is the rate determining step.

(b) (i)



(ii) *activation energy* is the minimum energy that particles must possess when they collide for a reaction to take place.

(iii) The presence of a catalyst provides an alternative pathway for the reaction to take place and this has a lower activation energy. Hence, more particles have energy more than the activation energy and the reaction rate increase.



(iv) The presence of a catalyst increase the rate constant. The rate constant is a function of activation energy. The lower the activation energy, the higher the rate constant.

3)

(d) (i) An instrumental method like a colorimeter is used.

In a colorimeter absorbance of different wavelengths is measured to find the wavelength shift from 400 – 500 nm. Time taken for this change is noted.

Since the time is related to rate, i.e. $\text{rate} \propto \frac{1}{\text{time}}$, the gradient of absorbance over time gives the rate of reaction. The experiment is repeated with different concentrations of $[\text{Zn}^{2+}(\text{aq})]$ and PAR.

(ii) Add aqueous bromine to PAR brown color will decolorize to show presence of phenol group.

4)

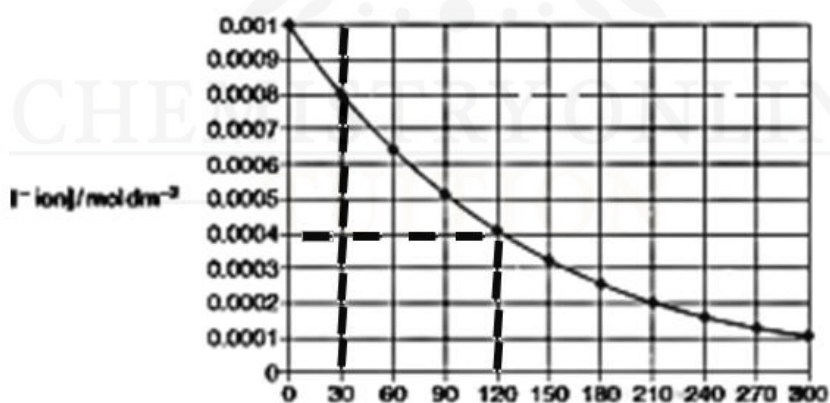
(a) colorless to reddish brown,

(b)

Case	Numerical value		
	a	b	c
Step 1 is the slowest overall	1	1	0
Step 2 is the slowest overall	1	1	1
Step 3 is the slowest overall	1	2	2

(c) $\text{rate} = 7.5 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$

(d)



From the graph, Half the = $120 - 30 = 90 \text{ s}$.

(e) Line 1 and 2: as $[\text{H}_2\text{O}_2]$ increases by $\frac{0.07}{0.05} = 1.4$ so does rate. So order

w.r.t. $[\text{H}_2\text{O}_2] = 1$.

Line 1 and 3 increases in rate (1.8) is also increase in $[\text{H}_2\text{O}_2]$. So rate is independent of $[\text{H}^+]$

Order w.r.t $[\text{H}_2\text{O}_2] = 1^{\text{st}}$ order.

Order w.r.t $[\text{H}^+] = \text{zero order}$.

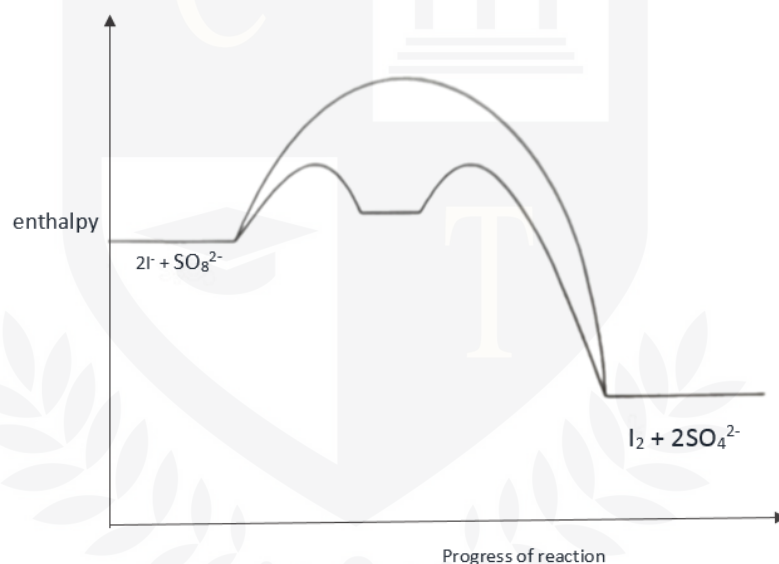
(f) the 1^{st} step. Equation: $\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{IO}^- + \text{H}_2\text{O}$

5)

(a) (i) homogeneous

(ii) Ions in reaction 2 and 3 are oppositely charged, thus attract each other and react easily.

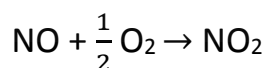
(iii)



(b) (i) Sulphur trioxide dissolves in rain water to produce H_2SO_4 , which damages buildings

(ii) The burning of fossil fuels.

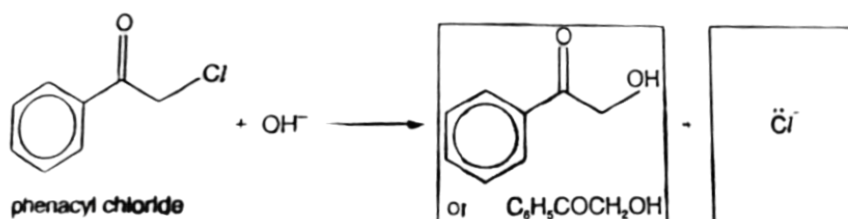
(iii) $\text{SO}_2 + \text{NO}_2 \rightarrow \text{SO}_3 + \text{NO}$



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6)

(a)

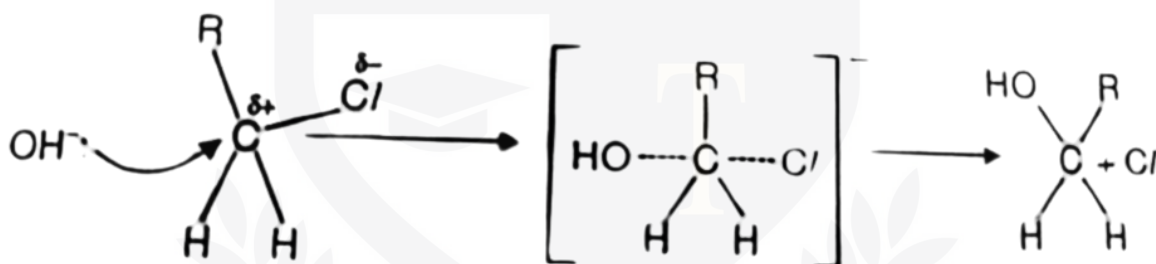


(b) (i) It is the power to which concentration is raised in the rate equation.

(ii) By comparing experiment 1 and 2, rate increases by the same ratio as concentration of R - Cl increases, hence $\text{Rate} \propto [\text{primary haloalkane}]$. It is observed in experiment 2 and 3 that rate is proportional to OH^- .

(iii) $\text{Rate} = k[\text{R} - \text{Cl}][\text{OH}^-]$

(iv)



Primary haloalkane undergoes $\text{S}_{\text{N}}2$ mechanism (Bimolecular nucleophilic substitution).

(c) (i) Reagent to check relative reactivity of R - Cl and R - C(=O) - Cl is silver nitrate solution.

add dilute aq. AgNO_3 solution to each of the above halogen

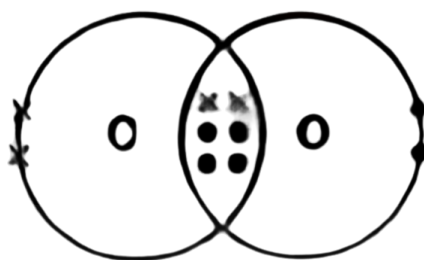
derivative, white precipitate of AgCl are formed at once with R - C(=O) - Cl.

R - Cl forms white ppt after some time as hydrolysis of R - Cl is slow.

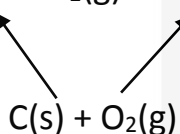
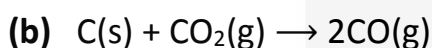
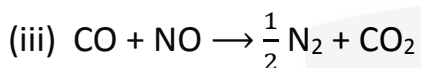
(ii) in acylhalide $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$, carbon atom is more positive as compared to carbon atom in haloalkane. Hence acid halides undergo faster hydrolysis as compared to haloalkanes.

7)

(a) (i)



(ii) This is due to the incomplete combustion of hydrocarbon fuels.



Let enthalpy change of the reaction be x.

$$\therefore x + (-394) = (-111) \times 2$$

$$x = -222 + 394$$

$$= +172 \text{ KJ mol}^{-1}$$

(c) (i) Ligand exchange reaction.

(ii) In transition element complexes, the central metal (ion) has a partially filled d – subshell. The d – subshell is split into different energy levels and the energy gap (ΔE) between these levels depends upon the ligands surrounding the central metal ion.

An electron at a lower energy level absorbs energy from the visible light and is promoted to a higher energy level. Hence, color observed is the complement of the color absorbed.

(iii) From Rows 1 and 3, it can be clearly seen that doubling the concentration of $[\text{Ru}(\text{H}_2\text{O})_2\text{Cl}_4]^{2-}$ doubles the rate of the reaction. Thus the concentration of $[\text{Ru}(\text{H}_2\text{O})_2\text{Cl}_4]^{2-}$ and the rate of the reaction are proportional to one another.

Increasing or decreasing the concentration of carbon monoxide does not effect the rate of reaction. Hence, order of reaction with respect to $[\text{Ru}(\text{H}_2\text{O})_2\text{Cl}_4]^{2-} = 1$ and order of reaction with respect to $[\text{CO}] = 0$.

$$\therefore \text{rate equation} = k[[\text{Ru}(\text{H}_2\text{O})_2\text{Cl}_4]^{2-}]$$

(iv) Mechanism 2, since it is the only mechanism that does not involve carbon monoxide in the rate determining step (i.e the slow reaction).

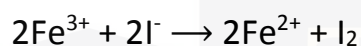
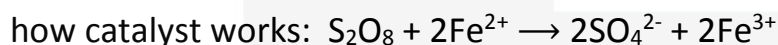
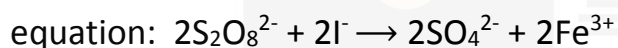
8)

(a) (i) If a catalyst is present in the same phase as the reactants. It is known as homogeneous catalyst.

If the phase of the catalyst is different from the phase of the reactants, It is known as heterogeneous catalyst.

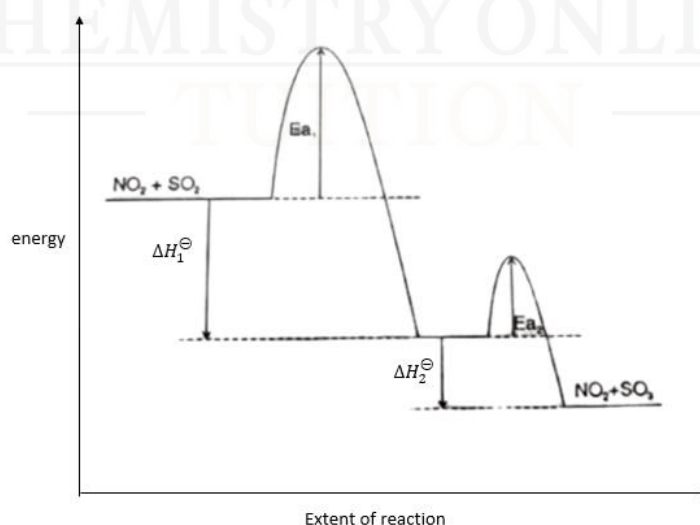
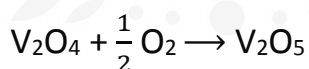
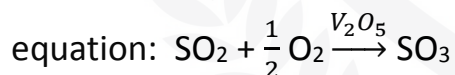
(ii) For homogenous catalysis:

Homogeneous catalyst: Fe^{2+}



For heterogeneous catalysis:

heterogeneous catalyst: V_2O_5 (vanadium (V) oxide).

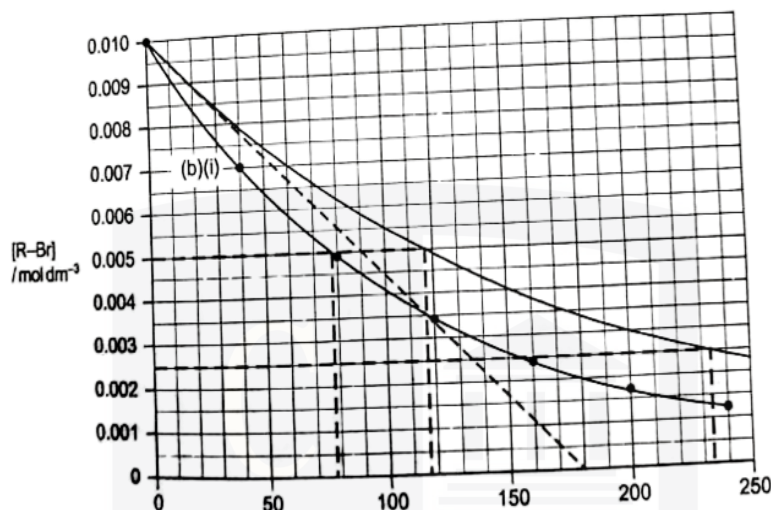


9)



(ii) Nucleophilic substitution

(b) (i)



(ii) From graph, using $[\text{NaOH}] = 0.1 \text{ mol / dm}^3$, the time taken for concentration of R – Br to fall from 0.01 to 0.005 mol / dm³ is approximately 118 minutes. Also, time taken for concentration of R – Br to fall from 0.005 to 0.0025 mol / dm³ is (233 – 118) = 115 minutes approximately. As half lives are approximately same and constant, hence reaction is of first order with respect to R – Br

(iii) From graph.

$$t_{1/2} \text{ for } 0.10 \text{ mol dm}^{-3} \text{ of NaOH} \approx 118 \text{ min}$$

$$t_{1/2} \text{ for } 0.15 \text{ mol dm}^{-3} \text{ of NaOH} \approx 78 \text{ min}$$

when concentration of NaOH increases by ratio = $\frac{0.15}{0.1} = 1.5$,

$$t_{1/2} \text{ decreases by ratio} = \frac{118}{78} \approx 1.5$$

since $t_{1/2}$ decreases 1.5 times when $[\text{NaOH}]$ is increased 1.5 times, therefore order of reaction with respect to $[\text{NaOH}]$ is 1.

(iv) initial Gradient of the curve at time, $t = 0$ using $[\text{NaOH}] = 0 \text{ mol/dm}^3$ can be approximated by,

$$\text{gradient} = \frac{0.01-0}{0-180} = 5.5 \times 10^{-5}$$

hence, initial rate = $5.5 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ mol}^{-1}$

$$\text{rate} = k[\text{R} - \text{Br}] [\text{NaOH}]$$

$$\begin{aligned} \Rightarrow k &= \frac{\text{rate}}{[\text{R} - \text{Br}] [\text{NaOH}]} \\ &= \frac{5.5 \times 10^{-5}}{0.01 \times 0.1} \\ &= 0.055 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1} \end{aligned}$$

10)

(a) (i) Using experiment 2 and 3, as the concentration of NO doubles, the rate of the reaction increases by approximately 4 times. Using experiment 1 and 2, as the concentration of O₂ doubles, the rate of the reaction approximately doubles, as well. Therefore order with respect to [NO] is second order and order with respect to [O₂] is first order.

(ii) The concentration of NO and O₂ in experiment 4 has increased by 3 times as compared to experiment 1.

$$\begin{aligned} \therefore \text{initial rate} &= (4.08 \times 10^{-3}) \times 3 \times 3^2 \\ &= 0.11 \text{ mol dm}^{-3} \text{ s}^{-1} \end{aligned}$$

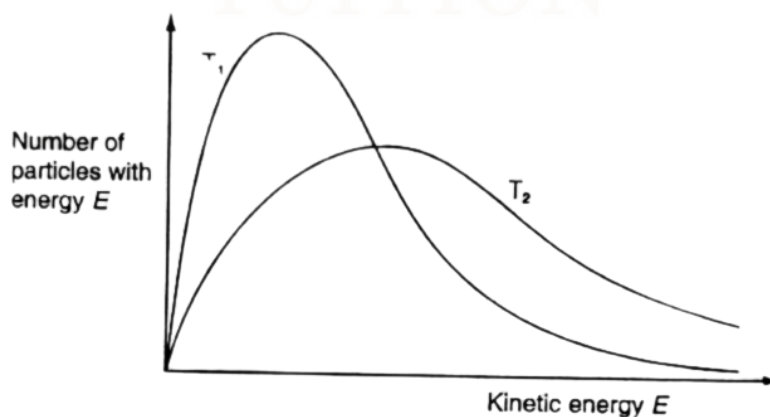
(iii) Rate = k[O₂][NO]²

(iv) Rate = k[O₂][NO]²

$$4.08 \times 10^{-3} = k(0.012)(0.032)^2$$

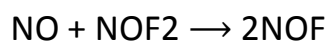
$$k = \frac{4.08 \times 10^{-3}}{(0.012)(0.032)^2} = 332.03 \text{ mol dm}^{-3} \text{ s}^{-1}$$

(b) (i)



(ii) The rate of the reaction and the energy of the particles increases. There are more particles which will have energy greater than activation energy and therefore more fruitful collisions can take place.

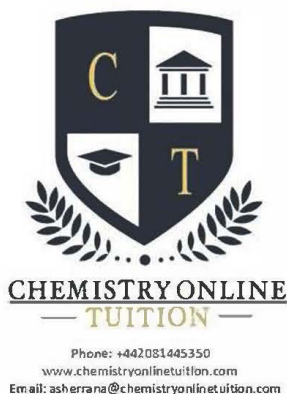
(c) $F_2 + NO \rightarrow NOF_2$ (rate determining slower step).



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