Theme: **Reaction Kinetics**

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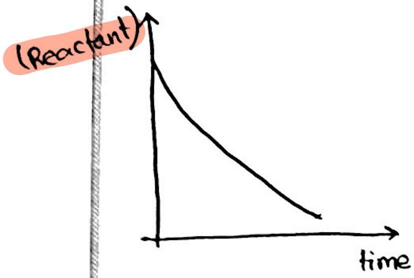
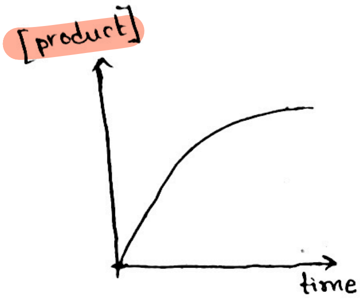
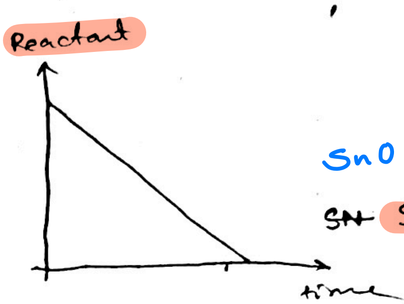
$$\text{Rate} = \frac{\text{change in conc. of reactant/product}}{\text{time}}$$

[Reactant] = $mol\,dm^{-3}s^{-1}$ OR $mol\,dm^{-3}min^{-1}$

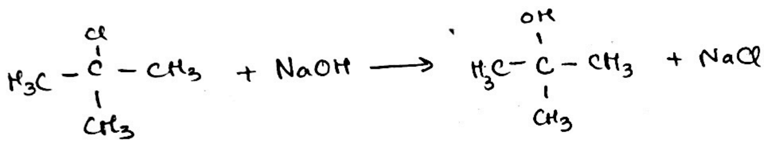






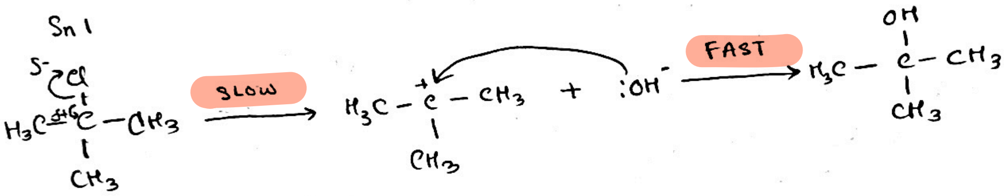
Sn 0 ?

~~SN~~ Sn 1



- only the reactant present in slow step can ef affect the rate of reaction.

Sn 1



$\text{Rate} \propto [\text{Reactant}]^n$

Define Order of Reaction :

It is the power to which concentration of ~~per~~ reactants are raised in rate ~~fo~~ equation.

$${}_mA + {}_nB + {}_pC \xrightarrow{D\text{(catalyst)}} pE + qF$$

* $\text{Rate} \propto [A]^m$
* $\text{Rate} \propto [B]^r$
* $\text{Rate} \propto [C]^0$
* $\text{Rate} \propto [D]$

$$\text{Rate} \propto [A]^m [B]^r [C]^0 [D]^s$$

$$\boxed{\text{Rate} = K[A]^m[B]^r[D]^s} \longrightarrow \text{Rate eq}^n$$

K → Rate constant

- overall constant = m + n + r + s

* With change in temperature the value Rate constant will changes.

K is constant given that te Temperature is constant.

T ↑ K ↑

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Q. $A + B \xrightarrow{C} D$

Expt. No	[A]	[B]	[C]	Rate $mol\,dm^{-3}s^{-1}$
1	0.200	0.100	0.300	5.00×10^{-3}
2	0.400	0.100	0.300	5.00×10^{-3}
3	0.400	0.200	0.300	2×10^{-2}
4	0.500	0.300	0.600	9×10^{-2}
5	0.500	0.700	0.900	?

$9 \times 10^{-2} = 2 \times 10^{-2} \times 1.5^2 \times 2^n$

$\Rightarrow 0.09 = 0.045 \times 2^n$

$\Rightarrow 2^1 = 2^n$

$\therefore n = 1$

i) ~~Rat~~ * From exp. 1 & 2 when concn A is doubled there is no change in rate of reacn thus ~~or~~ w.r.t. [A] is 0 order.

5.4 - ii) * From exp. 2 & 3 when con^n of B is ~~bo~~doubled ~~to~~ rate increases by 4 times, w.r.t. [B] it is 2nd order.

iii) * From exp. 3 & 4 due to increase in [B] by 1.5 time, the rate will increase by $(1.5)^2$ times. The overall increase in the rate 4.5 times. This indicates when [C] is doubled rate is also doubles. Thus, w.r.t. [C], it is 1st order

$4.5 = (1.5)^2 \times 2^n$

iv) $Rate = K \cancel{[A]^0} [B]^2 [C]^1$

~~Using values from~~

v) $Rate = K [B]^2 [C]$

$= 9 \times 10^{-2} \times \left(\frac{7}{3}\right)^2 \times \left(\frac{3}{2}\right)$

$= 0.735$

~~Use val~~

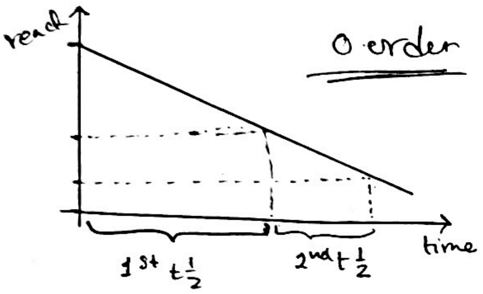
vi) Use values from exp. 3 to find a value of Rate constant & it's unit.

$$\frac{2\times10^{-2}}{mol\,dm^{-3}s^{-1}} = K\,\frac{[0.2]^2[0.3]}{mol^{2}\,dm^{-6}}$$

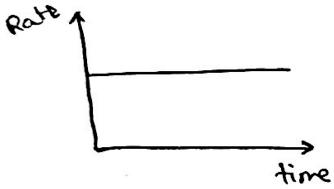
$$\therefore K = 5/3 \quad dm^{6}\,mol^{-2}\,s^{-1}$$

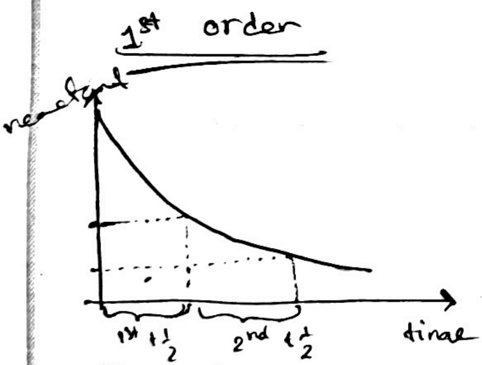
half life

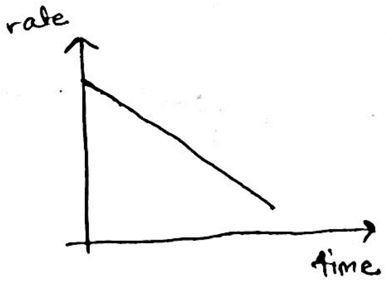
Half life: It is the time taken for the concⁿ of the reactant to become half of its initial value.



• for 0 order reaction, its successive half life decreases.



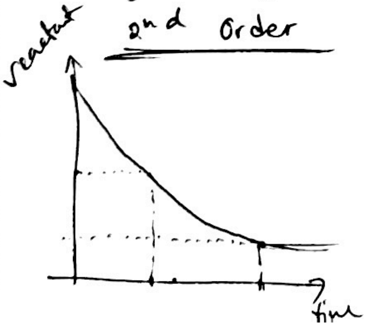


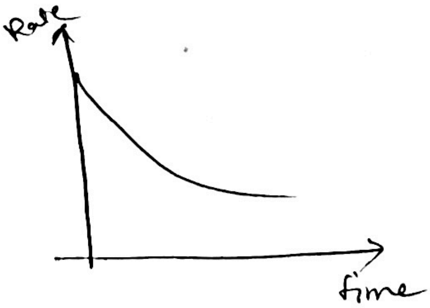


Note: Only applicable for 1st order

$$t\tfrac{1}{2} = \frac{\ln 2}{K \rightarrow \text{rate constant}}$$

$$t_{\frac{1}{2}} = \frac{\ln 2}{K}$$





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EXPLAINING ORDER OF REACTION USING REACTION MECHANISM

→ Define rate determining step : (r.d.s)

→ It is the slow step in the reaction mechanism.

→ Only the reactants that are available in the rate determining step will appear in the rate equation.

$$CH_3COCH_3 + I_2 \xrightarrow{H^+} CH_3COCH_2I + HI$$

Mechanism

$$CH_3COCH_3 + H^+ \underset{}{\overset{fast}{\rightleftharpoons}} CH_3-\overset{\overset{+}{O}H}{\overset{|}{C}}-CH_3$$

$$CH_3-\overset{\overset{+}{O}H}{\overset{||}{C}}-CH_3 \xrightarrow{slow} CH_3-\overset{OH}{\overset{|}{C}}=CH_2 + H^+$$

$$CH_3-\overset{OH}{\overset{|}{C}}=CH_3 + I_2 \xrightarrow{fast} CH_3-\overset{\overset{+}{O}H}{\overset{||}{C}}-CH_2I + I^-$$

$$CH_3-\overset{\overset{+}{O}H}{\overset{||}{C}}-CH_2I + I^- \xrightarrow{fast} CH_3-\overset{O}{\overset{||}{C}}-CH_2I + HI$$

• power is equal to no. of mol used

$$\therefore \quad Rate = K\,[CH_3COCH_3][H^+]$$

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

$$Rate = K\,[N_2O_5]$$

Reaction meachanism

$$N_2O_5 \xrightarrow{slow} NO_2 + NO_3$$

$$N_2O_5 \xrightarrow{fast} NO + NO_2 + O_2$$

$$\cancel{NO} + \cancel{NO_3} \xrightarrow{fast} 2NO_2$$

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

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Q1 The reaction 2 mols of ICl + 1 mol ~~HCl~~ 2H H₂ → 2HCl + 1 I_2

$$2ICl + H_2 \longrightarrow 2HCl + I_2$$

its 1st order w.r.t. ICl and 1st order ~~wrt~~ w.r.t to H_2 the reac^n mechanism has 2 steps only. The first step is ~~so~~ ~~slowest~~ ~~and the~~ much slower step than the 2nd step.

$$2ICl + H_2 \longrightarrow [ICl][H_2]$$

$$Rate = k[ICl][H_2]$$

$$\cancel{ICl \longrightarrow I_2 + Cl_2}$$

step 1 : $ICl + H_2 \xrightarrow{Slow} HCl + HI$

step 2 : $HI + ICl \xrightarrow{fast} HCl + I_2$

$$ICl + H_2 \longrightarrow 2HCl + I_2$$

Catalysis

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HOMOGENOUS CATALYSIS

During homogenous catalysis the catalyst changes it oxidation state

~~for an ion~~

For an ion or a chemical species to behave as a homogenous catalyst it electrod potential value (E_0) must be in between the electrode potential value of the reactants.

$S_2O_8^{2-} + 2I^- \rightarrow Fe^{2+}/Fe^{3+} \; 2SO_4^{2-} + I_2$

$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$

$2I^- + 2Fe^{3+} \rightarrow I_2 + 2Fe^{2+}$

$$S_2O_8^{2-} + 2I^- \xrightarrow{Fe^{2+}/Fe^{3+}} 2SO_4^{2-} + I_2$$

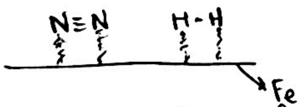
Fe^{2+}

$$S_2O_8^{2-} + 2Fe^{2+} \longrightarrow 2SO_4^{2-} + 2Fe^{3+}$$

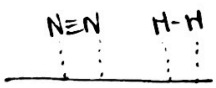
$$2I^- + 2Fe^{3+} \longrightarrow I_2 + 2Fe^{2+}$$

Heterogenous catalysis

~~Diffusion~~ ① Diffusion to the surface



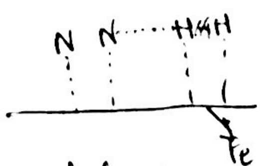
② Adsorption to the surface of the catalyst



when these reactant molecule are forming bonds with the surface of the catalyst energy is ~~prod~~ released.

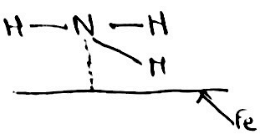
③ Reaction : The energy ~~produced by~~ is used to break the bond between the particles so new bonds can be formed.

(i)



The reactants will react with each other

(ii)



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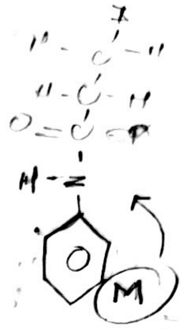
(4) Diffusing away from the surface

↑NH_3↑



M/J/17

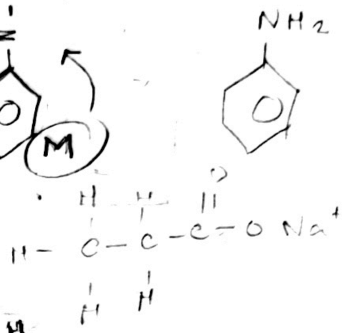
5. J JKL amine

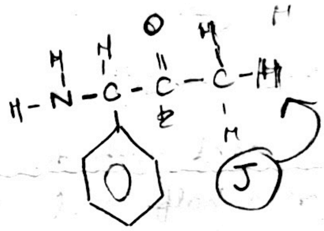
M amide

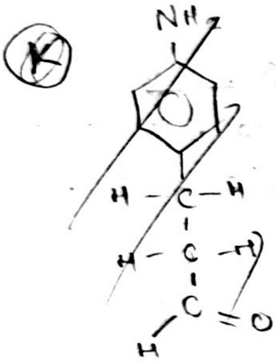
K aldehyde

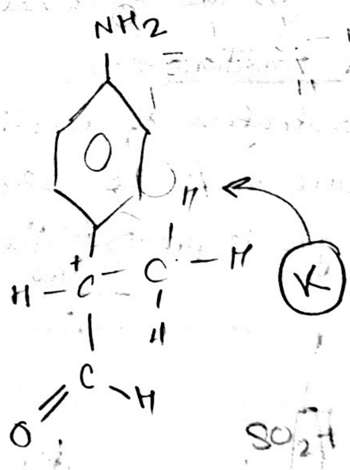
JL methyl ketone

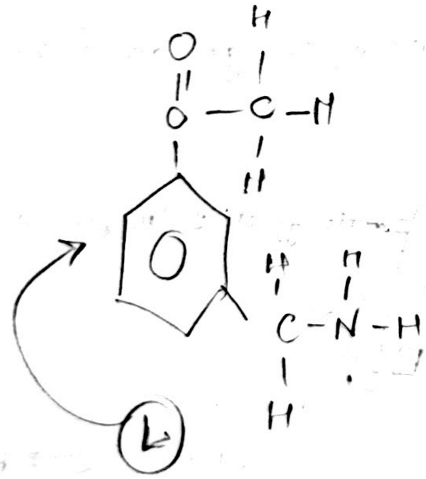
K phenyl amine











$SO_2 + NO_2 \rightarrow SO_3 + NC$

$NO + \frac{1}{2}O_2 \rightarrow NO_2$

$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$

$SO_2 + O_2 \rightarrow SO_3$

~~$I_2 + Fe$~~

$2NO + O_2 \rightarrow 2NO_2$

$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$

$SO_2 + NO_2 \rightarrow SO_3 + NO$

$2I^- + 2Fe^{3+} \rightarrow I_2 + 2Fe^{2+}$

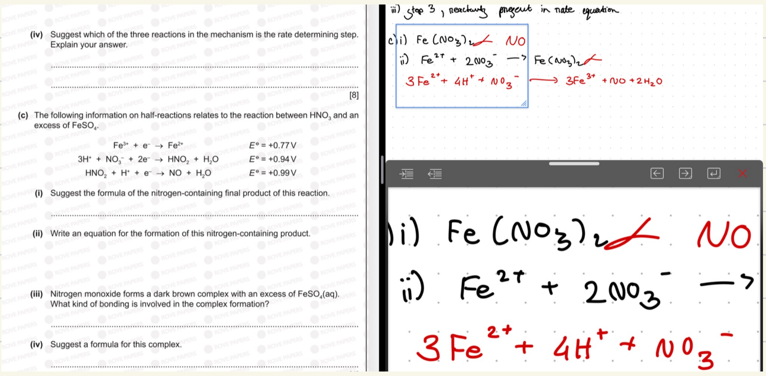
Misc Notes

Diffusion: nitrogen gas and hydrogen gas diffuse to the surface of the iron.
Adsorption: the reactant molecules are chemically adsorbed onto the surface of the iron. The bonds formed between the reactant molecules and the iron are:
- strong enough to weaken the covalent bonds within the nitrogen and hydrogen molecules so the atoms can react with each other
- weak enough to break and allow the products to leave the surface.

Reaction: the adsorbed nitrogen and hydrogen atoms react on the surface of the iron to form ammonia.
Desorption: the bonds between the ammonia and the surface of the iron weaken and are eventually broken.
Diffusion: ammonia diffuses away from the surface of the iron.

Catalysts CAN be a part of the r.d.s. however Intermediates CANNOT be part of r.d.s.

Why is it not possible to determine the order of reac^n wrt water in certain reactions
↳ BECAUSE water is the solvent OR its conc^n cannot change — me



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