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REACTION KINETICS

Rate of reaction: Change in conc. of reactant / product per unit time.

Found by measuring dec. in conc. of reactant over time OR inc. in conc. of product over time.

Unit: $mol\ dm^{-3}\ s^{-1}$

$$\text{rate of reaction} = \frac{\text{chance in conc.}}{\text{time}}$$

Rate equation

* found experimentally

$$\boxed{Rate = k[P]^m[Q]^n}$$

- k = rate constant
- [P] & [Q] = conc. of reactants
- m, n = order to which reactant is raised (can be 0, 1, 2)

NOTE: Rate equation doesn't include conc. of products ∵ this doesn't affect rate.

Order of reaction: Shows how conc. of a reactant affects rate.

→ when order of reaction w.r.t reactant = 0
  - ~~con~~ rate is independent of conc. of that reactant
  - not included in rate equation

→ when order of reaction w.r.t reactant = 1
  - rate ∝ conc. of that reactant

  rate ∝ [X] ~~⇒ rate = k_1[X]~~

→ when order of reaction w.r.t reactant = 2
  - rate ∝ square of conc. of that reactant

  rate ∝ $[X]^2$ ~~⇒ rate =~~

Overall order = sum of powers

Half-life ($t_{1/2}$): time taken for conc. of limiting reactant to become half its initial value.

Rate-determining step (RDS)

- slowest step in a reaction mechanism.
- any reactant appearing in RDS appears in rate equation.
- biomolecular reaction: 2 species involved in RDS.
- unimolecular reaction: 1 species involved in RDS.

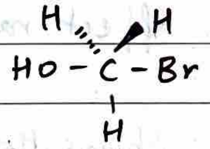
Intermediate: formed from the species that are involved in RDS.

eg. $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$

rate equation: rate = $k[CH_3Br][OH^-]$

⇒ both take part in RDS ⇒ biomolecular

intermediate =



Experimental determination of order of reaction

① using table of results

② using graphs

① **Table of results**

- choose 2 exp where conc of only 1 reactant changes.
- Compare conc. change vs. rate change.
- deduce order of reaction w.r.t that reactant.
- repeat for all reactants.

eg.

	$mol\ dm^{-3}$			$mol\ dm^{-3}\ s^{-1}$
exp. no.	Initial [A]	Initial [B]	Initial [C]	Initial Rate
1	0.20	0.10	0.40	0.80×10^{-3}
2	0.20	0.40	0.40	3.20×10^{-3}
3	0.10	0.80	0.40	1.60×10^{-3}
4	0.10	0.30	0.20	0.60×10^{-3}

From 1 & 2:

when [B] × 4, rate × 4 $\because 0.80 \times 10^{-3} \rightarrow 3.20 \times 10^{-3}$

$\therefore$ order w.r.t [B] = 1

From 2 & 3:

when [B] × 2, rate × 2 $\therefore 3.2 \times 10^{-3} \rightarrow 6.4 \times 10^{-3}$

when [A] $\times \frac{1}{2}$, rate $\times \frac{1}{4}$ $\because 6.4 \times 10^{-3} \rightarrow 1.6 \times 10^{-3}$

$\therefore$ order w.r.t [A] = 2

From 3 & 4:

when [B] $\times \frac{3}{8}$, rate $\times \frac{3}{8}$ $\therefore 1.60 \times 10^{-3} \rightarrow$ ~~[illegible]~~ 6×10^{-4}

when [C] $\times \frac{1}{2}$, rate × 1 ~~$\therefore 6.0 \times 10^{-4} \rightarrow$~~

or rate unaffected

$\therefore$ order w.r.t [C] = 0

overall order of reaction = 1 + 2 + 0 = 3

② Graphs

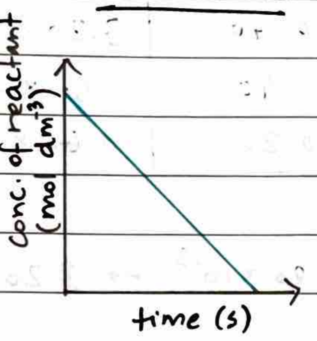
(i) concentration - time graphs

(ii) rate-concentration graphs / rate-time graphs : initial rate

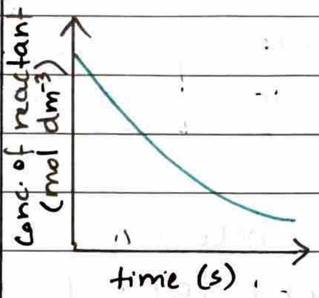
(iii) half-life

(i) Concentration-time graphs

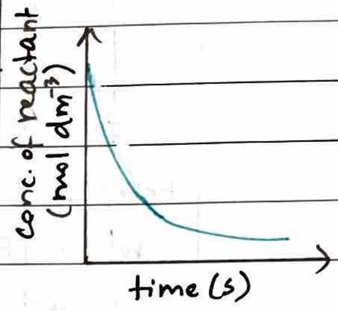
zero-order



first-order



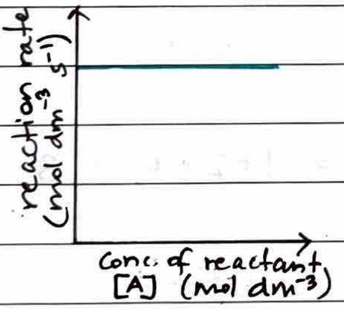
second-order



(ii) Initial rate

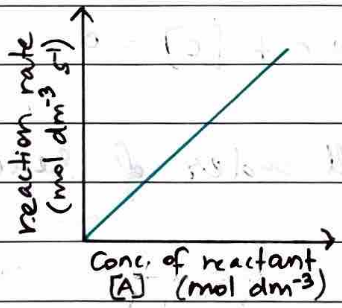
- progress of reaction can be followed by measuring initial rates of reaction using various initial conc. of each reaction.
- these rates are plotted against time - rate-time graph

zero-order



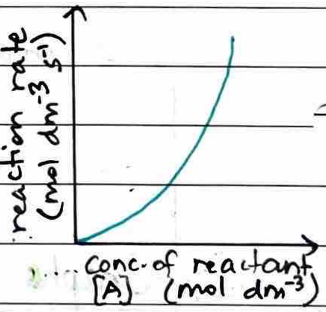
- rate doesn't depend on conc. of reactant.
- ∴ rate constant throughout reaction.
- rate equation:
  rate = k

first-order



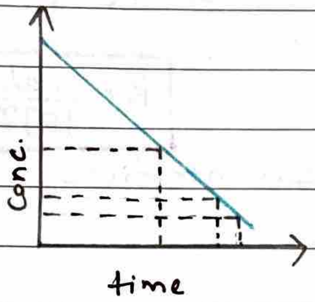
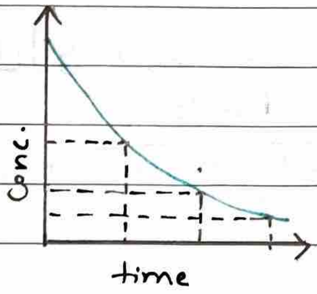
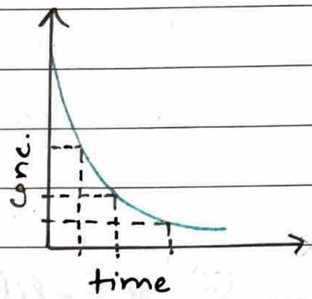
- rate ∝ conc. of reactant.
- rate ↓ as conc. ↓ when it gets used up in reaction.
- rate equation:
  rate = k[A]

second-order



- rate ∝ square of conc. of reactant.
- rate ↓↓ as conc. ↓ when it gets used up in reaction.
- rate equation:
  k[A]^2

(iii) Half-life

Zero-order	first-order	Second-order
		
- Successive $t_{1/2}$ dec. with time.	- ~~ks~~ successive $t_{1/2}$ remains constant throughout.	- ~~$t_{1/2}$~~ Successive $t_{1/2}$ inc. with time.

Calculating initial rate

- Using initial conc. of reactants in rate equation.

eg. $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$

rate = $k[CH_3Br][OH^-]$ $k = 1.75 \times 10^{-2}\ dm^{-2}\ mol^{-1}\ s^{-1}$

initial conc. of $CH_3Br = 0.0200\ mol\ dm^{-3}$

$OH^- = 0.0100\ mol\ dm^{-3}$

initial rate $= 1.75 \times 10^{-2} \times 0.02 \times 0.01 = 3.50 \times 10^{-6}$ $mol\ dm^{-3}\ s^{-1}$

Calculating units

for above equation, unit of k:

$$\frac{\cancel{mol}\ \cancel{dm^{-3}}\ s^{-1}}{\cancel{(mol\ dm^{-3})}\ (mol\ dm^{-3})}$$ (unit of rate) / (unit of conc. of reactants)

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

Calculating rate constant (k)

① Initial rates & rate equation

② Half life

(i) **Initial rate**

eg. $CaCO_3(s) + 2Cl^-(aq) + 2H^+(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$

~~14/22~~

$$rate = k[CaCO_3][Cl^-]$$

$$k = \frac{\text{initial rate}}{[CaCO_3][Cl^-]} \longrightarrow \text{initial concentrations}$$

$$\boxed{k = \frac{rate}{[P]^m[Q]^n}}$$

(ii) **Half-life**

→ only required to deduce k from half-life of first-order reaction.

→ for first-order reaction:

$$\boxed{t_{1/2} = \frac{0.693}{k}} \qquad \boxed{k = \frac{0.693}{t_{1/2}}}$$

Kinetics of multi-step reactions

- Reaction mechanism ⇒ steps involved in making & breaking of bonds during chemical reaction.
- RDS is slowest step of reaction mechanism, and reactants appearing in RDS appear in rate equation.

Predicting reaction mechanism

eg. $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ → reaction equation

$rate = k[NO_2]^{\textcircled{2}}$ → no. of molecules in RDS (stoichiometric coefficient) = power → rate equation

} known

- reaction is zero-order w.r.t to $CO(g)$ & 2nd-order w.r.t $NO_2(g)$
- ∴ 2 molecules of NO_2 involved in RDS.

possible mechanism:

step 1 : $\textcircled{2}NO_2(g) \rightarrow NO(g) + NO_3(g)$; slow RDS

step 2 : $NO_3(g) + CO \rightarrow NO_2(g) + CO_2(g)$; fast

$$\cancel{2NO_2} + \cancel{NO_3} + CO \rightarrow NO + \cancel{NO_3} + \cancel{NO_2} + CO_2$$

$$NO_2(g) + CO \rightarrow NO(g) + CO_2(g)$$

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Predicting reaction order & deducing rate equation

eg. $2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(l)$

Step 1: $NO(g) + NO(g) \longrightarrow N_2O_2(g)$; fast

Step 2: $N_2O_2(g) + H_2(g) \longrightarrow H_2O(l) + N_2O(g)$; slow RDS

Step 3: $N_2O(g) + H_2(g) \longrightarrow N_2(g) + H_2O(l)$; fast

→ reaction equation } known
→ mechanism

- 2nd step = RDS
- RDS consists of :
  - N_2O_2 formed from 2NO; N_2O_2 is an intermediate
  - $1\ H_2$ molecule

* rate eq. must only have reactants!

∴ 2nd-order w.r.t NO & 1st-order w.r.t H_2

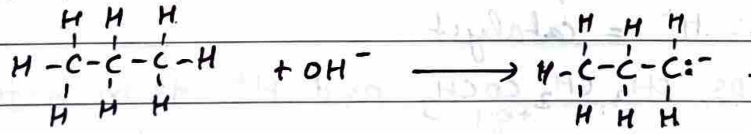
∴ rate = $k[NO]^2[H_2]$

∴ overall order = 3rd-order

Identifying RDS

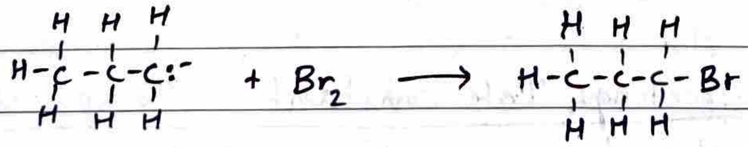
eg. $CH_3CH_2CH_3 + Br_2 + OH^- \rightarrow CH_3CH_2CH_2Br + H_2O + Br^-$

Step 1:



$H-C-C-C-H + OH^- \longrightarrow H-C-C-C:^- + H_2O$ ~~slow RDS~~

Step 2:



$H-C-C-C:^- + Br_2 \longrightarrow H-C-C-C-Br + Br^-$ ~~fast~~

rate = $k[CH_3CH_2CH_3][OH^-]$

→ mechanism } known
→ rate equation

- from rate eq, can be deduced that only $CH_3CH_2CH_3$ & OH^- are involved in RDS

∴ RDS = Step 1

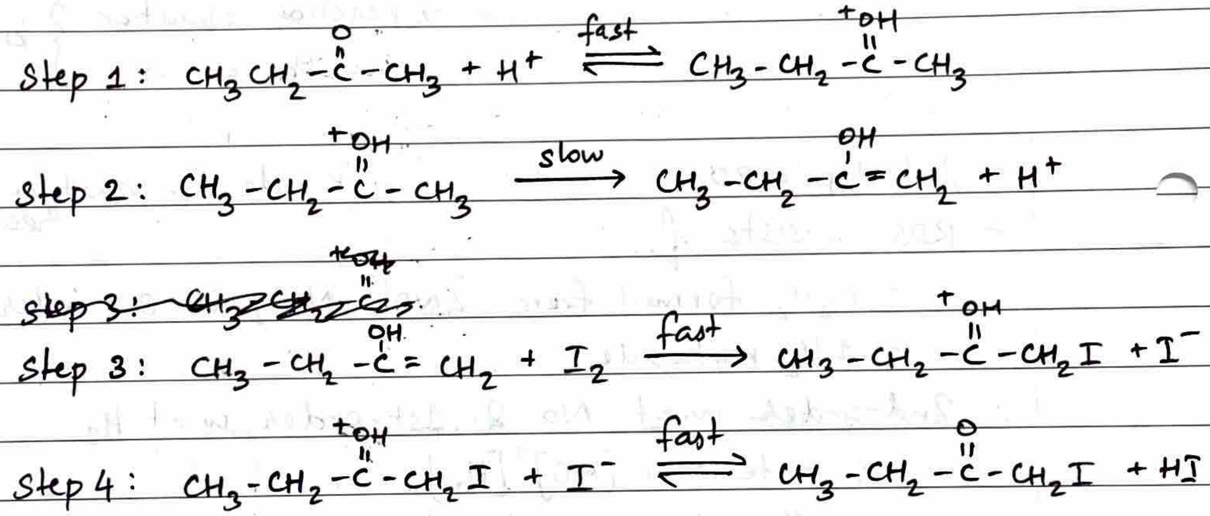
- not part of reaction equation but part of rate equation.

Identifying intermediates & catalysts

- catalyst: species which first appears on LHS, then RHS.
- intermediate: species which first appears on RHS, then LHS.

is formed RDS

eg. $CH_3CH_2COCH_3 + I_2 \xrightarrow{H^+} CH_3CH_2COCH_2I + HI$



Step 1: $CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_3 + H^+ \underset{}{\overset{fast}{\rightleftharpoons}} CH_3-CH_2-\overset{+OH}{\overset{\|}{C}}-CH_3$

step 2: $CH_3-CH_2-\overset{+OH}{\overset{\|}{C}}-CH_3 \xrightarrow{slow} CH_3-CH_2-\overset{OH}{\overset{|}{C}}=CH_2 + H^+$

~~step 3: $CH_3CH_2\overset{+OH}{\overset{\|}{C}}CH_3$~~

step 3: $CH_3-CH_2-\overset{OH}{\overset{|}{C}}=CH_2 + I_2 \xrightarrow{fast} CH_3-CH_2-\overset{+OH}{\overset{\|}{C}}-CH_2I + I^-$

step 4: $CH_3-CH_2-\overset{+OH}{\overset{\|}{C}}-CH_2I + I^- \overset{fast}{\rightleftharpoons} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2I + HI$

Rate = $k[CH_3CH_2COCH_3][H^+]$

- H^+ not part of reaction equation, but in rate equation
  $\therefore H^+$ = catalyst
- In RDS, $CH_3CH_2COCH_3$ and H^+ form intermediate
  $\therefore CH_3-CH_2-\overset{+OH}{\overset{\|}{C}}-CH_3$ = intermediate

Factor affecting Rate constant – Temperature

- at higher temp, greater proportion of molecules have $E \geq E_a$.
- rate constant and rate of reaction $\propto$ fraction of molecules w/ $E \geq E_a$.
- ~~at higher tem~~ $\therefore$ temp ↑ ⇒ rate constant ↑
  temp ↑ ⇒ rate of reaction ↑

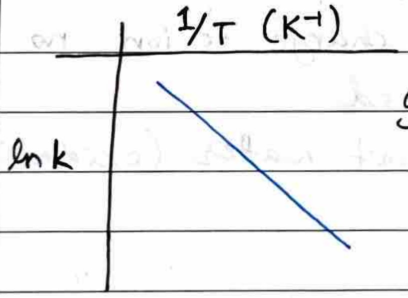
$$\boxed{\ln k = \ln A - \frac{E_a}{RT}}$$

- $\ln k$ = natural log of rate constant
- A = constant related to collision freq. & orientation of molecules
- E_a = activation energy (J)
- R = gas constant (8.31 $J\,K^{-1}\,mol^{-1}$)
- T = temperature (K)

constants

$$\boxed{\underset{\underset{y}{\downarrow}}{\ln k} = \underset{\underset{m}{\downarrow}}{\frac{-E_a}{R}}\;\underset{\underset{x}{\downarrow}}{\frac{1}{T}} + \underset{\underset{c}{\downarrow}}{\ln A}}$$

T ↑ ⇒ ln k ↑ ⇒ k ↑ ⇒ rate of reaction ↑



gradient = $\frac{-E_a}{R}$

intercept = ln A

catalysts:
inc. rate of reaction by providing an alternate pathway which has lower E_a.

Homogenous catalysts

same phase as reaction mixture.

eg. $CH_3COOH(aq) + CH_3OH(aq) \xrightarrow{H^+(aq)} CH_3COOC_2H_5(aq) + H_2O(l)$
(esterification); H^+ = homogenous catalyst ∵ in aq. state like reactants & products.

→ Homogenous catalysis often involves redox reactions, where ions involved in catalysis undergo changes in oxidation no. (transition elements good catalysts ∵ change ox. no.)

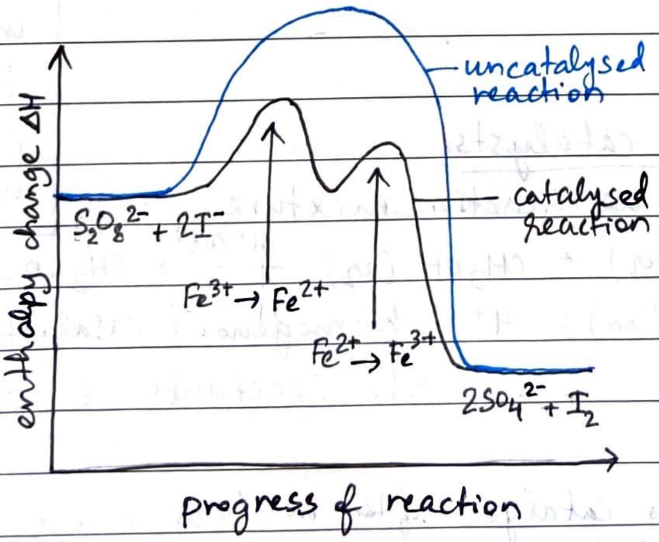
→ these catalysts are used in one step, then reformed in a later step.

Eg1: Iodine-peroxydisulfate reaction

$S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$

↳ v. slow reaction; peroxydisulfate ($S_2O_8^{2-}$) ions oxidise iodide to iodine.

- both $S_2O_8^{2-}$ & I^- have -ve charge ∴ lot of energy required for the ions to overcome repulsive forces & collide.
- Fe^{3+} (aq) is used as homogenous catalyst.
- catalysis involves 2 redox reactions:
  ① $Fe^{3+} \rightarrow Fe^{2+}$; reduction by I^-
  $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$
  ② $Fe^{2+} \rightarrow Fe^{3+}$; oxidation by $S_2O_8^{2-}$
  $2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$
- By reacting reactants w/ +ve charge Fe ion, no repulsive forces ∴ E_a lowered.
- order of the reactions doesn't matter (oxidation can occur before reduction)



pathways of 2-stage catalysed reaction

Eg2: Nitrogen oxides & acid rain

- fossil fuels contain sulfur; when burned, SO_2 released; SO_2 oxidised in air to SO_3; dil. H_2SO_4 formed by reaction w/ water = acidification of rain.

$$SO_3\,(g) + H_2O\,(l) \longrightarrow H_2SO_4\,(aq)$$

- nitrogen oxides act as catalysts in formation of acid rain by catalysing oxidation of $SO_2 \rightarrow SO_3$.

$$NO_2\,(g) + SO_2\,(g) \longrightarrow SO_3\,(g) + NO\,(g)$$

- formed NO gets oxidised to regenerate NO_2.

$$NO\,(g) + \tfrac{1}{2}O_2\,(g) \longrightarrow NO_2\,(g)$$

- regenerated NO_2 molecule oxidises another SO_2 molecule → $SO_3 \rightarrow H_2SO_4$ ... and so on.

Heterogenous catalysts

diff. phase to rest of reaction mixture.

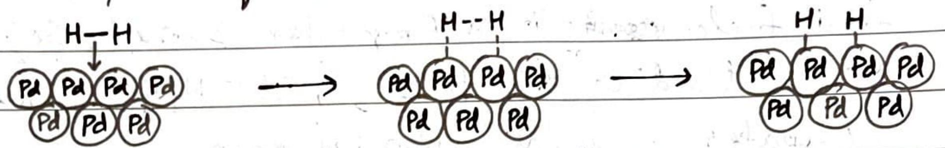
→ In heterogenous catalysis, molecules react at the surface of solid catalyst.

→ mode of action:

① adsorption (chemisorption) of reactants on catalyst surface
  - reactants diffuse to surface of catalyst
  - reactant is physically adsorbed onto surface by weak forces.
  - reactant is chemically adsorbed onto surface by stronger bonds. ~~forces~~
  - chemisorption causes bond weakening btwn the atoms of the reactants.

② desorption of products
  - bonds btwn products and catalyst weaken so much that the products break away from surface.

eg. adsorption of H_2 molecules onto Pd surface:



H atoms moving towards palladium surface.

- bond strengthening btwn H & Pd atoms.
- bond weakening btwn H atoms.

Eg 1: Iron in Haber process

reactants : N_2 & H_2 in gaseous state
catalyst : solid Fe

Mode of action:

i)- diffusion of N_2 and H_2 gas to Fe surface.

ii) adsorption of reaction molecules onto Fe surface by forming bonds btwn Fe & reactant atoms.
  - these bonds are so strong that they weaken covalent bonds btwn N atoms in N_2 & H atoms in H_2
  - but they are weak enough to break when catalysis has been completed.

iii) reaction takes place btwn adsorbed N & H atoms on Fe surface to form NH_3

iv) desorption occurs when bonds btwn NH_3 & Fe surface are weakened & eventually broken.

v) formed NH_3 diffuses away from Fe surface

Eg. 2: Heterogenous catalysts in catalytic converters

↳ catalytic removal of oxides of nitrogen from exhaust gases of car engines.

Catalysts speed up conversion of:

(i) nitrogen oxides (NO_y) → harmless N_2 gas

(ii) $CO \longrightarrow CO_2$

- catalytic converter has honeycomb structure containing small beads coated w/ Pt, Pd, Rh metals = heterogenous catalysts

Mode of action:

(i) adsorption of nitrogen oxides & CO onto catalyst surface.

(ii) weakening of covalent bonds within nitrogen oxides & CO.

(iii) formation of new bonds btwn:

- adjacent N atoms to form N_2 molecules
- CO and O atoms to form CO_2 molecules.

(iv) desorption of N_2 & CO_2 molecules which eventually diffuse away from metal surface.

Worked examples

1. Predicting reaction mechanism

(i) $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

rate = $k[NO_2]^2$

step 1: $2NO_2 \longrightarrow NO + NO_3$ (slow RDS)

step 2: $NO_3 + CO \longrightarrow CO_2 + NO_2$ (fast)

$$\cancel{2}NO_2 + \cancel{NO_3} + CO \longrightarrow NO + \cancel{NO_3} + CO_2 + \cancel{NO_2}$$

$$NO_2 + CO \longrightarrow NO + CO_2$$

2. (ii) $2N_2O_5 \longrightarrow 4NO_2 + O_2$

rate = $k[N_2O_5]$

step 1 : $N_2O_5 \rightarrow NO_2 + NO_3$ (slow RDS)

step 2 : $\underline{NO_3 + N_2O_5 \rightarrow 3NO_2 + O_2}$ (fast)

$N_2O_5 + \cancel{NO_3} + N_2O_5 \rightarrow NO_2 + \cancel{NO_3} + 3NO_2 + O_2$

$2N_2O_5 \rightarrow 4NO_2 + O_2$

(iii) $2N_2O \rightarrow 2N_2 + O_2$

rate = $k[N_2O]$

step1 : $N_2O \rightarrow \frac{1}{2}N_2 + NO$ (slow RDS)

step2 : $\underline{NO + N_2O \rightarrow O_2 + \frac{3}{2}N_2}$ (fast)

$N_2O + \cancel{NO} + N_2O \rightarrow \frac{1}{2}N_2 + \cancel{NO} + O_2$

$2N_2O \rightarrow 2N_2 + O_2$

(iv) $2NO + Cl_2 \rightarrow 2NOCl$

rate = $k[NO]^2[Cl_2]$

Step 1 : $NO + NO \rightarrow \overset{\text{inter-mediate}}{N_2O_2}$ (fast)

Step2 : $\underline{N_2O_2 + Cl_2 \rightarrow 2NOCl}$ (slow)

$2NO + Cl_2 \rightarrow 2NOCl$

or

step 1 : $2NO + Cl_2 \rightarrow NO_2 + NCl_2$ [illegible]w)

step 2 : $NO_2 + NCl_2 \rightarrow 2NOCl$ (fast)

2. Predicting reaction order & rate e

(i) $2HBr + O_2 \rightarrow H_2O_2 + Br_2$

mechanism : step 1 = $2HBr + O_2 \rightarrow H_2O_2 + Br_2$

~~rate = $k[O_2][HBr]^2$~~ step 1 = RDS

∴ rate = $k[HBr]^2[O_2]$

another proposed mechanism :

step 1 : $HBr + O_2 \rightarrow HO_2Br$ (slow)

step 2 : $HO_2Br + HBr \rightarrow 2HOBr$ (fast)

step 3 : $2HOBr \rightarrow H_2O_2 + Br_2$ (fast)

Step 1 = RDS ∴ rate = $k[HBr][O_2]$

another proposed mechanism : same as above, but slow step 2nd

step 2 = RDS ; HO_2Br = intermediate formed from 1 HBr & 1 O_2

∴ rate = $[HBr]^2[O_2]$