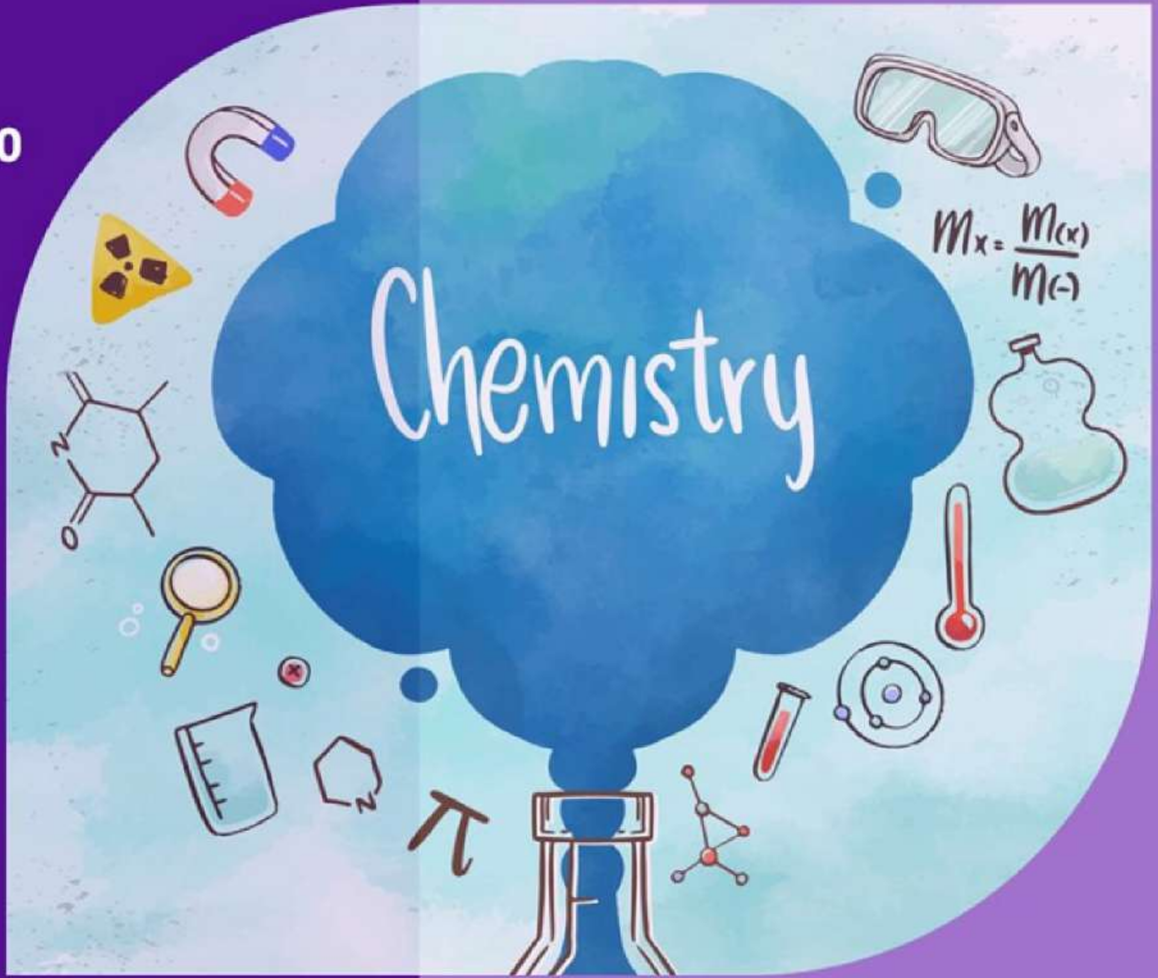
MEDICAL AND DENTAL ADMISSION PROGRAM 2020

CHEMISTRY

LECTURE : C-04

CHAPTER 4 : CHEMICAL CHANGE

(kinetics + thermodynamics)



উন্মেষ
মেডিকেল এন্ড ডেন্টাল এডমিশন কেয়ার

www.unmeshbd.com

Important topic from this chapter for Medical and Dental admission test

Importance	Topic	Admission test years
✪	Chemical reactions and green chemistry	MAT: 02-03
✪✪✪	Irreversible and reversible reaction	MAT: 10-11, 04-05, 02-03, 01-02, DAT: 10-11, 08-09
✪✪✪	Rate of reaction and activation energy	MAT: 08-09, 04-05, DAT: 04-05
✪✪✪	Catalyst ✓	MAT: 17-18, 16-17, 13-14, 08-09, DAT: 17-18
✪✪	Bio-catalyst/Enzyme ***	MAT: 11-12, 02-03; DAT: 16-17
✪✪✪	Law of conservation of mass and different types of heat change ✓	MAT: 18-19, 13-14, 10-11, 05-06, 03-04, DAT: 02-03
✪	Thermochemical laws	MAT: 06-07

Green chemistry

Other name:Clean/Benign/Sustainable Chemistry.

Founder: Paul Anastam and John C. Warner of USA.

Environment Friendly

- A → C
- $\boxed{B \rightarrow C}$ ✓
- D → C

12

✓Minimum pollution

✓Maximum production

✓minimum risk

12. Accidents prevention
1. Prevention
2. Atomic economy
3. Safer chemical synthesis
4. Safer chemicals design
5. Use of safer solvents and auxiliaries
6. Energy efficiency
7. Use of renewable raw materials
8. Reduction of derivatives
9. Catalysis
10. Degradation products design
11. Real-time analysis for pollution prevention

12 principle

12 principles of Green Chemistry have been identified internationally.

1. Prevent waste, ✓ E factor $= \frac{TW}{TP} = \frac{\text{total waste}}{\text{total product}}$ ⇓⇓
2. Maximize atom economy, ✓ $A.E = \frac{DP}{TP} \times 100\%$ ⇑⇑

(70-90%)

3. Use less hazardous processes,
4. Design safer chemicals,
5. Use safer solvents, → volatile organic solvent ✗ ✗ ✗
6. Design for energy efficiency, ✓

① Nonvolatile O.S
② ~~Non~~ Aqueous Ionic S
③ O.S Free production
④ Water based production

Greener Solvent

7. Use renewable feed stocks, ✓
   - petrol ✗
   - solar energy
8. Minimize derivatives,
9. Use catalysts,
10. Design for bio-degradation
11. Monitor pollution in real time
12. Prevent accidents

✓ $A \rightarrow B + C$ $\quad \frac{B \times 100\%}{B + C}$ ↑

✓ $D \rightarrow B + C + E$ $\quad \frac{B \times 100\%}{B + C + E}$ ↓

$Cl-Cl$
↓
$Cl^{\cdot}$
O_3

* Which solvent is better than CFC?

Chloro Fluoro Carbon → solvent

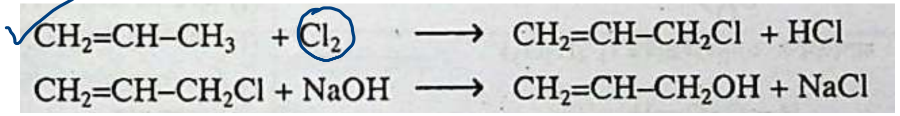
CFC < HCFC < HFC < Super critical CO_2

Liquid

*** Critical T → 31.25°c
Critical P → 72.9 atm

* Which one is greener process?

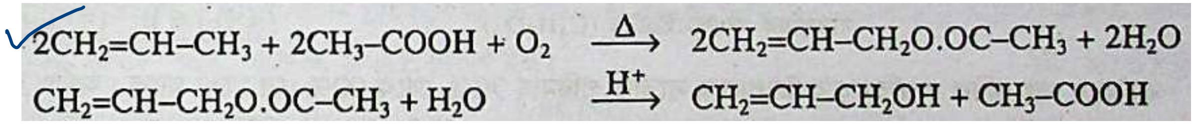
a



$CH_2{=}CH{-}CH_3 + Cl_2 \longrightarrow CH_2{=}CH{-}CH_2Cl + HCl$

$CH_2{=}CH{-}CH_2Cl + NaOH \longrightarrow CH_2{=}CH{-}CH_2OH + NaCl$

b



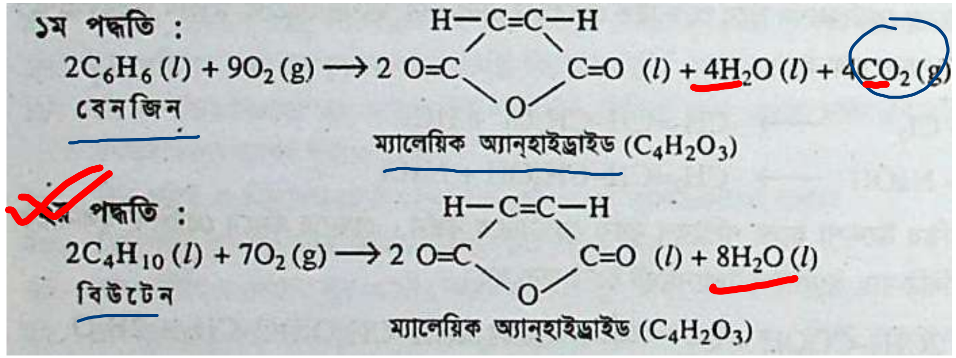
$2CH_2{=}CH{-}CH_3 + 2CH_3{-}COOH + O_2 \xrightarrow{\Delta} 2CH_2{=}CH{-}CH_2O.OC{-}CH_3 + 2H_2O$

$CH_2{=}CH{-}CH_2O.OC{-}CH_3 + H_2O \xrightarrow{H^+} CH_2{=}CH{-}CH_2OH + CH_3{-}COOH$

* which one is greener?

a

b



১ম পদ্ধতি :

$2C_6H_6\,(l) + 9O_2\,(g) \longrightarrow 2\,C_4H_2O_3\,(l) + 4H_2O\,(l) + 4CO_2\,(g)$

বেনজিন

ম্যালেয়িক অ্যানহাইড্রাইড ($C_4H_2O_3$)

২য় পদ্ধতি :

$2C_4H_{10}\,(l) + 7O_2\,(g) \longrightarrow 2\,C_4H_2O_3\,(l) + 8H_2O\,(l)$

বিউটেন

ম্যালেয়িক অ্যানহাইড্রাইড ($C_4H_2O_3$)

* what is smog?

smoke + fog = smog

*
fog = কুয়াশা
mist = কুয়াশা

× volatile organic solvent
× Flu gas (H_2S, SO_2, SO_3)

$+ H_2O \rightarrow$ Acid

pH ↓

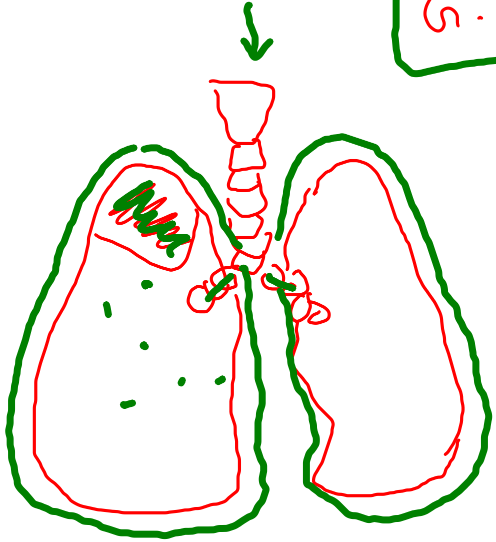
②

5 component
↓
• PANs
↓
photochemical smog

• Smog → pH – ②

G. Juice ↑

*mucous
↓
HCO_3^- + H^+
↓
H_2CO_3



Lungs

- Bronchitis
- → Pneumonia

HCO_3^- ↓↓

H^+ → epithelium inflammation

meningitis
encephalitis

alveolitis

lobe – pneumonia

Previous Question

Which is not a synonym of green chemistry? (MAT: 02-03)

(a) Clean Chemistry

[✓ (b) Chemical Chemistry]

(c) Benign Chemistry

(d) Sustainable Chemistry

Irreversible reaction:

- Irreversible reaction ends at some time.
- Reactants are completely converted into products.
- There is decrease in free energy in case of irreversible reaction. Change of free energy

$\Delta G = -ve$

$$(\Delta G) < 0$$

$$2KClO_3(s) \rightarrow 2KCl + 3O_2(g) \uparrow$$

$$C + O_2 \rightarrow CO_2 \uparrow$$

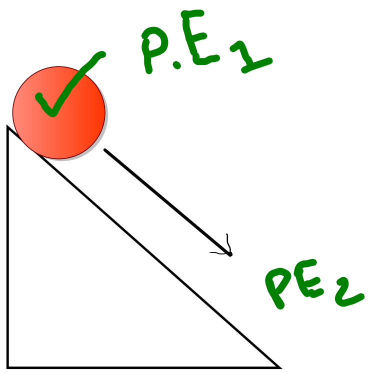
$\Delta G = 0$

Equilibrium

All Reactions are reversible

???

Berthollet

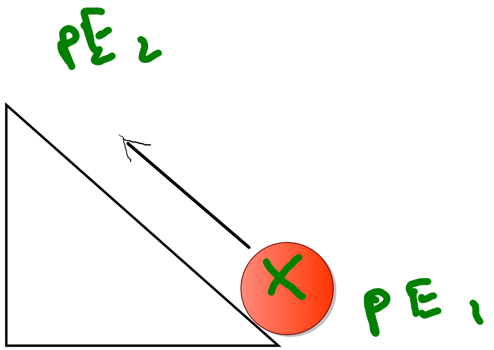


$\downarrow (PE_2 - PE_1) \uparrow$

$(-ve)$

$\Delta G = -ve$

Spontaneous
Irreversible



$\uparrow (PE_2 - PE_2) \downarrow$

$(+ve)$

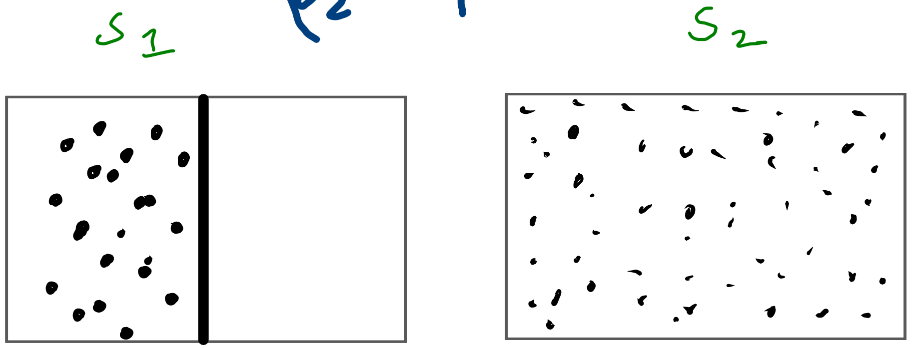
$\Delta G = +ve$

Non-spontaneous

$$\Delta G = \underset{\downarrow}{\Delta H} - \underset{\uparrow}{\boxed{T\Delta S}}$$

ΔG = change in Free energy
ΔH = change in Enthalpy
T = Temperature
ΔS = change in entropy

$(S_2 - S_1 = \Delta S = +ve)$



- **Entropy increases: solid → liquid → aqueous → gas**
- **Entropy increases when there are more moles of gaseous products than gaseous reactants.**
- **These two factors,**
  (1) a drive towards lower enthalpy and
  (2) a drive towards higher entropy,
  are what control all reactions in the universe.

কম — বেশি = $(-ve)$

$$\underset{\downarrow}{y} = \underset{\downarrow}{x} - \underset{\uparrow}{mz}$$

Spontaneity of reaction:

$T\Delta S$ -ve

ΔH	ΔS	ΔG	**Reaction**
$\Delta H < 0$ -ve	$\Delta S > 0$ +ve	Condition of spontaneity in all cases: $\Delta G < 0$	• Reaction will occur spontaneously at all temperature.
$\Delta H < 0$ ↓ -ve	$\Delta S < 0$ ↓ -ve		• Reaction will occur spontaneously at a low temperature. ↓
$\Delta H > 0$ ↑ +ve	$\Delta S > 0$ +ve ↑		• Reaction will occur spontaneously at a high temperature. ↑
$\Delta H > 0$ ↑	$\Delta S < 0$ ↓		• Reaction will not occur spontaneously at any temperature.

$$\Delta G = \Delta H - T\Delta S$$
$$= (-) - T(-y)$$
$$= (-) + (T)(y)$$

(T) ↓↓

↑↑

$$\underline{A}_{(g)} + \underline{B}_{(g)} \longrightarrow \underline{C}_{(g)}$$

$\Delta H = -y\ \text{kJ mol}^{-1}$

$T\Delta S$ ↑↑ $\underline{\underline{+ve}} > \Delta H$

$T\Delta S$ ↑ $+ve < \Delta H$

$$\boxed{\Delta G < 0}$$

Which chemical reaction will definitely react spontaneously?

- a) an endothermic reaction in which there is an increase in entropy
- b) an endothermic reaction in which there is a decrease in entropy
- [✓ c)] an exothermic reaction in which there is an increase in entropy
- d) an exothermic reaction in which there is a decrease in entropy

ΔH	ΔS	
+	+	] T ↑
+	−	] ×× Non spon.
$\boxed{-}$	$\boxed{+}$	] at any T

* $N_2 + 3H_2 \rightleftharpoons 2NH_3$ ΔH = −92.2 KJ

For this reaction, entropy, ΔS = −2 JK^{-1}

Determine the spontaniety of this reaction

at 27°C ✓✓ a b

$$\Delta G = \Delta H - T\Delta S$$

$$= -92.2\ kJ\,mol^{-1} - (300K)(-2\ JK^{-1})$$

$$= -92.2\ kJ\,mol^{-1} + 600\ J$$

$$= -92.2 \times 10^3\ J\,mol^{-1} + 600$$

$$= (-ve)$$

Reversible reaction:

- These reactions can be started from both directions.
- These reactions never complete.
- These reactions have a tendency to come into an equilibrium state.
- In the equation of a reversible reaction, sign of equality (=) is replaced by two opposite half arrows (⇌).
- If the rate of forward reaction becomes equal to the rate of backward reaction, the reaction reaches the equilibrium state.

$$H_2 + I_2 \overset{450°C}{\rightleftharpoons} 2HI$$

T, C, T

$$CuSO_4.5H_2O \overset{260°C}{\rightleftharpoons} CuSO_4 + 5H_2O$$

Bluevitriol (200°c)

In case of equilibrium

- $\Delta G = 0$
- $\Delta H = T\Delta S$

Pre~~vo~~ius Question

What is the color of hydrogen iodide? (MAT: 10-11,04-05)

[✓ (a) Light violet]
(b) Light green
(c) Light red
(d) Light yellow

deepviolet → I_2 100%.

$$H_2 + I_2 \rightleftharpoons \boxed{2HI} \rightarrow \text{colorless}$$

at equili. 20% 80%

↑
light violet

Poll Question-01

At what temperature hydrogen iodide is produced if hydrogen and deep violet iodine is kept in a closed container? (DAT: 10-11)

(a) $450°C$

(b) $550°C$

(c) $350°C$

(d) $250°C$

Methods of converting a reversible reaction into irreversible reaction

- By conducting reaction in an open conatiner or open place
- By removing the precipitate
- By removing one product chemically

product → gas / volatile

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons C_2H_5OH + CH_3COOH$$

$$CH_3COOC_2H_5 + NaOH \longrightarrow C_2H_5OH + CH_3COONa$$

$$NaCl\,(aq) + AgNO_3\,(aq) \longrightarrow NaNO_3\,(aq) + AgCl\,(s)\downarrow$$

$$A_{(s)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(s)}$$

Poll Question-02

Which one is applicable for transforming a reversible reaction to unidirectional? (MAT: 02-03)

(a) If reactants are solid or liquid and one product is gaseous
(b) One product is precipitated from solution
(c) If any product is transferred from the reaction
(d) All of the above

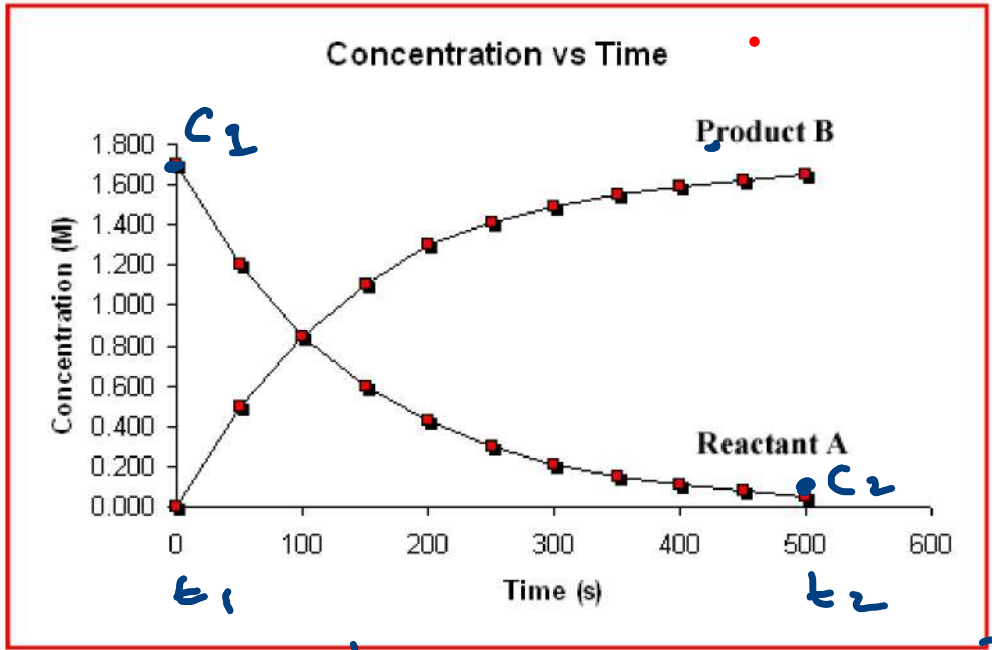
Rate of reaction

L. Wilhetmy

✓Rate of reaction = change of concentration / change of time

$r = \ominus \frac{dc}{dt}$ ✓ $r = \oplus \frac{dx}{dt}$

$\boxed{\text{Unit of rate of reaction = mol liter}^{-1}\text{ second}^{-1}}$



✓ $r = -\frac{C_2 - C_1}{t_2 - t_1}$ $\frac{mol L^{-1}}{s}$

$\boxed{aA + bB \longrightarrow cC + dD}$

$A \longrightarrow 2B$

$-\frac{d[A]}{dt} = +\frac{1}{2}\frac{d[B]}{dt} = r$

*** $\left[r = \ominus \frac{1}{a}\frac{d[A]}{dt} = \ominus \frac{1}{b}\frac{d[B]}{dt} = \oplus \frac{1}{c}\frac{d[C]}{dt} = \oplus \frac{1}{d}\frac{d[D]}{dt} \right]$

Initial concentration of a reactant is 2 $molL^{-1}$,becomes 1.5 $molL^{-1}$ after 10 second. What is the rate of the reaction ?

$$r = -\frac{dc}{dt}$$

$$= -\frac{(1.5-2)}{10}$$

$$= -\frac{(-0.5)}{10}$$

$$= 5 \times 10^{-2}\ molL^{-1}s^{-1}$$

✓N_2O_5 dissociates into NO_2 and O_2, after 6 second concentration of ✓NO_2 increases 3×10^{-3} molL^{-1} , calculate the rate of reaction ?

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

$$r_{NO_2} = +\frac{1}{4}\frac{dx}{dt}$$

$$= +\frac{1}{4}\frac{3\times10^{-3}}{6}$$

$$= +\frac{1}{4}\times\frac{1}{2}\times10^{-3}$$

$$= +\frac{1}{8}\times10^{-3}$$

Rate constant of a reaction:

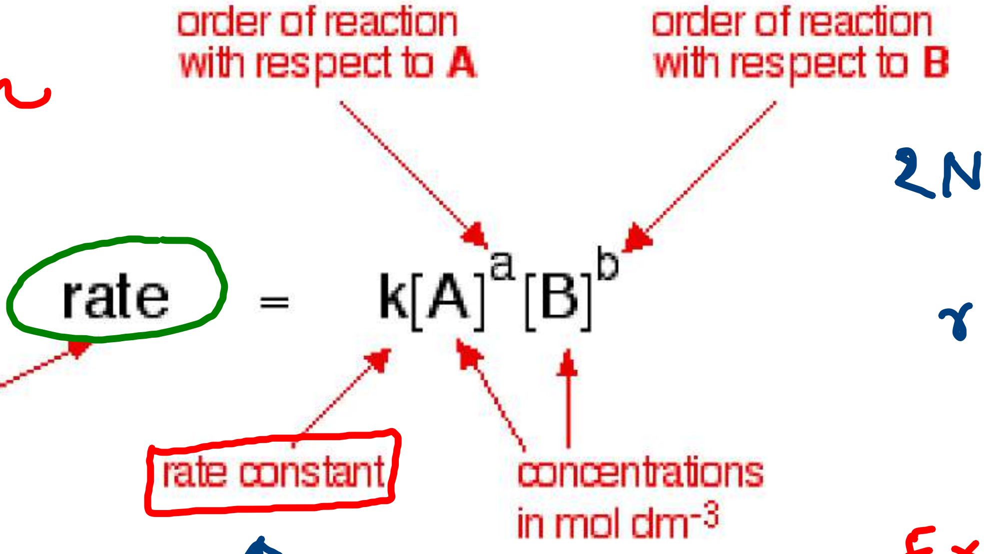
$aA + bB \rightarrow \text{product}$

Law of mass action

$\boxed{r} \propto [A]^a [B]^b$

$\uparrow$

$[T, C]$



order of reaction with respect to **A**

order of reaction with respect to **B**

$$\text{rate} = k[A]^a[B]^b$$

rate in mol dm^{-3} s^{-1}

rate constant

concentrations in mol dm^{-3}

mol L^{-1} s^{-1}

$\uparrow$

$[T]$

unit depends on order of reaction

$$r = k[A]^m [B]^n$$

m + n = order

$2N_2O_5 \longrightarrow 4NO_2 + O_2$

$r = k[N_2O_5]^2$ according to L of MA

Experimentally

$r = k[N_2O_5]^1$

$r \propto [N_2O_5]$

Order of Reaction

Order of reaction

order can be → 0, integer, fraction

For a Reaction $\boxed{A \rightarrow B}$

Experimentally

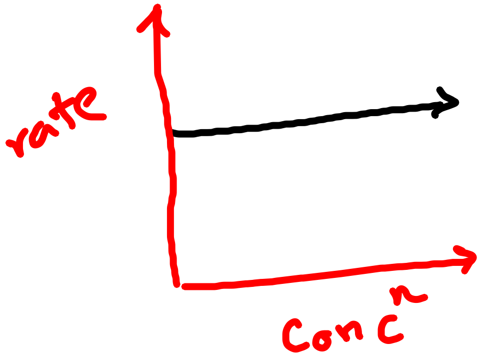
Relative rate vs. concentration

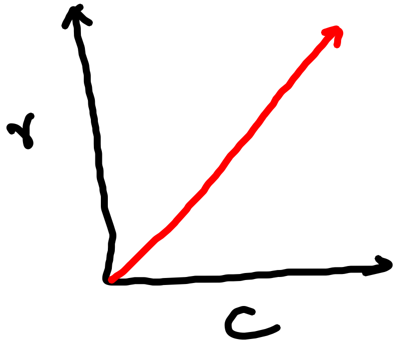
unit (k)

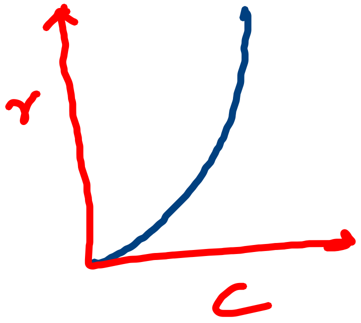
[A], *M*	Rate, M/s
1	1
2	1
3	1

[A], *M*	Rate, M/s
1	1
2	2
3	3

[A], *M*	Rate, M/s
1	1
2	4
3	9







$r \propto [C]^0$

$r = k[C]^0$

[0 order]

$r \propto [C]^1$

$r = k[C]^1$

[1st order]

$r \propto [C]^2$

$r = k[C]^2$

[2nd order]

Order of reaction

✓ Zero order reaction	- Rate of reaction doesn't depend on the concentration of reactant i.e. if , n=0 then unit of will be Ms^{-1} $r = \underline{k}[c]^0$
First order reaction	- Rate of reaction depends on 1st power of concentration of any reactant i.e. if , n=1 then unit of will be n=1 s^{-1}
Second order reaction	- Rate of reaction depends on 2nd power of concentration of any reactant i.e. if , n=2 then unit of will be $M^{-1}s^{-1}$
✓ Third order reaction	- Rate of reaction depends on 3rd power of concentration of any reactant i.e. if , n=3 then unit of will be $M^{-2}s^{-1}$ $r = k[c]^3$

$[mol L^{-1} = M]$ $r = Ms^{-1}$

$$\boxed{\begin{array}{l} A + B \rightarrow C + D \\ k = 2.2\ M^{-1}s^{-1} \end{array}}$$

$$k = \frac{Ms^{-1}}{M^3} = M^{-2}s^{-1}$$

Poll Question-03

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ what is the unit of rate of reaction for this reaction ?

3rd

(a) $M^{-1}s^{-2}$

(b) $M^{-2}s^{-1}$

(c) $M^{-2}s^{-2}$

(d) $M^{-1}s^{-1}$

$2N_2O_5 \longrightarrow 4NO_2 + O_2$

order = 1

0 order

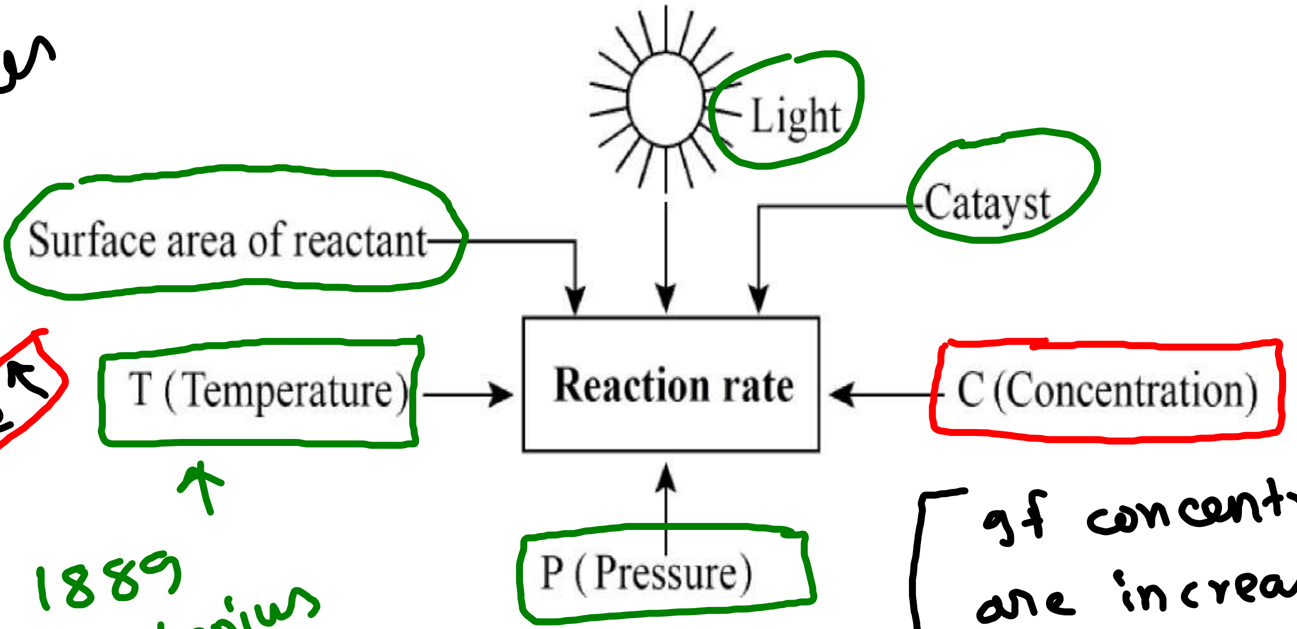
- $H_2 + Cl_2 \xrightarrow[UV]{h\nu} 2HCl$

Factors affecting rate of reaction:

conc^n ↑ & collision ↑ ← pressure

Temp↑ →

& more molecules will gain Ea → Rate ↑



↑ 1889 Arrhenius

10°C↑ → 2-3 times

For 0 order

$r \propto [c]^0$

If concentration of reactants are increased, reaction rate will increase for any reaction

a) True (except 0 order)

b) False ✓

Main factors:

(1) Concentration of reactant

(2) Pressure (for gaseous substance)

(3) Temperature

If T is increased for an exothermic reaction reaction rate

a) increase ✓ b) decrease

Arrhenius' equation

Arrhenius proved that, rate of almost all reactions increases two or three times with the increase of $10°C$ temperature generally

$$k = A.e - \frac{E_a}{RT}$$

$$\boxed{k = Ae^{-\frac{Ea}{RT}}}$$

activation energy

Rate constant

Arrhenious factor

✓ SF ← p. 2 → CR

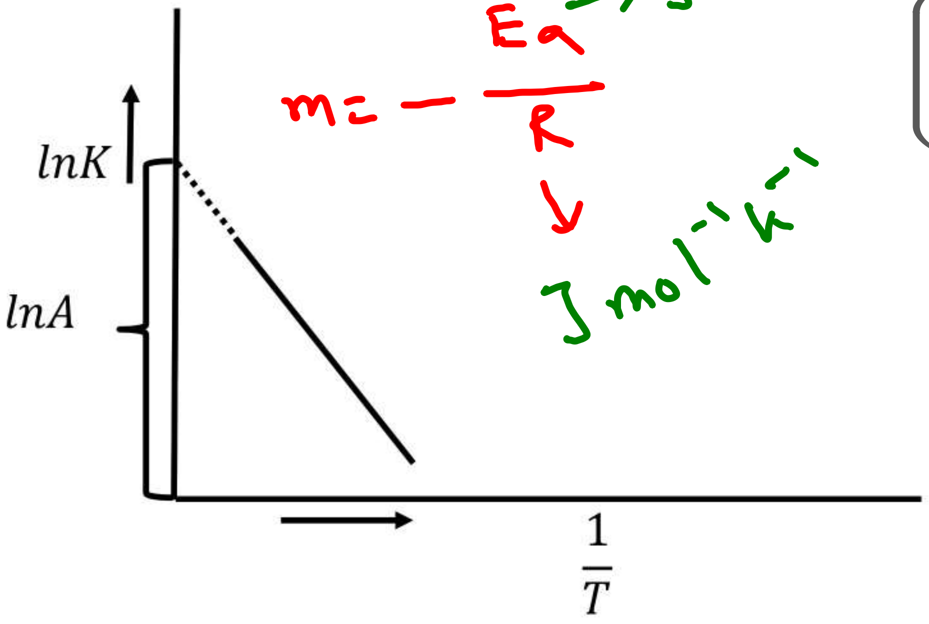
$$\checkmark\ \underline{\ln k} = \ln A - \frac{E_a}{RT}$$

$$\ln k = -\frac{E_a}{R}\,\frac{1}{T} + \ln A$$

$$\underline{y} = \underline{-m\ \ x} + \underline{C}$$

$k \propto T$

$k\uparrow \leftarrow T\uparrow$



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

$E_a \rightarrow J\,mol^{-1}$

$R \rightarrow J\,mol^{-1}K^{-1}$

what should be the unit of the slope?

$\downarrow$

$\boxed{K}$

Previous Question

Rate of reaction increases what times with the increase of each 10° C temperature? (MAT: 08-09, 04-05; DAT : 04-05)

[✓ (a) 2-3]
(b) 3-4
(c) 4-5
(d) 5-6

Activation energy

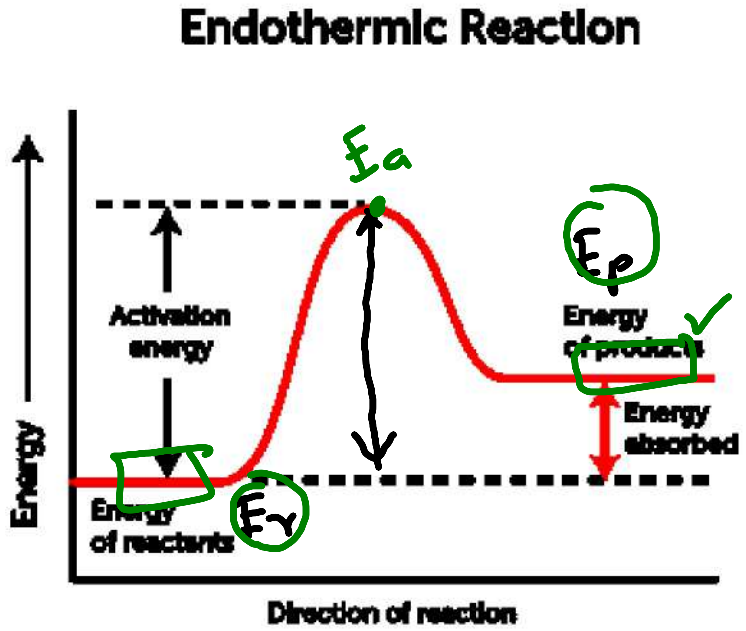
During reaction the required minimum energy for reactants is called activation energy

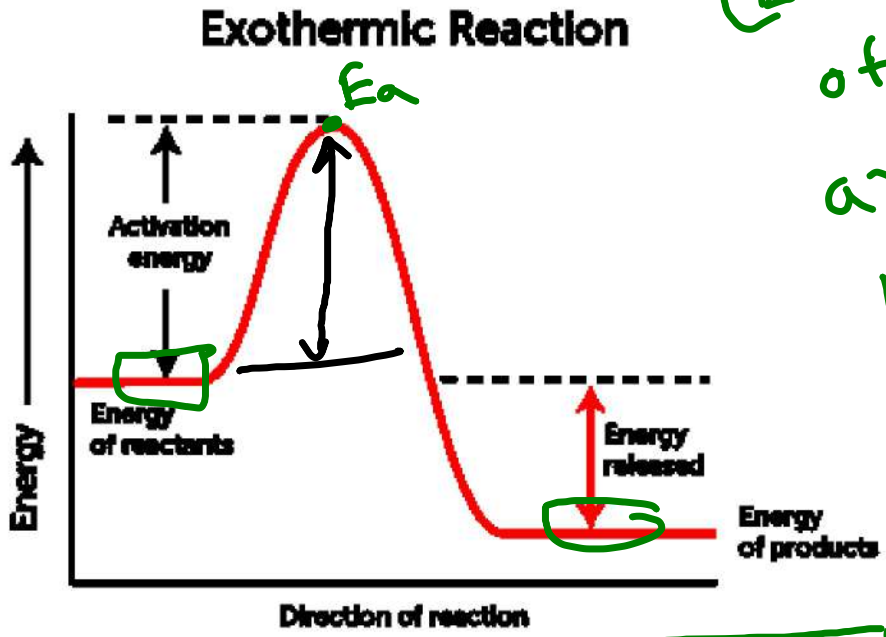
✓ Rate of reaction is inversely proportional to the activation energy

[Ea is independent of ΔH]

a) True

b) False





✓ $\boxed{\Delta H = E_p - E_r}$

$E_p > E_r$, $\Delta H = +ve$

$\boxed{\Delta H = E_p - E_r}$

$E_p < E_r$, $\Delta H = -ve$

Exothermic reaction	**Endothermic reaction**
$\Delta H = -ve$	$\Delta H = +ve$
$E_p < E_r$	$E_p > E_r$
(Bond formation) liberated energy > (Bond breaking) absorbed energy	absorbed energy > liberated energy

$\Delta H = \boxed{-ve}$

$\Delta H = \boxed{+ve}$

Bond breaking

THEORY OF REACTION

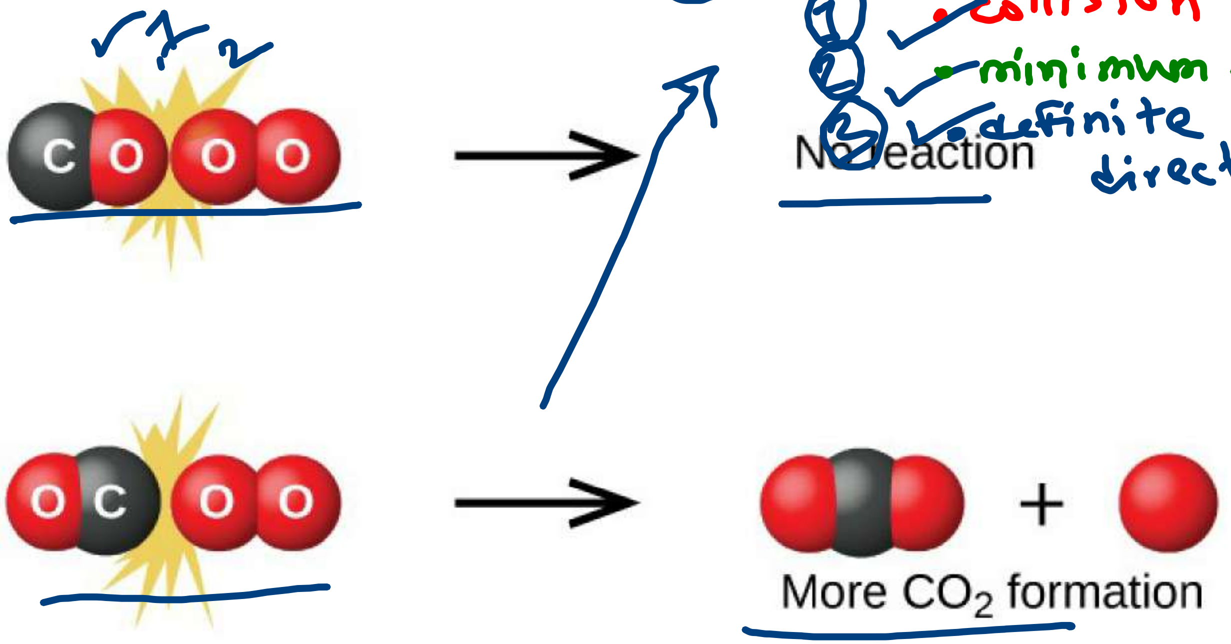
✓ ① Collision theory

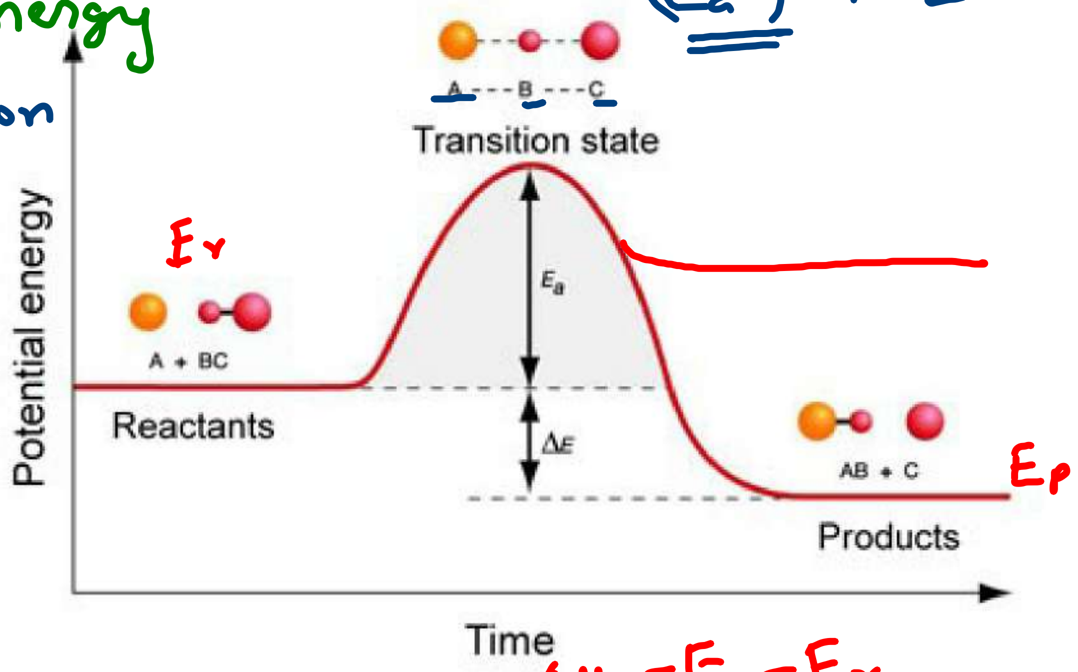
③ condition
- ① ✓ collision
- ② ✓ minimum energy
- ③ ✓ definite direction

② Transition state theory

✓ Activated complex

(E_a) P.E ↑↑





$E_r > E_p$

$\Delta H = E_p - E_r$
$= -ve$

Poll question : 04

Change of entropy of an exothermic reaction is -2 J/K ,then in which condition the reaction will occur spontaneously?

a) In all temperature

b) [✓ In low temperature]

c) In high temperature

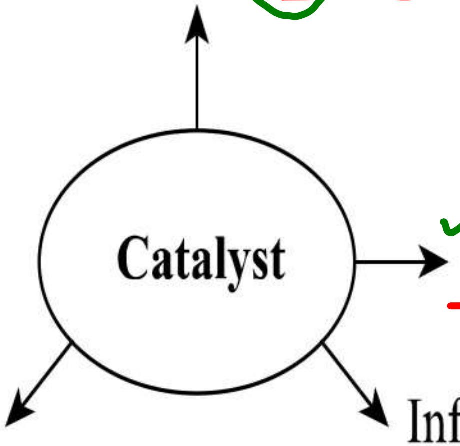
d) In no temperature

$\Delta S = -$ ↓

$\Delta H = -$ ↓

$\boxed{T} =$ ↓

Characteristics of catalyst



Time (No role at the begining or end of a reaction)

Catalyst

Selective

Influences a reaction even present in a small amount

3 'No'

(1) Can't start reaction.

(2) No change of total weight.

(3) No change of equilibrium

(4) No change after reaction

Berzelius

- Halogen
- Isomerism
- VF theory
- O/Inorganic

$$A + B \xrightarrow{Pt} C + D$$

r

Poll Question-05

Which one is not characteristic of catalyst? (MAT: 13-14)

(a) There is no change in total mass or structure at the end of reaction

[✓ (b) Catalyst can start or stop the reaction] (no)

(c) A little amount of catalyst is enough to affect the rate of reaction

(d) A catalyst is specific for a specific reaction

100%- Classification of catalysts 100%

✓ Positive catalyst	• MnO_2 . Metals • Mineral acid

✓ Negative Catalyst

P A G E S — Sodium benzoate

H_2SO_4

H_3PO_4

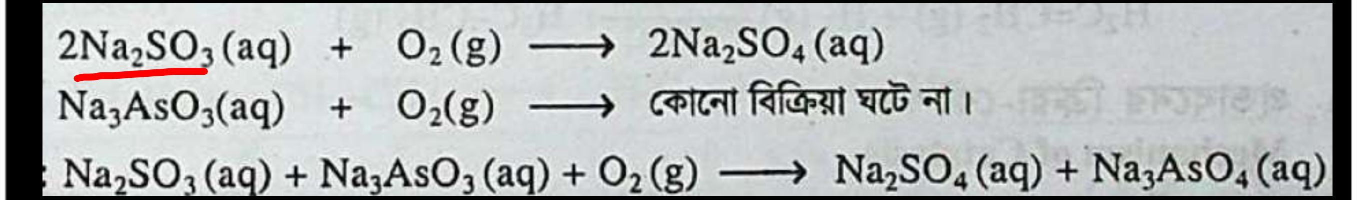
Anisole

Glycerine

Ethanol

Auto catalyst	~~Manganese~~ ion (Mn^{2+}) $(COOH)_2 + KMnO_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + CO_2 + H_2O$

Induced Catalyst



$2Na_2SO_3(aq) + O_2(g) \longrightarrow 2Na_2SO_4(aq)$

$Na_3AsO_3(aq) + O_2(g) \longrightarrow$ কোনো বিক্রিয়া ঘটে না।

$Na_2SO_3(aq) + Na_3AsO_3(aq) + O_2(g) \longrightarrow Na_2SO_4(aq) + Na_3AsO_4(aq)$

Catalyst poison & Catalyst promoter

Catalyst poison: dust, sulfur powder, arsenic oxide

Catalyst promoter: Mo, Al_2O_3, MgO, SiO_2

K_2O

অসাধু ব্যবসায়ী

Pd / $BaSO_4$ ***

***

for enzyme

inhibitor

activator

Effector

Haber bosch

NH_3

Mechanism of catalysis

Divided into two types. Such as-

All states same R C P

(a) Mechanism of homogenous catalysis: Formation of intermediate compound

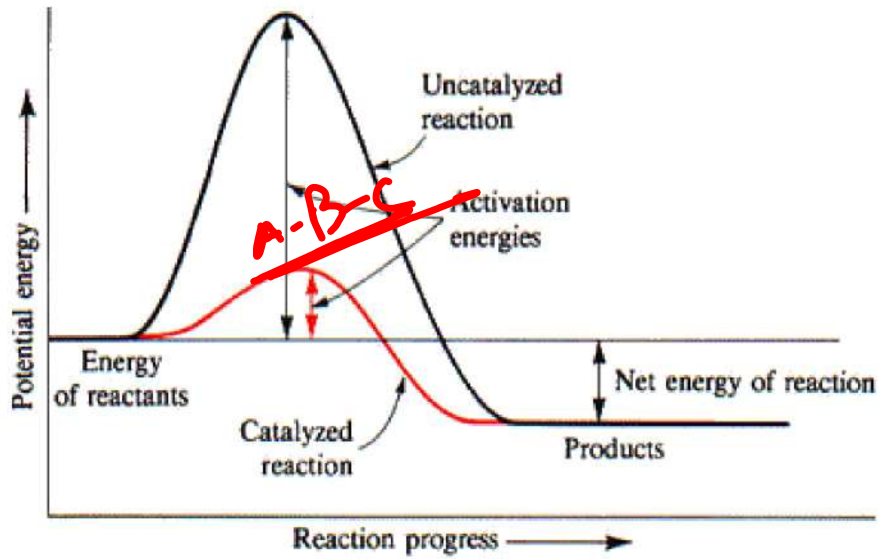
(b) Mechanism of heterogenous catalysis: Catalysis through adsorption ✓

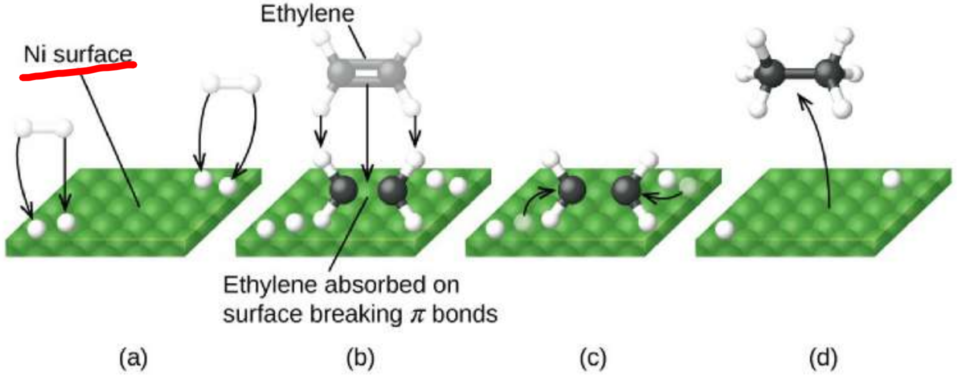
one of the state different

R C P

metal

$C_2H_4 + H_2 \xrightarrow[200°C]{Ni} C_2H_6$





4 step.

Homogenous catalysis	(i) In the manufacture of sulphuric acid by lead chamber process, sulphur dioxide gas is oxidized by oxygen in presence of NO gas as catalyst. It is an example of homogenous catalysis. $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$ (ii) In hydrolysis of cane sugar, mineral acid like HCl acid acts as catalyst. It is an example of homogenous catalysis. Inventase $\underset{sucrose}{C_{12}H_{22}O_{11}}(aq) + H_2O\ (l) \xrightarrow{H+(aq)} \underset{glucose}{C_6H_{12}O_6}(aq) + \underset{fructose}{C_6H_{12}O_6}(aq)$ (iii) Hydrolysis of ester: $R - COOR'(aq) + H_2O(1) \overset{[H^+]}{\rightleftharpoons} R - COOH(aq) + R'OH(aq)$ (iv) Degradation of ethanal vapour in the presence of iodine vapour: $CH_3 - CHO(g) \overset{I_2(g)}{\rightleftharpoons} CH_4(g) + CO(g)$
Heterogenous catalysis	(i) Oxidation of SO_2 in contact process in the presence of catalyst acute pt powder. $2SO_2(g) + O_2(g) \xrightarrow{Pt\ (solid)} 2SO_3(g)$ 2nd step (ii) The production of ethane and Dalda ghee or margarin from catalytic hydrogenation of carbon-carbon double bond (C=C) containing ethane gas and unsaturated vegetable oil like soyabean oil is a heterogenous catalysis. Here or powder acts as catalyst. $H_2C = CH_2(g) + H_2(g) \xrightarrow[150°C]{Ni} H_3C - CH_3\ (g)$

100%

Use of Homogenous and heterogenous catalysts industries:

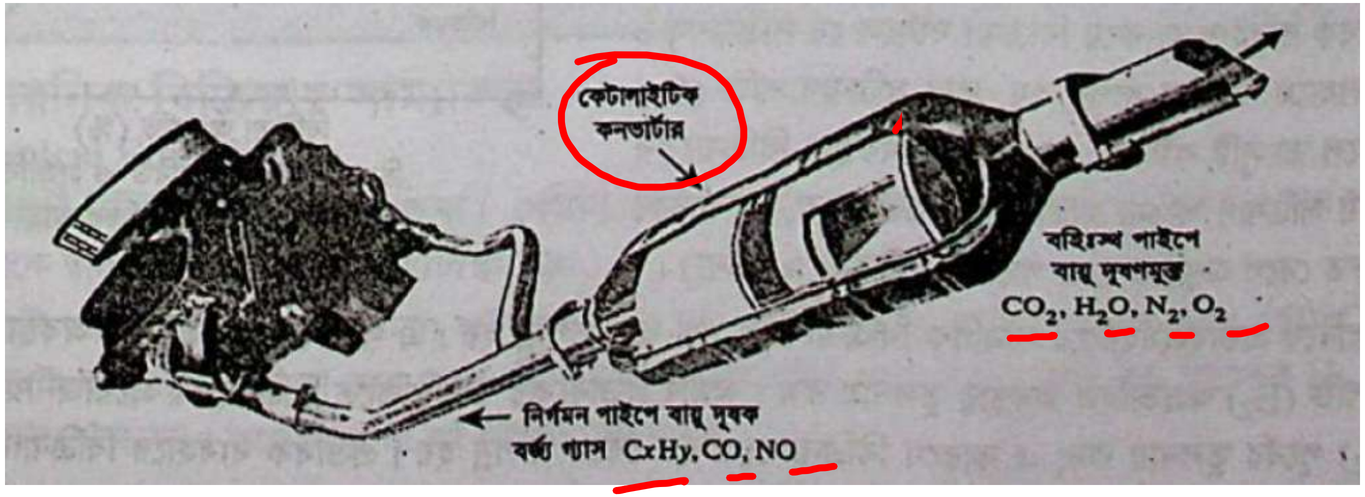
100%

Reactions	Catalyst used	Commercial processes	End product and uses
(a) Heterogenous gaseous			
1. $2SO_2 + O_2 \rightarrow 2SO_3$	Pt or V_2O_5	In contact process, manufacturing in 2nd step.	**Product**: different chemicals, fertilizers.
2. $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$	Pt or Rh	In Ostwald process, production from in 1st step.	**Product**: used for explosives, fertilizers, plastics, dyes and burnish.
3. $N_2 + 3H_2 \rightarrow 2NH_3$	Fe Promoter :Mo	In Haber's process of production.	**Product** used for fertilizers and production.
4. $CH_4 + H_2O \rightarrow CO + 3H_2$	Ni	Steam-alkane reforming process of gas synthesis.	**Product** gas used for , methanol.
5. $CO + 2H_2 \rightarrow CH_3OH$	ZnO and Cr_2O_3	Methanol production in industry.	Production of plastics, organic solvent, gum.
6. $CH_2 = CH_2 + H_2 \rightarrow CH_3 - CH_3$	Ni, Pd or Pt	Production of Dalda by hydrogenation of oil.	Used in hydrogenation of edible oil to produce solid fat.
(b) Homogenous reaction:			
1. Propylene, oxidizer	Mo complex	Propylene oxide synthesis.	Uses: polyester, polyurethane foams.
2. Buta-di-ene, HCN	Ni/P compound	Adiponitrile production	Uses: Production of nylons, fibre, plastic.

উন্মেষ
মেডিকেল এন্ড ডেন্টাল এডমিশন কেয়ার

Which catalyst is called warrior at Air pollution prevention ?

$\boxed{\text{Pt}}$



Previous Question

Which one is negative catalyst? (MAT: 08-09)

(a) Fe

[✓ (b) Alcohol]

(c) Cu

(d) MnO_2

PAGES

Previous Question

$CH_4 + H_2O \rightarrow CO + 3H_2O$; which catalyst is used in this reaction?

(MAT: 17-18)

(a) K_2O ✓

(b) [✓ Ni]

(c) Mo ✓

(d) Al_2O_3 ✓

Bio-catalyst/Enzyme (in yeast)

Name
Kuhn

Functional

High molecular weight globular tertiary protein

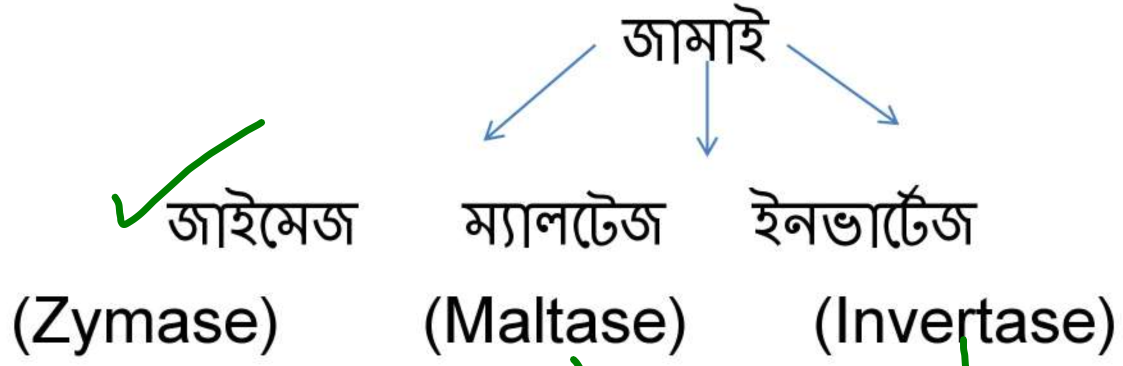
Human body has about 30,000 various types of enzymes

produce colloid in water

Temperature: 37°c $p^H = 7$

Pepsin - 2.0
Invertase - 4.5

Yeast


জামাই

✓ জাইমেজ (Zymase) → Glucose

ম্যালটেজ (Maltase) → Maltose

ইনভার্টেজ (Invertase) → Sucrose

২টা

Malt → Diastase → Starch

(Vinegar)

$$H_2CO_3 \xrightleftharpoons{\text{Carbonic anhydrase}} H^+ + HCO_3^-$$

360 lakh molecule/min

• Anticoagulant

Heparin

clotting prevent

• Blood Clot dissoluting agents

✓ MI → streptokinase

✓ • Stroke → urobilase

✓ tPA

tissue plasminogen activator

Poll Question-06

Which is not related to enzymatic action? (MAT: 11-12)

(a) Heat
(b) Pressure
(c) pH
[✓ (d) Time]

Reaction enthalpy and bond energy

$\boxed{\Delta H = \Delta E + P \times \Delta V,}$

↘ Greek word

(to warmin)

First law of thermo.

H= enthalpy
E= internal energy
P= pressure
V=volume

$\Delta G = \Delta H - T\Delta S$

2nd law

✓ Reaction enthalpy= heat of formation of product – heat of formation of reactant

when $\Delta H = \Delta E$,

a) isobaric system

✓ b) isochoric "

c) isothermal "

d) all

$[\Delta V = 0]$ volume constant

100%

Various thermal changes

100%

Exothermic ✓ *	Endothermic ✓	Exothermic or endothermic *
• Heat of combustion • Heat of neutralization • Heat of condensation	• Heat of atomization • Heat of melting • Heat of vapourization • Heat of sublimation	• Heat of reaction • Heat of solution • Heat of formation

- $\Delta H = -ve$
- $E_p < E_r$
- $\sum (BE)_{reactant} > \sum (BE)_{product}$

- $\Delta H = +ve$
- $E_p > E_r$
- $\sum (BE)_{reactant} < \sum (BE)_{product}$

Bond energy

E_p = P.E

E_r

Various thermal changes

$C_{(s)} + O_2 \rightarrow CO_2$ ΔH → formation

$CH_4\,(g) + O_2\,(g) \rightarrow CO_2\,(g)$, $\Delta H = -890.3$ KJ/mol → combustion

$C\,(\text{graphite}) \rightarrow C\,(g)$, $\Delta H = +717.2$ KJ/mol → sublimation

* $H_2O\,(\underline{s}) \rightarrow H_2O\,(\underline{l})$, $\boxed{\Delta H = +6\ \text{KJ/mol}}$ → melting

$H_2O\,(l) \rightarrow H_2O\,(\text{vap})$, $\boxed{\Delta H = +44\ \text{KJ/mol}}$ → heat of vaporisation

$\underline{\tfrac{1}{2} Cl_2\,(g)} \rightarrow \underline{Cl\,(g)}$, $\Delta H = +121$ KJ/mol ✓

atomisation

$$\boxed{\frac{\Delta H}{+ve} \quad \frac{\Delta S}{+ve} \quad \frac{T}{\uparrow}}$$

Heat of condensation (−ve)

* Heat of solution is exothermic or endothermic ?

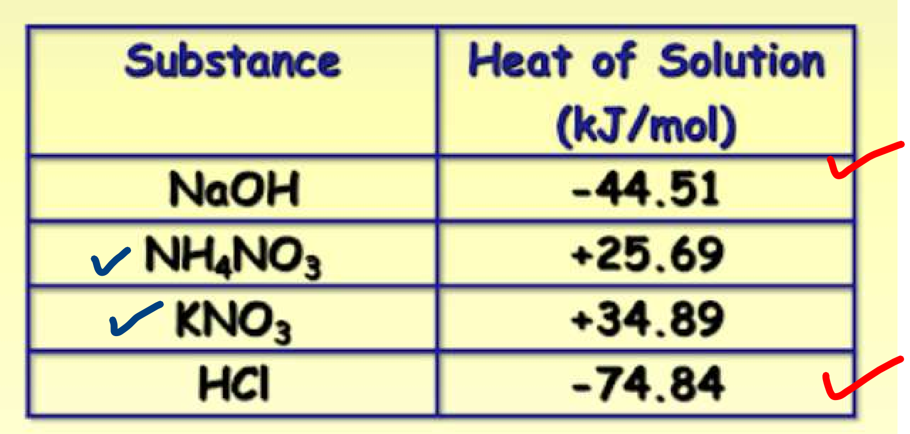
$(Na_2SO_4 \cdot 10H_2O)$

32.4°C

(NH_4Cl, $Pb(NO_3)_2$, $AgNO_3$, KI, $CuSO_4$, $KClO_3$, $HgCl_2$, NH_4NO_3, $NaCl$, K_2CrO_4, $K_2Cr_2O_7$, KBr, K_2CO_3, KNO_3, KCl, $NaHCO_3$) NO_3^-, WA, WB ΔH +ve

($znSO_4$, $FeSO_4$ $LiSO_4$, $Ca(OH)_2$, $CuSO_4$, $CaCl_2$ $NaOH$, $Ce_2(SO_4)_3$)

SA, SB, SO_4^{2-} — ΔH = -ve



Substance	Heat of Solution (kJ/mol)
NaOH	-44.51
✓ NH_4NO_3	+25.69
✓ KNO_3	+34.89
HCl	-74.84

✓ Exo

Endo

✓ Exo

Previous Question

What is the heat of melting of water? (MAT: 18-19)

[✓ (a) +6 $kJmol^{-1}$]

(b) +60 $kJmol^{-1}$

(c) – 6 $kJmol^{-1}$

(d) –60 $kJmol^{-1}$

Poll Question-07

Which one is exothermic ?

(a) H_2O (l) → H_2O (g) → vaporisation

[✓ (b) H_2O (g) → H_2O (l)] → condensation

(c) H_2O (s) → H_2O (l) → melting

(d) H_2O (s) → H_2O (g) → sublimation

Com

Neu

Con

$\Delta H = -ve$

Neutralization heat of various acids and bases:

Is neutralization heat of various acids and bases constant?

$SA + SB \longrightarrow salt + H_2O$

$H^+ + OH^- \longrightarrow H_2O \quad \Delta H = -57.3\ kJ\ mol^{-1}$

Neutralization heat of various acids and bases:

Acid	Base	Neutralization heat kj/mol
✓ HCl	* NaOH	-57.34
✓ H_2SO_4	* NaOH	-57.44
✓ HNO_3	* NaOH	-57.35
✓ HCl	* KOH	-57.43
✓ CH_3COOH	NaOH	✓ -55.14
✓ CH_3COOH	✓ NH_4OH	✓✓ -50.40
✓ HF	* NaOH	? $\boxed{-68.60}$

* **

F^- size ↓ → H.E ↑↑

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$; what is the reaction enthalpy of this reaction ?

C−H   Cl−Cl $\boxed{\text{C−Cl}}$ $\boxed{\text{H−Cl}}$

ভা   গ

ΔH = Bond Breaking − Bond formation

$= \{430.5 + 242.9\} - \{328 + 433\}$

$= -87 . . .$

Bond	Kj/mol
H-H	435.5
H-F	564
H-Cl	433
H-Br	366
H-I	299
C-H	430.53
C-Cl	328
Cl-Cl	242.90

Thermochemical laws

(1) Lavoisier and Laplace's law

$A + B \rightarrow C+D$; $\Delta H = + X$

$C+D \rightarrow A+B$; $\Delta H = - X$

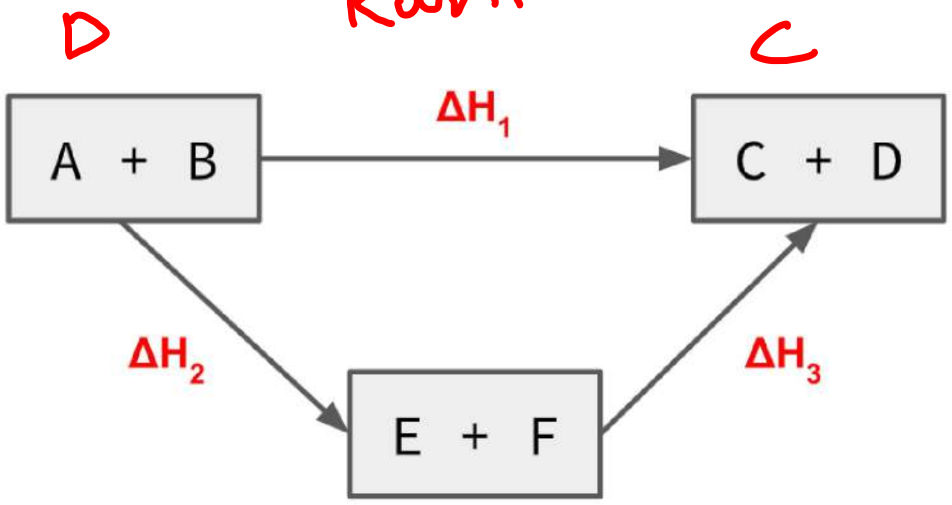
$$\begin{tikzcd} D \arrow[r] & C \arrow[l, bend left] \end{tikzcd}$$

Same

1840

(2) Hess's law of constant heat summation

Russian



Cumilla

$\Delta H_1 = \Delta H_2 + \Delta H_3$

What is the change of heat in conversion of graphite to diamond?

$C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g)$; $\Delta H = -393.4\ Kjmol^{-1}$

$C\ (diamond) + O_2\ (g) \rightarrow CO_2\ (g)$; $\Delta H = -395.3 Kjmol^{-1}$

$$\begin{tikzcd}
C(graphite) + O_2 \arrow[r] \arrow[d, "\Delta H"'] & CO_2 \arrow[dl, bend left] \\
C(diamond) + O_2 \arrow[ur]
\end{tikzcd}$$

$\Delta H_1 = -393.4$

$\Delta H_2 = +395.3 KJmol^{-1}$

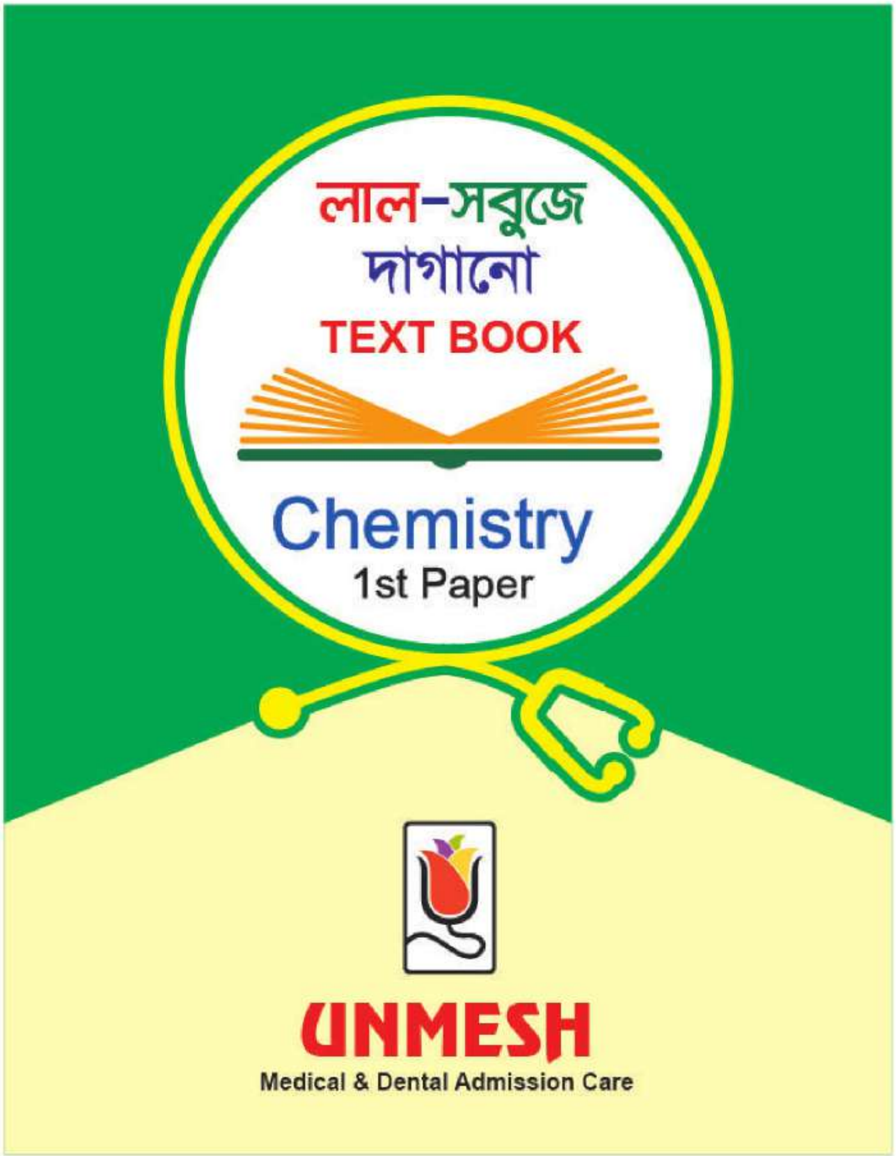
L & L

$$\boxed{\Delta H = \Delta H_1 + \Delta H_2}$$

$= (-393.4 + 395.3)\ KJmol^{-1}$

$= +1.9\ kjmol^{-1}$

লেগে থাকো সৎ ভাবে,
স্বপ্ন জয় তোমারই হবে।



লাল-সবুজে
দাগানো
TEXT BOOK
Chemistry
1st Paper

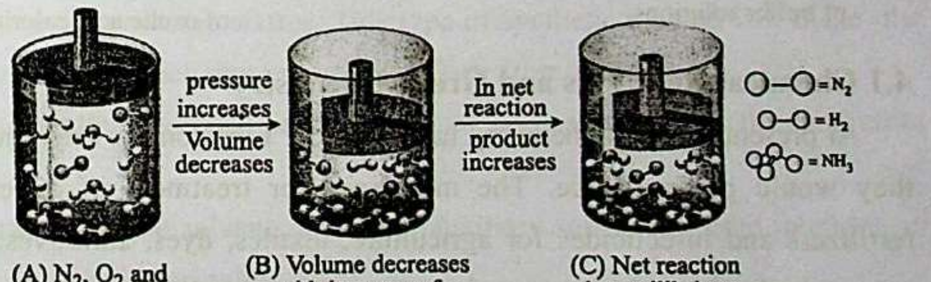
UNMESH
Medical & Dental Admission Care

Theoretical Lectures = 20
Class Activities = 8
Total Periods = 28

Chapter-4
Chemical Changes

Introduction : Ionic and covalent compounds in aqueous solutions generally undergo irreversible reactions such as precipitation, acid-base neutralizations and redox reactions. In different modern chemical industries, different essential pharmaceutical products, chemical fertilizers, intecticides, textile -dyes, building-materials and different polymer substances from covalent solid, liquid and gaseous substances are produced by reaversible synthesis, decomposition reactions. or replacement reactions in organic solvents together with use of heavy metal catalysts. Of these industries, some harmful and poisonous solvents, bye -products, some reactants and metallic catalysts can do dangerous harms to environment when those chemical substances are discharged as wastes in air and land. It is unlikely that all chemical processes will ever be completely benign, but awareness of the environmental problems, caused by chemical industries, has grown dramatically in recent years, giving rise to a movement called **'green chemistry'**.

Key words : Green chemistry, rate of reaction, activation energy, catalyst, enzyme, reaction equilibrium, active-mass. equilibrium constant, ionic product of water, dissociation constants of acids and bases, pH of a solution, buffer solution, internal energy, enthalpy, heat of neutralization, heat of formation, heat of reaction, heat of solution, bond-energy.



(A) N_2, O_2 and NH_3 gases are in equilibrium

(B) Volume decreases with increase of pressure no equilibrium

(C) Net reaction in equilibrium reactants produce products, decreases number of molecules

After reading this chapter, Students will be able–

1. To explain the concept of green chemistry relating to the occurance of reactions.
2. To describe the direction of reactions such as reversible reactions and irreversible reactions.
3. To evaluate the effect of changes of reaction factors like temperature, pressure and concentration of reactants on rate of reactions.
4. To explain the mechanism of catalysts in controlling rate of reactions with their proper use in reactions.

5. To explain the equilibrium and dynamic nature of equilibrium of reversible reactions.
6. To explain the expected changes of equilibrium in reversible reactions with the application of Le-Chatelier's principle.
7. To explain the importance of Le-Chatelier's principle in the industrial productions.
8. To explain the law of mass action.
9. To deduce equilibrium constants K_c and K_p from the Law of mass action and can also explain the relation between K_c and K_p.
10. To explain ionic product of water, acid dissociation constant, K_a and base dissocition constant, K_b.
11. To explain the strength of acids and bases with respect to their dissociation constants K_a and K_b.
12. To define and establish pH and pH scale of different solutions.
13. To explain buffer solutions and the mechanism of buffer solutions.
14. **Practical** : To prepare carbonate buffer solution with the explanation of buffer action on adding a little amount of acid and alkali to it separately.
15. To explain the importance of pH of blood in human body.
16. To explain the role of p^H in agriculture, chemical industry, toiletries and in taking medicine.
17. To select proper cosmetics after measuring the p^H of related cosmetics.
18. To explain the law of conservation of mass and energy together with thermal changes (like heat of reaction, heat of change of states, heat of atomization, heat of solution, heat of neutralization).
19. To explain that `the heat of neutralization of strong acid and strong base is constant.'
20. To calculate the heat of reaction by using bond energies.
21. To calculate the heat of reaction by the application of Lavoisier and Laplace's Law.
22. **Practical** : To determine the heat of solution of oxalic acid calorimetrically.

4.1 Chemical Reactions and Green Chemistry

At present, modern chemistry has made our lives longer, safer and more comfortable than they would otherwise be. The medicines for treatment of different diseases, chemical fertilizers and insecticides for agriculture, textiles, dyes, adhesives, building materials, and polymer substances that we use for construction are all the products of the different chemical industries. But these better benefits have not come without a price. Many chemical processes produce harmful and even hazardous wastes that must be dealt with. For example, reaction solvents and many bye-products that might evaporate into the air or leach into groundwater, if not disposed of properly. The hazardous chemical wastes may cause the existance of plant and animal kingdoms in danger. In the different industries, natural gas (CH_4) and coal are burnt as fuel for industrial furnaces. Coal contains sulphur. The chemical reactions that occur in furnaces are as follows :

MCQ-4.1 : How many principles are proposed for Green Chemistry by international chemists?
(a) 7 (b) 10 (c) 12 (d) 14

$$CH_4 (g) + 2O_2 (g) \rightarrow CO_2 (g) + 2H_2O (g)$$
$$C (s) + O_2 (g) \rightarrow CO_2 (g)$$
$$S (s) + O_2 (g) \rightarrow SO_2 (g)$$

You better know that the products like CO_2 and SO_2 gases get mixed with air from the furnace chimney as air pollutants.

It is unlikely that all chemical processes will ever be completely benign. but awareness of the environmental problems caused by chemistry has grown in recent years, giving rise to a movement called green chemistry.

Definition of Green Chemistry : Green chemistry is the design and implementation of chemical process in different industries that reduce waste and minimize or eliminate the generation of harmful and hazardous chemical substances towards environment.

The following twelve principles form the foundation of green chemistry.

(1) Prevent Waste. Chemical waste should be prevented rather than cleaned up after it has been created.

(2) Minimize atom economy. Industrial processes should minimize the incorporation of all reactant atoms into the final product to minimize left over wastes. For this, better chemical process should be implemented.

(3) Use less hazardous processes. For this, methods of chemical synthesis should use nontoxic reactants and generate nontoxic wastes. This type of synthetic method will make the lives of industrial workers and surrounding environment free from danger.

(4) Design safer chemicals. Chemical products should be designed from the beginning to have minimal toxicity.

(5) Use safer solvents. Industrial solvents and other auxiliary substances used in chemical reactions should be safe and used sparingly.

(6) Design for energy efficiency. Energy usage in chemical processes should be minimized, with reactions carried out at room temperature if possible.

(7) Use renewable feedstocks. For the better chemical processes, raw materials should come from renewable sources when feasible.

(8) Minimize derivatives. Industrial synthesis should be designed with minimal use of protecting groups to avoid extra steps and to reduce wastes.

(9) Use catalysis. Reactions should be catalytic rather than stoichiometric.

(10) Design for degradation. Industrial products should be designed to be biodegradable at the end of their useful life times.

(11) Monitor pollution in real time. Chemical processes should be monitored in real time during production of hazardous substances.

(12) Prevent accidents. Chemical substances and processes should minimize the probability for fires, explosions, or other accidents.

The 12 principles of green chemistry would not all be met in most applications. But they provide a goal to aim for and they can make chemists think more carefully about the environmental implications of their work. A major focus of the academic, industrial and government chemists who work in this new field is to develop methods that reduce or prevent the release of harmful substances into the environment.

To fully evaluate alternative methods, several green chemistry principles are taken into account, including the quantity of energy needed and the nature of the solvents required, when these factors are similar, then the **'atom economy' is considered.**

The `atom economy' means the proportion of reactant atoms that end up in the desired product. The atom economy is a useful criteria for choosing the more efficient synthetic route. The efficiency of a synthesis is quantified in terms of the percent atom-economy :

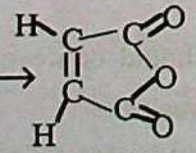
$$\%\ \text{atom economy} = \frac{\text{no.of moles} \times \text{molar mass of desired product} \times 100}{\text{sum of no. of moles} \times \text{molar massfor all products}}$$

Here an example of an industrial process that supports three principles of green chemistry such as -(i) prevent waste, (ii) maximize atom economy, and (iii) use less hazardous process, is given for clear conception about green chemistry :

Production of Maleic Anhydride : Maleic anhydride is a key industrial chemical used in the manufacture of medicine, pesticides, dyes, different polymers, and other important products : Consider two synthetic routes for production of maleic anhydride ($C_4H_2O_3$),– one route starting with benzene (C_6H_6), the other route with butane (C_4H_{10}); both the routes star with the proces of oxidation.

Route–1:

$2C_6H_6(l) + 9O_2(g) \rightarrow$



$(l) + 4H_2O(l) + 4CO_2(g)$

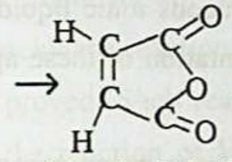
benzene

maleic anhydride ($C_4H_2O_3$)

MCQ-4.2 : The aims of green chemistry are :

(i) decrcase harmful wastes,
(ii) maximum products attain,

Route-2:

$2C_4H_{10}(g) + 7O_2(g) \longrightarrow$  $(l) + 8H_2O(l)$

butane

maleic anhydride ($C_4H_2O_3$)

(iii) use renewable feed stocks

which is correct?

(a) i, ii (b) ii, iii

(c) i, iii (d) i, ii and iii

At present, in most of the synthetic processes applied in different chemical industries, the highest percentage of productions lie in between 70% to 90%. Hence about 30% to 10% of the reactants remain out of the desired products.

Let us compare the efficiency of these two routes maleic anhydride synthesis in terms of percent atom economy (% AE):

$$\% \text{ AE} = \frac{\text{no. of moles} \times \text{ molar mass of desired product} \times 100}{\text{sum of no.of moles} \times \text{ molar mass for all products}}$$

For Route-1, $\% \text{ AE} = \dfrac{2 \text{ mol } C_4H_2O_3 \times 100}{(2\text{mol } C_4H_2O_3 + 4\text{mol } H_2O + 4\text{mol } CO_2)}$

$$= \frac{2 \times 98.06\text{g} \times 100}{(2\times 98.06\text{g} + 4\ 18.02\text{g} + 4 \times 44.01\text{g})} = 44.15\%$$

For Route-2, $\% \text{ AE} = \dfrac{2\text{mol } C_4H_2O_3 \times 100}{(2\text{mol } C_4H_2O_3 + 8\text{mol } H_2O)}$

$$= \frac{2 \times 98.06\text{g} \times 100}{(2\times 98.06 \text{ g} + 8 \times 18.02\text{g})} = 57.63\%$$

Conclusion : Clearly, from the perspective of atom economy–

(i) Route-2 is preferable for production of maleic anhydride; because a larger percentage of reactant atoms end up in the desired product maleic anhydride.

(ii) Route-2 is also a "greener" approach than route-1; because it avoids the use of the toxic reactant benzene.

(iii) Route-2 does not produce CO_2 gas, that contributes to global warming. Hence route-2 process is a better greener process.

A greener approach to working with organic solvents is now followed by greener chemists. Volatile organic solvents have many uses in paints and other coatings, in cleaning agents, and in propellants for hair spray, coocking oils, lubricants and so forth. But they also play a role in `smog' formation in air and may have adverse health effects. In the region of 'smog' in air, pH lowers to a value of 2, as it contains acidic $SO_2$ gas; causing bronchitis and pneumonia due to inflammation of the lung. The word `smog' originates from two words smoke and fog. These concerns have led to the development of 'greener' processes, such as

***

organic

the use of (i) non-volatile organic solvents, (ii) nonaqueous ionic liquid solvents, (iii) solvent-free and (iv) water based methods. With the implementation of these approaches, atmospheric emissions and worker exposure are greatly reduced.

Now different polymers are produced from petroleum-based monomers such as ethylene and substituted ethylene. But green chemists are devising polymers based on corn, sugarcane and even cashew nut shells. Before being embraced as a 'green' technology, however, the total impact of growing, transporting, and manufacturing must be assessed.

Students' Work - 4.1 : Green chemistry Based :

Problem – 4.1: What is green chemistry? [C. B. 2017; Di. B. 2017; Ctg.B. 2017; Syl. B. 2015]

Problem–4.2(a) : Glyeerine is obtained as bye-product is the manufacturing process of bio-diesel from vegetable-oil. This glycerine is converted to propalene glycol which is used in automobile engine as an antifreeze. This process is a greener process; here calculate%AE for the reaction : **[Ans. 80.85%]**

$$CH_2OHCH(OH)CH_2OH + H_2 \xrightarrow[\text{Copper chromite}]{CuCrO_2} Ch_3CH(OH)CH_2OH + H_2O$$

Problem–4.2(b) : Ethylene oxide is prepared from ethylene by old process and new greener process is as per following equations. Ethylene oxide is a smoke–maker and by hydrolysis of ethylene oxide antifreeze ethylene glycol is produced. Calculate % AE in each case :

(a) Old process : $C_2H_4+Cl_2 + Ca(OH)_2 \rightarrow C_2H_4O + CaCl_2 + H_2O$ **[Ans. 25.43%]**

(b) Greener process : $C_2H_4 + \frac{1}{2}O_2 \rightarrow \xrightarrow[250^\circ C]{\text{Ag Catalyst}} C_2H_4O$ [Ans. 100%]

Problem–4.2(c) : Two synthetic processes of maleic anhydride are as follows :

(i) $2C_6H_6 + 9O_2 \rightarrow 2C_4H_2O_3 + 4H_2O + 4CO_2$

(ii) $2C_4H_{10} + 7O_2 \rightarrow 2C_4H_2O_3 + 8H_2O$.

Which process will be a greener process; explain it from % AE calculation.

4.2 Reaction Direction : Irreversible Reaction and Reversible Reaction.

In lower classes such as class nine and class ten, you have already known that the thermal decomposition of lime stone or calcium carbonate in a closed reaction chamber is a reversible reaction. $CaCO_3 (s) \overset{\Delta}{\rightleftharpoons} CaO (s) + CO_2 (g)$

According to some chemists all reactions are reversible in proper conditions. But in reality in some cases backward reaction is so slow in comparison to forward reaction that its occurrence can not be proved. Such reactions are taken as irreversible reactions. **Example :** Water is produced by the reaction of H_2 and O_2. The reaction does not stop incomplete. It proceeds till either O_2 gas or H_2 gas is fully consumed. It is an irreversible reaction.

$$2H_2(g) + O_2(g) \xrightarrow{\Delta} 2H_2O\ (g)$$

Moreover, when pure water is heated, water vapour is produced; no free O_2 gas or H_2 gas can be detected in water vapour. So this reaction should be treated as irreversible at that temperature. So according to direction of reaction, all reactions are classified into two classes : (i) irreversible reactions and (ii) reversible reactions.

1. Irreversible reaction : When in a chemical reaction all the reactants are converted to the products, or in other words the reaction proceeds in one direction, then the reaction is called an **irreversible reaction.** In this type of reaction an arrow (⟶) may be used in place of equal sign (=).

Example : When potassium chlorate ($KClO_3$) is heated it dissociates into Potassium chloride KCl and O_2 gas. Conversely (KCl) and O_2 gas do not react with each other to produce $KClO_3$. So it is an irreversible reaction.

$$2KClO_3\ (s) \xrightarrow{\Delta} 2KCl\ (s) + 3O_2(g)$$

Similarly when carbon burns in oxygen, the whole amount of carbon burns and CO_2 gas is produced. It is an irreversible reaction

$$C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g)$$

2. Reversible reaction : When a chemical reaction proceeds both in forward and backward directions, then the reaction is called reversible reaction.

Example : When hydrogen and iodine are heated at 450°C in a sealed container, then some hydrogen iodide is produced due to following reaction.

$$H_2(g) + I_2(g) \xrightarrow{450^\circ C} 2HI(g)$$

On the other hand when pure hydrogen iodide is heated to 450°C in a sealed container, then some hydrogen iodide dissociates to produce hydrogen and iodine.

$$2HI(g) \xrightarrow{450^\circ C} H_2(g) + I_2\ (g)$$

So the above two reactions are reversible reactions. Reversible reactions are expressed by two oppositly half arrows (⇌).

$$H_2(g) + I_2(g) \xrightleftharpoons{450^\circ C} 2HI(g)$$

Some More Example of Reversible Change

1. Dissociation of ammonium chloride : When solid ammonium chloride (NH_4Cl) is heated in a sealed container, then it dissociates into ammonia gas (NH_3) and hydrogen chloride (HCl) gas. As the time passes, the amount of ammonia gas and hydrogen chloride gas increases, so also the rate of the reverse reaction to produce NH_4Cl also increases. After certain time the rates of forward reaction and backward reaction become equal and equilibrium is attained.

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl\ (g)$$

2. Dehydration of hydrated copper sulphate : When blue vitriol or blue coloured crystalline hydrated copper sulphate is heated to about 260°C, then white coloured powdered anhydrous copper sulphate and steam are produced. When it is cooled, anhydrous copper sulphate absorbs 5 molecules of water from the atmosphere and turns into blue coloured hydrated copper sulphate again. It is also a reversible chemical change.

✓

$$\underset{\text{blue crystal}}{CuSO_4.5H_2O(s)} \underset{\Delta}{\overset{260°C}{\rightleftharpoons}} \underset{\text{white powder}}{CuSO_4(s) + 5H_2O(g)}$$

Characteristics of reversible reaction :

(1) A reversible reaction can start from both sides

(2) Reversible reactions never complete i.e. hundred percent reactants are not converted into products or products are not completely converted into previous reactants.

(3) Reversible reactions show tendency to come into an equilibrium state.

(4) In the equation of a reversible reaction sign of equality (=) is replaced by two opposite half arrows ($\rightleftharpoons$) sign.

(5) A reversible reaction will be in equilibrium state when rate of forward reaction becomes equal to rate of backward reaction.

* Theoretically, all reactions are reversible. But in reality in some cases the backward reaction is so slow in camparison to forward reaction that its occurance can not be proved. Such reactions are taken as irreversible.

4.2.1 Interconversion of Reversible & Irreversible Reactions

Method of converting a reversible reaction into irreversible reaction : A reversible reaction is an incomplete reaction. This incomplete reaction can be completed or made into irreversible. Reversible reactions can be made into irreversible by the following 3 methods :

(1) **For gaseous product** : When the reactants are solid or liquid and one product is gaseous, then this product can be easily removed from the reaction area and the reaction becomes irreversible.

Example : The dissociation of calcium carbonate in a closed container is reversible. But when the reaction is carried out in an open container, the reaction turns irreversible. Because one product CO_2 is a gas and it escapes as soon as it is produced.

$$CaCO_3(s) \overset{\Delta}{\rightleftharpoons} CaO(s) + CO_2(g) \text{ (in closed container)}$$

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g) \text{ (in open container)}$$

(2) **Precipitation** : When one product is precipitated from solution, the reaction becomes irreversible. Because the precipitate is a solid state which is different from reaction medium (solution).

Example : When barium chloride solution is added to sodium sulphate solution, then barium sulphate precipitates out and is thus removed from the reaction area. Hence the reaction becomes irreversible and proceeds to completion.

$$Na_2SO_4(aq) + BaCl_2(aq) \longrightarrow 2NaCl(aq) + BaSO_4(s)$$

(3) **One product removed chemically** : When one product is chemically removed from the reaction, the reaction becomes irreversible.

Example : Ethanoic acid reacts with ethanol to produce ethyl ethanoate and water. If conc. H_2SO_4 is added to reaction mixture, it absorbs water; so backward reaction cannot take place.

$$CH_3COOH(l) + C_2H_5OH(l) \xrightarrow{\text{conc.}H_2SO_4} CH_3COOC_2H_5\ (l) + H_2O(l)$$

$$H_2SO_4\ (l) + H_2O(l) \longrightarrow H_2SO_4.H_2O(l)$$

Again acidic hydrolysis of ethyl ethanoate, the products are ethanoic acid and ethyl alcohol. If alkali NaOH is added to the reaction mixture then it reacts with ethanoic acid and the backward reaction cannot take place. Then hydrolysis of ethyl ethanoate goes to completion.

$$CH_3COOC_2H_5(l) + H_2O(l) \xrightarrow{\text{dil, HCl}} CH_3COOH(l) + C_2H_5OH(l)$$

$$CH_3COOH(l) + NaOH(aq) \longrightarrow CH_3COO\text{-}Na\ (aq) + H_2O(l)$$

4.3 Rate of Reaction

The rate of a reaction means how fast a reaction is taking place. Since during the reaction the concentration of the reactant decreases and the concentration of product increases. So the rate of reaction may be defined in terms of concentration as follows :

Definition : The rate of decrease of concentration of reactant or rate of increase of concentration of product in unit time is called rate of a reaction.

$$\text{Rate of reaction} = \frac{\text{change in concentration of reactant or product}}{\text{time needed for that change}}$$

Mathematical Expression : Let us consider a general reaction $A \longrightarrow B$. Let the concentration of the reactant 'A' after time, 't' from the beginning of reaction be 'c' and after a very small time 'dt' be $(c - dc)$. So the change of concentration of reactant in time dt is

$(c - dc) - c = - dc$.

$\therefore$ Rate of the reaction $= \frac{-dc}{dt}$

Again if the concentration of product 'B' after time 't' be x and after $(t + dt)$ be $(x + dx)$, then the change of concentration of 'B' in time 'dt' is $(x + dx) - x = dx$.

So the rate of reaction $= \frac{dx}{dt}$

$\therefore$ Rate of reaction $= \frac{-dc}{dt} = \frac{dx}{dt}$

Where c = concentration of reactant A after time t;

x = concentration of product B after time t.

Unit of Rate of Reaction

$$\text{Since rate of reaction} = \frac{\text{change of concentration of reactant or product}}{\text{time needed for this change}}$$

$$\text{So unit of rate of reaction} = \frac{\text{concentration}}{\text{time}} = \frac{\text{mol L}^{-1}}{\text{second}} = \text{mol L}^{-1}\,\text{s}^{-1}$$

4.3.1 The Rate Law or the Rate Equation

Rate of Reaction from Law of Mass Action : According to law of mass action, at a constant temp. the rate of a reaction at any moment is directly proportional to each reactant concentration term 'active-mass', with each term raised to the power of its stoichiometric coefficient in the balanced equation. Here concentration term 'active-mass' means molar concentration (molL^{-1}) for reactant solution and partial–pressure for gaseous reactant.

Here two general equations for reactions :

$nA \longrightarrow \text{Product}$

$\therefore$ Rate of reaction $\alpha\ [A]^n$

or, $\frac{-dc}{dt} = \frac{dx}{dt} = K \times [A]^n$ .... (1)

$aA + bB \longrightarrow \text{Product}$

$\therefore$ Rate of reaction $\alpha\ [A]^a \times [B]^b$

or, Rate of reaction $= k \times [A]^a \times [B]^b$ ......(2)

Here equations (1) and (2) are general rate equations for reactions and k is a constant.

Similarly, as per law of mass action for reaction like :

$$2A + B \longrightarrow C + 3D;$$ we get rate of reaction = $k \times [A]^2 \times [B]$

Exception : In many cases the rate equations of the reactions as per law of mass action may not be same or similar to the rate equations of the reactions as per experimental observed results. For example the rate equation of thermal dissociation of $N_2O_5(g)$ deduced from balanced equation and Law of mass action is not identical or same as the rate of reaction deduced from experimental observation result.

* Balanced equation : $2N_2O_5\,(g) \longrightarrow 4NO_2\,(g) + O_2\,(g)$

* From Law of mass action, rate of reaction = $k \times [N_2O_5]^2$

* From experimental result, rate of reaction = $k \times [N_2O_5]$

The Rate Law : From experimental observation-result the relation between the rate of reactions and molar concentrations of one or more reactants of different reactions have been determined. This type of co-related equations are called the rate laws or the rate equations.

Example :	**Rate equation of reaction :**
(1) $H_2(g) + I_2\,(g) \xrightarrow{\Delta} 2HI\,(g)$	reaction rate = $k \times [H_2] \times [I_2]$
(2) $2N_2O_5\,(g) \xrightarrow{\Delta} 4NO_2(g) + O_2(g)$	reaction rate = $k \times [N_2O_5]$
(3) $2NO\,(g) + 2H_2(g) \xrightarrow{\Delta} N_2(g) + 2H_2O\,(g)$	reaction rate = $k \times [NO]^2 \times [H_2]$

* Balanced general equation : $aA + bB \longrightarrow cC + dD$

* From Law of mass action, rate of reaction, $r = k \times [A]^a \times [B]^b$

* From Expt-Obsn, result, rate of reaction, $r = k \times [A]^m \times [B]^n$

Here 'm' and 'n' are the power of molar concentration of reactant 'A' and 'B' respectively as per experimental observation result. Here (m + n) value is called **'reaction-order.'**

* Note that coefficients 'a', 'b' of balanced equation have no relation with reaction rate and reaction order.

Rate Constant of a Reaction : Suppose, a general equation of a reaction is :

$aA + bB \longrightarrow cC + dD$. If the power of molar concentration of A and B as per experimental observation be m and n respectively; then according to rate law,

the rate of reaction (r) = $k \times [A]^m \times [B]^n$; here k is a constant.

$$\therefore k = \frac{\text{rate of reaction } (Ms^{-1})}{[A]^m \times [B]^n}$$

Now if concentration of each reactant is 1 molar, then $[A] = [B] = 1\ molL^{-1}$;

Hence rate of reaction = $k \times 1 \times 1 = k$;

i.e. 'rate of reaction' becomes equal to 'rate constant of reaction'.

Definition of Rate Constant : The rate of reaction of unit molar concentration of each reactant is called rate constant of that reaction. Rate constant is also called **specific reaction rate**.

Characteristics of Rate Constant of a Reaction :

(1) The value of rate constant of a reaction at a particular temp. is constant. But with change of temp. the value of rate constant also changes.

(2) At a particular temp. the value of rate constant (k) of different reactions are different.

(3) If the value of rate constant is high then rate of that reaction is high or more and with decrease of rate of reaction decreases the value of rate constant.

Followings are the similarities and dissimilarities between rate of reaction and rate constant :

Rate of Reaction	Rate Constant
(1) The rate of increase of product per unit time is called its rate of reaction. $\therefore$ rate of reaction $= \frac{dx}{dt}$.	(1) Rate constant of a reaction is the rate of reaction of unit molar concentration of each reactant.
(2) Rate of reaction changes with change of temperature.	(2) Rate constant is also changed with change of temp.
(3) At constant temp. with change of concentrations of reactants, rate of reaction changes.	(3) At constant temp. with change in concentration of reactants, rate constant does not change.
(4) Rate of reaction depends on concentration of each reactant.	(4) Rate constant (k) does not depend on concentration of reactants.
(5) Unit of reaction rate is $molL^{-1}\ s^{-1}$ or, Ms^{-1}; (For gaseous reaction, $atm.s^{-1}$)	(5) Unit of rate constant depends on order of reaction as per rate law or, rate equation.

Graphical Explanation of Rate of Reaction :

In 1850 L. Wilhetmy proved that the rate of reaction depends mainly on the concentration of reactants. When reaction occurs, the concentration of the reactant gradually decreases and that of the product gradually increases. So if the molar concentrations of reactant and product are plotted against time, a graph like Fig 4.I is obtained. From the plotting curve of the reactant concentration versus time, it is seen that in time $(t_2 - t_1)$ the concentration of the reactant is decreased by $(c_2 - c_1)$; here $c_1 > c_2$.

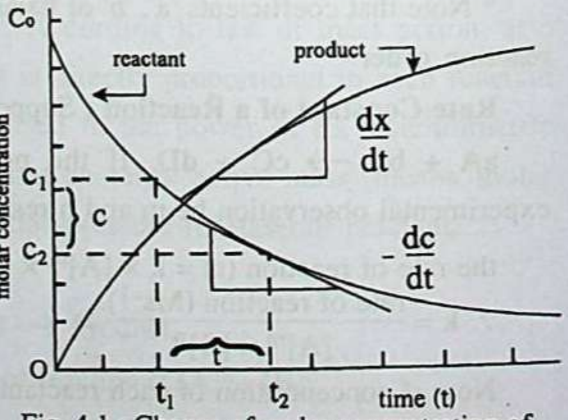


Fig. 4.1 : Change of molar concentration of reactant and product with time.

$$\therefore \text{ Rate of reaction} = \frac{(c_2 - c_1)}{(t_2 - t_1)} = \frac{-dc}{dt}$$

Calculation of rate of reaction : If a tangent is drawn at any point on the graph, the slope of that straight line will be equal to $\frac{-dc}{dt}$; which is the rate of reaction.

Similarly slope of a tangent drawn at a point on the curve for product will give the same rate of reaction and is equat to $\frac{dx}{dt}$

$$\therefore \text{ rate of reaction} = \frac{-dc}{dt} = \frac{dx}{dt}$$

★ From the graph it is seen that at the beginning, the rate of reaction is high and with increase of time it decreases. So the rate of any reaction depends on time.

★ In other-words the rate of a reaction is not constant or fixed; but rate of reaction depends on change of molar concentration of the reactants against change of reaction-time.

Significance of negative sign : The negative sign in case of rate of reaction of reactants means (i) the concentration of reactant decreases with increase of time of reaction. (ii) Besides this, the rate of reaction can never be of the negative value. So the value of rate of reaction makes positive by placing negative sign on right side of the equation of rate of reaction.

For example, look at the thermal decomposition of gaseous dinitrogen pentoxide (N_2O_5) to produce the brown gas nitrogen dioxide (NO_2), a common air pollutant, and molecular oxygen gas :

$$\underset{\text{colourless}}{2N_2O_5\,(g)} \xrightarrow{\Delta} \underset{\text{brown}}{4NO_2\,(g)} + \underset{\text{colourless}}{O_2\,(g)}$$

Changes in concentration as a function of time can be determined by measuring the increase of pressure, as 2 moles gaseous reactant are converted to 5 moles gaseous products, Alternately concentration changes can be monitored by measuring the intensity of the brown colour due to NO_2 gas. Reactant and product concentrations as a function of time at 55°C are listed in Table-4.1 below :

Table-4.1 : Change of concentrations with time at 55°C for decomposition of N_2O_5

Time (s)	N_2O_5 (mol)	NO_2 (mol)	O_2 (mol)	Comment
0	0.020	0	0	Note that the concentrations of NO_2 and O_2 increase as the concentration of N_2O_5 decreases.
100	0.0169	0.0063	0.0016	
200	0.0142	0.0115	0.0029	
300	0.0120	0.0160	0.0040	
400	0:0101	0.0197	0.0049	
500	0.0086	0.0229	0.0057	

The Reaction rate can be defined either **as the increase in the concentration of a product per unit time or as the decrease in the concentration of a reactant** per unit time. Let us look first at product formation. In the decomposition of N_2O_5, the rate of formation of O_2 gas is given by the equation :

$$\text{Rate of formation of } O_2 = \frac{\Delta[O_2]}{\Delta t} = \frac{\text{Conc. of } O_2 \text{ at time } t_2 - \text{Conc. of } O_2 \text{ at time } t_1}{(t_2 - t_1)}$$

Where the square brackets surrounding O_2 denote its molar concentration, $\Delta[O_2]$ is the change in the molar concentration of O_2; Δt is the change in the time, and $\Delta[O_2]/\Delta t$ is the average rate of change in the molar concentration of O_2 gas during the interval from time t_1 to t_2. During the time period 300 to 400 seconds, for example, the average rate of reaction of formation of O_2 is 9×10^{-6} M/s:

$$\text{Rate of formation of } O_2 = \frac{\Delta[O_2]}{\Delta t} = \frac{0.0049\text{M} - 0.0040\text{M}}{400\text{s} - 300\text{s}} = 9 \times 10^{-6} \text{ M/s}$$

Reaction Rate with different moles of Reactants and Products :

The general equation of this type of reaction is :

$$aA + bB \longrightarrow cC + dD$$

Here rate of reaction is expressed as follows :

$$\text{Rate of reaction, } r = -\frac{1}{a}\cdot\frac{d[A]}{dt} = -\frac{1}{b}\cdot\frac{d[B]}{dt}$$

$$= +\frac{1}{c}\cdot\frac{d[C]}{dt} = +\frac{1}{d}\cdot\frac{d[D]}{dt}$$

Example : $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

$$\therefore \text{ rate of reaction, } r = -\frac{d[N_2]}{dt} = -\frac{1}{3}\cdot\frac{d[H_2]}{dt} = +\frac{1}{2}\cdot\frac{d[NH_3]}{dt}$$

MCQ–4.3 : Initial concentration of a reactant is 0.1ML^{-1}. After 20s, if concentration of it becomes 0.05ML^{-1}, what is the rate of reaction?

(a) 1.5×10^{-2} $\text{ML}^{-1}\text{ s}^{-1}$

(b) 2.5×10^{-3} $\text{mol L}^{-1}\text{s}^{-1}$

(c) $2.05\text{molL}^{-1}\text{ s}^{-1}$

(d) 2.05×10^{-2} molL^{-1}

Worked Example–4.1 : In reaction A⟶B; initial concentration of A is 0.275 molL^{-1}. After starting reaction within 5 min 20 sec. concentration of A decreases to 0.125 molL^{-1}. In this period calculate rate of reaction.

Solution : Average rate of reaction = $\dfrac{\text{change in concentration of A}}{\text{time used for that change}}$

$$\text{Or, } \frac{-\Delta A}{\Delta t} = -\frac{([A_2] - [A_1])}{\Delta t} = -\frac{(0.125 - 0.275)\text{ molL}^{-1}}{320\text{s}} = 4.6875 \times 10^{-4} \text{ molL}^{-1}\text{s}^{-1}$$

$\therefore$ Average rate of reaction = 4.6875×10^{-4} $\text{molL}^{-1}\text{ s}^{-1}$.

Worked Example-4.2 : Finding relative rates of product formation :

Ethanol (C_2H_5OH), the active ingredient in alcoholic beverages and an octane booster in gasoline, is produced by the fermentation of glucose. The balanced equation is :

$$C_6H_{12}O_6\ (aq) \longrightarrow 2C_2H_5OH\ (aq) + 2CO_2\ (g)$$

(a) How is the rate of formation of ethanol related to the rate of consumption of glucose?

(b) Write this relationship in terms of $\Delta[C_2H_5OH]/\Delta t$ and $\Delta[C_6H_{12}O_6]/\Delta t$.

Strategy : To find relative rates, look at coefficients in balanced chemical equation.

Solution : According to given balanced equation of fermentation, 2 moles of ethanol are produced from 1 mole of reactant glucose. Therefore , the rate of formation of ethanol is twice the rate of consumption of reactant glucose.

(b) Since the rate of formation of ethanol is $\Delta[C_2H_5OH]/\Delta t$ and the rate of consumption of glucose is $-\Delta[C_6H_{12}O_6]/\Delta t$ (note the minus sign indicating decrease of reactant's concentration), we can write : $\Delta \frac{[C_2H_5OH]}{\Delta t} = -2 \times \frac{\Delta[C_6H_{12}O_6]}{\Delta t}$

Worked Example–4.3 : Nitrogen penta oxide dissociates into NO_2 and O_2 gases :

$$2N_2O_5\ (g) \rightleftharpoons 4NO_2\ (g) + O_2\ (g)$$

If concentration of NO_2 increases to 3.0×10^{-3} $molL^{-1}$ in 6 sec, then what is rate of reaction?

Solution : Rate of reaction $= +\frac{1}{4} \times \frac{[NO_2]}{\Delta t}$; Here $[NO_2] = 3 \times 10^{-3} molL^{-1}$ $\Delta t = 6$ sec.

$$\therefore \text{Rate of reaction} = \frac{1 \times 3.0 \times 10^{-3}\ molL^{-1}}{4 \times 6\ sec} = 1.25 \times 10^{-4}\ molL^{-1}.\ s^{-1}.$$

Student's Work- 4.2 : Reaction Rate Based.

Problem–4.3(a) : What is rate of reaction? [B. B. 2015]

Problem–4.3(b) : What are the differences between rate of reaction and rate constant?

Problem–4.4 : Calculate (a) the average rate of decomposition of N_2O_5 and (b) the average rate of formation of O_2 gas during the time interval 200 to 300 seconds using the data in Table-4.1 **Ans.** (a) 2.2×10^{-5} M/s; (b) 1.1×10^{-5} M/s

Problem – 4.5 : Write the rate of reaction for the given equations :

(1) $H_2 + I_2 \longrightarrow 2HI$ (3) $4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$

(2) $2N_2O_5 \longrightarrow 4NO_2 + O_2$ (4) $A + 2B \longrightarrow 2C + D$

Problem–4.6 : The oxidation of iodide ion by arsenic acid, (H_3AsO_4,) is given by the following balanced equation :

$$3I^-(aq) + H_3AsO_4\ (aq) + 2H^+\ (aq) \longrightarrow I_3^-\ (aq) + H_3\ AsO_3\ (aq) + H_2O\ (l)$$

(a) If $-\Delta\ [I^-]/\Delta t = 4.8 \times 10^{-4}$ M/s, what is the value of $\Delta\ [I_3^-]\ \Delta t$ during the same time interval? [**Ans.** 1.6×10^{-4} M/s]

(b) What is the average rate of consumption of H^+ ion during that same time interval? [**Ans.** 3.2×10^{-4} M/s

Problem–4.7 : Dissociation equation of N_2O_5 is : $2N_2O_5\,(g) \rightleftharpoons 4NO_2\,(g) + O_2\,(g)$; if in this reaction concentration of NO_2 increases to 5.25×10^{-2} mol L^{-1} within 2 min 15 sec; then what is the rate of reaction of it? [**Ans.** 9.722×10^{-5} mol L^{-1} s^{-1}]

Problem–4.8 : In acidic hydrolysis of ethyl acetate ($CH_3COOC_2H_5$), the reactant concentration falls from 1.0 mol L^{-1} to 0.5 mol L^{-1} in 40 minutes. What is the reaction rate? [**Ans.** 2.08×10^{-4} mol L^{-1} s^{-1}]

Problem–4.9 : In 5 minutes, 0.1 molL^{-1} H_2O_2 solution dissociates to concentration 0.08 mol L^{-1}. What is its reaction rate? [**Ans.** 3.33×10^{-5} molL^{-1} s^{-1}.]

Problem–4.10 : On mixing a definite concentration of H_2O_2 solution with KI solution, 1.0×10^{-2} molL^{-1} I_2 is liberated in 5 minutes, What is the rate of this oxidation reaction? [**Ans.** 3.33×10^{-5} molL^{-1} s^{-1}]

Problem–4.11 : In reaction, $N_2\,(g) + 3H_2(g) \longrightarrow 2NH_3\,(g)$, the concentration of product NH_3 in 1 minute 40 seconds is 3.5×10^{-3} MolL^{-1}, Calculate its rate of reaction. [**Ans.** 1.75×10^{-5} moll^{-1} s^{-1}]

Problem–4.12 : The rate of reaction of NH_3 production is 4.25×10^{-2} molL^{-1}. s^{-1}; in the reaction $N_2\,(g) + 3H_2(g) \longrightarrow 2NH_3\,(g)$. Calculate the rate of each reactant taking part in this reaction.[**Ans:** $d[N_2]dt = 2.125 \times 10^{-2}molL^{-1}$ s^{-1}; $d[H_2]/dt = 6.375 \times 10^{-2}$ molL^{-1} s^{-1}]

Problem–4.13 : The rate of production of NO in the reaction : $4NH_3\,(g) + O_2(g) \xrightarrow{900°C\ Pt} 4NO(g) + 6H2O(g)$, is 5.25×10^{-3} molL^{-1} s^{-1}. What will be the rate of reaction of reactant NH_3 and production of steam? [**Ans.** $NH_3 = 5.25 \times 10^{-3}$ molL^{-1} s^{-1}; steam $= 7.875 \times 10^{-3}$ molL^{-1} s^{-1}.]

Problem–4.14 : In reaction, $2A \longrightarrow 3B + C$, if the rate of production of B is 2.75×10^{-2} molL^{-1} s^{-1} then what will be the rate of reaction with respect to 'A' and 'C' ? [**Ans.** $A = 1.8332 \times 10^{-2}$ molL^{-1} s^{-1}. $C = 9.166 \times 10^{-3}$ molL^{-1} s^{-1}.]

Know More : In chemical kinetics, together with (i) rate of reaction, (ii) rate constant; one more important term like (iii) order of reaction is closely associated. The unit of rate constant depends on order of reaction.

Definition of Order of Reaction : Order of reaction is the sum of the exponents (or powers) to which molar concentration terms of the reactants are raised so as to that exponents (powers) may be equal to experimental rate of the reaction.

1007 -

Calculation of order of reaction : Suppose a general equation of a reaction :

$$aA + bB \longrightarrow \text{Product.}$$

From experimental result, rate of reaction = $k \times [A]^m \times [B]^n$

Taking $(m + n) = x$. So here order of the reaction = x.

(1) When, from experimental result, $x = 0$, then the reaction is called **zero-order** reaction. In zero order reaction, rate of reaction does not depend on concentration of reactants,

For example,

$H_2(g) + Cl_2(g) \xrightarrow{h\vartheta} 2HCl(g)$; [sunlight catalysed reaction]

Rate of reaction = $k \times [H_2]^{\circ} \times [Cl_2]^{\circ} = k$.

Unit of k = $molL^{-1}.\ s^{-1}$ (unit of reaction rate)

(2) When, from experimental result, $x = 1$, then the reaction is called **first order** reaction. In 1st order reaction, rate of reaction depends on 1st power of concentration of any one reactant. For example.

$$2N_2O_5\ (g) \xrightarrow{\Delta} 4NO_2\ (g) + O_2\ (g)$$

$\therefore$ Rate of reaction = $k \times [N_2O_5]^1$

$\therefore$ Unit of k = $\dfrac{\text{unit of reaction rate}}{\text{unit of } [N_2O_5]} = \dfrac{Ms^{-1}}{M} = s^{-1}$

(3) When, from experimental result, $x = 2$, then the reaction is called **second order** reaction. In 2nd order reaction, rate of reaction depends on 2nd power of concentration of one reactant or more reactants. For example :

$H_2(g) + I_2(g) \longrightarrow 2HI(g)$; $\quad 2NOCl(g) \longrightarrow 2NO(g) + Cl_2(g)$

$2NO_2(g) \longrightarrow 2NO(g) + O_2\ (g)$; $\quad NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

$\therefore$ Rate of reaction = $k \times [H_2]^1 \times [I_2]^1$;

$\therefore$ unit of k = $\dfrac{\text{unit of reaction rate}}{\text{unit of } [H_2] \times [I_2]} = \dfrac{M.s^{-1}}{M^2} = M^{-1}.s^{-1}$

(4) When, from experimental result, $x = 3$, then the reaction is called **thir** **reaction.** In **3rd order reaction,** rate of reaction depends on 3rd power of concent one reactant or more reactants. For example.

$2NO\ (g) + O_2(g) \longrightarrow 2NO_2(g)$; $\quad 2NO\ (g) + Cl_2(g) \longrightarrow 2NOCl(g)$

$\therefore$ Rate of reaction = $k \times [NO]^2 \times [O_2]^1$;

Unit of k = $\dfrac{\text{unit of reaction rate}}{\text{unit of } [NO]^2 \times [O_2]^1} = \dfrac{M.s^{-1}}{M^3} = M^{-2}\ s^{-1}$

4.3.2 Factors that Affect the Rate of a Reaction

The rate of a reaction depends on following three primary factors :

(i) temperature, (ii) pressure and (iii) concentration of the reactants.

(I) Affect of Temperature on Rate of Reaction

Temperature often has a major affect or reaction rate. When reactant concentrations are held constant, the rate of reaction nearly doubles with each rise in temperature of 10K (or 10°C). In fact, for many reactions near at room temperature, an increase of 10°C causes a doubling or tripling of the rate.

By experiment it is found that the precipitation rate of sulphur in reaction between sodium thiosulphate and HCl acid becomes double at 30°C to the rate of precipitation at 20°C. The rate of most reactions becomes approximately double with the rise of 10°C temperature

$$Na_2S_2O_3\ (aq) + 2HCl\ (aq) \longrightarrow S\ (s) + 2NaCl\ (aq) + SO_2\ (g) + H_2O\ (l)$$

Explanation for Affect of Temperature on Rate of Reaction

With increase of temperature in a reaction the following affects occur.

★ (i) Speed of reactant molecules or atoms or ions increases.

★ (ii) Collision rate among the molecules or particles increases.

★ (iii) More reactant molecules or particles can get activation energy for the reaction.

(A) Activation Energy : It is clear that only those molecules can participate in a reaction, which have acquired atleast some definite higher energy than the average energy of the molecules. This excess energy necessary for particular molecule to react is known as **activation energy**.

The difference between the average energy of reactant molecules and the necessary higher energy which a reactant molecule must possess to enable it to take part directly in a reaction is known as activation energy of the reaction. The molecules which possess atleast the amount of activation energy are called activated molecules.

In 1889, Swedish chemist Svante Arrhenius inroduced a mathematical equation co-relating the above factors with rate of reaction as follows : It is known as Arrhenius equation for rate of reaction :

$$\underset{\substack{\uparrow\\ \text{rate}\\ \text{constant}}}{k} = \underset{\substack{\uparrow\\ \text{steric}\\ \text{factor}}}{P.}\quad \underset{\substack{\nwarrow\\ \text{rate}\\ \text{collision}}}{Z.}\quad \underset{\substack{\nwarrow\\ \text{fraction of molecules with}\\ \text{activated energy to react}}}{e - E_a/RT}$$

Again P × Z combinely denoted by constant

MCQ–4.4 : Factors which affect the rate of reaction are :
(i) temperature, (ii) concentration,
(iii) pressure,
Which will be correct?
(a) i, iii (b) ii, iii9
(c) i, iii (d) i, ii and iii

'A' called frequency factor or 'pre-exponential factor or Arrhenius factor, then that equation will be :

$$k = A \times e^{-E_a/RT}$$

Where, E_a = activation energy of reactant, R = gas constant = $8.3 JK^{-1} mol^{-1}$, T = Kelvin temp. In accord with the minus sign in the exponent, rate constant decreases as E_a increases and increases as T increases.

By taking exponential logarithm on both sides, we get:

$$\text{In}k = \text{In}\,A - \frac{E_a}{RT}$$

$$\text{In}k = \frac{-E_a}{R} \times \frac{1}{T} + \text{In}A \text{ .... (1)}$$

This equation is related to linear equation,

y = mx + c, Here slope of the straight line,

$m = - E_a/R$, [fig: 4.2]

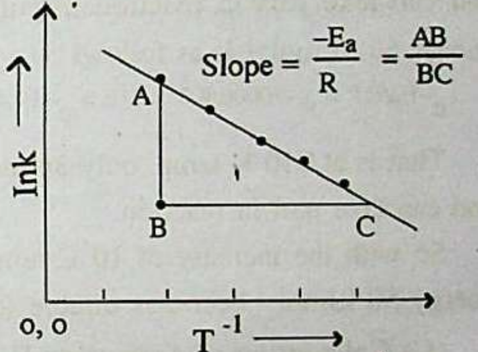


Fig- 4.2 : Ink against T^{-1}

Conclusions : From equation (1) it is seen that :

★ (i) With the increase of temperature (T), the rate constant (k) of a reaction increases.

★ (ii) With the decrease of activation energy (E_a), the rate constant increases,

★ (iii) A graph In k against T^{-1} will be a straight line. Its slope is $\frac{-E_a}{R}$

From slope, $\frac{-Ea}{R}$ the activation energy of a reaction can be calculated.

Again, when k_1 and k_2 are the rate constant of a reaction at temperature T_1 and T_2, we get from equation (1):

$$\text{In}\frac{k_2}{k_1} = \frac{E_a}{R} \times \frac{(T_2 - T_1)}{T_1 \times T_2}, \quad \text{where } T_2 > T_1 \text{ .... (2)}$$

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R} \times \frac{(T_2 - T_1)}{T_1\,T_2}, \quad \text{where } T_2 > T_1 \text{ .... (3)}$$

From the equation (3), it is seen that :

★ (i) If the values of rate constant k_1 and k_2 are known at temp. T_1 and T_2, then activation energy, E_a of that reaction can be calculated.

★ (ii) If the activation energy (E_a) of a reaction and rate constant k_1 at T_1 are known, then rate constant k_2 at any temp. T_2 can be calculated.

(B) Comparison of Reaction Rates at two different Temperatures :

Example : Suppose the activation energy of molecules of a reaction is 50 $kJmol^{-1}$. Show that the rate of reaction becomes double when temperature of the reaction increases from 300K (27°C) to 310 K (37°C).

Solution : According to Arrhenius equation, fraction of molecules with activated energy 50 $kJmol^{-1}$ = 50,000 J mol^{-1} to react at 300 K temp. can be calculated as follows :

$e^{-E_a/RT} = e^{-50000/8.3 \times 300}$ From question : $E_a = 50\ kJ = 50 \times 1000\ J$

$= e^{-20.08} = 1.90 \times 10^{-9} = \frac{19}{10^{-10}}$ $R = 8.3\ JK^{-1}\ mol^{-1}$; $T = 300\ K$

That is at 300 K temp. only 19 molecules out of 10^{10} molecules get that activation energy and can take part in reaction. Again at 310 K temp. fraction of molecules with activated energy 50 kJ mol^{-1} is as follows :

$$e^{-Ea/RT} = e^{-50000/8.3 \times 310} = e^{-19.48} = 3.63 \times 10^{-9} = \frac{36.3}{10^{10}}$$

That is at 310 K temp. only 36 molecules out of 10^{10} molecules get that activation energy and can take part in reaction.

So with the increase of 10°C temp. for a reaction the rate of the reaction with activation energy 50 $kJmol^{-1}$ becomes double (approximately).

(C) Calculation of Activation Energy :

Worked Example– 4.4 : At different temp. the rate constants (k) of dissociation of HI in gaseous state, are determined.With this results lnk values are plotted against T^{-1}(kelvin inverse). Thus the straigt line obtained, has slope $-2.24 \times 10^4 K$. What is the activation energy of this reaction?

Strategy : For lnk vs T^{-1} graph, slope $= \frac{-Ea}{R}$; because related equation is

$\ln k = \frac{-E_a}{R} \times \frac{1}{T} + \ln A.$ Here, slope $= -2.24 \times 10^4$ K

$R = 8.314\ Jmol^{-1}K^{-1}$

Solution : Activation energy, $E_a = -$ slope × R;

$\therefore\ E_a = -(-2.24 \times 10^4 K) \times 8.314\ Jmol^{-1}K^{-1}$

or, $E_a = 18.62336 \times 10^4\ Jmol^{-1}$

or, $E_a = 186.2336\ kJ.mol^{-1}$

$\therefore$ Activation energy, $E_a = 186.2336\ kJ.mol^{-1}$

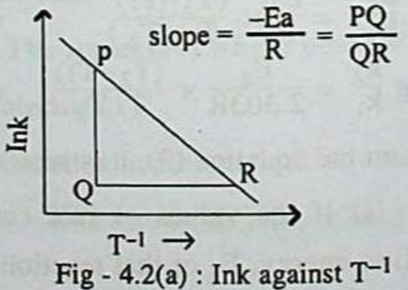


Fig - 4.2(a) : lnk against T^{-1}

Worked Example–4.5 : At different kelvin temp. (T) the rate constants (k) of thermal dissociation of N_2O_5 (g) are determined. Then with this data logk vs T^{-1} graph is drawn; the slope of the straight line obtained, is -96.5×10^2 K. Calculate the activation energy of this dissociation reaction.

Strategy : For logk vs T^{-1} graph, slope $= \frac{-E_a}{2.303R}$, because related equation is

$$\log k = \frac{-E_a}{2.303R} \times \frac{1}{T} + \log A$$

Solution : Activation energy, $E_a = -\text{slope} \times 2.303R$;

$\therefore E_a = -(-96.5 \times 10^2\ \text{K}) \times 2.303 \times 8.314\text{J mol}^{-1}.\ \text{K}^{-1}$

or, $E_a = 1847.7 \times 10^2\ \text{J mol}^{-1}$

or, $E_a = 184.77\ \text{kJmol}^{-1}$

$\therefore$ Activation energy, $E_a = 184.77\ \text{kJ.mol}^{-1}$

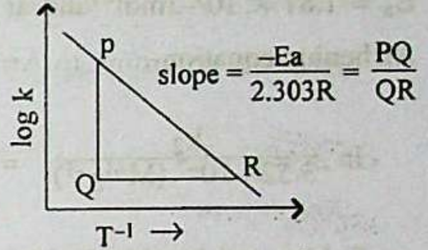


Fig-4.2 (b) : log Ḳ vsT^{-1}

Here, slope $= -96.5 \times 10^2$ K
$R = 8.314\ \text{Jmol}^{-1}\text{K}^{-1}$

Worked Example : 4.6 : Using Arrhenius Equation :

Rate constants for the gas phase decomposition of hydrogen iodide,

$2HI\ (g) \longrightarrow H_2\ (g) + I_2\ (g)$, at 283°C and 508°C are respectively

$k_1 = 3.52 \times 10^{-7}\ M^{-1}\ s^{-1}$ and $k_2 = 3.95 \times 10^{-2}\ M^{-1}s^{-1}$,

(a) Calculate E_a from the rate constants at 283°C and 508°C.

(b) Calculate the rate constant at 293°C using the rate constant at 283°C (given) and the value of E_a obtained in part (a).

Strategy : (a) E_a can be calculated from $\ln \frac{k_2}{k_1} = \frac{-E_a}{R} \times \frac{(T_1 - T_2)}{T_1 \times T_2}$

(b) To calculate k_2 at T_2 values of k_1 at T_1 and E_a are to be used in above equation.

Solution : (a) Substituting the values of $k_1 = 3.52 \times 10^{-7}\ (M^{-1}\ s^{-1})$ at $T_1 = 556K\ (283°C)$ and $k_2 = 3.95\ 10^{-2}\ (M^{-1}s^{-1})$ at $T_2 = 781K\ (508°C)$ in the following equation :

$$\ln \frac{k_2}{k_1} = \frac{-E_a}{R} \times \frac{T_1 - T_2}{T_1 \times T_2} \quad \text{or,} \quad \ln \frac{3.95 \times 10^{-2}\ (M^{-1}\ s^{-1})}{3.52 \times 10^{-7}\ (M^{-1}s^{-1})}$$

$$= \frac{-Ea \times (556 - 781)K^{-1}}{8.314(JK^{-1}mol^{-1}) \times 556 \times 781}$$

MCQ–4.5 : What is the unit of rate of reaction?

(a) $mol.L^{-1}s^{-1}$ (b) $mol\ L.s^{-1}$

(c) $mol.dm^3\ s^{-1}$ (d) mol^{-1} [illegible] or, $11.628 = \dfrac{-Ea \times (-5.18 \times 10^{-4})}{8.314 \text{ JmoL}^{-1}}$

or, $E_a = 1.87 \times 10^5 \text{ Jmol}^{-1}$; or, $E_a = 187 \text{ kJ mol}^{-1}$

(b) On using the known values for $k_1 = 3.52 \times 10^{-7}$ (M^{-1} s^{-1}) at $T_1 = 556$ K (283°C) and $E_a = 1.87 \times 10^5$ $\text{Jmol}^{-1}$and at $T_2 = 566$ K (293°C), k_2 will be calculated from the above Arrhenius equation :

$$\ln \frac{k_2}{3.52 \times 10^{-7} (M^{-1}s^{-1})} = \frac{-1.87 \times 10^5 \text{ J mol}^{-1}(556 - 566) \text{ K}^{-1}}{8.314 \text{ Jk}^{-1} \text{ mol}^{-1} \times 566 \times 556} = 0.715$$

Taking anti ln of both sides we get :

$$\frac{k_2}{3.52 \times 10^{-7}(M^{-1}s^{-1})} = e^{0.715} = 2.04 \quad \therefore k_2 = 2.04 \times 3.52 \times 10^{-7} (M^{-1}s^{-1})$$

or, $k_2 = 7.18 \times 10^{-7}$ $M^{-1}s^{-1}$

Note, in this temperature range, a rise in temperature of 10 K doubles the rate constant.

Worked Example–4.7 : HI is produced from H_2 and I_2 as per following equation :

$$H_2(g) + I_2(g) \rightleftharpoons 2H1(g)$$

The rate constants of this reaction at 227°C and 257°C are respectively 1.95×10^{-4} L mol^{-1} s^{-1} and 1.75×10^{-3} L mol^{-1} s^{-1}. Calculate the activation energy of this reaction.

Strategy : Arrhenius equation, $\log \frac{k_2}{k_1} = \frac{Ea}{2.303R} \times \left[\frac{T_2 - T_1}{T_1T_2}\right]$ will be used.

Solution : $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \times \left[\frac{T_2 - T_1}{T_1T_2}\right]$

or, $\log \dfrac{1.75 \times 10^{-3}}{1.95 \times 10^{-4}} = \dfrac{E_a \times 10^3}{2.303 \times 8.314}\left[\dfrac{530 - 500}{500 \times 530}\right]$

$\therefore E_a = 161.18 \text{ kJ.mol}^{-1}$

$\therefore$ Activation energy = $161.18 \text{kJ.mol}^{-1}$

here,

at 227°C, $k_1 = 1.95 \times 10^{-4} \text{ L.mol}^{-1} \text{ s}^{-1}$

at 257°C, $K_2 = 1.75 \times 10^{-3} \text{ L.mol}^{-1} \text{ s}^{-1}$

$T_1 = (227 + 273) \text{ K} = 500\text{K}$

$T_2 = (257 + 273) \text{ K} = 530\text{K}$

$R = 8.314 \times 10^{-3} \text{ kJmol}^{-1}\text{K}^{-1}$

$E_a = ?$

Worked Example–4.8 : At 45°C the rate constant of a reaction is double of rate constant at 35°C of that reaction. Calculate the activation energy of that reaction.

Solution : From Arrhenius equation :

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \times \left[\frac{T_2 - T_1}{T_1 T_2}\right];$$

$$\text{or, } \log \frac{2k_1}{k_1} = \frac{E_a \times (318 - 308)}{2.303 \times 8.314 \times 308 \times 318}$$

$$\text{or, } \log 2 = \frac{E_a \times 10}{2.303 \times 8.314 \times 308 \times 318}$$

$$\text{or, } E_a = \frac{0.301 \times 2.303 \times 8.314 \times 308 \times 318}{10}$$

here, $T_1 = (35 + 273)K = 308K$

$T_2 = (45 + 273)K = 318K$

$R = 8.314\ JK^{-1}.\ mol^{-1}$

Suppose at T_1 rate constant $= k_1$

at T_2, rate constant $= k_2 = 2k_1$

$E_a = ?$

or, $E_a = 56447.96\ Jmol^{-1}.$ $\therefore E_a = 56.45\ kJmol^{-1}$

$\therefore$ Activation energy, $E_a = 56.45\ kJmol^{-1}$.

Worked Example – 4.9 : The rate constant of $2N_2O_5\,(g) \rightleftharpoons 4NO_2(g) + O_2\,(g)$ reaction at 25°C and 65°C are respectively $3.46 \times 10^{-5}\ s^{-1}$ and $4.87 \times 10^{-3}\ s^{-1}$. What is activation energy of this reaction?

Solution : From Arrhenius equation :

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \times \frac{(T_2 - T_1)}{T_1 T_2}$$

$$\text{or, } \log \frac{4.87 \times 10^{-3}}{3.46 \times 10^{-5}} = \frac{E_a \times (338 - 298)}{2.303 \times 8.314 \times 298 \times 338}$$

$$\text{or, } \log 1.407 \times 10^2 = \frac{E_a \times 40}{19.147 \times 1.007 \times 10^5}$$

$$\text{or, } 2.1482 = E_a \times 2.07459 \times 10^{-5}$$

$$\text{or, } E_a = \frac{2.1482}{2.07459 \times 10^{-5}} = 10.3549 \times 10^4\ Jmol^{-1}$$

$\therefore$ Activation energy, $E_a = 103.549 kJmol^{-1}$

Here, $T_1 = (25 + 273)\ K = 298\ K$

$T_2 = (65 + 273)\ K = 338\ K$

$k_1 = 3.46 \times 10^{-5}\ s^{-1}$

$k_2 = 4.87 \times 10^{-3}\ s^{-1}$

$R = 8.314\ Jmol^{-1}\ K^{-1}$

$E_a = ?$

Student's Work- 4.3 : Arrhenius Equation Based :

Problem–4.15 (a) : Scientist Arrhenius established the fact that the rate of a reaction becomes double at the increase of 10°C temperature. Explain its causes.

Problem–4.15 (b) : Establish the equation $\ln \frac{k_2}{k_1} = \frac{-E_a}{R} \times \left[\frac{T_1 - T_2}{T_1 \times T_2}\right]$ $k = p.z.e^{-Ea/RT}$, where k_1 and k_2 are reaction rates at T_1 and T_2.

Problem–4.15 (c) : The slope of the straight line obtained by plotting log k vs T^{-1} at different temperatures for a reaction is -2.872×10^3 K. Then calculate activation energy of that reaction. [Ans. 55 kJ mol^{-1}]

Problem–4.15 (d) : The slope of the straight line drawn by plotting logk vs T^{-1} at different temperature for a reaction : $Ag_2CO_3(s) \rightleftharpoons Ag_2O(s) + CO_2(g)$ is – 82K. Then calculate its activation energy. **[Ans.** 1.57 kJ mol^{-1}]

Problem–4.15 (e) : The slope of the straight line drawn by plotting lnk vs T^{-1} at different temperatures for reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ is -2.24×10^4K.

Calculate its activation energy. **[Ans.** 186.23 kJ mol^{-1}]

Problem–4.16 : Rate constants for the decomposition of gaseous dinitrogen pentoxide are $3.7\times10^{-5}\ s^{-1}$ at 25°C and $1.7 \times 10^{-3}\ s^{-1}$ at 55°C. $2N_2O_5(g) \longrightarrow 4NO_2 + O_2(g)$

(a) What is the activation energy for this reaction in kJ/mol? **[Ans.** 103.67 kJ/mol]

(b) What is the rate constant at 35°C **[Ans.** $1.44 \times 10^{-4}\ s^{-1}$]

Problem–4.17(a) : The thermal decomposition of hydrogen iodide has rate constants of 9.51×10^{-9} L.mol^{-1}. s^{-1} at 500K and 1.10×10^{-5} L.mol^{-1} s^{-1}at 600K. Find E_a of this reaction in kJ/mol. $2HI(g) \xrightarrow{\Delta} H_2(g) + I_2(g)$ **[Ans.** 1.76×10^2 kJ/mol]

Problem–4.17(b) : For reaction : $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$; the rate constants at 275°C and 500°C are respectively 3.5×10^{-7} L.mol^{-1} s^{-1} and 3.92×10^{-2} L.mol^{-1} s^{-1}

Calculate its activation energy. **[Ans.** 182.019 kJ mol^{-1}]

Problem–4.17(c) : For reaction : $2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$; the rate constants at 27°C and 37°C are respectively $2.25 \times 10^{-3}\ s^{-1}$. and $4.75 \times 10^{-3}\ s^{-1}$. Calculate activation energy of it. **[Ans.** 57.775 kJ mol^{-1}]

Problem-4.18 : The reaction, $2NOCl(g) \longrightarrow 2NO(g) + Cl_2(g)$ has an E_a of 1.00×10^2 kJ/ mol and a rate constant of 0.286 L. mol^{-1} s^{-1} at 500 K. What is the rate constant of that reaction at 490K? **[Ans.** 0.17505L. mol^{-1} s^{-1}]

Problem–4.19 : The rate of a reaction at 45°C becomes double the rate of that reaction at 35°C. Calculate the activation energy of that reaction. ($R = 8.314\ JK^{-1}\ mol^{-1}$)

[Ans. 56.44 kJ mol^{-1}]

Problem–4.20 : Of the reaction, $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$; the reaction rates at 45°C and 85°C are 2.25×10^{-5} L.mol^{-1} s^{-1} and 3.75×10^{-5} L mol^{-1} s^{-1}. Calculate the activation energy of this reaction. **[Ans.** 12.1kJ mol^{-1}]

Problem – 4.21 : Of the reaction, $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$; the reaction rates at 700K and 800 K are 1.3Lmol^{-1} s^{-1} and 23.0 L.mol^{-1} s^{-1}. Calculate the activation energy of this reaction in kJ/mol unit. **[Ans.** 133.76 kJ/mol]

(2) Affect of Pressure on Reaction Rate

Pressure has no affect on the rate of reaction taking part in liquid or solid phase. But for gaseous state increase of pressure will reduce the volume. Then concentration of the reactant increases and **collision among the gas molecules also increases. For this reason the rate of reaction increases.** However, it should be remembered that the rate constant of the reaction remains unchanged. For example in the industrial manufacture of ammonia gas by Haber's synthesis process the rate of production of ammonia is increased with increase of pressure.

The equation of ammonia synthesis by Haber's process is as follows :

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

From law of mass action;

$Kp = \frac{(P_{NH_3})^2}{P_{N_2} \times (P_{H_2})^3}$; Here P_{NH_3}, P_{N_2} and P_{H_2} are the partial pressure of NH_3 gas N_2 gas, H_2 gas at equilibrium state.

Suppose at equilibrium mixture, mole fractions of each component are respectively X_{NH_3}, X_{N_2} and X_{H_2}, and total pressure of the gas mixture is P atm; then –

Partial pressure of each component gas = mole fraction × total pressure

$\therefore P_{N_2} = X_{N_2} \times P; \quad P_{H_2} = X_{H_2} \times P; \quad P_{NH_3} = X_{NH_3}, \times P.$

Putting these values in the above equation, we get :

$$Kp = \frac{(X_{NH_3} \times P)^2}{(X_{N_2} \times P) \times (X_{H_2} \times P)^3} = \frac{(X_{NH_3})^2}{X_{N_2} \times (X_{H_2})^3 \times P^2}$$

So the unit of Kp is P^{-2} such as atm^{-2} or $N^{-2}\ m^4$. As Kp is constant, with the increase of pressure (P), the mole fraction of ammonia (X_{NH_3}) must be increased and mole fractions of N_2 and H_2 must be decreased. So with the increase of pressure in gaseous reactions like ammonia synthesis, the product will be increased and hence rate of reaction increases.

Think More : In which reaction, more production is possible at lower pressure?

(a) $H_2(g) + I_2\ (g) \rightleftharpoons 2HI(g)$ (b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(c) $N_2(g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$ (d) $N_2\ (g) + O_2\ (g) \rightleftharpoons 2NO(g)$

(3) Affect of Concentration of Reactants on Reaction Rate

With the increase of concentration of the reactant molecules or ions, collision rate among molcules or ions or particles increases, hence rate of reaction increases.

$\therefore$ reaction rate α (varies as) concentration of reactant

It has been experimentally proved that the rate of reaction is proportional to the concentration of reactants. So if the concentration of reactants is high, the rate of reaction will also be high. For low concentration of reactants the rate of reaction will decrease.

Example : When sodium thiosulphate and HCI acid react; precipitation of sulphur takes place. With the increase of concentration of reactants precipitation rate of sulphur increases.

$Na_2S_2O_3\ (aq) + 2HCl\ (aq) \longrightarrow S\ (s) + 2NaCl\ (aq) + SO_2(g) + H_2O\ (l)$

The following data in the Table–4.2 proves that with the increase of concentration mol/L of sodium thiosulphate; the required time (in second) for precipitation decreases that is, reaction rate increases.

Table – 4.2 : Effect of concn. of $Na_2S_2O_3$ on precipitation reaction rate

Concentration of $Na_2S_2O_3$ (Mol/L)	0.01	0.02	0.04	0.04	0.1
Required time for complete precipitation (s) :	98	51	24	12	10

4.3.3 Activation Energy of Exothermic & Endothermic Reactions

Activation Energy : In every reaction new substance is produced. During reaction old bonds between atoms are broken and new bonds are formed with energy change. So in a reaction, reactant molecules requires a minimum energy to convert into product molecules. The minimum energy required for reactant molecules, during reaction is called **activation energy**.

Only the activated molecules can take part in the reaction and other molecules can not react till they acquire necessary activation energy. When two activated molecules come in contact with each other, they form **'transitional activated complex'**. At initial stage the reactant molecules have average potential energy E_A and average transitional activated complex has potential energy E_x; then difference between two energies $(E_x - E_A)$ is the necessary activation energy. In fig-4.3 (a,b) activation energy is shown.

* When activation energy is high then it is hardly acquired by minimum number of molecules. So rate of reaction becomes less.

* When activation energy is lower then more molecules acquire this minimum activation energy easily. So rate of that reaction becomes more.

* Reaction with lower activation energy occurs at less temperature. But reaction with high activation energy requires high temperature.

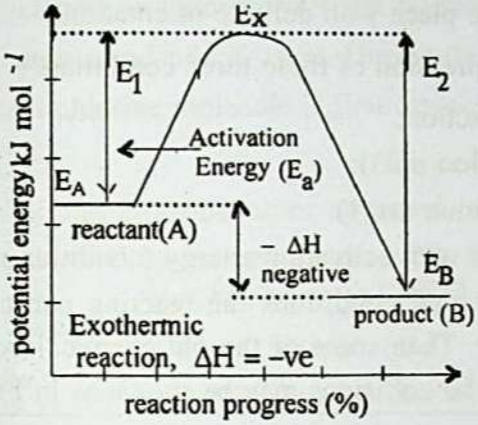


Fig- 4.3(a) : Activation Energy graph for exothermic reaction

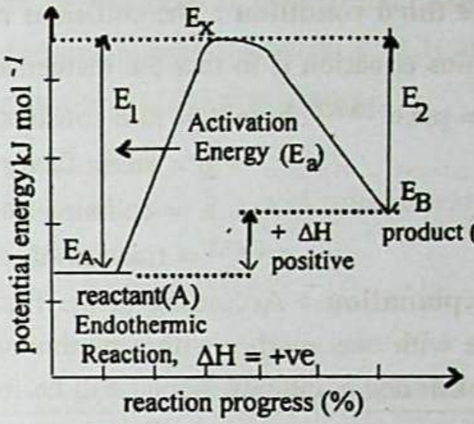


Fig- 4.3(b) : Activation Energy graph for endothermic reaction

* When potential energy of reactant (E_A) is more than that of product (E_B); then residual energy ($E_A - E_B$) comes out [fig-4.3(a)]; this type of reaction is called **exothermic reaction**.

* When potential energy of reactant (E_A) is less than that of product (E_B) i.e. product has higher energy, then required excess energy is absorbed from surroundings [fig-4.3 (b)]; this type of reaction is called **endothermic reaction**.

* The heat produced in exothermic reaction or absorbed in endothermic reaction, is called **reaction heat or enthalphy** (ΔH). In exothermic reaction, ΔH is negative and in endothermic reaction, ΔH is positive.

In exothermic reaction, the reactant molecules get more random movements and more molecules gain activation energy. So rate of exothermic reaction becomes more, the reaction completes rapidly. On the otherhand in endothermic reaction the initial potential energy of reactant is less than that of product i.e. $E_A < E_B$. So during occurance of the reaction, some amount of energy ($E_B - E_A$) is absorbed by product molecules. So temperature reduces and movement of reactant molecules also decreases. Hence the rate of endothermic reaction comparatively less.

* **Calculation of Activation Energy :** See article-4.3.2 (c), Worked example–4.4 and 4.5.

4.3.4. Collision Theory of Chemical Reaction

Collision theory was first successfully applied to explain the bimolecular reactions in gaseous phase. But later it was found to be applicable also to the reactions in solution.

For a reaction to take place :

* The first condition :	The particles (atoms, ions or molecules) taking part in a reaction must collide with one another.
* The second condition :	The collisions must take place with minimum amount of energy.

(3) The third condition : The collisions must take place with definite orientation.

Arrhenius equation is in fact the mathematical expression of these three conditions :

$k = p.z.e^{-Ea/RT}$ here, k = rate constant of a reaction;

p = steric factor (condition no.3);

z = collision rate (condition no. 1)

$e^{-Ea/RT}$ = fraction of molecules with activation energy (condition no.2)

Explanation : According to the first and second conditions the reacting particles must collide with one another with a minimum energy. Then some of the old chemical bonds will be broken down and new bonds will be formed. The collisions may be shown as in Fig. 4.4.

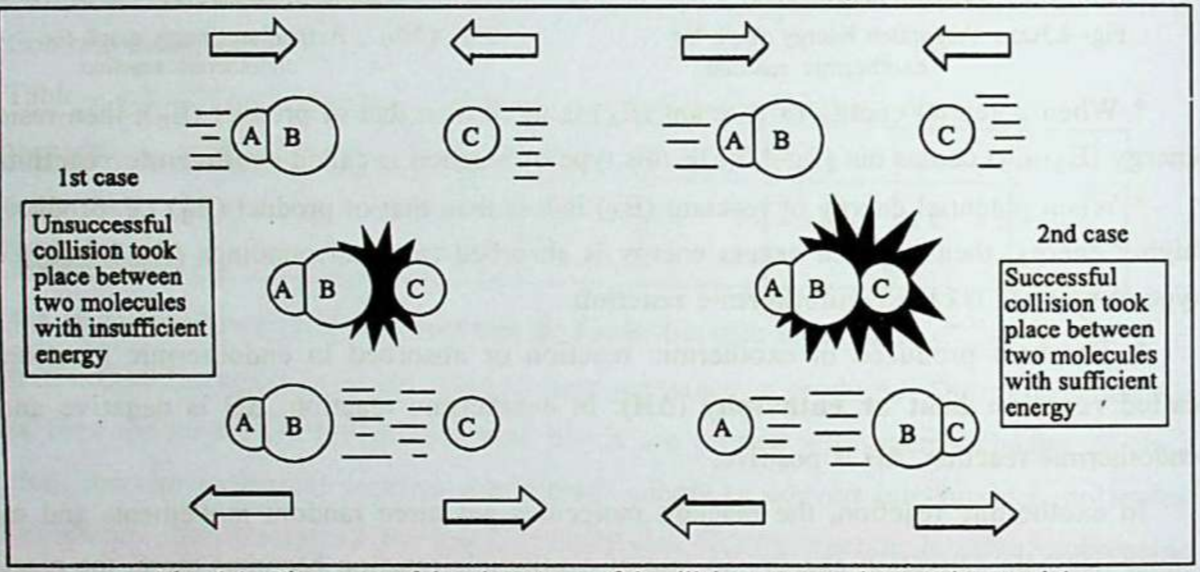


Fig- 4.4 : The successful and unsuccessful collisions among the reacting particles

From the figure it is clear that in the first case the collision took place with insufficient energy. So the breaking of old bonds between the atoms did not occur. The molecules returned to their original state. But in the second case the collision took place with sufficient energy. So the bond between A and B broke down and a new bond between B and C was formed to produce molecule BC.

According to the third condition, the collision has to take place in definite orientation. This may be explained as follows :

The attacking reactant must come in contact with the particular central atom, with which bond breaking and formation will take place in a suitable orientation. If this central atom is attached to a large group and the attacking reactant comes from that side, then the reactant will not be able to come in contact with that central atom due to the hindrance created by that large group. **The hindrance of large group to the approaching reactant is known as steric hindrance.** Avoiding this hindrance, for breaking of old bond and formation of new bond, collision should take place in proper orientation.

For example in chloroform ($CHCl_3$) molecule one carbon atom is bonded tetrahedrally to three Cl–atoms and one H-atom. During the photochemical reaction between $CHCl_3$ and Cl_2, the reactant chlorine molecule is first dissociated into two active chlorine atoms.

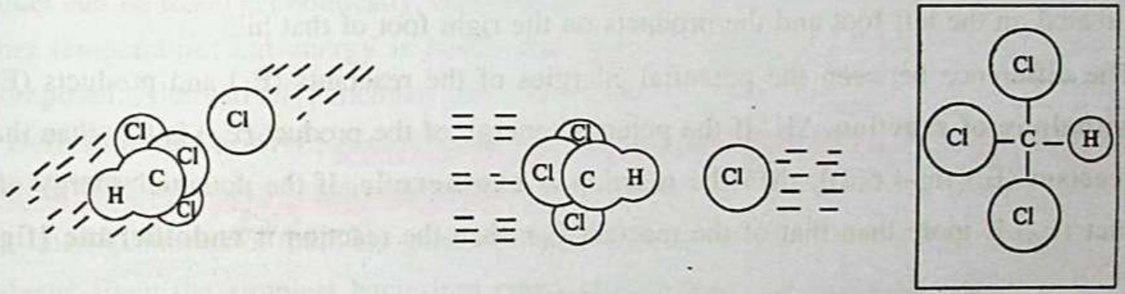
$$Cl_2 \text{ or } Cl : Cl \xrightarrow{h\vartheta} 2Cl.$$

Now if the chlorine atom approaches the chloroform ($CHCl_3$) molecule towards the suitable side of H-atom, then the reaction takes place easily.

$$Cl_3C\text{–}H + Cl\cdot \longrightarrow Cl_3C. + HCl$$

$$Cl_3C. + \dot{C}l \longrightarrow Cl_3C\text{–}Cl \text{ or } CCl_4$$

If the chlorine atom approaches the chloroform molecule towards the unsuitable side of chlorine atoms, then no reaction will take place. In fig. 4.5, collision from unsuitable side and suitable side are shown.



Collision from the side of Cl-atom (unsuitable for reaction)

Collision from the side of H-atom (suitable for reaction)

Fig. 4.5 : Collision between Cl atom and $CHCl_3$ molecule in different orientations

4.3.5 Activation Energy and Activated Complex or Transition State Theory

From the Arrhenius equation. it is clear that only those molecules can participate in a reaction, which have acquired atleast some definite higher energy than the average energy of the molecules. This excess energy necessary for particular molecule to react is known as activation energy.

Activation Energy : The difference between the average energy of reactant molecules and the necessary higher energy which a reactant molecule must possess to enable it to take part directly in a reaction is known as activation energy of the reaction. The molecules which possess atleast the amount of activation energy are called **activated molecules.**

Only the **activated molecules** can take part in the reaction and other molecules can not react till they acquire necessary activation energy. When two activated molecules come in contact with each other, they form **transitional activated complex**. Then the activated complex decomposes to the main product. For example.

$$A + BC \rightarrow AB + C$$

Here when 'A' molecule approaches 'BC' molecule, a bond between A and B gradually forms and the bond between B and C gradually becomes weak. At certain stage A, B and C form an activated complex with partial bonds, which then decomposes to AB and C.

$$\underset{\text{activated molecule}}{A} + \underset{\text{activated molecule}}{B—C} \longrightarrow \underset{\text{activated complex}}{[A......B.......C]} \longrightarrow \underset{\text{products}}{A—B + C}$$

Potential energy of the activated complex is the highest and higher than that of reactants and products. The difference of energy of the activated complex and the reactants (A + B–C) is the activation energy ΔE_1. It is evident that for the formation of products from the reactants, the reactants must overcome an energy barrier which is known as **'Energy–hill'** or **'Potential-hill'**. The activated complex is situated on top of this energy-hill and the reactants are situated on the left foot and the products on the right foot of that hill.

The difference between the potential energies of the reactants (E_1) and products (E_2) is the **enthalphy of reaction,** ΔH. If the potential energy of the product (E_p) is less than that of the reactant (E_r)[fig-4.6(a)], then the reaction is **exothermic**. If the potential energy of the product (E_p) is more than that of the reactant E_r); then the reaction is **endothermic** [fig-4.6 (b)],

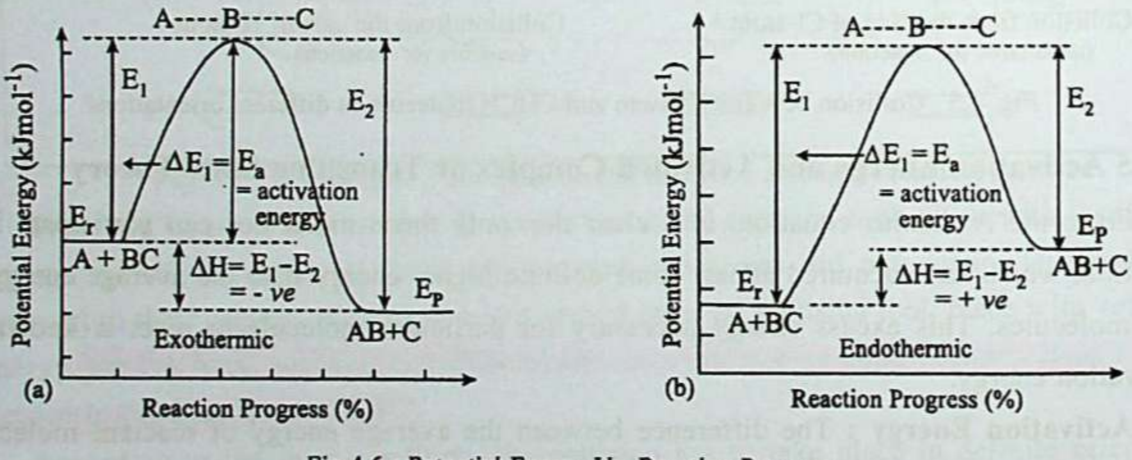


Fig-4.6 : Potential Energy Vs. Reaction Progress
[activation energy and transition activated complex state]

Then from both the diagrams, it is clear that the value of reaction enthalphy **ΔH** depends on difference between reactant potential energy (E_r) and product potential energy (E_p) and is equal to $\Delta H = (E_r - E_p) = (E_1 - E_2)$

Relation between Activation energy and Rate of reaction : The rate of a reaction is the rate of formation of its activated complex. Hence the higher is the activation energy, the lower is the rate of the reaction; and vice versa. Because if the activation energy is high, then it becomes difficult for reactant molecules to acquire this high amount of energy; then that reaction becomes slow. On the otherhand, if the activation energy is low, then many more reactant molecules can able to acquire this energy and more molecules can take part in reaction. So the rate of the reaction becomes high. So rate of a reaction is inversely proportional to the amount of activation energy.

4.4 Catalysts & Their Classification, Catalyst Promotor & Catayst Poison

From the previous discussion we have known that concentration of reactants, pressure and temperature. have affects on the rate of different reactions. Increase of temperature and pressure consume more energies in the systems.

In the industrial process for example, a higher rate often determines whether a new product can be made economically. Sometimes, we can speed up a reaction sufficiently with a higher temperature; but energy is costly and many substances are heat sensitive and easily decomposed. Alternatively, chemists can often employ a catalyst.

Definition of Catalyst : A catalyst is a substance that increases or decreases the rate of reaction without being consumed in the reaction. Because catalysts are not consumed, only very small quantities of them are generally required. Nature is the master designer and user of catalysts. Even the simplest bacterium employs thousands of biological catalyst, known as enzmes, to speed up its callular reactions. Every organism relies on enzymes to sustain its life.

The effect of catalyst on the rate of reaction is known as catalysis.

Each catalyst has its own specific way of functioning, but in general, a catalyst effects a **lower activation energy,** which in turn makes the rate constant larger and the rate higher. Two important points are associated with function of catalysts.

*A catalyst speeds up the **forward and reverse** reactions both. A reaction with a catalyst **does not produce more product** than one without a catalyst, but it produces the product **more quickly.**

* A catalyst effects a **lower activation** energy by providing a **diferent mechanism** for the reaction, a new and lower energy pathway.

(A) Classification of Catalysts :

Based on the function, the catalysts are classified into following 4 classes :

(1) Positive Catalyst : A catalyst which can accelerate the rate of a reaction, is called a positive catalyst. For example, decomposition of potassium chlorate ($KClO_3$) to KCl and O_2 gas is accelarated by a small amount of MnO_2. So here MnO_2 acts as positive catalyst.

$$2KClO_3\,(s) \xrightarrow{MnO_2,\,\Delta} 2KCl\,(s) + 3O_2\,(g)$$

(2) Negative Catalyst : A catalyst which can retard the rate of a reaction, is called a negative catalyst. For example decomposition of hydrogen peroxide (H_2O_2) is retarded by the presence of a few drops of phosphoric acid (H_3PO_4).

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g) \text{ [dissociation normal]}$$

$$2H_2O_2(aq) \xrightarrow{H_3PO_4} 2H_2O(l) + O_2(g) \text{ [dissociation retarded]}$$

(3) Auto Catalyst : When one of the products of a particular reaction can act as a catalyst for remaining reaction, then the phenomenon is known as auto–catalysis and the catalytic product is called auto-catalyst. For example, when potassium permanganate ($KMnO_4$) is added to a warm solution of oxalic acid mixed with dilute H_2SO_4, the reaction is slow at the beginning. But after some time, when some $MnSO_4$ is produced, the rate of reaction increases. Here $MnSO_4$ produced in this reaction, acts as auto-catalyst for the remaining reaction.

$$2KMnO_4 + 3H_2SO_4 + 5(COOH)_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

(4) Induced Catalyst : When a chemical reaction induces another reaction to occur, then this phenomenon is called induced catalysis and the reacting substance responsible for it is called induced catalyst. For example when O_2 is passed through the solution of sodium sulphite (Na_2SO_3) and sodium arsenite (Na_3AsO_3) separately, then Na_2SO_3 is oxidised to sodium sulphate (Na_2SO_4) but no reaction occurs with sodium arsenite. Again when O_2 is passed through a mixed solution of Na_2SO_3 and Na_3AsO_3 then both are oxidised to Na_2SO_4 and sodium arsenate (Na_3AsO_4) respectively.

Separately : $2Na_2SO_3(aq) + O_2(g) \longrightarrow 2Na_2SO_4(aq)$

$2Na_3AsO_3(aq) + O_2(g) \longrightarrow$ No reaction

On mixing : $[Na_2SO_3 + Na_3AsO_3] + O_2(g) \longrightarrow Na_2SO_4 + Na_3AsO_4$

Here the reaction of Na_2SO_3 and O_2 induces sodium arsenite to react with O_2. So here sodium sulphite (Na_2SO_3) is the induced catalyst for the second reaction.

★ **Catalyst–Promoter :** When a substance which itself does not act as catalyst, but increases the catalytic action of a catalyst, is called a catalyst promoter. For example, in Haber's process of ammonia synthesis, Fe-powder acts as catalyst. If Fe catalyst is mixed with a small amount of molybdenum powder (Mo), then catalytic activity of Fe-powder is greatly increased. Hence Mo powder acts as catalyst promoter.

$$N_2(g) + 3H_2(g) \xrightarrow{Fe,\ Mo,\ \Delta} 2NH_3(g)$$

* **Catalyst–Poison** : When a substance can reduce or even completely destroy the effectiveness of a catalyst, then it is called catalyst–poison. For example, in contact process of H_2SO_4 production, catalyst Pt is used in oxidation of SO_2 to SO_3. If arsenic oxide (As_2O_3) is present in SO_2 gas even in small amount, then catalytic action of Pt is greately reduced. So As_2O_3 is a catalyst-poison in this reaction.

$$2SO_2(g) + O_2(g) \xrightarrow{Pt,\ \Delta} 2SO_3(g)$$

(B) Classification of Catalysts : Based on the like or unlike physical state or phase of reactants, and catalysts used in the reaction, there are two general catagories of catalysts (i) homogeneous catalysts and (ii) heterogeneous catalysts. Similarly catalysis processes are of two types like (i) homogeneous catalysis and (ii) heterogeneous catalysis.

(A) Homogeneous Catalysis : When the catalyst and the reactants are in the same phase or physical state, then the catalysis is called homogeneous catalysis and the catalyst is called homogeneous catalyst.

Example :

(i) In gaseous phase : In the manufacture of sulphuric acid by chamber process, sulphur dioxide gas is oxidised by oxygen in presence of NO gas as catalyst. Here catalyst, reactants and product all are in gaseous phase.

$$2SO_2(g) + O_2(g) \xrightarrow[\Delta]{NO(g)} 2SO_3(g)$$

(ii) In liquid phase : In hydrolysis of cane sugar, mineral acid like HCl acid acts as catalyst. Here catalyst, the reactants and the products all are present in liquid state (in solution).

$$\underset{\text{sugar}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{HCl\ (aq)} \underset{\text{glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{fructose}}{C_6H_{12}O_6(aq)}$$

(B) Heterogeneous catalysis : When the catalyst and the reactants are in different physical states or phases, then it is called heterogeneous catalysis and the catalyst is called heterogeneous catalyst. Generally in most of the catalytic reactions catalysts are in solid state and the reactants and products are in liquid or gaseous state.

Example : (i) In the contact process for manufacture of H_2SO_4 acid, SO_2 gas is oxidised by oxygen to SO_3 gas with Pt powder as catalyst.

$$2SO_2(g) + O_2(g) \xrightarrow{Pt\ (solid)} 2SO_3(g)$$

(ii) One of the most important examples of heterogeneous catalysis is the addition of H_2 gas to the carbon-carbon double bonds (C=C) of organic compounds to form C–C bonds. The petroleum, plastics, food industries frequently use **catalytic hydrogenation**. The conversion of vegetable oil into margarine is one example.

The simplest hydrogenation converts ehylene to ethane in presence of metal catalyst like Ni, Pd or Pt.

$$H_2C = CH_2(g) + H_2\,(g) \xrightarrow[150\,°C]{Ni} H_3C\text{–}CH_3\,(g)$$

4.4.1 Mechanism of Catalysis

Perhaps you may be in confusion or astonished how the catalysts affect reaction rate without taking part in reactions directly :

In practice, catalysts rander their catalytic action through the different processes without their any change in atomic structures finally. The processes of catalytic actions or mechanisms are broadly of two types :

(a) Catalysis through formation of intermediate compounds : It occurs in homogeneous catalysis.

(b) Catalysis through adsorption : It occurs in heterogeneous catalysis.

(A) Homogeneous catalysis : Formation of intermediate compound : This mechanism is effective in homogeneous catalysis. In this mechanism the catalyst reacts with one reactant to form in unstable intermediate compound. This intermediate compound then reacts with other reactant to produce the final product and the catalyst is regenerated. This then again reacts in the similar way. Therefore in the first step the catalyst is consumed and in the last step, it is regenerated. So total amount of the catalyst remains unchanged.

For example; Catalysis by NO gas in oxidation of SO_2 gas by air, nitric oxide reacts first with one reactant oxygen to form nitrogen dioxide; an intermediate compound. This reacts with the second reactant sulphur dioxide to produce the final product sulphur trioxide and catalyst NO gas is regenerated, which reacts with further oxygen.

1st step : $\underset{\text{catalyst}}{2NO\,(g)} + \underset{\text{reactant-1}}{O_2\,(g)} \longrightarrow \underset{\text{inter. compd.}}{2NO_2\,(g)}$

2nd step : $\underset{\text{Inter. compd.}}{2NO_2\,(g)} + \underset{\text{reactant-2}}{2SO_2(g)} \longrightarrow \underset{\text{final product}}{2SO_3\,(g)} + \underset{\text{catalyst}}{2NO\,(g)}$

Total reaction : $2NO\,(g) + 2SO_2\,(g) + O_2(g) \longrightarrow 2SO_3\,(g) + 2NO\,(g)$

$$\text{or, } 2SO_2\,(g) + O_2\,(g) \xrightarrow{NO(g)} 2SO_3\,(g)$$

(B) Heterogeneous catalysis : Catalysis through adsorption : Heterogeneous catalysis is effective through adsorption mechanism on solid catalyst surface; here the reactant molecules are gases or liquids. The mechanism of heterogeneous catalysis is often complex.

Important steps, however, frequently imvolve as follows. With a general gaseous reaction it is explained below : $A_2\,(g) + B_2\,(g) \xrightarrow{\text{catM}} 2AB\,(g)$

Ist Step : The gaseous reactant molecules (A_2 and B_2) are first attached properly on the catalyst metal (cat M) surface ; This process is called **adsorption.**

Here the reactant molecules (A_2 and B_2) get attached with vacant d-orbitals of the metal by a weak chemical bonding forming an unimolecular layer.

2nd Step : At this adsorbed stage, the covalent bonds of the gaseous molecules become weak. With proper orientation, number of collision among the molecules increases and form activated metal complex catM–A with lower activation energy.

3rd Step : At this stage, other reactant molecule (B_2) and activated complex catM–A form product molecule (A–B) with new covalent bond residing on the metal surface then. The energy evolved from bond formation is absorbed by metal catalyst and it is transferred to reactant molecules later on.

4th or Last Step : Finally detachment of product molecules (2AB) from the catalyst metal surface occurs.

Example : Let us take the catalytic hydrogenation of compounds with C=C double bonds, a reaction used in the food industry to convert unsaturated vegetable oils to solid fats called margarine. The reaction is catalyzed by tiny particles of metals such as Ni, Pt or Pd. The hydrogenation of ethene ($CH_2{=}CH_2$) gas follows the same mechnism shown below :

In these cases, as per figure-4.7, at first the reactants molecules are adsorbed on the metal catalyst surface. At the 2nd step, adsorption facilitates the rate-determining step by breaking the strong H-H bond in the H_2 molecule. Because the H-H bond breaking is accompanied by the simultaneous formation of bonds from the separating H-atoms to the surface of metal atoms,

The activation energy for the process is lowered. The H-atoms then move about on the surface until they encounter the C-atoms of the adsorbed C_2H_4 molecule. Subsequent stepwise formation of two new C–H bonds first forming C_2H_5 group metal bonded and finally a second H-atom bonds to the C_2H_5 group to form product ethane C_2H_6 molecule. At the 4th step, the resulting C_2H_6 molecule is detached from the metal surface.

$$\text{H–H(g)} + 2\,\text{catM(s)} \longrightarrow 2\,\text{catM–H} \quad \text{[H atom is adsorbed on metal surface]}$$

$$\text{catM–H} + H_2C = CH_2\,(g) \longrightarrow H_3C - \dot{C}H_2 \text{ or } \dot{C}_2H_5$$

$$\text{catM–H} + \dot{C}H_2 - CH_3 \longrightarrow H_3C - CH_3 + \text{CatM}$$

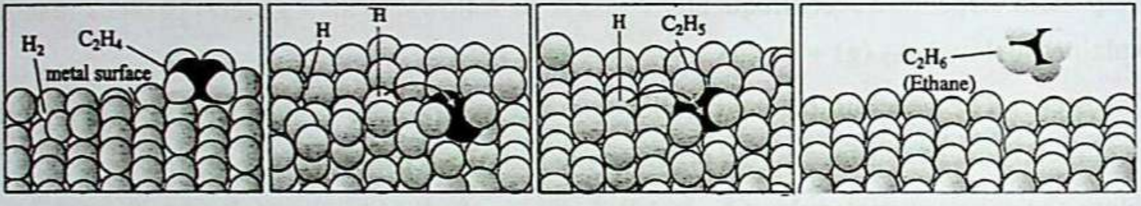


Fig 4.7 : Proposed mechanism for the catalytic hydrogenation of ethene (C_2H_4) on a metal catalyst surface. [H-atom bonded to metal surface]

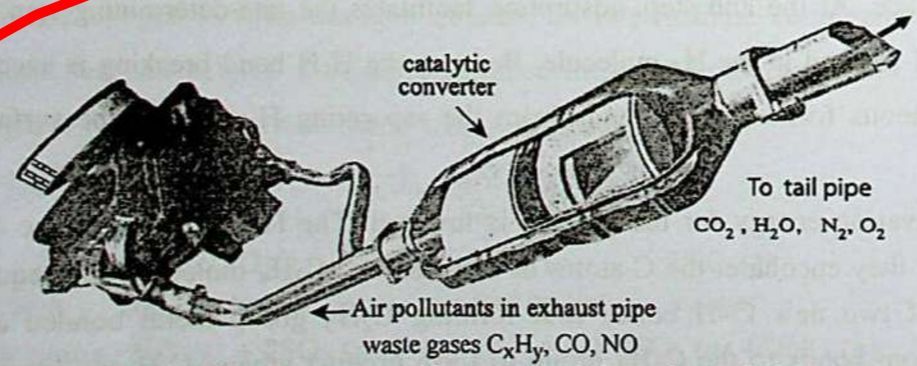
Importance of Catalysts : (1) Catalysts are enormously important, both in the chemical industry and in living organisms. (2) Nearly all industrial processes, for the manufacture of essential chemicals, use catalysts to favour the formation of specific products at lower reaction temperature, thus it reduces energy costs. (3) In environmental chemistry, catalysts such as nitric oxide (NO) play a role in the formation of air pollutants NO_2 gas. On the otherhand, metal catalysts such as platinum (Pt) in automobile catalytic converters, are potent weapons in the battle to control air pollution.

Automobile exhaust emissions contain air pollutants such as unburned hydrocarbons (C_xH_y), carbon monoxide (CO) and nitric oxide (NO) gases. Carbon monoxide results from the incomplete combustion of hydrocarbon fuels, and nitric oxide is produced when atmospheric N_2 gas and O_2 gas combine at the high temperatures present in an automobile engine. Catalytic converters help to convert the offending pollutants to carbon dioxide (CO_2) water, nitrogen and oxygen as follows :

$$C_xH_y(g) + (4 + y/4)\,O_2\,(g) \xrightarrow{Pt} xCO_2\,(g) + y/_2\,H_2O(g)$$

$$2CO(g) + O_2(g) \xrightarrow{Pt} 2CO_2\,(g);$$

$$2NO\,(g) \xrightarrow{Pt} N_2\,(g) + O_2\,(g)$$



Fig–4.8 : The exhaust gases from automobile engine and their conversion to CO_2, H_2O, N_2 and O_2 gases.

(4) Most of the catalysts used in industrial chemical processes are heterogeneous. Then such catalysts can be easily separated from the reaction products. On the otherhand, some homogeneous catalysts are used in the production of polymers. In the table –4.3 some examples for heterogeneous catalysts and homogeneous catalysts used in the various industries are shown below :

100%.

Table 4.3 : Catalysts used in Industries :

Reaction :	**catalyst**	**commercial processes**	**End-product : commercial uses**
Heterogeneous Catalysis : 1. $2SO_2 + O_2 \rightarrow 2SO_3$	Pt or V_2O_5	In contact process, H_2SO_4 manufacturing in 2nd step.	**Product :** H_2SO_4 used for fertilizers, chemicals.
2. $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$	Pt and Rh	In Ostwald process, HNO_3, production from NH_3 in 1st step	**Product :** HNO_3 used for fertilizers, plastics, dyes, explosives.
3. $N_2 + 3H_2 \rightarrow 2NH_3$	Fe, K_2O and Al_2O_3	Haber's process. NH_3 production	**Product :** NH_3 used for fertilizers and HNO_3.
4. $CH_4 + H_2O \rightarrow CO + 3H_2$	Ni catalyst	Steam-hydrocarbon reforming process, H_2 gas synthesis.	**Product :** H_2-gas used for NH_3, methanol production.
Homogeneous Catalysis : 1. Propylene, oxidizer	Mo (VI) complexes	Propylene oxide synthesis	**Product :** Propylene oxide used for polyester, polyurethane foams.
2. Butadiene, HCN	Ni/P compounds	Adiponitrile production	**Used :** nylons, fibre, plastic

4.4.2 Activation Energy of Catalyzed Reaction

The activation energy diagram of a non-catalyzed and a catalyzed reactions are shown in Fig. 4.9. It is seen from the figure that the activation energy of the catalyzed reaction is less than that of the non-catalyzed reaction. The explanation is that the energy of activated complex in a non-catalyzed reaction is high and the formation of this complex is difficult. So the reaction is slow.

With catalyst the whole reaction proceeds through another route. The energy of the activated complex in this route is low and it is formed easily. So the catalyzed reaction is fast. Hence an alternate definition of catalyst is given as follows :

Catalyst : A catalyst for a reaction is a substance which provides an alternate route for that reaction, in which the activation energy is less than that of the non-catalyzed reaction.

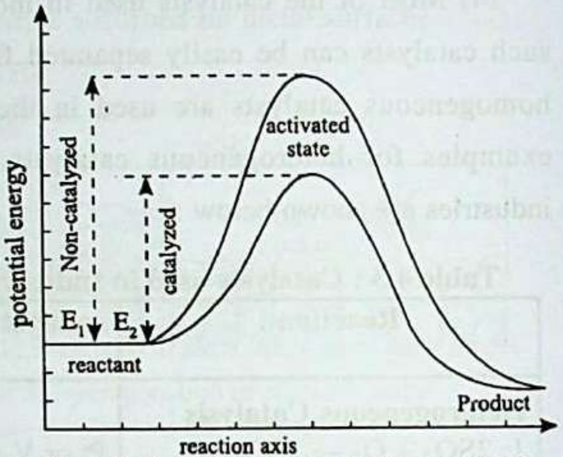


Fig 4.9 : Activation energy of a catalyzed and non-catalyzed reactions

4.4.3 Bio-Catalyst, Enzyme

Definition : Enzymes are complex nitrogen containing organic compounds with very high molecular masses secreted by living plant and animal cells. They are globular proteins. They are very active organic catalysts. Many complex reactions take place in plants and animals under the influence of different enzymes. Enzymic activity occurs on particular reaction.

How enzyme acts : There are some active sites in enzyme molecules. Due to these sites enzymes acquire the power of catalysis. Each enzyme is active for one particular organic reaction. When the size and shape of a reactant molecule becomes similar to active site and shape of the enzyme, then the reactant molecule (S) is engulfed in active site of the enzyme (E). Thus activated complex (E–S) is formed. At this stage product complex (E–P) is formed by bond weakening. Finally the product molecule (P) is released by breaking product complex. Thus catalysis continues.

$$E + S \overset{\text{fast}}{\rightleftharpoons} E\text{–}S \longrightarrow E - P \xrightarrow{\text{slow}} E + P$$

Some enzyme-catalyzed reactions are mentioned below :

(1) An enzyme named 'diastase' converts starch by hydrolysis into maltose sugar.

$$\underset{\text{starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{diastase}} \underset{\text{maltose}}{n\,C_{12}H_{22}O_{11}}$$

(2) The enzyme 'maltase' converts maltose sugar by hydrolysis into glucose.

$$\underset{\text{maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{maltase}} \underset{\text{glucose}}{2C_6H_{12}O_6}$$

(3) The enzyme 'zymase' dissociates glucose into ethanol and CO_2 gas

$$\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow{\text{zymase}} \underset{\text{ethanol}}{2C_2H_5OH} + 2CO_2$$

(4) The enzyme 'eurease' converts urea by hydrolysis to ammonia and CO_2 gas.

$$\underset{\text{urea}}{H_2NCONH_2} + H_2O \xrightarrow{\text{eurease}} 2NH_3 + CO_2$$

Characteristics of a Catalyst :

(i) A catalyst does not participate directly in the reaction. Hence it remains unchanged in composition and mass at the end of the reaction.

(ii) A small quantity of catalyst is sufficient to effect large quantity of the reactants.

(iii) A catalyst does not initiate or stop a reaction, it only accelerates or retards a reaction and does not disturb other catalysts.

(iv) A catalyst is generally specific for a particular reaction.

(v) Catalyst generally lowers the activation energy of a reaction.

4.5 Chemical Equilibrium

Definition : When the rate of a forward reaction is equal to that of the backward reaction, then the state is known as chemical equilibrium.

Example : When a mixture of H_2 gas and iodine is heated to a temperature, 450°C in a sealed container, then hydrogen and iodine react to form hydrogen iodide. Since with the increase of time the amounts of hydrogen and iodine decrease, then the rate of this reaction gradually decreases.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Initially there was no hydrogen iodide, so there was no backward reaction. But when the forward reaction starts to form HI and gradually its amount increases, the backward reaction *i. e.* dissociation of HI into H_2 and I_2 begins to occur. After some time the rates of forward and backward reactions become equal. This state of both the reactions is called **chemical equilibrium.**

Again if we heat pure hydrogen iodide in a sealed container, similar situation arises.

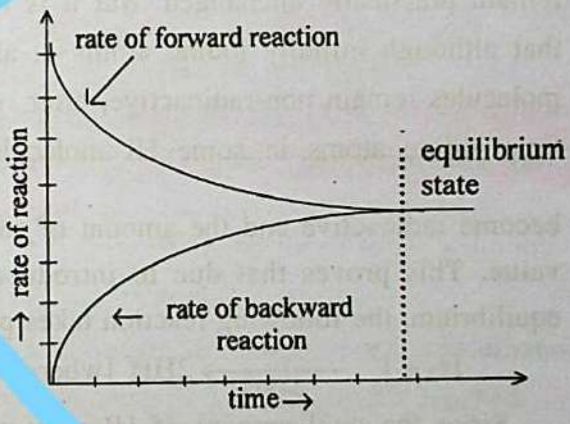


Fig. 4.10. Change of rates of forward and backward reactions with time and attainment of chemical equilibrium

Then the dissociation of hydrogen iodide to hydrogen and iodine is the forward reaction and formation of hydrogen iodide from hydrogen and iodine is the backward reaction.

$$2HI(g) \overset{\Delta}{\rightleftharpoons} H_2(g) + I_2(g)$$

At one stage the chemical equilibrium will be reached when the rates of these two reactions (forward and backward) will be same. In both the cases at equilibrium the ratio of these substances will be the same. This is the condition of equilibrium.

~~**Expt. No.– 02**~~

~~**Name of Expt. : Determination of pH of branded toothpastes and their useability.**~~

~~**Date** .... **Time.** ....~~

~~**A.** **Aim :** To know if different branded tooth pastes contain pH properly.~~

~~**B.** **Required substances :** 1. Different branded toothpastes such as pepsoden, White plus, Colgate.~~

~~**C.** **Required Apparatus :** (i) Beaker, (ii) Glass rod, (iii) wash bottle, (iv) p^H meter. (v) Universal Indicator strips or solution.~~

~~**D.** **Procedure :** Follow the procedure of Expt. No-1~~

~~**E.** **Experimental Data :**~~

~~Sample of tooth paste~~	~~pH of the branded sample~~	~~Approved pH value~~	~~Sample's pH more/less~~	~~Comment on expt. Result~~
~~1. Brand-1~~ ~~2. Brand-2~~ ~~3. Brand-3~~	~~1. 8~~ ~~2. 8~~ ~~3. [illegible]~~	~~8~~	~~1. normal~~ ~~2. normal~~ ~~3. more~~	~~Brand-1, 2 mantain normal pH. Useable for all. Brand 3 has more pH, so it is not for baby.~~

~~**Expt. No. 03** : Determination of pH of cold cream/snow of different brands.~~

~~Follow above two **Expt. No. 1 and 2** and do this experiment in group with the guidance of teacher.~~

4.18 Law of Conservation of Mass and Energy

We know from laws of chemical combination that in every chemical reaction, the total mass of the reactants is equal to total mass of the product after the completion of the reaction. This is known as conservation of mass in chemical reaction. Because the different atoms present in the reactant molecules with different bonds break their old bonds to form new molecules known as product, with new bonds among those atoms with the exchange of heat energy in reaction conditions. Here during the chemical process, the atoms change their relative positions practically with new bond formation.

Every chemical reaction occurs with exchange of heat energy. **Hence every chemical reaction is associated with law of conservation of mass** of the atoms and also the **conservation of the energy** of the atoms bonded in reactant and product molecules.

When any chemical reaction occurs, then heat energy is absorbed or produced. Moreover, that change of energy may be in the form of light or any other way. But in every case, conservation of energy change must occur.

The change of energy in chemical reaction is discussed in first law of Thermodynamics.

The law of conservation of energy is stated as follows :

'**Energy is transformed from one form to another, but it can not be created or destroyed.**' This law is applicable to every chemical reaction. For example, Methane burns in oxygen to form carbon di-oxide, water and heat energy.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) + 890.3 \text{ kJ}$$

Here, the heat energy produced from burning of methane, is called **internal energy** of substance. Depending on internal energy of reactant and product, heat is produced or absorbed during the occurrence of any chemical reaction. So the **chemical reactions are classified into two classes.**

(i) **Exothermic Reaction** and (ii) **Endothermic Reaction.**

In exothermic reaction, the internal energy of the product is less than that of reactant. Again, in endothermic reaction the internal energy of the product (E_p) becomes more than internal energy of the reactant (E_r). This change of internal energy in exothermic reaction and endothermic reaction is shown with a symbol, ΔH known as enthalpy change or hat change by enthalpy diagram in figure–4.29 (A), 4.29 (B)

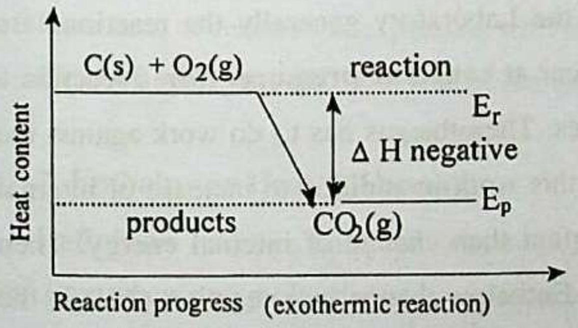


Fig 4.29 (A) exothermic reaction, $E_r > E_p$

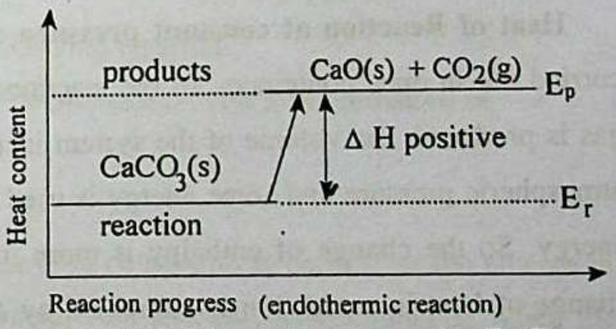


Fig 4.29 (B) endothermic reaction $E_r < E_p$

Internal energy : Every substance contains some energy; it is stored as potential energy and kinetic energy. The total energy stored in a substance is called **internal energy** of that substance. Internal potential energy is due to the relative positions of ions, atoms or molecules in different bond formation and in crystalline lattice.

Again internal kinetic energy is the sum of different forms of kinetic energies stored in atoms or molecules such as translational energy, rotational energy and vibrational energy, electronic energy etc.

The internal energy expressed by 'E' depends on the nature of the substance, temperature and pressure. When a substance absorbs heat from surroundings, its internal energy increases, also its temperature increases. Similarly when a substance gives up energy to surroundings, its internal energy decreases, also its temperature decreases. The internal energy (E) of a substance cannot be measured, but its changes (ΔE) can be measured.

At constant pressure the change of internal energy (ΔE) in a chemical reaction is expressed as : $\Delta E = E_p - E_r$; here the symbol 'Δ' is pronounced as 'delta' means measurable.

Enthalpy : Enthalpy or heat content is a thermodynamic function, which is the sum of internal energy of a system and product of pressure and volume change of system. It is denoted by 'H' and is given by : $H = E + P \times \Delta V$.

Where E is the internal energy, P is the pressure and ΔV is the volume change of the system.

When solid or liquid is heated its volume does not increase appreciably. But when a gas at constant pressure is heated its volume increases to a great extent. So the heat supplied at constant pressure (q_p) is used partly to increase the internal energy (ΔE) and partly for doing the work for expansion of the volume (ΔV). Here both the changes are expressed together by the term enthalpy change, ΔH. Then we can write :

$q_p = \Delta E + P\Delta V = \Delta H$; or, $q_p = \Delta H$ Here, $P\Delta V$ = work done for volume expansion .

Heat of Reaction at constant pressure : In the Laboratory generally the reactions are carried out in open containers, so the reactions occur at **constant pressure.** If in a reaction a gas is produced, the volume of the system increases. Then the gas has to do work against the atmospheric pressure and some energy is used for this work in addition to increase of internal energy. So the change of enthalpy is more important than change of internal energy. Then change of heat in a reaction is expressed by ΔH. Enthalpy change in a reaction (ΔH) is the difference of enthalpy of the products (H_p) and reactants (H_r).

$\therefore\ \Delta H = H_p - H_r$

When a reaction occurs in closed container, there is no increase of volume during absorption of heat then, $\Delta V = 0$; and $\Delta E = \Delta H$. For example, in case of solids and liquids the expansion of volume is negligible ($\Delta V = 0$), and for gaseous reactions, when more numbers of reactants and products are equal.

We know, $\Delta H = H_p - H_r$; if $H_p > H_r$, then ΔH is positive. Then the reaction is endothermic and the products are less stable than reactants. At that stage, if gaseous reaction occurs, then mole number of products is greater than that of reactants.

If $H_p < H_r$, then ΔH is negative. Then the reaction is exothermic and the products are more stable than reactants. Here if gaseous reaction occurs, then mole number of products is less than that of reactants.

4.18.1 Different Types of Enthalpy Change or Heat Change

There is a change of enthalpy in those processes, in which heat is evolved or absorbed. These processes may be physical change or chemical change. So there are many types of enthalpy changes.

(1) Important enthalpy changes in chemical process are : (i) enthalpy of formation. (ii) enthalpy of combustion. (iii) enthalpy of decomposition. (iv) enthalpy of neutralisation etc.

(2) Important enthalpy changes in physical processes are : (i) enthalpy of sublimation. (ii) enthalpy of fusion. (iii) enthalpy of vapourisation. (iv) lattice enthalpy etc.

1. Heat of reactions :

Definition : The change in enthalpy which occurs in a reaction according to the balanced equation in proper mole ratio of the related reactants, is called the **heat of reaction.** For example, H_2 gas and Cl_2 gas react in the 1 :1 mole ratio to form 2 moles of HCl gas and evolves 184 kJ heat.

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \qquad \Delta H = -184 \text{ kJ}$$

Here heat of reaction is expressed with the following equation :

Heat of reaction, $\Delta H°$ = [Heat of formation of products] – [Heat of formation of reactants]

2. Enthalpy or Heat of Formation

Definition : The enthalpy or heat of formation of a compound is defined as the change in enthalpy when one mole of that compound is formed from its constituent elements. When the reaction is carried out at standard condition (at 25°C and I atm pressure), the enthalpy change is called **standard enthalpy of formation.** It is denoted by H_f^θ. For example :

When carbon and oxygen react, they produce CO_2. The enthalpy change of the reaction (ΔH) at 25°C or 298 K and 1 atm pressure is -393.5 kJ mol^{-1}.

$$C(s) + O_2(g) \longrightarrow CO_2(g); \qquad \Delta H_f^\theta = -393.5 \text{ kJ}$$

By definition, enthalpy of formation of element is zero.

$\therefore$ Enthalpy change in reaction, ΔH = [Enthalpy of CO_2] – [Enthalpy of C + Enthalpy of O_2]

$$= H_f(CO_2) - [H_f(C) + H_f(O_2)]$$

$$= H_f(CO_2) - [0 + 0];\ [\because H_f \text{ of element is zero}]$$

$$= H_f(CO_2)$$

[Here 'H_f' means enthalpy of formation]

Since enthalpy change of above reaction, $\Delta H = -393.5$ kJ; So enthalpy of formation of CO_2, $H_f = -393.5$ kJ.

Hence the standard enthalpy of formation of CO_2 is – 393.5 kJ mol^{-1}.

So, **enthalpy of formation of a compound can be calculated from the enthalpy of reaction.**

Calculation of Enthalpy of Reaction from Enthalpy of Formation

Enthalpy of a reaction can be easily calculated from enthalpy of formation of reactants and products with the help of the following equation.

Enthalpy of a reaction = [Total enthalpy of formation of products] –
[Total enthalpy of formation of reactants]

For example, At STP the enthalpy of formation of $CO_2(g)$ and $H_2O(l)$ are – 393.5 $kJmol^{-1}$ and – 286 $kJmol^{-1}$. The enthalpy of combustion of liquid ethanol is– 1367 kJ mol^{-1}. Calculate the enthalpy of formation of liquid ethanol.

Here, the thermochemical reaction for combustion of ethanol may be written as follows :

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l);\ \Delta H = -1367 \text{ kJ}$$

Here, Enthalpy of reaction = [Total enthalpy of formation of products] –
[Total enthalpy of formation of reactants]

$$\therefore \Delta H = [2 \times H_f(CO_2) + 3 \times H_f(H_2O)] - [H_f(C_2H_5OH) + 3 \times H_f(O_2)]$$

$$\text{Or, } -1367 \text{ kJ} = [2 \times (-393.5) + 3 \times (-286)] \text{ kJ} - [H_f(C_2H_5OH) - 0] \text{ kJ}$$

$$\text{Or, } -1367 \text{ kJ} = [-787 - 858 - H_f(C_2H_5OH)] \text{ kJ}$$

$$\text{Or, } H_f(C_2H_5OH) = [1367 - (787 + 858)] = [1367 - 1645] = -278 \text{kJ}$$

$\therefore$ Standard enthalpy of formation of ethanol is – 278 $kJmol^{-1}$.

3. Enthalpy of Sublimation Definition :

Definition : Enthalpy of sublimation of a substance is defined as the change in enthalpy when one mole of that solid substance becomes vapour directly on heating. It is denoted by

ΔH°_{subl}. **Example :** When one mole of solid iodine sublimes, it absorbs 62.3 kJ heat, so its enthalpy of sublimation is + 62.3 kJ. Similary enthalpy of sublimation of potassium is + 90 kJ mol^{-1}.

$I_2(s) \longrightarrow I_2(g)$; $\Delta H^\circ_{subl} = +62.3 \text{ kJ mol}^{-1}$

$K(s) \longrightarrow K(g)$; $\Delta H^\circ_{subl} = +90 \text{ kJ mol}^{-1}$

$C(graphite) \longrightarrow C(g)$; $\Delta H^\circ_{subl} = +712.02 \text{ kJ mol}^{-1}$

Heat or Enthalpy of Melting or Fusion :

Definition : The amount of heat needed to melt one mole of solid substance to its liquid is called its heat of melting or fusion (ΔH°_f)

The heat of fusion of ice is + 6 kJ mol^{-1}

$H_2O(s) \longrightarrow H_2O(l)$ $\Delta H^\circ = +6 \text{ kJ mol}^{-1}$

4. Heat of vapourization :

The amount of heat needed to vapourize one mole of a substance at its boiling point, is called heat of vapourization of that substance. It is denoted by ΔH°_{vap}.

$H_2O(l) \longrightarrow H_2O(vap)$ $\Delta H^\circ_{vap} = +44.0 \text{ kJ mol}^{-1}$

$C_6H_6(l) \longrightarrow C_6H_6(vap)$ $\Delta H^\circ_{vap} = +31.37 \text{ kJ mol}^{-1}$

On the otherhand, the amount of heat given out or evolved, when one mole of vapour of a substance is condensed to its liquid, is called its **heat of condensation.** It is opposite to that of vapourization; but the value of ΔH°_{condn} is negative

$H_2O(vap) \longrightarrow H_2O(l)$ $\boxed{\Delta H^\circ_{condn} = -44.0 \text{ kJ mol}^{-1}}$

5. Heat of Atomization : The amount of heat absorbed by one mole of a substance to convert into its atoms, at gaseous state is called its heat of atomization (ΔH°_{atom}).

$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$ $\Delta H^\circ_{atom} = +121 \text{ kJ mol}^{-1}$

Note, here it means per mote of chlorine atom, but not per mole of chlorine molecule.

6. Enthalpy of Solution or Heat of Solution :

The enthalpy or heat of solution of a solute is defined as the change in enthalpy of the system, when 1 mole of solute is dissolved in sufficient amount of solvent, so that further dilution of that solution produces no more change of enthalpy. Generally 200 – 450 mole solvent is sufficient for 1 mole solute for this purpose.

If any reaction occurs between the solvent and solute, then the heat of solution is negative, i.e, the dissolution is an exothermic process. On the other hand if no reaction occurs between the solvent and solute, then the heat of solution is generally positive, i.e. heat is absorbed during the dissolution.

For example, when the solute forms hydrate with water then ΔH is negative. e.g., anhydrous $CuSO_4$ forms a penta hydrate with water, so the heat of solution of anhydrous copper sulphate in water is negative. It is denoted by ΔH°_{soln}.

$$CuSO_4(s) + aq \longrightarrow CuSO_4.5H_2O(aq); \quad \Delta H^\circ_{soln} = -66.04 \text{ kJ}$$

Similarly anhydrous $CaCl_2$ forms a hexahydrate with water, so the heat of solution of anhydrous $CaCl_2$ is negative.

$$CaCl_2(s) + aq \longrightarrow CaCl_2.6H_2O(aq); \quad \Delta H^\circ_{soln} = -75 \text{ kJ}$$

But hydrated $CaCl_2$ does not form any more hydrate in water, so its heat of solution is positive.

$$CaCl_2.6H_2O(s) + aq \longrightarrow CaCl_2.6H_2O(aq); \quad \Delta H^\circ_{soln} = +19.06 \text{ kJ}$$

7. Heat of Neutralization :

The amount of heat produced in neutralization reaction between acid and base to form one mole of water at room temperature (25°C, 298K), is called heat of neutralization. Neutralization reaction is an exothermic reaction.

For example, at 25°C one mole dilute HCl acid reacts with one mole dil. NaOH to produce one mole water with elimination of 57.34 kJ heat.

$$\underset{1\text{mol}}{HCl(aq)} + \underset{1\text{mol}}{NaOH(aq)} \longrightarrow NaCl(aq) + \underset{1\text{ mol}}{H_2O(l)}; \ \Delta H^\circ rxn = -57.34\text{kJ}$$

4.19 Heat of Neutralization of Strong acid and Strong base

(A) Heat of neutralization of strong acid and strong base is constant and it is – 57.34 kJ approx. In aqueous solution strong acid like HCl acid and strong base like NaOH are completely ionized as follows :

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq); \ NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

When a strong acid reacts with a strong base, the cation of the base and the anion of the acid remain unchanged, they are called **spectator ions**. In reality the hydrogen ion (H^+) of the acid and the hydroxide ion (OH^-) of the base combine to produce water.

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

The heat of reaction between strong acid and strong base is, in fact, the heat of this ionic reaction. Hence in all cases heat of neutralization value is the same.

(i) Neutralization reaction between NaOH and HCl

$$(Na^+ + OH^-) + (H^+ + Cl^-) \longrightarrow (Na^+ + Cl^-) + (H^+ + OH^-) = Na^+ + Cl^- + \boxed{H_2O}$$

(ii) Neutralization reaction between KOH and HNO_3 :

$$(K^+ + OH^-) + (H^+ + NO_3^-) \longrightarrow (K^+ + NO_3^-) + (H^+ + OH^-) = (K^+ + NO_3^-) + \boxed{H_2O}$$

So heat of neutralization of strong acid and strong base is the heat of reaction of 1 mol H^+ ion and 1 mol OH^- ion to form 1 mol of water (H_2O) and heat of this reaction is – 57.34 kJ approximately.

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \qquad \Delta H = -57.34 \text{ kJ}$$

In the following table 4.1 the heats of neutralisation of some strong acids with some strong bases have been mentioned. They are practically constant.

75%.. ionize

Table 4.1 : Heat of neutralization of some strong acids with strong bases at 25°C

Acid		**Strong base**	**Heat of Neutralization (kJ)**
HCl	(Strong)	NaOH	– 57.34
H_2SO_4	(Strong)	NaOH	– 57.44
HNO_3	(Strong)	NaOH	– 57.35
HCl	(Strong)	KOH	– 57.43
CH_3COOH	(weak)	NaOH	–55.14
HF	(weak)	NaOH	– 68.60

★ **Exceptions :** Between acids and bases, when any one of the two is weak then their heat of neutralization is less than standard value – 57.34 kJ mol^{-1}

(B) Heat of neutralization of weak acid and strong base is less than – 57.34 kJ.

Acetic acid (CH_3COOH) is a weak acid. So its decimolar solution ionizes about 5% only. But NaOH is a strong base; it ionizes about 100% in decimolar solution. Practically it is found that the heat of neutralization of CH_3COOH with NaOH is about –55.14 kJ. This is because in aqueous solution acetic acid is partially ionized.

During the neutralization reaction acetic acid is gradually ionized and some energy (about 2.2 kJ) is used up for this ionization. Hence the heat of neutralization is numerically less by this amount from the ideal value (–57.34 kJ).

$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$ [5% ionizes in aqueous soln.]

$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$ [100% ionizes in aq. soln.]

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$

(C) Heat of neutralization of strong acid and weak base :

If the base is weak like NH_4OH, it is incompletely ionized and during the neutralization process it becomes fully ionized. Therefore some energy is used up in this process. Hence the heat of neutralization of strong acid with weak base is numerically lower than – 57.34 kJ. e.g.

$$\underset{\text{weak base}}{NH_4OH(aq)} + \underset{\text{strong acid}}{HCl(aq)} \rightleftharpoons NH_4Cl(aq) + H_2O(l); \qquad \Delta H = -51 \text{ kJ}$$

If both the base and the acid are weak, then more energy is needed for the complete ionization of both acid and base and hence the heat of neutralization becomes numerically more lower than – 57.34 kJ e.g.

$$\underset{\text{weak base}}{NH_4OH(aq)} + \underset{\text{weak acid}}{CH_3COOH(aq)} \rightleftharpoons CH_3COONH_4(aq) + H_2O(l); \quad \Delta H = -44 \text{ kJ}$$

*** (D) Heat of neutralization of HF acid and NaOH is more than – 57.34 kJ.**

The explanation for excess heat of neutralization of HF acid and NaOH is the summation of general value of heat of neutralization together with excess hydration energy of fluoride (F^-) ion.

(i) Firstly hydrofluoric acid (HF) ionises 16% and sodium hydroxide (NaOH) ionize completely in aqueous solution. So hydrogen ion (H^+) and hydroxide ion (OH^-) neutralize together in molar proportion producing one mole of water with the evolution of heat by less than –57.34 kJ.

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq) \qquad \text{[about 16\% ionization]}$$

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq) \qquad \text{[100\% ionization]}$$

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

(ii) Secondly as the size of fluoride (F^-) ion is the smallest negative ion; its charge density is more. Therefore association of F^- ion with water molecules is closest and strong; so its hydration energy is maximum. Hence, hydration energy of F^- ion is a little bit more than any other negative ions. So excess hydration energy of F^- ion is added up to neutralization value. As a result the summation of heat energy becomes – 68.6 kJ.

$$HF(aq) + NaOH(aq) \longrightarrow Na^+(aq) + F^-(aq) + H_2O(l) \qquad \Delta H = -68.6 \text{ kJ}$$

It is to be noted that due to the association of positive ion and negative ion with water molecules in aqueous solution and thereby the energy liberated is called the **hydration energy of ion.**

Students Work – 4.15 : Heat of Neutralization Based :

Problem –4.52(a) : Heat of neutralization of strong acid and strong base is constant; explain. [D. B. 2015; J. B. 2015]

Problem –4.52(b) : Heat of neutralization of HF acid and NaOH is more than constant value; explain why. [D. B. 2015]

Problem –4.52(c) : Heat of neutralization of weak acid (CH_3COOH) and strong base (NaOH) is less than – 57.34 kJ; explain. [R. B. 2016; J. B. 2016; Di. B. 2016]

Problem –4.53(a) : (1) 0.1M HCl + 0.1M NaOH; (2) 0.1MHF + 0.1M NaOH; whether heat of neutralization of mixture.(1) and (2) will be same? explain. [C. B. 2017]

Problem –4.53(b) : (1) KOH + HNO_3; (ii) NaOH + HF; Between mixture.(1) and (2) which will have more heat of neutralization; explain. [Ctg. B. 2017]

Problem –4.53(c) : (1) 1M NaOH + 1M H_2SO_4; (2) 1M NaOH + 0.1MCH_3COOH; explain the cause of difference in heat of neutralization between mixture (1) and (2). [Syl. B. 2017]

Problem –4.53(d) : HCl + NaOH $\rightarrow$ NaCl + H_2O; $\Delta H = -57.34$kJ. Here if HCl acid is replaced by HF acid, discuss change of ΔH value of that reaction. [Madrasa. B. 2017]

4.20 Bond Energy and Heat of Reaction

Bond Energy : When a chemical bond is formed between the atoms, some energy is released. The same amount of energy will be needed to break the bond. This amount of energy associated with bond formation is called bond energy and is a measure of the strength of that bond.

Definition : The amount of energy required to break one mole of a bond of a particular type between two atoms in the gaseous state is called bond energy or enthalpy of that bond. Bond enthalpy is expressed in kJ mol^{-1} unit.

For example, if X–Y bond present in one mole of a compound is broken down and H_b kilo joule amount of energy is needed in this process, then the bond energy or bond enthalpy of X–Y bond is H_b kJ mol^{-1}. $X{-}Y(g) \longrightarrow X(g) + Y(g); \quad \Delta H = H_b \text{ kJ mol}^{-1}$

For exmaple, 435 kJ amount of energy is needed to break H–H bonds present in one mole of H_2 molecules. So the H–H bond energy or bond enthalpy is 435.5 kJ mol^{-1}.

$$H_2(g) \longrightarrow 2H(g) ; \qquad \Delta H = 435.5 \text{ kJ mol}^{-1}$$

For example, the bond energy of C–H bond is 430 kJ mol^{-1}. This value does not change appreciably in CH_4, CH_3Cl, C_2H_6 etc. The average bond energies of some bonds have been listed in Table 4.7

From these bond enthalpy values, not only the stability or instability of a compound can be ascertained, but also the heat of all types of reactions can be calculated.

Heat of Reaction : Heat of reaction includes all types of reactions such as exothermic reactions and endothermic reactions, which include heat of formation, heat of combustion, heat of decomposition, heat of neutralization etc.

Table 4.7 : Average bond energy

Bond	kJ mol $^{-1}$
H—H	435.5
H—F	564
H—Cl	433
H—Br	366
H—I	299
C—H	430.53
C—Cl	328
Cl—Cl	242.9
O=O	498.4
O—H	462.5
N—H	391
C—C	344
C=C	615
C≡C	812
C=C	724

Calculation of Bond Energy : The bond energy is defined as the amount of energy required to break one mole of particular bond between to atoms in the gaseous state of a compound. Bond energy is calculated from (i) sublimation energy, (ii) energy of atomization, (iii) energy of formation and (iv) number of bonds. When a compound contains more than one type of bonds, then the average bond energy is calculated as follows :

Average bond energy = Total bond dissociation energy ÷ total bond number

∴ Bond energy=[sublimation energy+atomization energy–bond formation energy] ÷ bond numbers

For example, let us calculate the C–H bond energy in the methane (CH_4) molecule. Here the following enthalpy changes occur :

(1) $C(graphite) \longrightarrow C(g)$; Sublimation energy of graphite, $\Delta H = 717.02$ kJ

(2) $2H_2(g) \longrightarrow 4H(g)$; Atomization energy of H_2, $\Delta H = (2x\ 435.5) = 871.0$ kJ

(3) $2H_2(g) + C(g) \longrightarrow CH_4(g)$; Formation energy of CH_4, $\Delta H = -75.09$ kJ

∴ For bond dissociation of CH_4; $CH_4(g) \xrightarrow{\Delta} C(g) + 4H(g)$

∴ Bond dissociation energy of CH_4, ΔH = (Sublimation energy + atomization energy – energy of formation of CH_4)

$= (717.02 + 871.0 - (-75.09) = 1663.11$ kJ

So, C–H bond energy = $(1663.11 \div 4)$ kJ [∴ 4 bonds in CH_4]

$= 415.78$ kJ mol^{-1}

Again the compounds which contain C–H bond together with C–O, C–C bonds or other bonds, their bond energy can be calculated for those cases, with the following equation :

Bond energy : ΔH = Sublimation energy of graphite (C) + Atomization energy of all other elements– Formation energy of compound – (C–H bond energy × C–H bond numbers)

Calculation of Heat of Reaction from Bond energy : In all compounds, the bond energy of a particular bond is approximately same. Depending on this fact, we can calculate bond energy of a particular bond by subtracting bond energies of product from the total bond energies of reactants.

This method is commonly used for the covalent bonded gaseous organic compounds.

Heat of Reaction = (Heat of formation of reactants) – (Heat of formation of products)

For example, heat of reaction of the following reaction can be calculated with use of bond energies : $CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(l) + HCl(g)$; $\Delta H = ?$

Here, we know C–H bond energy = 430.53 kJ mol^{-1}

Cl–Cl bond energy = 242.90 kJ mol^{-1}, and C–Cl bond energy = 328 kJ and H–Cl bond energy = 433 kJ mol^{-1},

Bond energies of reactants and products are as follows :

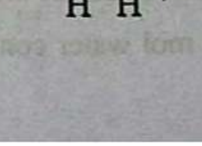
Reactants,	kilo Joul, (kJ)	Products	kilo Joule (kJ)
4 C–H	4× 430.53	3 C–H	3× 430.53 = 1291.59
1 Cl–Cl	=1722.12	1 C–Cl	328.00
	242.90	1 H–Cl	433.00
Total bond energies of reactants :	= 1965.02	Total bond energies of products :	= 2052.59

∴ Heat of reaction; $\Delta H = (1965.02 - 2052.59) = -87.57$ kJ mol^{-1}

Worked Example-4.69 : The heat of sublimation of carbon is 717 kJ mol^{-1}, the heat of atomization (or dissociation) of H_2 molecule is 435.5kJ mol^{-1}, C–C bond enthalphy is 343.9kJ mol^{-1} and C–H bond enthalpy is 430.5 kJmol^{-1}. Calculate the heat of formation of ethane (C_2H_6).

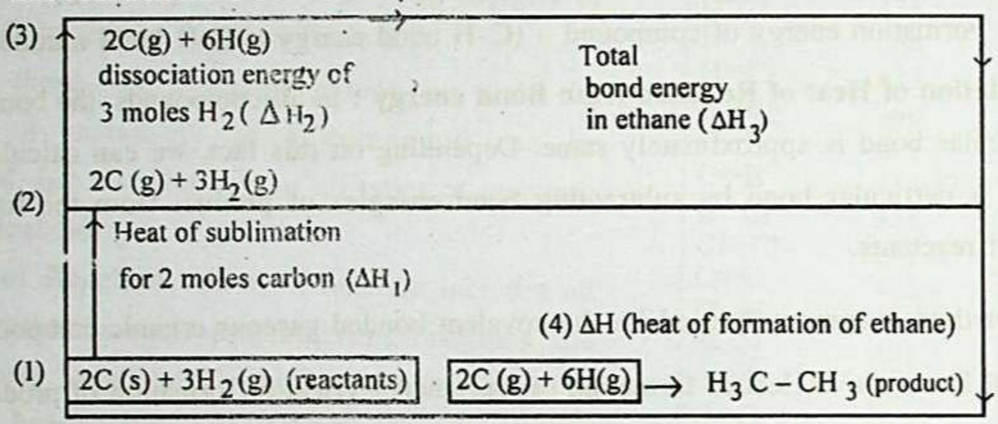
Solution : The reaction for the formation of ethane is as follows :

$2C(s) + 3H_2(g) \longrightarrow C_2H_6(g)$ or $H_3C–CH_3(g)$



Let heat of the reaction or heat of formation of ethane be ΔH.

In this case 2 moles carbon sublime, 3 moles H–H bonds are broken down and one mole C–C bond and six mole C–H bonds are formed. In the following enthalpy diagram different routes for this reaction have been shown.



According to Hess's Law, from this enthalpy diagram we get :

$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$ [Here ΔH_1 and ΔH_2 are positive and ΔH_3 is negative. From the data given, we see;

ΔH_1 = Heat of sublimation of 2 moles carbon = 717 × 2 = 1434 kJ (positive)

ΔH_2 = Heat of dissociation of 3 moles H_2 gas = 435.5 × 3 = 1306.5 kJ (positive)

In ethane molecule there are one C–C bond and six C–H bonds formed.

Hence $\Delta H_3 = (343.9 \times 1 + 430.5 \times 6) = 2936.9$ kJ (negative)

$\therefore \Delta H = (1434 + 1306.5 - 2936.9) = -196.6$ kJ

Ans. Heat of formation of ethane = -196.6 kJ mol^{-1}

Worked Example–4.70 : Calculation of Bond–energy from Heat of Reaction :

Calculate bond–energy of O–H bond from following reaction enthalpy or heat :

$H_2(g) \longrightarrow 2H(g)$; $\Delta H = 104$ kcal (i)

$O_2(g) \longrightarrow 2O(g)$; $\Delta H = 120$ kcal (ii)

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g)$, $\Delta H = -58$ kcal .....(iii)

Solution : Dividing eqn. (ii) by 2, $\frac{1}{2}O_2(g) \longrightarrow O(g)$, $\Delta H = 60$ kcal (iv) Adding (i) and (iv) eqn, $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow 2H(g) + O(g)$, $\Delta H = (104 + 60) = 164$ kcal ...... (v)

Writing eqn. (iii) oppositely, $H_2O(g) \longrightarrow H_2(g) + \frac{1}{2}O_2(g)$, $\Delta H = 58$ kcal (vi)

Adding (v) and (vi) eqn, $H_2O(g) \longrightarrow 2H(g) + O(g)$, $\Delta H = 222$ kcal

Two O–H bonds are present in one molecule water (H_2O).

So 1 mol water contain 2 mol O–H bonds.

Hence to break 2 mol O–H bonds energy required = 222 kcal.

∴ to break 1 mol O–H bonds energy required = 111 kcal.

So, O–H bond energy = 111 kcal mol^{-1}.

Note that, 1 kcal = 4.186 kJ energy.

Worked Example–4.71 : Calculation of Heat of Reaction from Bond-Energy :

Bond energy of H–H, O=O and O–H are respectively 434.7, 493.24 and 463.98 kJ mol^{-1}. Calculate heat of reaction : $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O$.

Solution : From given equation, it is clear that in this reaction; 2 O–H bonds form after breaking 1 H–H bond and $\frac{1}{2}$ (O=O) bond.

∴ Heat of reaction, $\Delta H = -2\,\Delta H\,(O\text{–}H) + \Delta H\,(H\text{–}H) + \frac{1}{2}\,\Delta H\,(O{=}O)$ ....(i)

Given, $\Delta H\,(O\text{–}H) = 463.98\ kJmol^{-1}$, $\Delta H\,(H\text{–}H) = 434.7\ kJmol^{-1}$

$\Delta H\,(O{=}O) = 493.24\ kJmol^{-1}$.

∴ From eqn (i), we get, $\Delta H = (-2 \times 463.98) + 434.7 + (\frac{1}{2} \times 493.24) = -246.64\ kJmol^{-1}$.

∴ Heat of reaction = – 246.64 J mol.

4.20.1 Standard Heat or Enthalpy of Formation

Definition : The standard heat or enthalpy of formation of a compound is the change in heat at standard states like 298K temp and 1atm pressure, when one mole of that compound is formed from its constituent elements. It is denoted by $H°_{f.}$ For example,

At 25°C and 1 atm pressure when carbon and oxygen react to form CO_2 gas. Here heat produced, is 393.5 kJ.

$$C\,(s) + O_2\,(g) \longrightarrow CO_2(g);\ \Delta H° = -393.5\ kJmol^{-1}$$

Here Heat of reaction = Heat of formation of CO_2 compound = $H°_{f.}$

∴ $H°_{f.}$ = [Enthalpy of formation of CO_2] – [Enthalpy of C + Enthalpy of O_2]

or, $H°_{f.} = [H(CO_2) - H(C) - H(O_2)]$; here 'H' means enthalpy of formation of each substance.

Worked Example–4.72 : At standard state, heat of formation of CO_2 (g) and H_2O (*l*) are respectively – 393.5 kJ and – 286 kJ. At 25°C combustion heat of liquid ethanol is – 1366.9 kJ; then calculate heat of formation of liquid ethanol.

Solution : Thermochemical combustion reaction of ethanol is written as :

$C_2H_5OH\,(l) + 3O_2(g) \longrightarrow 2CO_2\,(g) + 3H_2O\,(l);\ \Delta H = -1366.9\ kJ$

Enthalpy or heat of reaction, ΔH = [Enthalpy of product] – [Enthalpy of reactant]

$\therefore\ \Delta H = [2 \times H(CO_2) + 3 \times H(H_2O)] - [H(C_2H_5OH) + 3 \times H(O_2)]$

$= [2 \times H(CO_2) + 3 \times H(H_2O)] - [H(C_2H_5OH) + 0]$

$= [2 \times H(CO_2) + 3 \times H(H_2O)] - H\ (C_2H_5OH)$ ... ... (1)

Given, $H(CO_2) = -393.5kJ$ and $H(H_2O) = -286kJ$, $\Delta H = -1366.9$ kJ

Suppose, $H(C_2H_5OH) = xkJ$

Now putting different values in equation (1), we get :

$-1366.9 = [2 \times (-393.5) + 3 \times (-286]-x)]kJ$

$-1366.9 = (-787 - 858 - x)$ kJ

$x = (-787 - 858 + 1366.91)$ kJ $= (-1645 + 1366.9)$ kJ

$\therefore\ x = -278.1$ kJ

So standard heat or enthalpy of formation of liquid ethanol = – 278.10 kJ.

Worked Example–4.73 : Calculate heat of formation of acetylene from followings and give analysis whether it is exothermic or endothermic. :

(1) $C\,(s) + O_2\,(g) \longrightarrow CO_2(g);\quad \Delta H = -393.5$ kJ

(2) $H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O(l);\quad \Delta H = -286$ kJ

(3) $C_2H_2\,(g) + \frac{5}{2}O_2\,(g) \longrightarrow 2CO_2(g) + H_2O\,(l);\quad \Delta H = -1304$ kJ

Solution : From eqn. (1) and (2), heat of formation of CO_2, H_2O are – 393.5 and – 286 $kJmol^{-1}$. Suppose, heat of formation of acetylene = x $kJmol^{-1}$

We know, Heat of reaction, ΔH = (enthalpy of product) – (enthalpy of reactant)

∴ From equation (3), we get :

$\Delta H = [2 \times H(CO_2) + H(H_2O)] - [HC_2H_2 + \frac{5}{2} \times H(O_2)]$

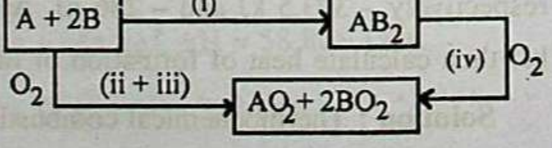
or, $-1304 = [2 \times (-393.5) + (-286)]\ kJ - \left[x + \frac{5}{2} \times 0\right]$ kJ

or, $-1304 = [-787.0 - 286]kJ - xkJ$

or, $x = [-1073.0 + 1304]kJ = +231kJ$, ∴ Heat of formation of acetylene = + $231kJmol^{-1}$

Analysis : Here calculated heat of formation of acetylene is positive. So it is an endothermic reaction,

Worked Example 4.74 : Combustion enthalpy of A, B and AB_2 are respectively – 394.55 kJ, – 594.78 KJ and – 1109.17kJ. Calculate ΔH_f of AB_2 from the given flow diagram :



Solution : Reactions of different steps with value of ΔH :

(ii) $A + O_2 \longrightarrow AO_2;$ $\Delta H = -\ 394.55 kJmol^{-1};$

(iii) $2B + 2O_2 \longrightarrow 2BO_2;$ $\Delta H = -\ 594.78 kJmol^{-1};$

(iv) $AB_2 + 3O_2 \longrightarrow AO_2 + 2BO_2$ $\Delta H = -\ 1109.17\ kJmol^{-1};$

From given diagram and question, main product is AB_2

Now writing equations with (iv) as reverse and other two as follows :

(1) $AO_2 + 2BO_2 \longrightarrow AB_2 + 3O_2;$ $\Delta H = +\ 1109.\ 17 kJmol^{-1};$

(2) $A + O_2 \longrightarrow AO_2;$ $\Delta H = -\ 394.55\ kJmol^{-1};$

(3) $2B + 2O_2 \longrightarrow 2BO_2$ $\Delta H = -\ 594.78\ kJmol^{-1};$

Adding (1), (2), (3) equations, we get :

$$AO_2 + 2BO_2 + A + O_2 + 2B + 2O_2 \longrightarrow AB_2 + 3O_2 + AO_2 + 2BO_2;\ \Delta H = 119.84\ kJ\ mol^{-1}$$

Excluding like components from both sides, we get –

$\therefore A + 2B \longrightarrow AB_2;$ $\Delta H = 119.84\ kJmol^{-1}$

$\therefore$ Heat of formation of AB_2, $H^\circ_{f.} = 119.84\ kJmol^{-1}$.

Worked Example–4.75 : Calculation of Heat of Reaction from Heat of Formation :

Oxyacetylene welding torches burn acetylene gas (C_2H_2). Heat of formation of $C_2H_2(g)$, $H_2O(g)$ and $CO_2(g)$ are $-\ 227.4\ kJ\ mol^{-1}$, $-241.8\ kJ\ mol^{-1}$ and $-393.5\ kJ\ mol^{-1}$ respectively. Calculate the standard heat of combustion of acetylene to produce $CO_2(g)$ and $H_2O(g)$.

Strategy : Write the appropriate balanced equation and then use the given data.

Solution : The balanced equation is :

$2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(g),$ $\Delta H = ?$

Putting the heat of formation of related compounds in the following equation :

Heat of reaction, ΔH° = [Heat of formation of products] –

[Heat of formation of reactants]

$\therefore \Delta H^\circ = [4\Delta H^\theta_f\ (CO_2) + 2\Delta H^\theta_f\ (H_2O)] - [2\Delta H^\theta_f\ (C_2H_2)];\ [\therefore \Delta H^\theta_f(O_2) = 0]$

$= (4\ mol) \times\ (-393.5\ kJ/mol) + (2\ mol) \times (-241.8\ kJ/mol) - (2\ mol) \times (-227.4\ kJ/mol)$

$= -\ 1602.8\ kJ$

From equation, for 2 mol acetylene heat energy = – 1602.8 kJ

$\therefore$ For 1 mol acetylene heat energy = $(-1602.8 \div 2) = -\ 801.4 kJ$

Worked Example– 4.76 : Two hydrocarbons P and Q each containing two C-atoms respectively are sp^3 and sp^2 hybridised. Here standard heat of formation of compound Q, CO_2, $H_2O\ (l)$ are respectively – 84, – 393 and – 220 $kJmol^{-1}$. Standard combustion heat of compound P is – 1370 $kJmol^{-1}$. [Ctg. B. 2016]

(a) Calculate standard heat of formation of hydrocarbon P of stem.

(b) Which of P and Q compounds will be a better fuel; explain mathematically.

Solution : (a) Calculation of heat of formation of P hydrocarbon :

As per stem, hydrocarbon with two C–atoms sp^3 hybridised is C_2H_6

From question, heat of combustion of C_2H_6 or P = – 1370 $kJmol^{-1}$

Equation of combustion of C_2H_6 is :

$$C_2H_6\ (g) \quad + \quad \frac{7}{2}O_2\ (g) \quad \longrightarrow \quad 2CO_2\ (g) \quad + \quad 3H_2O(g)$$

$$\text{or, } 2C_2H_6\ (g) \quad + \quad 7O_2\ (g) \quad \longrightarrow \quad 4CO_2\ (g) \quad + \quad 6H_2O(g)$$

Heat of formation ($\Delta H^\circ_{f.}$) of C_2H_6 is calculated from its heat of combustion;

Heat of reaction, ΔH° = (Heat of formation of products)– (Heat of formation of reactants).

$$\therefore\ 2 \times (-\ 1370)\ kJ = [4\Delta H^\circ_f\ (CO_2) + 6\Delta H^\circ_f\ (H_2O)] - [2\Delta H^\circ_f\ (C_2H_6) + 0]$$

$$\therefore\ 2\ \Delta H^\circ_{f.}(C_2H_6) = 2 \times 1370\ kJ + 4 \times (-393)\ kJ + 6 \times (-\ 220)\ kJ$$

$$2\ \Delta H^\circ_{f.}(C_2H_6) = (2740 - 2892)\ kJ = -\ 152\ kJ$$

$$\therefore\ \Delta H^\circ_{f.}(C_2H_6) = (-\ 52 \div 2)\ kJ = -\ 76\ kJmol^{-1}$$

$\therefore$ Standard heat of formation of C_2H_6 = – 76 $kJmol^{-1}$

Solution–(b) : Which of P and Q compounds is a good fuel?

As per given stem, sp^3 hydridised two C–atoms' hydrocarbon is C_2H_6 and sp^2 hybridised two C–atoms' hydrocarbon is C_2H_4. Heat of combusion of C_2H_4 is to be calculated from given data. Combustion equation of C_2H_4 is :

$$C_2H_4\ (g) + 3O_2 \longrightarrow 3CO_2(g) + 2H_2O(g)$$

$$\therefore\ \Delta H = 2\Delta H\ (CO_2) + 2\Delta H\ (H_2O) - \Delta H(C_2H_4) + 0$$

$$\text{or, } \Delta H = 2\times (-393)\ kJ + 2\times (-220)\ kJ + 84\ kJ$$

$$\text{or , } \Delta H = (-\ 786 - 440 + 84)\ kJ = (-\ 1226 + 84)\ kJ$$

$$\text{or, } \Delta H = -\ 1142\ kJ$$

Again gram molecular manss of C_2H_4 = 28g

∴ Heat produced from 28g C_2H_4 combustion = 1142kJ

∴ Heat produced from 1.0g C_2H_4 combustion = (1142 ÷ 28) = $\boxed{40.7\ \text{kJ/g}}$

From question, heat of combustion of C_2H_6 = – 1370 kJmol^{-1}

Gram molecular mass of C_2H_6 = 30g

∴ Heat produced from 30g C_2H_6 combustion = 1370 kJ

∴ Heat produced from 1.0g C_2H_6 combustion = (1370 ÷ 30) = $\boxed{45.7\ \text{kJ/g}}$

So from 1.0g of P and Q, heat produced are respectively 45.7 kJ and 40.7 kJ. Between two hydrocarbons, as a good fuel C_2H_6 is better,

Student's Work–4.16 : Heat of Reactions Based :

Problem–4.54(a) : Combustion reactions of carbon disulphide (CS_2), carbon and sulphur are the followings : [C. B. 2017]

(i) $CS_2(s) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g)$ $\Delta H = -1060.4$ kJ

(ii) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -393.5$ kJ

(iii) $S(s) + O_2(g) \longrightarrow SO_2(g)$; $\Delta H = -296.1$kJ

(a) As per reaction (ii) of stem, how many litre of O_2 is required at STP to produce 1200 kJ heat? **[Ans.** 68.31 LO_2**]**

(b) Calculate heat of formation of CS_2 using data of given stem and explain the reaction of CS_2 formation is an exothermic or endothermic reaction.

[Ans : $\Delta H = +74.7$ kJmol^{-1} endothermic**]**

Problem-4.54(b) : Standard heat of combustion of acetic acid, carbon and hydrogen are –871.5 kJ, –393. 7 kJ and – 285.85 kJ. Calculate the heat of formation of acetic acid from these data. **[Ans:** – 487.6 kJ mol^{-1}**]**

Problem-4.54(c) : Heat of combustion of C_2H_5OH (*l*), C(s) and H_2(g) are respectively –1367kJ mol^{-1}, – 393.5 kJ mol^{-1} and – 285.85 kJ mol^{-1} Calculate the heat of formation of ethanol. **[Ans.** – 62.2 kJ mol^{-1}**]**

Problem-4.54(d) : The heat of combustion of methane (CH_4) is – 890.3 kJ mol^{-1}. Calculate the amount of mass of methane needed to produce 1335.45 kJ heat and also calculate the volume of oxygen in litre needed for that reaction at STP.

[Ans. 24 g CH_4; 67.2L O_2 gas**]**

Problem–4.55 : The standard heat of formation of $CH_4(g)$, $C_2H_6(g)$, $CO_2(g)$ and $H_2O(g)$ are – 74.89, – 84.52, – 393.30 and –220.20 kJ mol^{-1} respectively. From this given data, calculate which of the gases CH_4 and C_2H_6, will be better as a fuel value and explain why.

[**Ans.** Heat of combustion of $CH_4 = -47.43$ kJ/g; that of $C_2H_6 = -45.42$ kJ/g. So CH_4 is more useful.]

Problem-4.56(a) : Calculate the heat of reaction ΔH° in kilojoules for the synthesis of lime (CaO) from limestone ($CaCO_3$), an important step in the manufacture of cement. The heat of formation of $CaCO_3(s)$, CaO(s) and $CO_2(g)$ are –1207.6 kJ/mol, –634.9 kJ/mol and –393.5 kJ/mol respectively. [**Ans.** 179.2 kJ; reaction is endothermic.]

Problem-4.56(b) : Calculate the heat of reaction of preparation of ethylene (C_2H_4) from acetylene (C_2H_2). Here the combustion enthalpies of acetylene, H_2 gas, and ethylene are – 1299 kJ/mol, –286.18 kJ/mol and –1411 kJ/mol respectively. [**Ans.** –174.18 kJ]

4.21 Lavoisier and Hess's Laws

There are two thermo chemical laws which are based on 1st law of thermo dynamics or law of conservation of energy. They are as follows :

(1) Lavoisier and Laplace's Law

(2) Hess's Law of constant heat summation

(1) Lavoisier and Laplace's Law

The first law of thermo chemistry expressed by Lavoisier and Laplace in 1780 is as follows :

'The change of enthalpy in a reaction is exactly equal to the change of enthalpy of the reaction in the opposite direction, but their signs of enthalpy changes are opposite'.

Example-1 : In the preparation of one mole of CuO from copper metal and gasous oxygen 157 kJ heat is evolved.

$$Cu(s) + 1/2\, O_2(g) \xrightarrow{\Delta} CuO(s) \qquad \Delta H = -157 \text{ kJ}$$

In the opposite reaction, that is decomposition of CuO, same amount of heat is absorbed.

$$CuO(s) \xrightarrow{\Delta} Cu(s) + 1/2\, O_2(g); \qquad \Delta H = +157 \text{ kJ}$$

So all thermo chemical equations can be reversed, then the sign of the heat change is also reversed, but its numerical value remains constant. Here the values of ΔH in two reactions are equal but opposite in signs.

To explain the opposite signs of the change of enthalpy is the bond formation and bond dissociation, the two opposite reactions. In the first case, to form CuO molecule, bond formation between Cu atom and O atom occurs, bond formation is an exothermic reaction. In the second case, to dissociate CuO molecule into its elements, absorption of heat energy is required, it is an endothermic reaction which is opposite of exothermic. So in every case change of heat is 157 kJ numerically.

(2) Hess's Law of constant heat summation

Russian scientist G.H. Hess (1840) put forward an important thermo chemical law, which is known by his name. **Hess's Law of constant heat summation is as follows :**

If a reaction can take place by single step or several steps, the overall change in enthalpy is the same which ever route is followed with same initial reactants and final products.

In other words, the net enthalpy change in a reaction does not depend on the path by which the reaction takes place.

Explanation : Let us suppose that a reactant 'A' may be converted to a product 'C' through two different paths or routes. These reactions with enthalpy changes have been shown in fig 4.30.

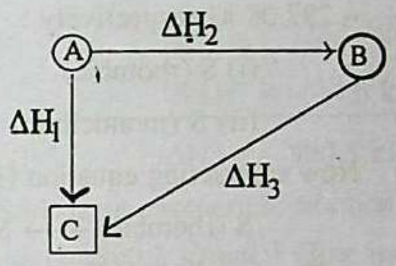


Fig.4.30 : Explanation of Hess's Law with enthalpy diagram.

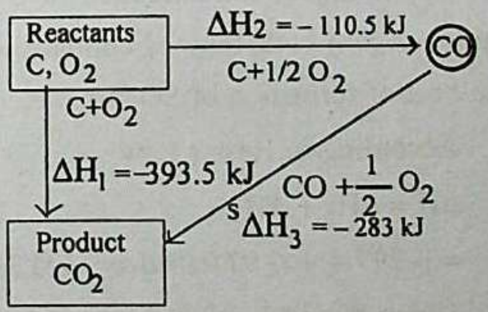
(i) Ⓐ $\xrightarrow{\Delta H_1}$ $\boxed{C}$: (by single step)

(ii) Ⓐ $\xrightarrow{\Delta H_2}$ Ⓑ $\xrightarrow{\Delta H_3}$ $\boxed{C}$: (by two steps)

So according to Hess's Law we get :

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

Example : CO_2 gas may be prepared from carbon and oxygen in single step and in two steps :



Single step reaction :

$C(s) + O_2(g) \longrightarrow CO_2(g); \Delta H_1 = -393.5$ kJ

Double steps reactions :

(i) $C(s) + 1/2\ O_2(g) \longrightarrow CO(g); \Delta H_2 = 110.5$ kJ

(ii) $CO(g) + 1/2\ O_2(g) \longrightarrow CO_2(g)\ ; \Delta H_3 = 283.0$ kJ

Adding (i) and (ii) we get the single step reaction :

$$C(s) + O_2(g) \longrightarrow CO_2(g); (\Delta H_2 + \Delta H_3) = [-110.5 + (-283.0)] = -393.5\text{kJ}$$

$$\therefore \Delta H_1 = (\Delta H_2 + \Delta H_3) = -393.5 \text{ kJ}$$

Thus we see that both in single step and in double steps reactions, the enthalpy change is the same. That is the algebric sum of enthalpy changes of multiple steps is equal to the enthalpy change in a single step of a reaction.

4.21.1 Application of Hess's Law

There are many applications of Hess's Law. Here addition, subtraction and multiplication processes can be applied in thermochemical equations. Some applications are discussed below:

(1) Determination of enthalpy of slow reactions : Some reactions are so slow that their heat changes or enthalpies cannot be determined by any experiment. For example the conversion of rhombic sulphur to monoclinic sulphur is so slow that heat of this reaction can not be determined experimentally. But the heat of combustion of both types of sulphur can be determined. Using these data and Hess's law we can calculate the heat of conversion of rhombic sulphur to monoclinic sulphur.

Heat of combustion of rhombic sulphur and monoclinic sulphur are – 296.79 kJ and – 297.08 kJ respectively :

(i) $S\ (\text{rhombic}) + O_2(g) \longrightarrow SO_2(g) \quad \Delta H_1 = -296.79\ \text{kJ}$

(ii) $S\ (\text{monoclinic}) + O_2(g) \longrightarrow SO_2(g) \quad \Delta H_2 = -297.08\ \text{kJ}$

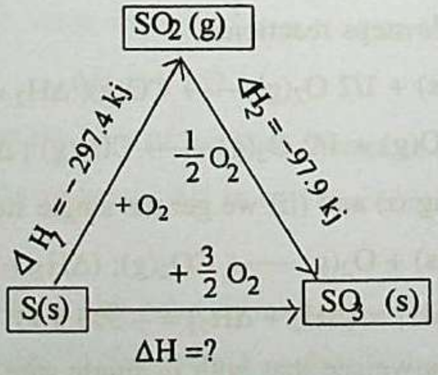
Now subtracting equation (ii) from (i), we get :

$$S\ (\text{rhombic}) \longrightarrow S\ (\text{monoclinic}) \qquad \Delta H = +\,0.29\ \text{kJ}$$

∴ To convert rhombic sulphur to monoclinic sulphur + 0.29 kJ heat will be absorbed.

(2) Determination of Heat of Formation : There are many cases where the heat of formation can not be determined by the calorimetric method. In such cases the heat of formation can be determined by an indirect method and that is based on Hess's Law i.e algebraic summation of heat of reactions.

For example, the oxidation of S into SO_2 has the heat of formation, $\Delta H_1 = -297.4$ kJ mol^{-1}. Again enthalphy of combustion of SO_2 forming SO_3 is $\Delta H_2 = -\,97.9$ kJ mol^{-1}. Now the heat of formation of SO_3 from element S and O_2 can be calculated in the following way :



According to Hess's Law :

$\Delta H = \Delta H_1 + \Delta H_2$

$= [-297.4 + (-97.9)]\ \text{kJ} = -395.3\ \text{kJ}$

The same result can be derived by means of thermochemical calculations :

(i) Conversion of S to SO_2 :

$S(s) + O_2(g) \longrightarrow SO_2(g);\ \Delta H_1 = -\,297.4\ \text{kJ}$

(ii) Conversion of SO_2 to SO_3 : $SO_2(g) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g);\ \Delta H_2 = -97.9\ \text{kJ}$

Adding equations (i) and (ii), we get,

$S(s) + \frac{3}{2} O_2(g) \longrightarrow SO_3(g)$; $\Delta H = (\Delta H_1 + \Delta H_2) = (-297.4 - 97.9)$ kJ $= -395.3$ kJ

$\therefore$ Heat of formation of $SO_3(g)$ is $- 395.3$ kJ.

Worked Example– 4.77 : On combustion of natural gas methane with O_2 gas CO_2 and water are produced. Using following given data, calculate heat of combustion of methane.

$CH_4(g) + O_2(g) \longrightarrow HCHO(g) + H_2O(g)$ $\quad \Delta H^\circ = - 275^\circ 6$ kJ

$HCHO(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$ $\quad \Delta H^\circ = - 526^\circ 7$ kJ

$H_2O(g) \longrightarrow H_2O(l)$ $\quad \Delta H^\circ = - 44.0^\circ$ kJ

Strategy : Hess's Law is to be used here

Solution :

$CH_4(g) + O_2(g) \longrightarrow HCHO(g) + H_2O(g)$ $\quad \Delta H^\circ = - 275.6$ kJ

$HCHO(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$ $\quad \Delta H^\circ = - 526.7$ kJ

$2[H_2O(g)] \longrightarrow H_2O(l)]$ $\quad 2[\Delta H^\circ = - 44.0$ kJ

Adding, $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ $\quad \Delta H^\circ = - 890.3$ kJ

$\therefore$ Heat of conbustion of CH_4, $\Delta H^\circ = - 890.3$ kJ. mol^{-1}. So it is an exothermic reaction.

Worked Example–4.78 : Heat of combustion of methane is -890.3 $kJmol^{-1}$ How much O_2 in gram will be needed for comustion of CH_4 to produce 1500 kJ heat?

Solution : Equation of CH_4 combustion with O_2 is :

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$; $\quad \Delta H = - 890.3$ kJ

1 mol $\quad$ 2mol $= 2 \times 32g$

From equation, 890.3 kJ heat is produced from burning methane with 64g O_2

$\therefore$ 1500 kJ heat is produced from burning methane with $\frac{64 \times 1500}{890.3}$ g $= 107.8288g$ O_2

Student's Work – 4.17 : Hess's Law Based :

Problem-4.57 : Calculate the enthalphy change for conversion of graphite carbon to diamond with the help of the following data. **[Ans. 1.9 kJ/mol]**

(i) $C\ (graphite) + O_2(g) \longrightarrow CO_2(g)$; $\quad \Delta H_C = -393.4$ kJ/mol

(ii) $C\ (diamond) + O_2(g) \longrightarrow CO_2(g)$; $\quad \Delta H_C = -395.4$ kJ/mol.

Problem-4.57(a) : The industrial degreasing solvent methylene chloride (CH_2Cl_2) is prepared from methane by reaction with chlorine;

$CH_4(g) + Cl_2(g) \longrightarrow CH_2Cl_2(g) + 2HCl(g)$

Use the following data to calculate ΔH° in kilojoules for preparation of CH_2Cl_2 :

$CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$; $\quad \Delta H^\circ = -98.3$ kJ

$CH_3Cl(g) + Cl_2(g) \longrightarrow CH_2Cl_2(g) + HCl(g)$; $\quad \Delta H^\circ = -104$ kJ $\quad$ **[Ans. –202 kJ]**

Problem– 4.58 (b) : During discharging of Lead-acid battery following reactions occur :

$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$

Calculate discharging enthalpy from following two reactions :

(i) $Pb(s) + PbO_2(s) + 2SO_3(l) \longrightarrow 2PbSO_4(s)$; $\Delta H^\circ = -775$ kJ

(ii) $SO_3(l) + H_2O(l) \longrightarrow H_2SO_4(aq)$; $\Delta H^\circ = -113$ kJ [**Ans.**. – 549 $kJmol^{-1}$]

Problem–4.58 (c) : Calculate heat of combustion of $C_6H_{12}O_6$:

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$$

Given, $\Delta H^\circ_{f.}$ of $C_6H_{12}O_6 = -1275.0$ kJ, $\Delta H^\circ_{f.}$ of $CO_2 = -393.5$kJ, $\Delta H^\circ_{f.}$ of $H_2O(l) = -285.85$ kJ, $\Delta H^\circ_{f.}$ of $O_2 = 0$. [**Ans.** – 2801 $kJmol^{-1}$ of glucose]

Problem–4.58 (d) : Equation of NO_2 synthesis is as follows :

$$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g); \Delta H = ?$$

Calculate heat of formation of NO_2 from following two reactions

$N_2(g) + O_2(g) \longrightarrow 2NO(g)$; $\Delta H^\circ = +180$ kJ

$2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$; $\Delta H^\circ = +112$ kJ [**Ans.** + 68 kJ]

Practical : Student's Work.

With the guidance of a teacher, the following experiment is to be done by the students in groups.

Expt. No. 14

Date :........

4.22 Name of Expt. To determine Heat of Solution of Oxalic acid calorimetrically

(A) Principle : The enthalpy or heat of solution of a solute is defined as the change in enthalpy of the system, when I mol of solute is dissolved in sufficient amount of solvent, so that further dilution of that solution produces no more change of enthalpy. When one mole of oxalic acid is dissolved in sufficient solvent water and the total volume is made into one kilogram, then heat needed to rise temperature for each degree celcius is one kilocalorie i.e. 4.2 kilojoules (4.2 kJ). So when total change of temperature is t°C for preparation of one mole oxalic acid for 1000g solution, then heat of solution of oxalic acid will be 4.2 × t kJ. Again for preparation of 100 g solution of 0.1 mol oxalic acid,—

Heat change = 0.42 × t kJ

$$\therefore \text{Heat of solution of oxalic acid} = \frac{0.42 \times t \text{ kJ}}{0.1}$$

$$= 0.42 \times t \times 10 \text{ kJ.}$$

(B) Required Chemicals :

(1) Oxalic acid ($C_2H_2O_4.2H_2O$)' (2) water.

MCQ-4.21 : Which has negative value always? [J. B. 2015]

(a) heat of combustion.

(b) heat of reaction.

(c) heat of formation,

(d) heat of solution

(C) Required Apparatus : (1) Beaker (250 mL). (2) Thermometer, (3) Glass rod, (4) Stand with clamp. (5) Measuring cylinder.

(D) Procedure :

(1) Molecular mass of hydrated oxalic acid. ($HOOC–COOH.2H_2O$) is 126. So powdered 0.1 mol oxalic acid or 12.6 g oxalic acid powder is to be weighed in digital balance.

(2) In one 250 mL beaker take 87.4 mL water with measuring cylinder.

(3) A thermometer is placed in water of the beaker (fig 4.31) At this stage temperature of water (t°C) is recorded.

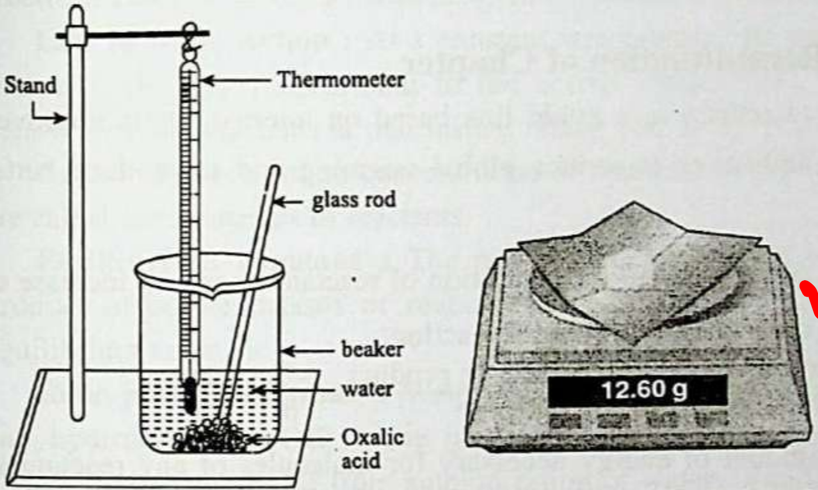


Fig. 4.31. Determination of heat of solution of oxalic acid calorimetrically

What is calorimetry? The unit of of heat is calorie; the term 'metry' means measurement. The instrumental process to measure heat produced or absorbed in a reaction is known as **calorimetry.** The instrument is called calorimeter which can oppose rediation of heat.

(4) Now add 12.6 g of oxalic acid, already weighed into water taken in the beaker. Stir with a glass rod slowly to dissolve the oxalic acid.

(5) When all the oxalic acid dissolves, then record the temperature of the solution ($t_2^{\circ}C$) from the thermometer.

(6) Now calculate the heat of solution of oxalic acid with the change of temperature recorded.

(E) Observation data :

Amount of oxalic acid taken = 12.6 g

Mass of water taken in beaker = 87.4 mL or gram

Concentration of solution prepared = 1M

Initial temperature of water, $t_1^{\circ}C$ = x (suppose)

Temperature of oxalic acid solution, ($t_2^{\circ}C$) = y (suppose)

MCQ–4-22 : Which one is exothermic process?

(a) $H_2O(l) \rightarrow H_2O$ (g)

(b) H_2O (g) $\rightarrow H_2O$ (*l*)

(c) H_2O (s) $\rightarrow H_2O$ (*l*)

(d) H_2O (s) $\rightarrow H_2O$ (g)

Calculation : Change of temperature, $t^{\circ}C = (t_1 - t_2)^{\circ}C = (x - y)^{\circ}C = z^{\circ}C$

∴ Heat of solution of anhydrous oxalic acid,

$$\Delta H = 0.42 \times t^{\circ}C \times 10 \text{ kJ/mol}$$
$$= 0.42 \times z \times 10 \text{ kJ/mol}$$

Heat of solution of anhydrous oxalic acid is an endothermic change. So the heat of solution of anhydrous oxalic acid is positive.

Heat of anhydrous oxalic acid, $\Delta H = + 18.94$ kJ/mol

Precautions :

(1) Dissolve anhydrous oxalic acid in water in a short time by stirring with a glass rod.

(2) Stir the glass rod carefully to save thermometer bulb from breaking by hit.

(3) Stirring the mixture of oxalic acid and water, should be uniform surrounding the thermometer.

Recapitulation of Chapter

Green Chemistry : Green chemistry is a guide line based on internationally approved twelve principles for chemical industries to reduce global warming and to produce better global environment.

Rate of reaction : The rate of decrease of concentration of reactant or rate of increase of concentration of product in unit time is called rate of a reaction.

$$\text{Rate of reaction} = \frac{\text{concentration change of reactant or product}}{\text{time needed for that change}} = \frac{-dc}{dt} = \frac{dx}{dt}$$

Activation Energy : The amount of energy necessary for molecules of any reactant to take part in the chemical reaction is called the activation energy for the related reaction.

Catalyst : A substance, which accelerates or retards the rate of a chemical reaction and remains unchanged in composition and mass is called a catalyst. The process of accelerating or retarding the reaction is known as catalysis.

Enzymes : Enzymes are tertiary globular proteins secrerated by living plant and animals cells, which can accelerate the organic reactions specially in living organism.

Homogeneous and heterogeneous catalysis : When the catalyst and the reactants are in the same phase, then the catalysis is called homogeneous catalysis. When the catalyst and the reactants are in different physical states, then it is called heterogeneous catalysis. The activation energy of a catalyzed reaction is less than that of a non-catalyzed reaction.

Industrial Uses of catalysts : With the use of catalyst large amount of chemical compounds may be produced in a relatively short time. This reduces the production cost to a great extent in industry. Different catalysts are used in chemical industries.

Reversible reaction : In case of a reversible reaction the reactants react with one another to produce some products and again these products react with one another to produce the reactants back.

Equilibrium of chemical reaction : When a reaction among the reactants proceeds, after some time the rate of reaction of the reactants to produce the products equals to the rate of reaction of the products to produce the reactants back. This state is called equilibrium of a reversible chemical reaction.

Irreversible reaction : When in a reaction all the reactants are converted to products, or in other words the reaction proceeds in one direction, then the reaction is called an irreversible reaction.

Dynamic Equilibrium : Even after attainment of equilibrium, both forward and backward reactions continue to occur, with same rate. So equilibrium is dynamic.

Law of Mass Action : At a constant temperature, the rate of a chemical reaction at any instant is directly proportional to the active masses (i.e., molar concentration or partial pressure) of the reactants at that instant taking part in the reaction.'

Active Masses : Molar concentration of reactants or partial pressures of gaseous reactants are called active masses of reactants.

Equilibrium constant : The ratio of the product of active masses of product to the product of active masses of reactants at equilibrium state of the reaction is called the equilibrium constant.

Ionic product of water : Water ionizes very slightly to produce hydronium ion (H_3O^+) and hydroxide ion (OH^-). The product of molar concentrations of hydronium ions and hydroxide ions produced from autoionization of water, is called ionic product (K_w).

Dissociation constant of acid (K_a) : The mole fraction of a acid dissociated in aqueous solution out of the total moles of acid dissolved in that aqueous solution is called dissociation constant (K_a) of acid.

Dissociation constant of base (K_b) : The mole fraction of a base dissociated in aqueous solution out of the total moles of base dissolved in that aqueous solution is called dissociation constant (K_b) of base.

Arrhenius Concept of acid-base : An acid is a hydrogen containing compound which gives hydrogen ion (H^+) in aqueous solution. A base is a substance which gives hydroxide ion (OH^-) in aqueous solution.

Bronsted-Lowry Concept or Protonic Concept : An acid is any substance (molecule cation or anion) which is capable of donating proton to any other substance. A base is any substance (molecule, cation or anion) which is capable of accepting proton from any other substance.

Conjugate base : The base, which is formed after the removal of a proton from an acid, is called the conjugate base of that acid.

Conjugate acid : The acid, which is formed by the addition of a proton to a base, is called the conjugate acid of that base.

Relation of conjugate acid and base : The stronger the acid, the weaker is its conjugate base. Again the stronger the base, the weaker is its conjugate acid.

Classification of acids : Based on constituent elements inorganic acids may be classified in two classes (1) Hydracids and (2) Oxoacids or oxyacids.

Strength of acids : The strength of hydracids depends mainly on the size of the anion or conjugate base. The larger the conjugate base, the weaker base it is and hence the stronger is the acid. The strength of oxoacids depends mainly on two factors— (1) Oxidation state of the central element and (2) electronegativity or size of the central element. The higher the oxidation state, the stronger is the acid. When the oxidation state of the central elements are same, then only the more electronegativity or smaller size of the central element determines the comparative more strength of that acid.

Indicator : Some organic compounds are used to detect the end point or equivalence point in the acid-base titrations. These organic compounds show one colour in acidic medium and another colour in basic medium. Such compounds are called acid-base indicators. Indicators are methyl orange, litmus etc.

Buffer solution : The solution of two compounds, whose pH remains same, even after addition of small amount of base or acid, is called buffer solution.

Thermo chemical equation : A chemical equation expressing states of chemicals and heat change during the reaction is called thermo chemical equation.

Exothermic reaction : The chemical reactions, in which heat is evolved, are called exothermic reactions. Example of exothermic reaction is burning of fuels.

Endothermic reaction : The chemical reactions, in which heat is absorbed from the surroundings, are called endothermic reactions. Formation of HI is an endothermic change.

Internal energy : The total energy stored in a substance is called internal energy of that substance. It is the summation of internal potential energy and internal kinetic energy both.

Enthalpy or heat content : It is a thermodynamic function, which is sum of internal energy of a system and product of pressure and volume change of the system. It is expressed as : $H = E + P \times \Delta V$.

(i) Heat content of reactants > Heat content of products $\longrightarrow$ Exothermic reaction

(ii) Heat content of reactants < Heat content of products $\longrightarrow$ Endothermic reaction

Heat of Atomization : The amount of heat absorbed by one mole of a substance to convert into its atoms at gaseous state is called heat of atomization.

Heat of reaction : The change in enthalpy that occurs in a reaction according to the balanced equation in proper mole ratio of the related reactants, is called the heat of reaction.

Heat of formation of a compound : Enthalpy or heat of formation of a compound is defined as the change in enthalpy when one mole of that compound is formed from its constituent elements. When the reaction is carried out at standard condition at 25°C and 1 atm pressure the enthalpy change is called standard enthalpy of formation. Enthalpy of a reaction = [Total enthalpy of formation of products] – [Total enthalpy of formation of reactants]

Enthalpy of combustion : It is defined as the change of enthalpy, when one mole of the substance (element or compound) is burnt completely in oxygen at a definite temperature and pressure. When the combustion is carried out at S.T.P, the change of enthalpy is called standard enthalpy of combustion of that substance.

Heat of solution of a solute : It is defined as the change in enthalpy of the system, when 1 mole of solute is dissolved in sufficient amount of solvent, so that further dilution of that solution produces no more change of enthalpy.

Heat of vapourisation : It is the amount of heat absorbed in transforming one mole of the substance from liquid state to its vapour at its boiling point and at 1 atm pressure.

Heat of sublimation : It is defined as the change in enthalpy when one mole of the solid substance directly becomes vapour on heating.

Heat of neutralization : It is defined as the change of heat or enthalpy during the formation of one mole of water by the neutralization reaction of required amounts of an acid and a base. Heat of neutralization of strong acid with strong base is constant and it is approximately –57.34 kJ.

Bond enthalpy : The amount of energy required to break one mole of particular bond between two atoms in the gaseous state is called bond energy or enthalpy of that particular bond.

Heat of Reaction = (Total bond energies in reactants – Total bond energies in products.)

Lavoisier and Laplace's Law : 'The change of enthalpy in a reaction is exactly equal to the change of enthalpy in the opposite reaction, but their signs are opposite.'

Hess's Law of constant heat summation : 'If the initial reactants and final products remain same in a reaction, then the net change of enthalpy in that reaction will remain same, whether the reaction takes place in a single step or in several steps.'

Calorie : The amount of heat needed to increase 1°C (14.5°C – 15.5°C) of one gram of water, is called one calorie. Again 1 calorie = 4.186 J (joule).

Answer to MCQ's :

4.1 (c) 4.2(d) 4.3 (b) 4.4 (d) 4.5 (a) 4.6 (c) 4.7 (d) 4.8 (d) 4.9 (a)
4.10 (d) 4.11 (d) 4.12 (c) 4.13 (c) 4.14 (b) 4.15. (d) 4.16 (b) 4.17 (b) 4.18 (a)
4.19 (c) 4.20 (c) 4.12 (a) 4.22 (b)