Engineering Chemistry

Module -1

A) Laws of thermodynamics - entropy change (selected processes) – spontaneity of a chemical reaction and Gibbs free energy - heat transfer;

B) Kinetics - Concept of activation energy and energy barrier - Arrhenius equation- effect of catalysts (homo and heterogeneous) – Enzyme catalysis (Michaelis-Menten Mechanism).

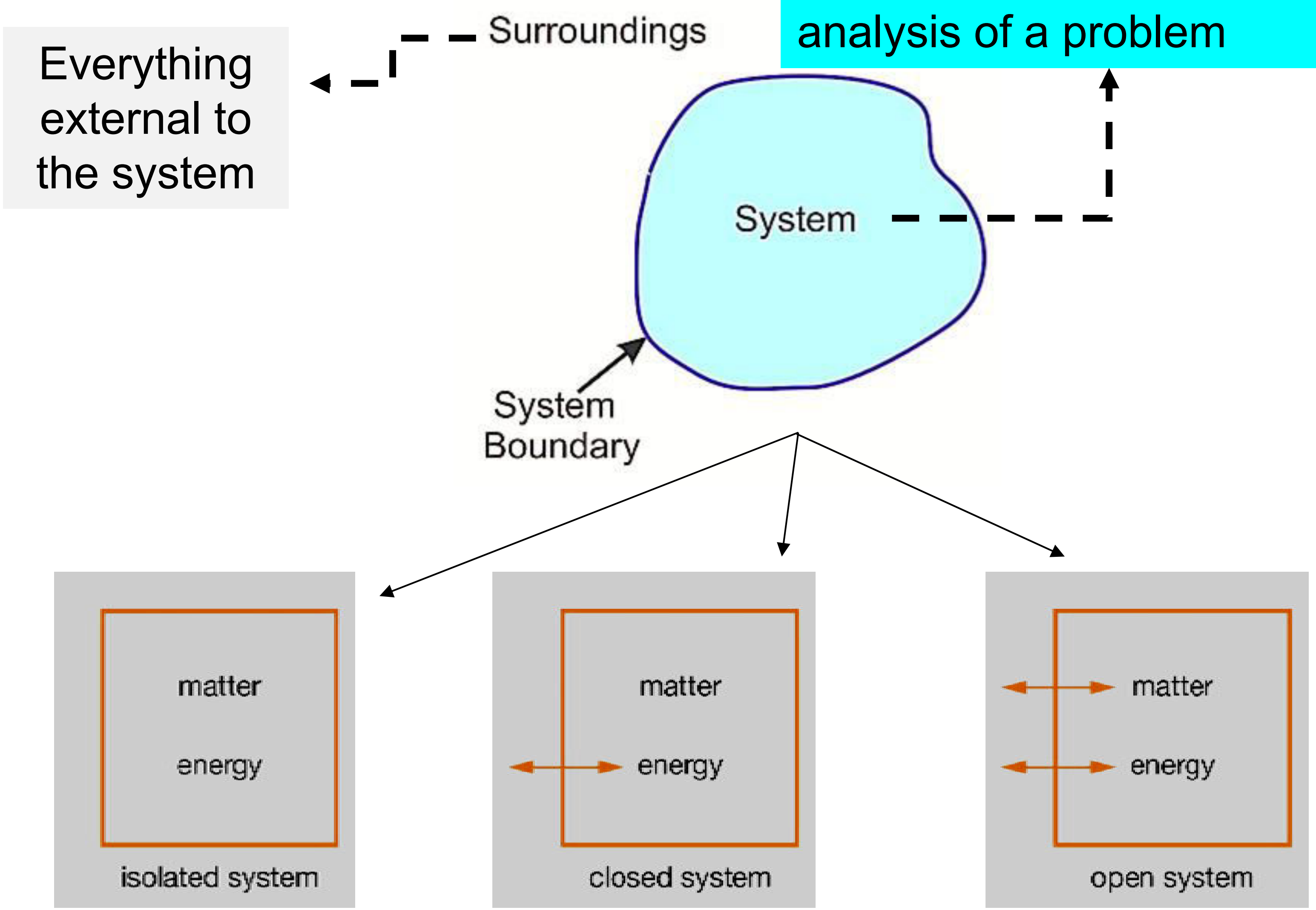
Part-A
Thermodynamics

Thermodynamics: Basic Terminologies

Thermodynamic Systems:

the quantity of matter or a region in space upon which attention is concentrated in the analysis of a problem

Everything external to the system



Properties of a system:

\# **Intensive Properties:**

Intensive properties do not depend on the amount of matter in a sample.

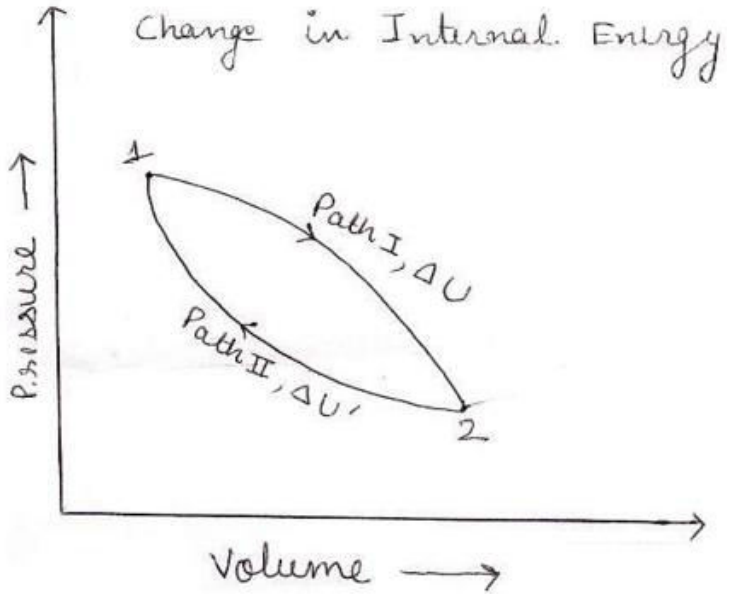
\# **Extensive Properties**

Extensive properties depend on how much matter a sample contains.

Thermodynamics: Basic Terminologies

State function:

Depends on the initial state & final state; **independent of the path used** to reach from. Example: **T** (Temperature), **P** (Pressure), **U** (Internal energy), **H** (Enthalpy) etc.



Path function:

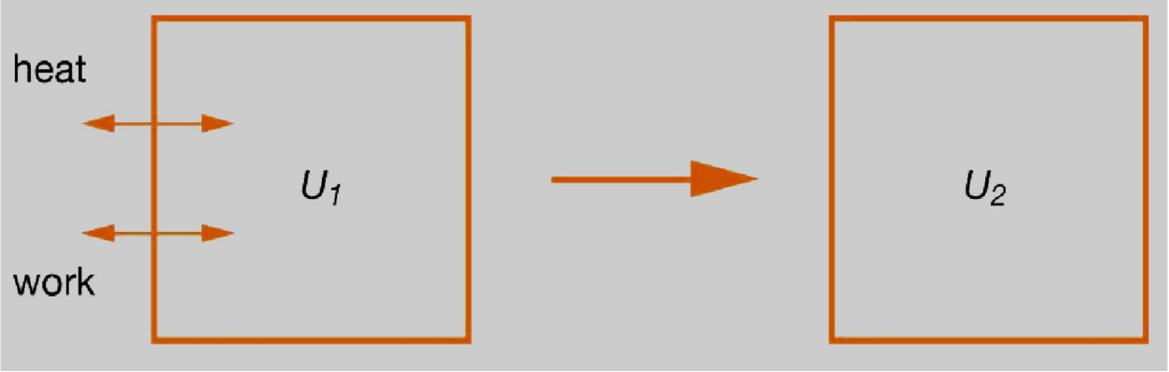
Depends on the path between the initial & final state

Example: **W** (work done), **q** (heat transferred) etc.

Internal energy (U)

= Kinetic energy + Potential energy

- It's a **state function** & an **extensive property** of the system.
- Internal energy of a system changes when **energy is transferred** into or outside the system in the form of ***heat or work***



- $$\Delta U_{system} = U_{final\ state} - U_{initial\ state}$$

Thermodynamics: Basic Terminologies

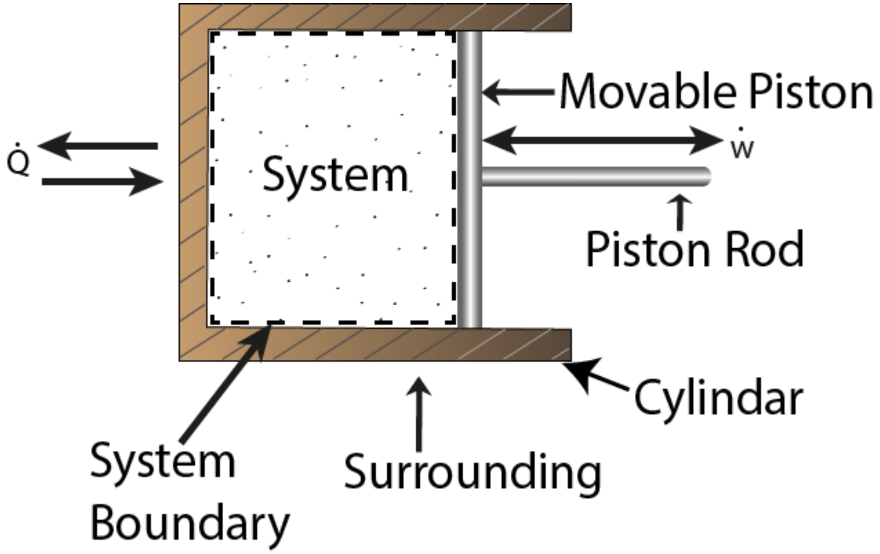
State of a system

- The state of thermodynamic variables such as pressure, temperature, volume, composition which describes the system is called **state of the system.**
- when one/more variables undergo change, the system is said to have undergone a change of state

- **Adiabatic** – no heat transferred
- **Isothermal** – constant temperature
- **Isobaric** – constant pressure
- **Isochoric** – constant volume

Work done on/by the system

W (Work) = F (force) x w (distance moved in the direction of force)



- **Gas is heated ⇒** it will expand and pushes the piston, thereby doing work on the piston.

The work done (dw) when the system expands by dV against a pressure P_{ex}:

$dw = -P_{ex}dV$

Total work done by the system to expand from volume V_i to V_f: $\mathbf{W = -\int_{v_i}^{v_f} P_{ex}dv}$

- This is an example of the **system doing the work on the surrounding**

Reversible Process in Thermodynamics

- ❑ **A thermodynamic process is reversible if the process can be turned back such that both the system and the surroundings return to their original states, with no other change anywhere else in the universe**.
- ❑ In reality, no such processes as reversible processes can exist.
- ❑ ***A change can be reversed by an infinitesimal modification of a variable.***

Example 1:

Thermal equilibrium of two systems with the same temp.

- If the temperature of either system is lowered infinitesimally, then energy flows into the system with the lower temperature.
- If the temperature of either system at thermal equilibrium is raised infinitesimally, then energy flows out of the hotter system

Example 2:

Reversible expansion:

Suppose a gas is confined by a piston.

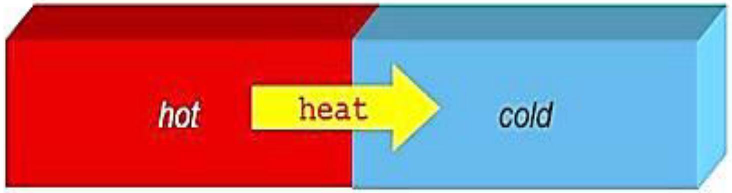
external pressure (P_{ex}) = pressure (P) of the confined gas.

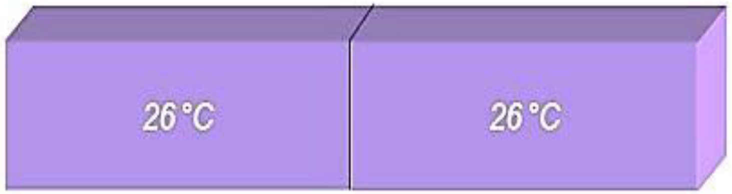
- Such a system is in mechanical equilibrium with its surroundings because an infinitesimal change in the external pressure in either direction causes changes in volume in the opposite directions.

$$\mathrm{dw} = -P_{ex}dV = -pdV$$

$$\mathrm{W} = -\int_{v_i}^{v_f} \mathrm{pdv}$$

0th Law of Thermodynamics

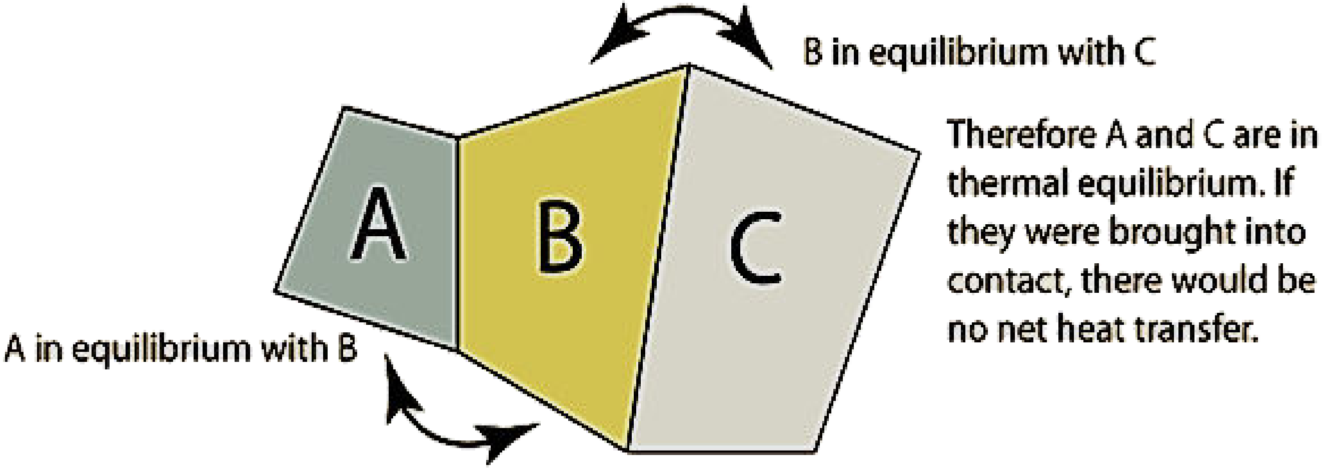




- Two physical systems are in **thermal equilibrium** if there is no net flow of heat (thermal energy) between them when they are connected by a path permeable to heat.

- According to 0th law:

If **two systems** are in **thermal equilibrium** with a **third system**, then those two systems are in thermal equilibrium with each other.



- The 0th law of thermodynamics defines thermal equilibrium and forms a basis for the definition of temperature.

1st Law of Thermodynamics

- It's the law of conservation of energy

❑ **The energy of an isolated system remains constant. Whenever a quantity of energy (some form) disappears, an exactly equivalent quantity of energy (some other form) must make an appearance.**

☐ **Heat (q)** and **work (w)** are equivalent ways of changing the internal energy of a system

→ Example:

- If a weight has been raised/lowered in the surroundings, transfer of energy happens by doing the work.
- If ice melts in the surroundings, it indicates the transfer of energy as heat. $\Delta U = q + w$

☐ For a system, if w = work done on a system, q = energy transferred as heat to a system & ΔU = resulting change in internal energy

The signs of **w** and **q**:

✔ +ve if **energy is transferred to the system** as work/heat

✔ -ve if **energy is lost** from the system.

Therefore,

change in internal energy (ΔU) of a system = heat added to the system (q) - **the work done *by* the system (w)**

$$\boxed{\Delta U = q - w}$$

Enthalpy & Heat Capacity

- If the change of a system is brought about at constant pressure, there will be change in volume.

V_i = volume of initial state, V_f = volume of final state.

Work done by the system, $w = -P\,(V_f - V_i)$

$$\therefore \Delta U = q + w$$

$$\text{or, } \Delta U = q - P\,(V_f - V_i)$$

$$\Rightarrow U_f - U_i = q - P\,(V_f - V_i)$$

$$\Rightarrow (U_f + PV_f) - (U_i + PV_i) = q$$

- The quantity **(U + PV)** is called the **enthalpy (H)** of the system

$$\Rightarrow H_f - H_i = q$$

ΔU = ΔH – PΔV

or ***ΔH = ΔU + PΔV***

,

- Heat capacity (**C**) of a system b/n any two temperatures – the quantity of heat (q) required to raise the temperature of the system from the lower temperature (T_1) to the higher temperature (T_2) divided by the temperature difference.

$$\boldsymbol{C = \frac{q}{T_2 - T_1}}$$

- If mass of the system is 1 g, the heat capacity is called the **specific heat of the system.**
- For 1 mol of substance, the heat capacity is termed as '**molar heat capacity**'

$$C = \frac{dq}{dT}$$

- Molar heat capacity varies with temperature

- **Molar heat capacity at constant volume**

@ constant volume w = 0 & ΔU = q

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v$$

Heat Capacity

- ❑ **Molar heat capacity at constant pressure (C_p)**

$$\Delta U = q - w$$

@ constant pressure, there is change in volume & some work is done

$$\Delta U = q - P\,(V_f - V_i)$$

$$\text{or, } q = \Delta U + p\Delta V$$

➡ As quantity (U+PV) is the enthalpy (H) of the system ⇒

$$\boxed{C_p = \left(\frac{\partial H}{\partial T}\right)_p}$$

- ❑ **Relationship between C_p & C_v**

For a system, $\Delta H = \Delta U + \Delta(PV)$

$$\text{or, } \frac{\Delta H}{\Delta T} = \frac{\Delta U}{\Delta T} + \frac{\Delta(PV)}{\Delta T}$$

$$\text{or, } \boxed{C_p = C_v + \frac{\Delta(PV)}{\Delta T}}$$

- ▪ **For ideal gas**, PV = RT (for 1 mole)

$$\Delta(PV) = R\,\Delta T$$

$$C_p = C_v + \frac{R\Delta(T)}{\Delta T} \qquad \text{or, } C_p = C_v + R$$

$$\text{or, } \boxed{C_p - C_v = R}$$

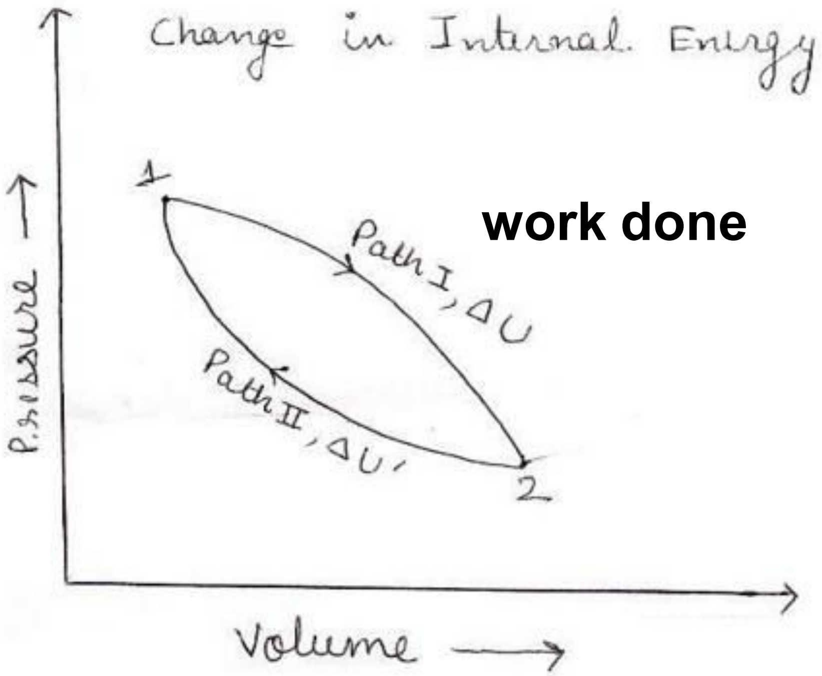
C_V = 3/2 R (**For monoatomic ideal gas**)

C_P = 5/2 R (**For monoatomic ideal gas**)

Heat capacity ratio, $\gamma = \frac{C_p}{C_v}$ **= 5/3 for a monoatomic ideal gas**

Application of 1st Law to the Expansion Work

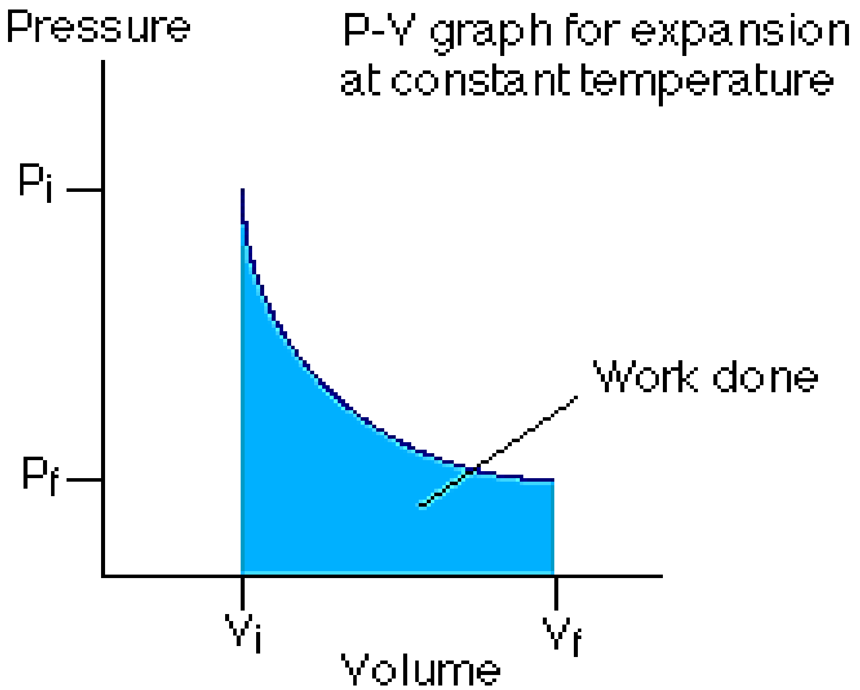
☐ Isothermal Process (constant temperature)



work done

Pressure-volume diagram

- In an isothermal process, the temperature stays constant, so **the pressure and volume are inversely proportional** to one another.



⇒ **For an ideal gas,**

The internal energy (U) ∝ Temperature (T)

if T = fixed, ΔU = 0 (according to 1st law, which deals with ΔU)

As, $\Delta U = q - w = 0$

$\Rightarrow$ **q = w**

\# **Magnitude of w** depends on whether the expansion is **reversible** or **irreversible**.

- If the **system does work**, the energy comes from **heat flowing into the system from the surrounding**
- If **work is done on the system**, **heat flows out** of the system **to the surrounding**.

Application of 1st Law to the Expansion Work

☐ Reversible isothermal expansion:

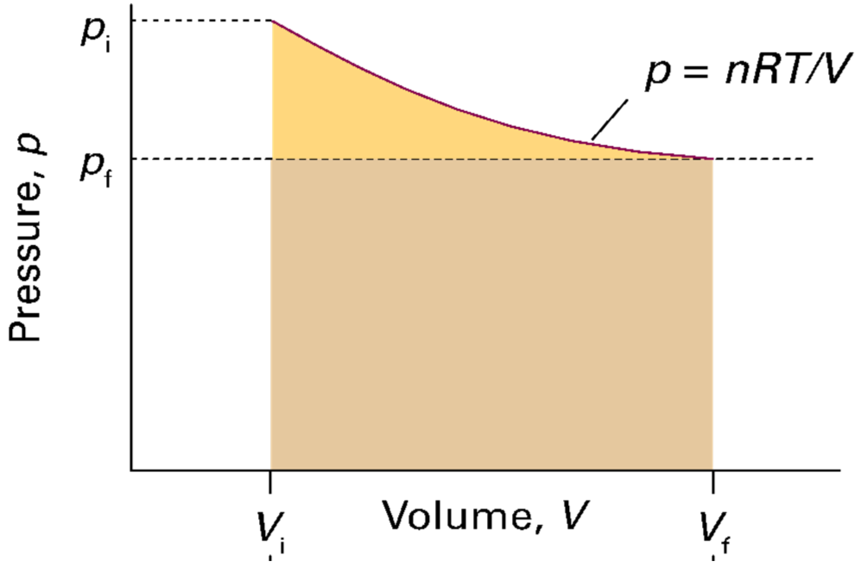
$$w = \int_{v_i}^{v_f} P\,dv = \int_{v_i}^{v_f} \frac{nRT}{V}\,dv \qquad (\text{as } PV = nRT)$$

(throughout the expansion, $P_{ex} = P$ as the expansion is reversible)

- Work done by the n moles of gas can be evaluated as:

$$w = -nRT\ln\frac{V_f}{V_i} = -nRT\ln\frac{P_i}{P_f}$$

(since $\frac{V_f}{V_i} = \frac{P_i}{P_f}$ in an isothermal expansion of a perfect gas)



☐ Relations for Irreversible Isothermal expansion

a) Free expansion (expansion in vacuum)

$$w = -\int_{v_i}^{v_f} P_{ex}\,dv = 0$$

a) Volume of the gas expands against a constant pressure.

$$w = -\int_{v_i}^{v_f} P_{ex}\,dv = -P_{ex}\,(V_f - V_i)$$

☐ The work done by a perfect gas when it expands **reversibly and isothermally** is equal to the area under the isotherm $p = nRT/V$.

☐ The work done during the **irreversible expansion** against the same final pressure is equal to the rectangular area shown slightly darker. **Note that the reversible work done is greater than the irreversible work done.**

Numerical from of 1st Law

- **Example 1**: Calculate w and ΔU for the conversion of 1 mole of water at 100 °C to steam at 1 atm pressure. Heat of vaporisation of water at 100 °C is 40670 Jmol^{-1}

Solution:

P = 1 atm = 101325 Nm^{-2}

V$_i$ = vol. of 1 mole of liquid water at 1 atm pressure

= 18 ml = 18 × 10^{-6} m^3

V$_f$ = vol. of 1 mole of steam at 100 °C at 1 atm pressure

= (22.4 dm^3 × 373)/273 = 30.60 dm^3 = 0.0306 m^3

w = P (V$_f$ - V$_i$)

= 101325 Nm^{-2} [0.0306 m^3-(18 × 10^{-6})m^3]

= 101325 Nm^{-2} × 0.0306 m^3 = 3100 Jmol^{-1}

Since, conversion of water to steam is accompanied by increase in volume, work is done by the system on the surroundings.

Hence, **w = – 3100 Jmol^{-1}**

- **Example 2**: 1 mole of an ideal gas expands against a constant external pressure of 1 atm from a volume of 10 dm^3 to a volume of 30 dm^3. Calculate the work done by the gas in Joules.

Solution:

$$w = -P_{ex}\Delta V$$

$$= -(1\ atm)(30\ dm^3 - 10dm^3)$$

$$= -20\ dm^3\ atm$$

R = 8.314 Jmol-^{1}K^{-1} = 0.08206 dm^3 atm K^{-1} mol^{-1}

1 atm = $\dfrac{8.314\ J\ mol^{-1}K^{-1}}{0.08206\ dm^3\ mol^{-1}K^{-1}}$

Therefore,

$$w = -20\ dm^3\ atm$$

$$= -20\ dm^3 \times \frac{8.314\ J\ mol^{-1}K^{-1}}{0.08206\ dm^3\ mol^{-1}K^{-1}}$$ = – **2026 J**

2^{nd} Law of Thermodynamics

- **Why we need for the 2nd law of thermodynamics?**

→ The 1^{st} law of thermodynamics does not tell us anything about **the direction of change**. The direction of spontaneous change of a process is defined by the 2^{nd} law of thermodynamics

❑ 2^{nd} law of thermodynamics

- Heat does not flow spontaneously from a cool body to a hotter body.
- The entropy (**S**) of an isolated system increases in the course of a spontaneous change.

$$\Delta S_{tot} > 0$$

Where, $S_{tot} = S + S_{sur}$

S = the entropy of the system of interest, &

$\boldsymbol{S_{sur}}$ = the entropy of the surroundings

\# ***Note:*** *when considering applications of the 2nd law – it is a statement about the* ***total entropy*** *of the overall isolated system (**the 'universe'**), not just about the entropy of the system of interest.*

☐ The **1^{st} law** uses the **internal energy** to identify ***permissible*** **changes**

☐ The **2^{nd} law** uses the **entropy** to identify which of these **permissible changes are *spontaneous***.

→ A **spontaneous process** points towards the **direction** in which the ***total entropy increases***.

☐ Entropy (**S**) is a **state function.**

☐ Thermodynamic definition of entropy

→ The thermodynamic definition of entropy concentrates on the change in entropy (**d*S***) that occurs as the result of a physical or chemical process.

→ dq_{rev} is the energy transferred as heat reversibly to the system at the absolute temperature *T*.

$$\boxed{dS = {}^{dq_{rev}}/_{T}, \qquad \Delta S = \int_i^f \frac{dq_{rev}}{T}}$$

Entropy

- Process that leads to an increase in entropy ($\Delta S > 0$)

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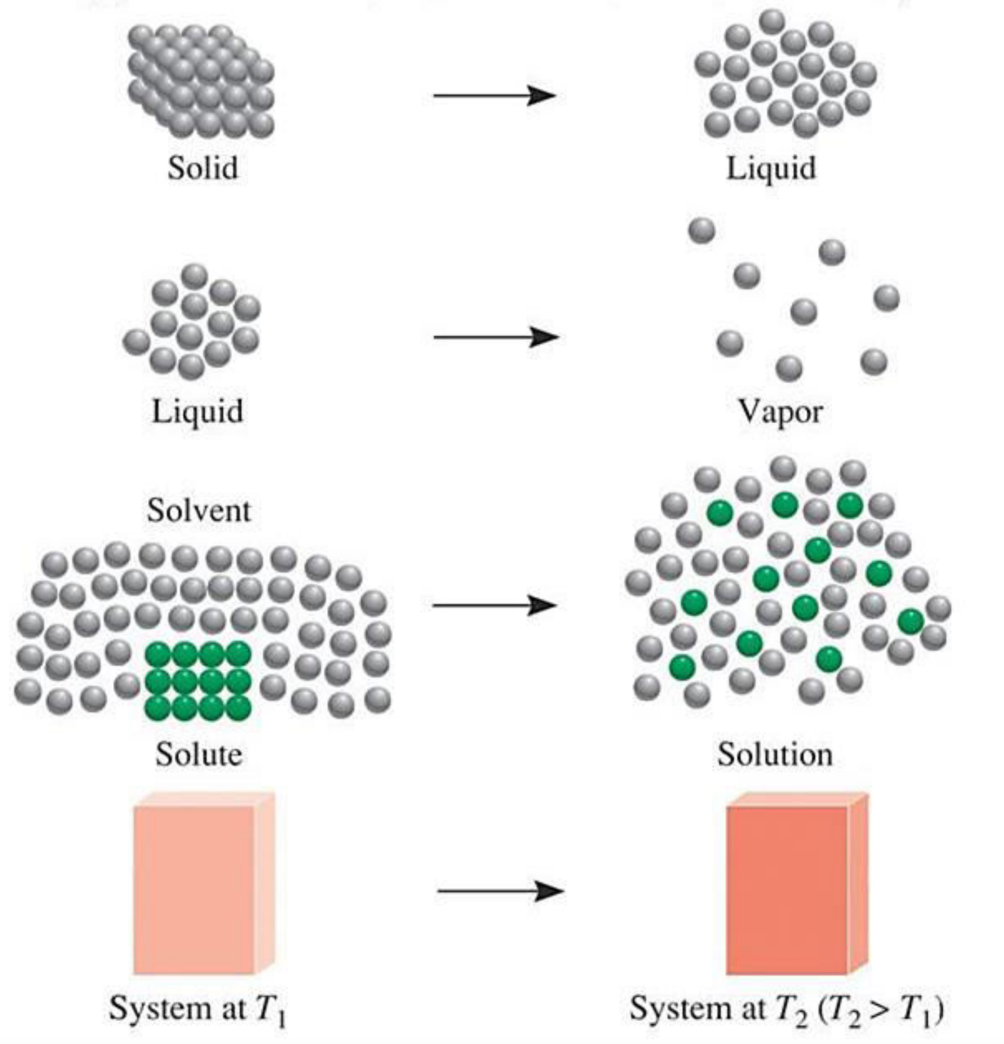


☐ **Entropy change for the *system* of an isothermal expansion of a perfect gas**

$\Delta U = 0$, $q = -w \Rightarrow q_{rev} = -w_{rev}$

as, $w_{rev} = -\, nRT \ln (V_f / V_i)$

[from the expression of work done in a reversible isothermal expression]

$\therefore q_{rev} = nRT ln(V_f/V_i)$

$$\text{as } dS = {}^{dq_{rev}}\!/_{T}$$

$$\Rightarrow \boxed{\Delta S = nRln(V_f/V_i)}$$

$$\boxed{\Delta S_m = nRln(V_f/V_i)}$$

☻ Notice the increasing ***disorder*** in above processes

Entropy

Total Entropy change in irreversible (spontaneous) process of a perfect gas

✔ example: ***Isothermal*** expansion of an ideal gas at constant temperature into **vacuum**

As, w = 0, $\Delta U = 0 \Rightarrow q = 0$ [from 1st law]

$\Rightarrow$ no heat is absorbed by or removed from the surrounding,

Hence, $\Delta S_{surrounding} = 0$

$$\Delta S_m = R ln(V_f/V_i)$$

As, $S_{total} = S_{system} + S_{surrounding}$

$$\therefore \Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}$$
$$= R ln(V_f/V_i) + 0$$
$$= R ln(V_f/V_i)$$

→ As $V_f > V_i$, this spontaneous (irreversible) isothermal expansion of a gas is accompanied by the increase in entropy.

Isothermal *Reversible* expansion

$w = -p\Delta V$ & $q_{rev} = p\Delta V$

$$\therefore S_{total} = \Delta S_{system} + \Delta S_{surrounding}$$
$$= \left(\frac{q_{rev}}{T}\right) + \left(-\frac{q_{rev}}{T}\right)$$
$$= 0$$

Clausius inequality $\boxed{dS \geq \frac{dq}{T}}$

- In an isolated system, there is no heat transfer and $dq = 0$, thus $dS \geq 0$

$\Rightarrow$ ***all natural processes are spontaneous & irreversible.***

- Reversible process:

$$dS_{total} = dS_{system} + ds_{surrounding} = 0$$

$\Rightarrow$ spontaneous in neither direction and is at equilibrium

- Irreversible process

$$dS_{total} > dS_{system} + ds_{surrounding} > 0$$

$\Rightarrow$ ***All spontaneous process occurring in Nature are irreversible and entropy of the universe is increasing continuously.***

Spontaneity of a Chemical Reaction

- A **spontaneous reaction** is a reaction that favors the formation of products at the conditions under which the reaction is occurring. Spontaneous processes may be fast or slow, but they occur without outside intervention.

Ex. **i) Conversion of graphite to diamond is slow;**

ii) A burning fire is relatively a fast reaction.

- "In any spontaneous process there is always an increase in the entropy of the universe"
- For a given change to be spontaneous, $\Delta S_{universe}$ must be positive.

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

Gibbs Free Energy

- **Free energy** *is energy that is available to do work*. The free energy change of a reaction is a mathematical combination of the enthalpy change and the entropy change.

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$$

- **The change in enthalpy, change in entropy and change in free energy of a reaction are the driving forces behind all chemical reactions.**

Conditions for Spontaneity of a Chemical Reaction (Changes in **Enthalpy** (ΔH), **Entropy** (ΔS), and **Free Energy** (ΔG))

- **A spontaneous reaction is one that releases free energy, and so the sign of ΔG must be negative. Since both ΔH and ΔS can be either positive or negative, depending on the characteristics of the particular reaction, there are four different possible combinations as shown in the table below.**

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$$

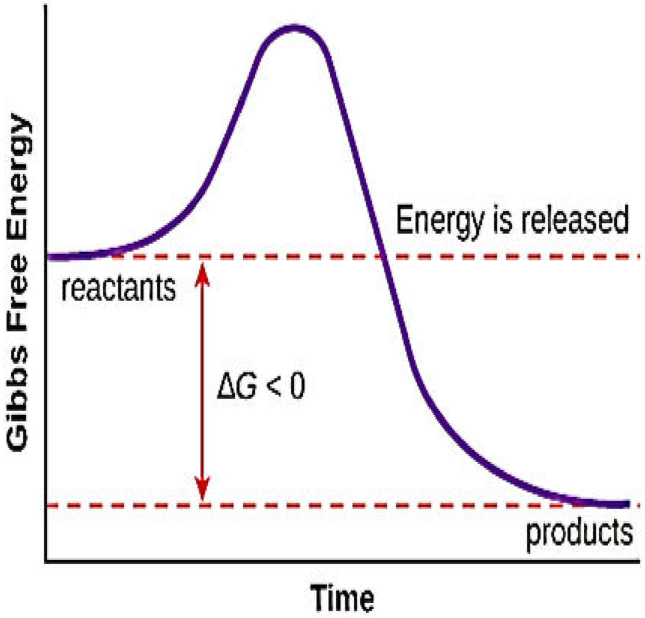
ΔH°	ΔS°	ΔG°
Negative	Positive	**Always negative**
Positive	Positive	**Negative at higher temperatures, positive at lower temperatures**
Negative	Negative	**Negative at lower temperatures, positive at higher temperatures**
Positive	Negative	**Always positive**

Change in Free Energy @ different conditions

☐ In an exothermic reactions

- commonly **spontaneous**

because dH < 0 & then dG < 0 provided TdS is not so negative that it outweighs the decrease in enthalpy.



☐ At chemical equilibrium,

☐ $dG = 0$

☐ *In an endothermic reaction:*

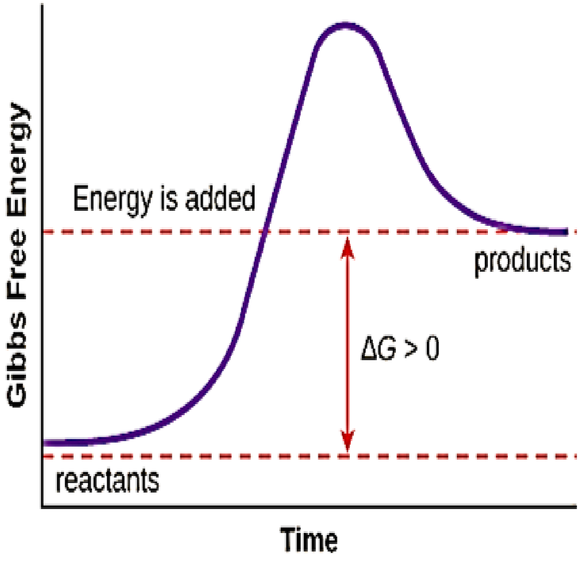
dH > 0

but if such a reaction is to be spontaneous at constant temperature and pressure, G must decrease.

- as dG = dH − TdS

it is possible for dG to be negative provided that the entropy of the system increases so much that TdS outweighs dH.

⇒ **Endothermic reactions** are therefore driven by the ***increase of entropy*** of the **system**



Solved problem-1

Q. How can you say that the following reaction is spontaneous or not? Justify the answer using the standard entropy values given in the table.

Standard Entropy Values at 25°C

Substance	S° (J/K. mol)
H_2 (g)	131.0
O_2 (g)	205.0
H2O (l)	69.9

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

Ans: From the absolute entropies of substances, we can calculate the entropy change by

$\Delta S^o =$ **S° of Products – S° of Reactants**

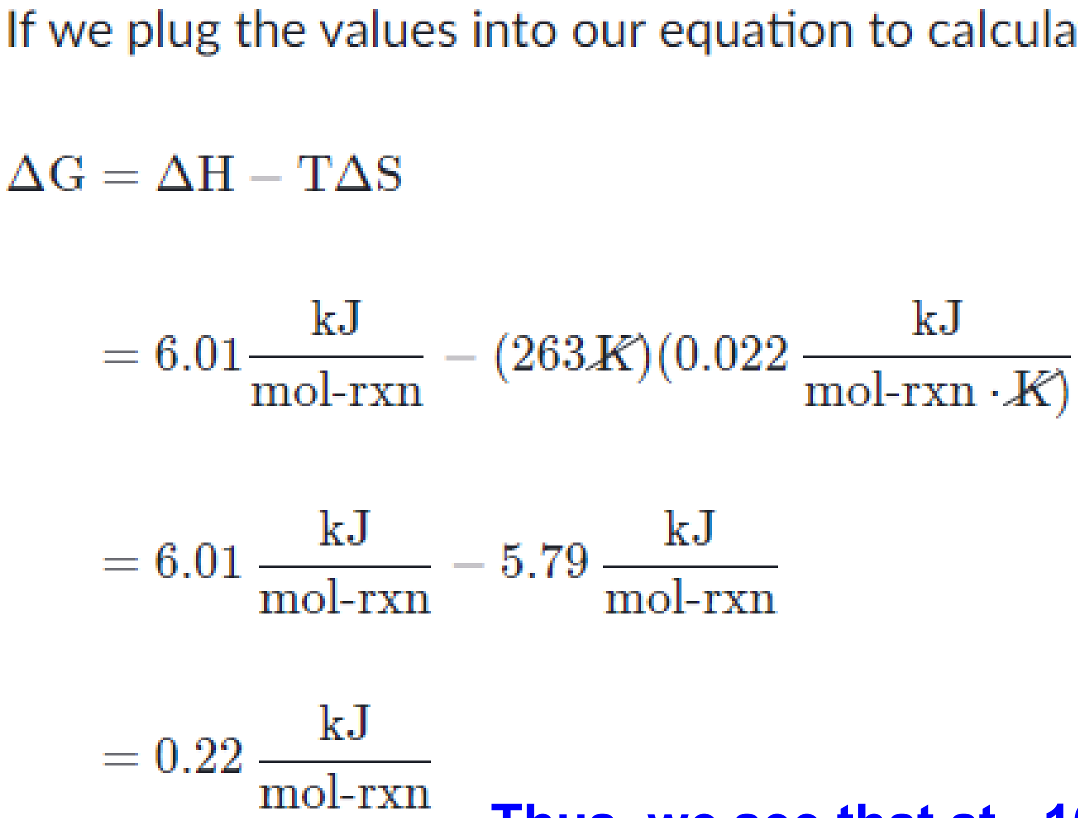
$$\Delta S^o = 2(69.9) - [2(131.0) + 1(205.0)] = -327\ \mathrm{J/K \cdot mol}$$

The entropy change for this reaction is highly negative because three gaseous molecules are being converted into two liquid molecules. According to the drive towards higher entropy, the formation of water from hydrogen and oxygen is an unfavorable reaction. In this case, the reaction is highly exothermic and the drive towards a decrease in energy allows the reaction to occur.

Solved problem-2

Q.2. What is ΔG for the melting of ice at -10 ∘C if the H = 6.01 kJ/mol and S = 0.022 kJ $K^{-1}mol^{-1}$

T= −10∘C + 273 = 263 K



If we plug the values into our equation to calculate ΔG, we get:

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

$$= 6.01 \frac{\text{kJ}}{\text{mol-rxn}} - (263\,\cancel{K})(0.022 \frac{\text{kJ}}{\text{mol-rxn} \cdot \cancel{K}})$$

$$= 6.01 \frac{\text{kJ}}{\text{mol-rxn}} - 5.79 \frac{\text{kJ}}{\text{mol-rxn}}$$

$$= 0.22 \frac{\text{kJ}}{\text{mol-rxn}}$$

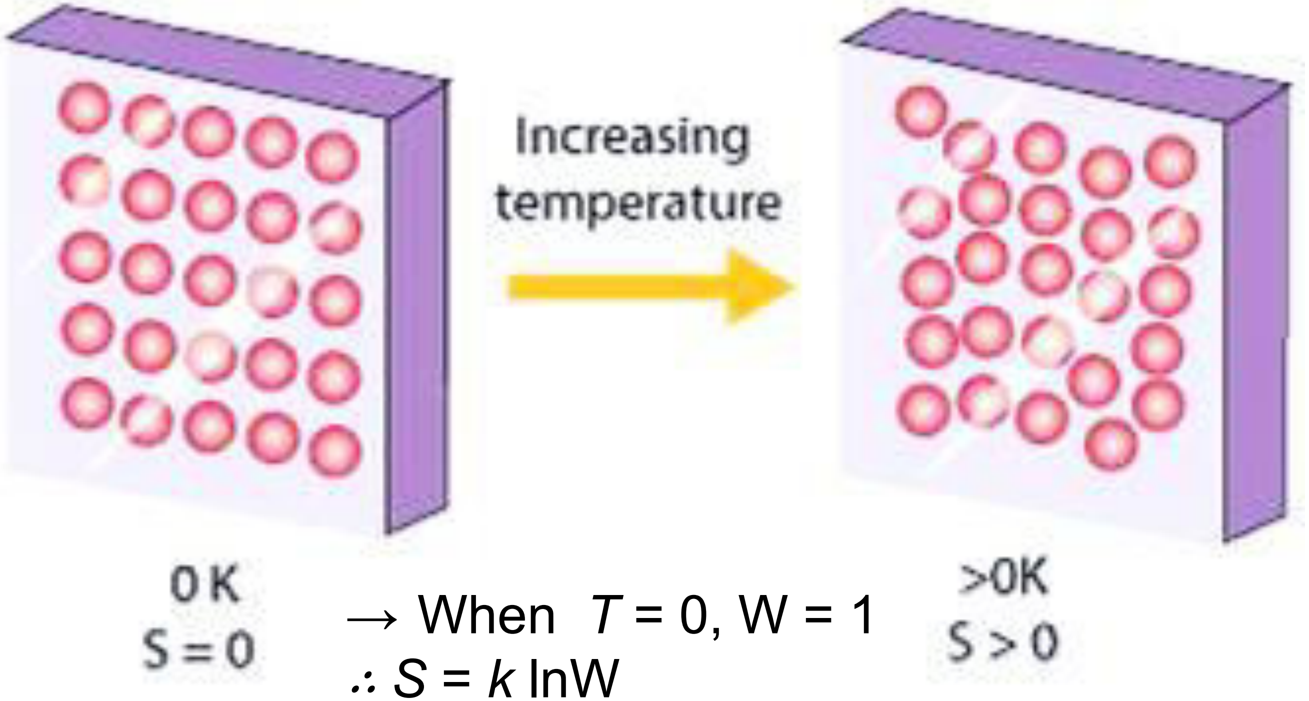
Thus, we see that at −10 ∘C, the Gibbs free energy change ΔG is positive for the melting of water. Therefore, we would predict that the reaction is *not* spontaneous at −10 ∘C.

3rd Law of Thermodynamics

- At $T = 0$, all energy of thermal motion has been quenched and in a perfect crystal all the atoms/ions are in a regular, uniform array.
- The localization of matter and the absence of thermal motion suggest that such materials also have zero entropy.
  - Statistical or microscopic definition of entropy:

$$\boxed{S = k \ln W}$$

where, **S** = the entropy,
k = Boltzmann constant,
W = the number of microstates or the total number of ways a molecular state can be distributed over the energy states for a specific value of total energy.



→ When $T = 0$, W = 1

$$\therefore S = k \ln W = 0$$

⇒ if the value zero is ascribed to the entropies of elements in their perfect crystalline form at $T = 0$, then all perfect crystalline compounds also have zero entropy at $T = 0$

☐ **Third law of thermodynamics:**

The entropy of all perfect crystalline substances is zero at $T = 0$.

Module 1

Part-B

Chemical Kinetics

What is Chemical kinetics?

- Chemical kinetics is the branch of chemistry which deals with the study of rates (or fastness) of chemical reactions, the factors affecting it and the mechanism by which the reactions proceed.

The rate of a chemical reaction might depend on variables such as

- pressure,
- temperature, and
- the presence of a catalyst,

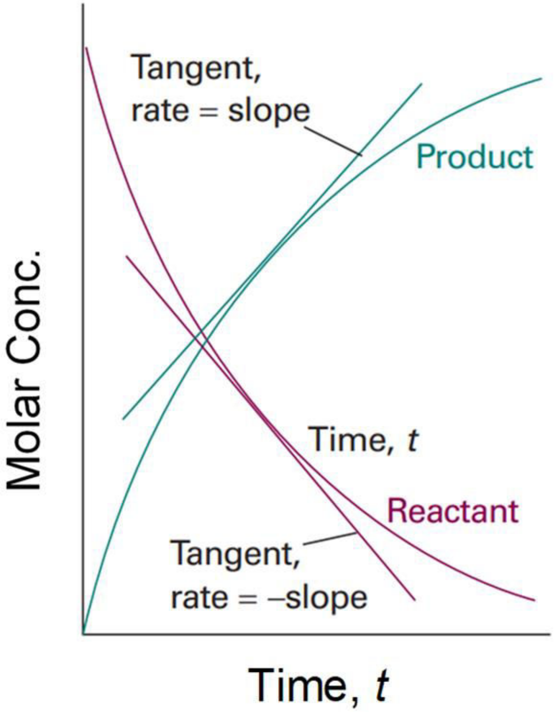
It is to be contrasted with thermodynamics, which deals with the direction in which a process occurs but in itself tells nothing about its rate

The rates of reactions

- The change in concentration of reactants or products per unit time.

- Here, the instantaneous rate of disappearance of one of the reactants (A or B) at a given time, t (at constant volume) is −d[R]/dt. Similarly, the rate of formation of one of the products is d[P]/dt. (***Note the change in the sign***)

- The negative sign indicates that the concentration is decreasing with time.



The rates of reactions

Consider a general reaction,

$$A + B \rightarrow C$$

The rate of reaction will be:

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt}$$

Consider another general reaction:

$$aA + bB \rightarrow cC + dD$$

where a, b, c d are stoichiometric coefficients

The rate of reaction will be:

$$\frac{-1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

The rates of reactions

Sample Questions:

Write rate expressions for the following reactions:

1. NO_2 (g) + CO (g) → NO (g) + CO_2 (g)
2. 2HI (g) → H_2 (g) + I_2 (g)

Solution:

1. $$-\frac{d[NO_2]}{dt} = -\frac{d[CO]}{dt} = \frac{d[NO]}{dt} = \frac{d[CO_2]}{dt}$$

2. $$-\frac{1}{2}\frac{d[HI]}{dt} = \frac{d[H_2]}{dt} = \frac{d[I_2]}{dt}$$

Rate laws and rate constants

- The rate law is the relationship between the rate and the concentration, which are related by a proportionality constant k, known as ***rate constant***.

aA + bB → cC + dD

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

where m and n are order of reaction in A and B, respectively k is the rate constant.

This above equation is called the ***rate law of the reaction***.

Rate laws and rate constants

☐ Important points about rate laws and rate constant:

- ✔ Rate law is a result of experimental observation. You **CANNOT** look at the stoichiometry of the reaction and predict the rate law (*unless the reaction is an elementary reaction*).
- ✔ The rate law is not limited to reactants. It can have a product term, For example: **rate = $k[A]^m[B]^n[C]^c$**
- ✔ The rate constant is independent of the concentrations but depends on the temperature.
- ✔ The units for k vary. Determine units for k by considering units for rate and for concentration.

Order of a reaction

A + B → C

For rate = $k[A]^m[B]^n$

Where, m is the order of reaction in A, n is the order of reaction in B. m and n can be integers, fractions, negative or positive.

***The overall reaction order is the sum of the exponents in the rate law*.**

✔ m = **0** (Zero order $k[A]^0$)
✔ m = **1** (First order $k[A]^1$)
✔ m = **2** (Second order $k[A]^2$)

Examples:

$H_2 + Cl_2 \rightarrow 2HCl$. Rate = $k[H_2]^0\,[Cl_2]^0$ **(Zero order)**
$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$ Rate = $k[SO_2Cl_2]^1$ **(First order)**
$NO_2 \rightarrow 2\,NO + O_2$ Rate = $k[NO_2]^2$ **(Second order)**
$2NO(g) + 2H_2(g) \rightarrow 2N_2\,(g) + 2H_2O\,(g)$ Rate = $k[NO]^2\,[H_2]^1$ **(Third order)**
$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$ Rate = $[CH_3COOC_2H_5]^1[H_2O]^0$ **(pseudo-first-order)**

Integrated rate laws

Since rate laws are in differential form, we must integrate them to find out the concentration as a function of time.

Integrated first-order rate law:

A → B

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]$$

Separate concentration and time terms

$$\frac{d[A]}{[A]} = -kdt$$

Integrating over the limits $[A]^0$ to $[A]^t$ and 0 to t,

$$\int \frac{d[A]}{[A]} = -k\int dt$$

$$\int_{[A]0}^{[A]t} \frac{d[A]}{[A]} = -k\int_0^t dt$$

$$\ln[A]_t - \ln[A]_0 = -kt$$

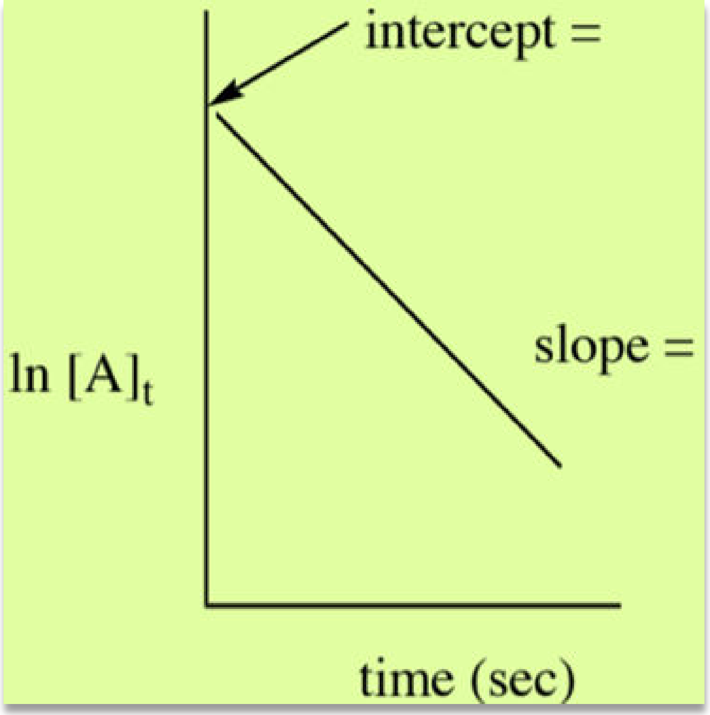
Continue….

Integrated rate laws

$$\ln[A]_t = -kt + \ln[A]_0$$

Straight line equation (y = mx+c)

If we plot ln $[A]_t$ versus time, then we will get a straight line having negative slope (-k). Rate constants can be determined from experiment by plotting data in this manner.



Pseudo First Order Reaction

- A pseudo first-order reaction can be defined as a second-order or bimolecular reaction that is made to behave like a first-order reaction.
- This reaction occurs when one reacting material is present in great excess or is maintained at a constant concentration compared with the other substance.

$$A + B \rightarrow C$$

So, if component B is in large excess and the concentration of B is very high as compared to that of A, the reaction is considered to be a **pseudo-first-order reaction** with respect to A and if component A is in large excess and the concentration of A is very high as compared to that of B, the reaction is considered to be pseudo-first order with respect to B.

For example:

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

$$\text{Rate} = k\,[CH_3COOC_2H_5]$$

The concentration of water is very high and thus does not change much during the course of the reaction.

Temperature dependence of reaction rates

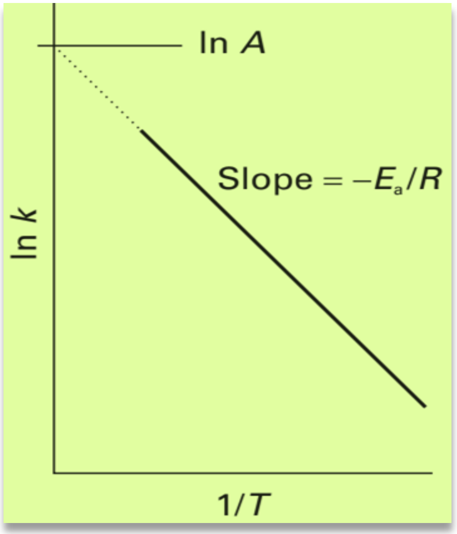
The rate constant of most reactions increases with increase in the temperature.

Arrhenius equation

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

where, A is the pre-exponential factor and E_a is the activation energy.

- A plot of ln k against 1/T is a straight line when the reaction follows the behavior described by the Arrhenius equation.
- The higher the activation energy, the stronger the temperature dependence of the rate constant (i.e., the steeper the slope).
- If a reaction has zero activation energy, its rate is independent of temperature.



If we plot the graph ln k vs 1/T, we will get the value of A from the intercept at infinite T (i.e.; 1/T=0) and the value of E_a from the slope.

Energy barrier: interpretation of Arrhenius parameters

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

One can rewrite the above equation as:

$$k = Ae^{-\frac{E_a}{RT}}$$

To interpret E_a, lets us consider the collision between molecules of reactants A and B:

Collision theory:

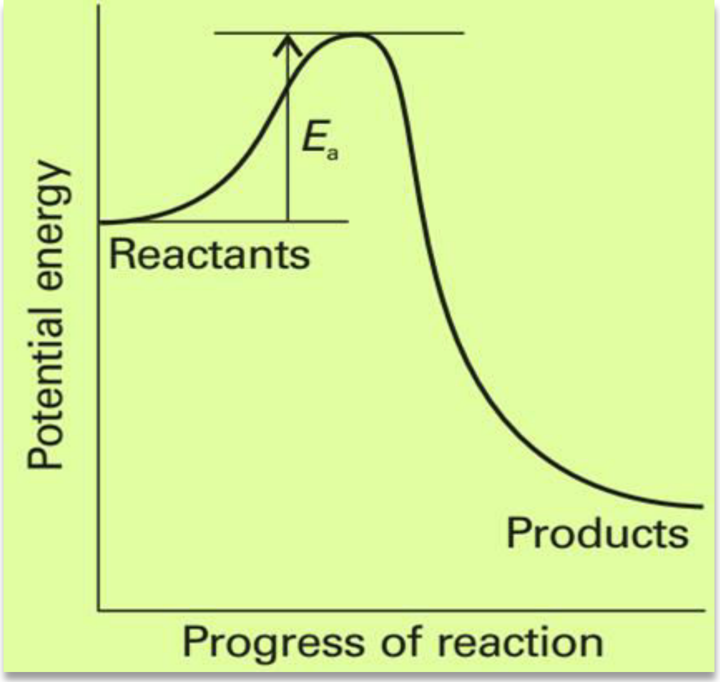
1. The rate of a reaction is proportional to the rate of reactant collisions:
2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.
3. The collision must occur with adequate energy to permit mutual penetration of the reacting species’ valence shells so that the electrons can rearrange and form new bonds (and new chemical species).

Collision theory

- But all the collision will not lead to the product. Only the molecules which are having sufficient energy ($E \geq E_a$) can cross the energy barrier.
- The minimum energy necessary to form a product during a collision between reactants is called the activation energy (E_a).
- The kinetic energy of reactant molecules plays an important role in a reaction because the energy necessary to form a product is provided by a collision of a reactant molecule with another reactant molecule.
- If the activation energy is much larger than the average kinetic energy of the molecules, the reaction will occur slowly: Only a few fast-moving molecules will have enough energy to react.
- If the activation energy is much smaller than the average kinetic energy of the molecules, the fraction of molecules possessing the necessary kinetic energy will be large; most collisions between molecules will result in reaction, and the reaction will occur rapidly.

Collision theory

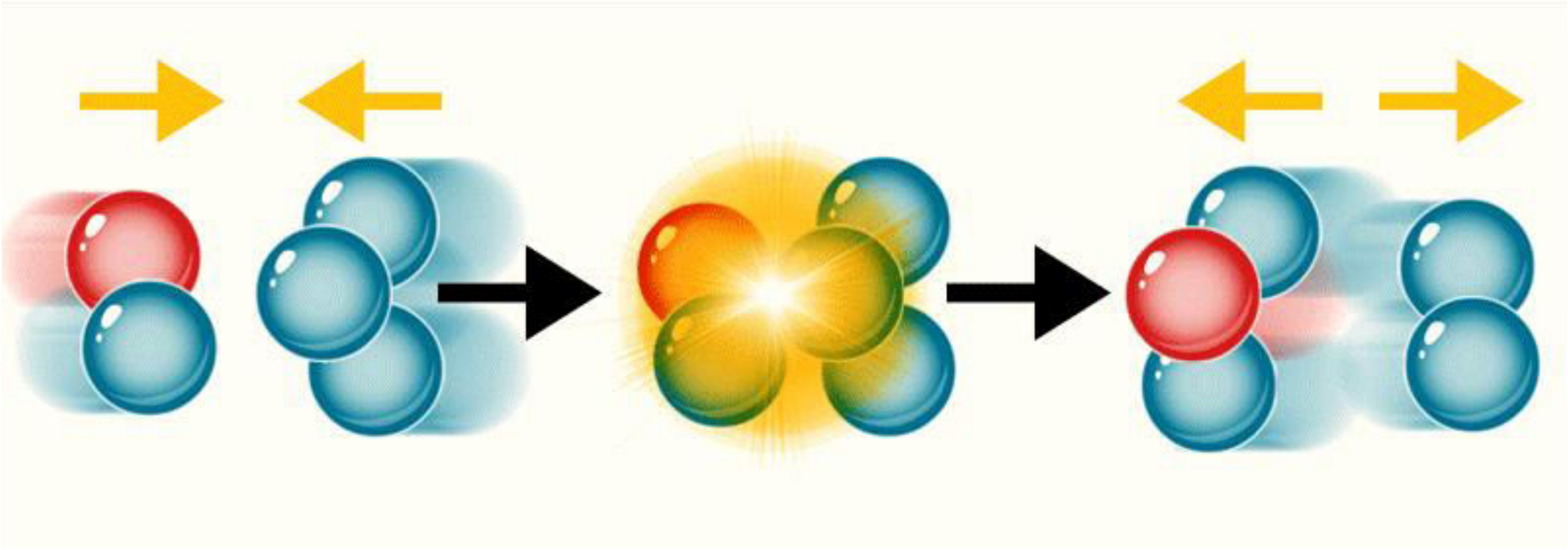
- The potential energy rises to a maximum and the cluster of atoms that corresponds to the region close to the maximum is called the **activated complex.**
- After the maximum, the potential energy falls as the atoms rearrange in the cluster and reaches a value characteristic of the products.
- The peak of the potential energy corresponds to the activation energy $E_{a..}$This crucial configuration is called the **transition state** of the reaction.
- The pre-exponential factor is a measure of the rate at which collisions occur irrespective of their energy. Hence, the product of A and the exponential factor, $e^{-E_a/RT}$, gives the rate of successful collisions.



A potential energy profile for an exothermic reaction. The height of the barrier between the reactants and products is the activation energy of the reaction.

Collision theory

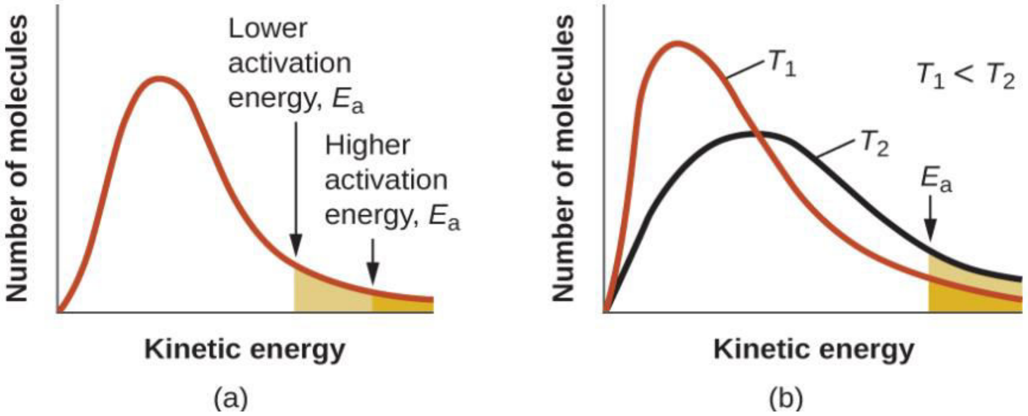
Both postulates of the collision theory of reaction rates are accommodated in the Arrhenius equation. The frequency factor A is related to the rate at which collisions having the correct orientation occur. The exponential term is related to the fraction of collisions providing adequate energy to overcome the activation barrier of the reaction.



Collision theory

Quantitatively, for two reactions at the same temperature

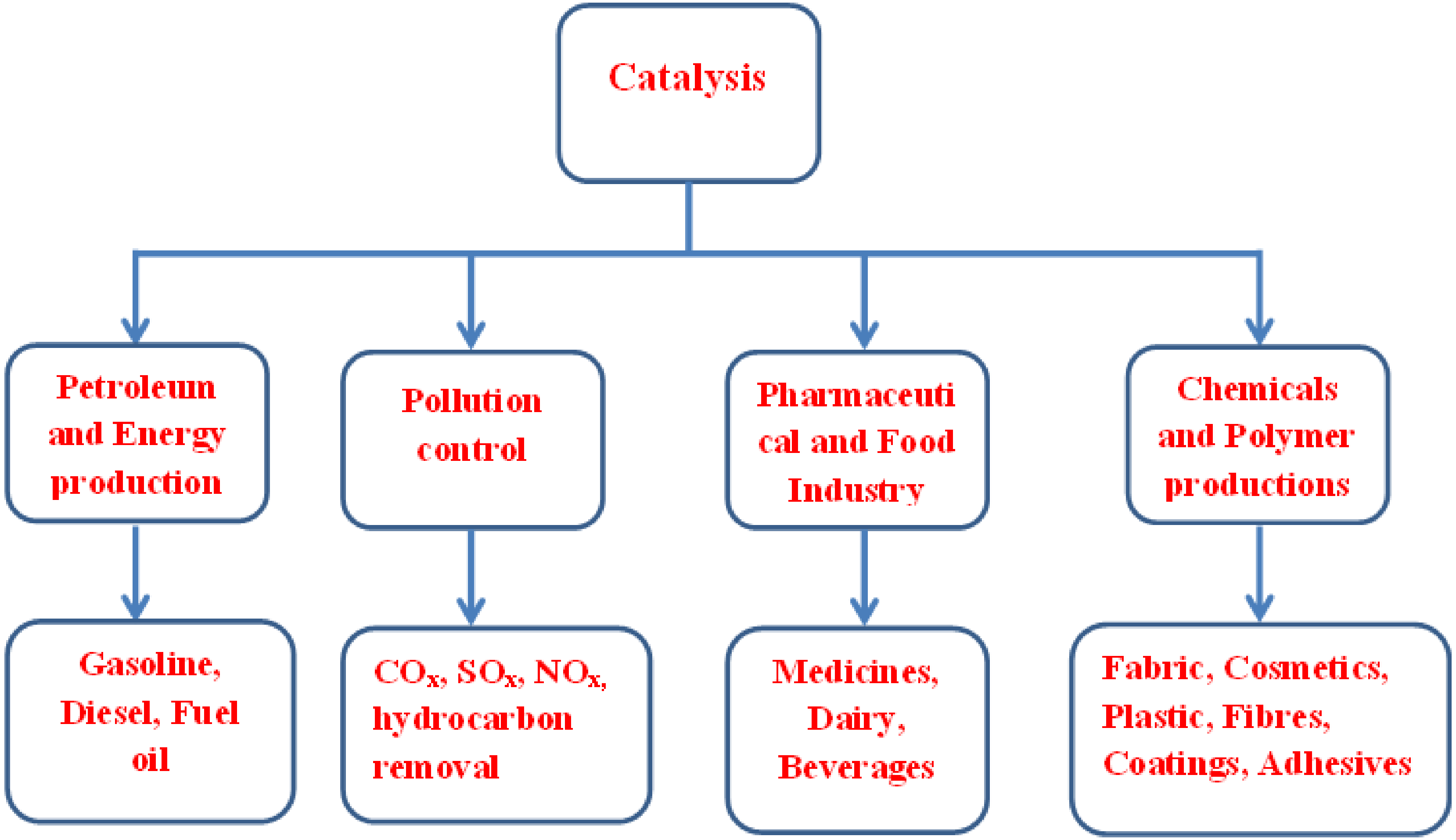
- ✔ The reaction with the higher activation energy has the lower rate constant and the slower rate. The larger value of E_a results in a smaller value for $e^{-\frac{E_a}{RT}}$ reflecting the smaller fraction of molecules with enough energy to react.
- ✔ The reaction with the smaller E_a has a larger fraction of molecules with enough energy to react. This will be reflected as a larger value of $e^{-\frac{E_a}{RT}}$, a larger rate constant, and a faster rate for the reaction.



(a) As the activation energy of a reaction decreases, the number of molecules with at least this much energy increases, as shown by the shaded areas.
(b) At a higher temperature, T_2, more molecules have kinetic energies greater than E_a, as shown by the yellow shaded area.

Catalysis

The science and technology of catalysis is of great significance as it affects our daily life. Four major sectors of the world economy; petroleum and energy production, chemicals and polymer production, food industry and pollution control, involve catalytic processes.



- Catalysis
  - Petroleum and Energy production
    - Gasoline, Diesel, Fuel oil
  - Pollution control
    - CO_x, SO_x, NO_x, hydrocarbon removal
  - Pharmaceutical and Food Industry
    - Medicines, Dairy, Beverages
  - Chemicals and Polymer productions
    - Fabric, Cosmetics, Plastic, Fibres, Coatings, Adhesives

Definition of Catalysis

“A catalyst is a chemical entity which by virtue of its presence in a reacting system increases or decreases the rate of the reaction, itself remaining unchanged in chemical properties or mass at the end of a reaction.”

The phenomenon of alteration of the rate of a reaction by a catalyst is known catalysis.

The **term catalysis**, proposed in **1835 by Jöns Jakob Berzelius (1779-1848),** comes from the Greek words **kata meaning down** and **lyein meaning loosen**.

The economic significance of the catalyst industry is enormous. The catalytic processes contribute greater than 30-40% of global GDP. The global catalyst market size was estimated at USD 34.0 billion in 2019 and is expected to reach USD 35.1 billion in 2020.

Characteristics of Catalysts

(1) The catalyst remains unchanged (in mass and chemical composition) in the reaction.

(2) A small quantity of the catalyst is required.

(3) The catalyst does not change the equilibrium constant but the equilibrium approaches earlier.

Catalytic reactions

Catalysts work by providing alternative mechanism involving a different transition state of lower energy. Thereby, the activation energy* of the catalytic reaction is lowered compared to the uncatalyzed reaction as shown in Figure below:

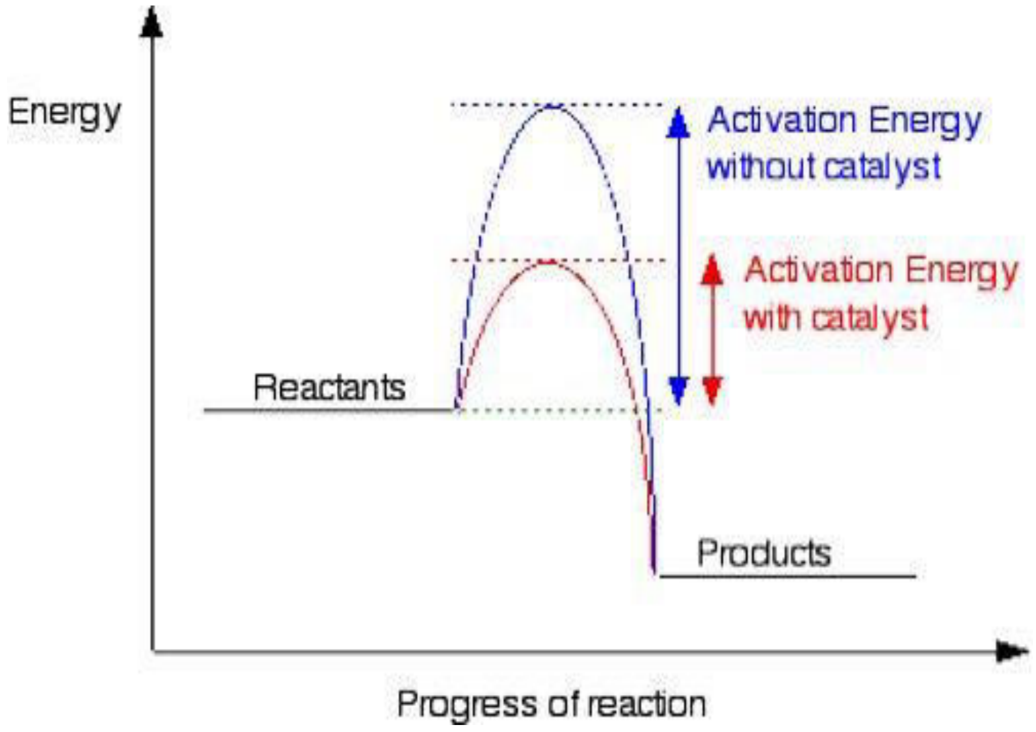


Figure: Schematic diagram to illustrate the effect of catalyst on activation energy of reactions

Types of catalysis

Following are the main types of catalysis:

1. **Heterogeneous catalysis**
2. **Homogeneous catalysis**
3. **Enzyme catalysis**

1. Heterogeneous catalysis

If the catalyst is present in a **different phase** than the reactants is called **heterogeneous catalyst and the phenomenon is known heterogeneous catalysis.**

In heterogeneous catalysis the reactions take place at the interface of two phases. The catalyst is, often a solid and adsorbs a liquid or a gas. This type of catalysis is of great importance in many industrial processes.

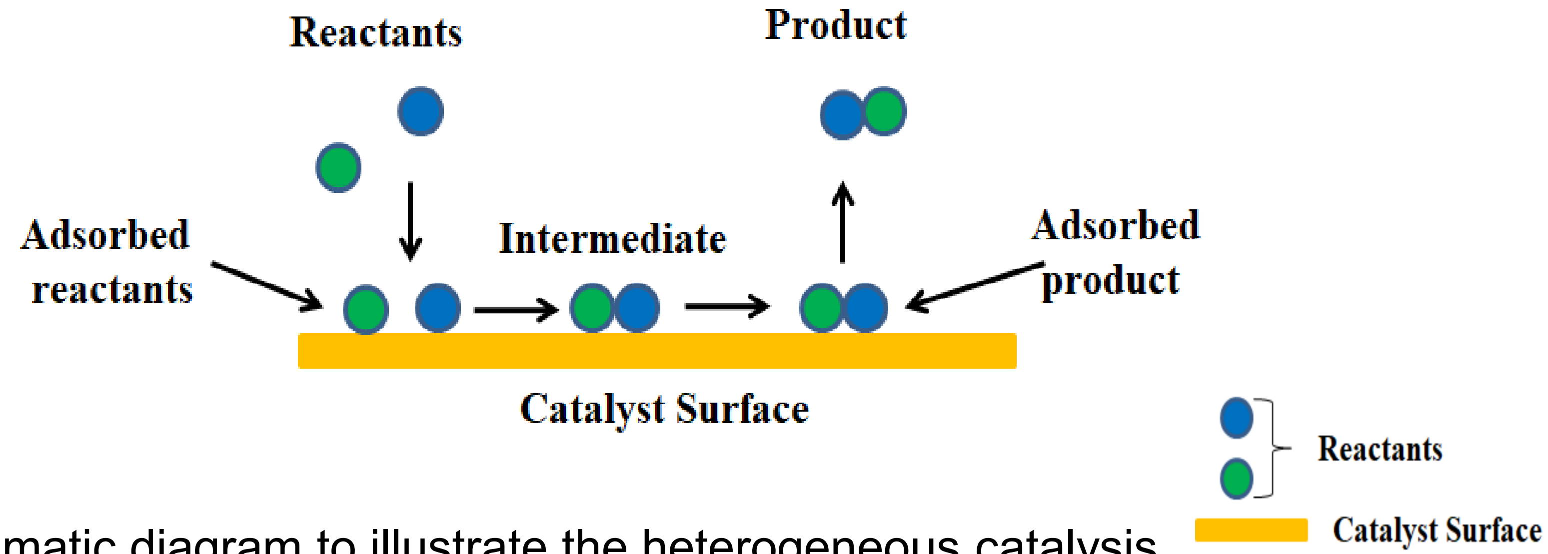


Figure: Schematic diagram to illustrate the heterogeneous catalysis.

Examples of Heterogeneous catalyst

(a) Manufacture of ammonia by the Haber process. Iron (Fe) acts as catalyst.

$$\mathbf{N_2\ (g) + 3H_3\ (g) \rightarrow 2NH_3\ (g)}$$

(b) Manufacture of sulphuric acid by the Contact process. Vanadium pentoxide (V_2O_5) or platinum are catalysts for the production of SO_3 (g) from SO_2 (g) and O_2 (g).

$$\mathbf{2SO_2\ (g) + O_2\ (g) \rightarrow 2SO_3\ (g)}$$

(c) Catalysts used in many reactions in the petroleum and polymer industries. **There are cases of heterogeneous catalysis where a reaction in the liquid phase is catalysed by a substance in the solid state.** An example is the decomposition of H_2O_2 (aqueous) by MnO_2 (s).

$$\mathbf{2H_2O_2\ (aq) \rightarrow 2\ H_2O\ (l) + O_2\ (g)}$$

(d) Examples of reactions in which both the reactant and the catalyst are in the solid phase. The decomposition of $KClO_3$ is catalysed by solid MnO_2.

$$\mathbf{2\ KClO_3\ (s) \rightarrow 2KCl\ (s) + 3O_2\ (g)}$$

2. Homogeneous catalysis

In a reaction, if the catalyst is present in the **same phase** as the reactants, it is called a **homogeneous catalyst and the phenomenon is homogeneous catalysis**. Such catalysis can take place in gaseous reaction or reactions in solution.

These chemicals help in attaining the equilibrium more quickly by increasing the rates of both the forward and reverse reactions to an extent.

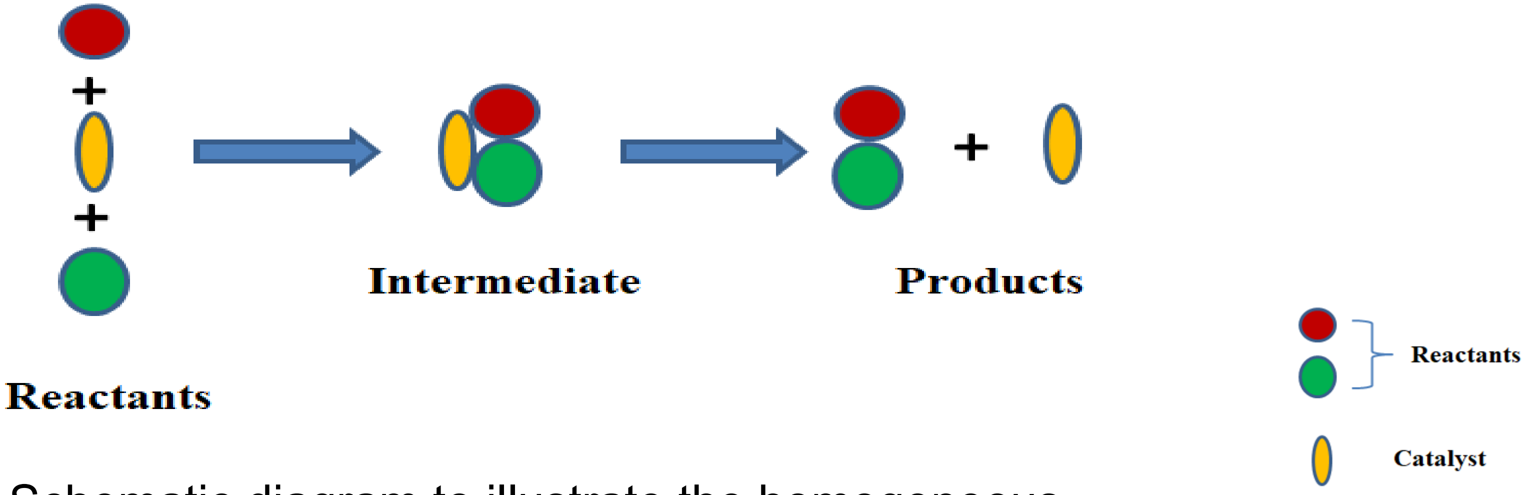


Figure: Schematic diagram to illustrate the homogeneous catalysis.

Examples of homogeneous catalysis in the gas phase

(a) Oxidation of sulphur dioxide, SO_2, by oxygen to sulphur trioxide, SO_3, in presence of nitric oxide, NO, in the Chamber Process for sulphuric acid manufacture.

$$\mathbf{2SO_2\ (g) + O_2\ (g) \rightarrow 2SO_3\ (g)}$$

here, **NO** acts as a catalyst.

(b) The following reaction in the gas phase is catalyzed by traces of chlorine gas, particularly in presence of light.

$$\mathbf{2N_2O\ (g) \rightarrow 2N_2\ (g) + O_2\ (g)}$$

In presence of light chlorine forms chlorine radicals, which react with N_2O forming the intermediate radical ClO*. The proposed mechanism is:

Step 1: $N_2O\ (g) + Cl^*\ (g) \rightarrow N_2\ (g) + ClO^*(g)$

Step 2: $2ClO^*(g) \rightarrow Cl_2\ (g) + O_2\ (g)$

Examples of homogeneous catalysis in the solution phase

(a) Hydrolysis of ester in the presence of acid and alkali:

$$CH_3COOC_2H_5\ (l) + H_2O\ (l) \rightarrow CH_3COOH\ (aq) + C_2H_5OH\ (aq)$$

(b) Hydrolysis of sucrose (cane sugar) into glucose and fructose in presence of minerals acids acting as catalysts:

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

Enzyme catalysis

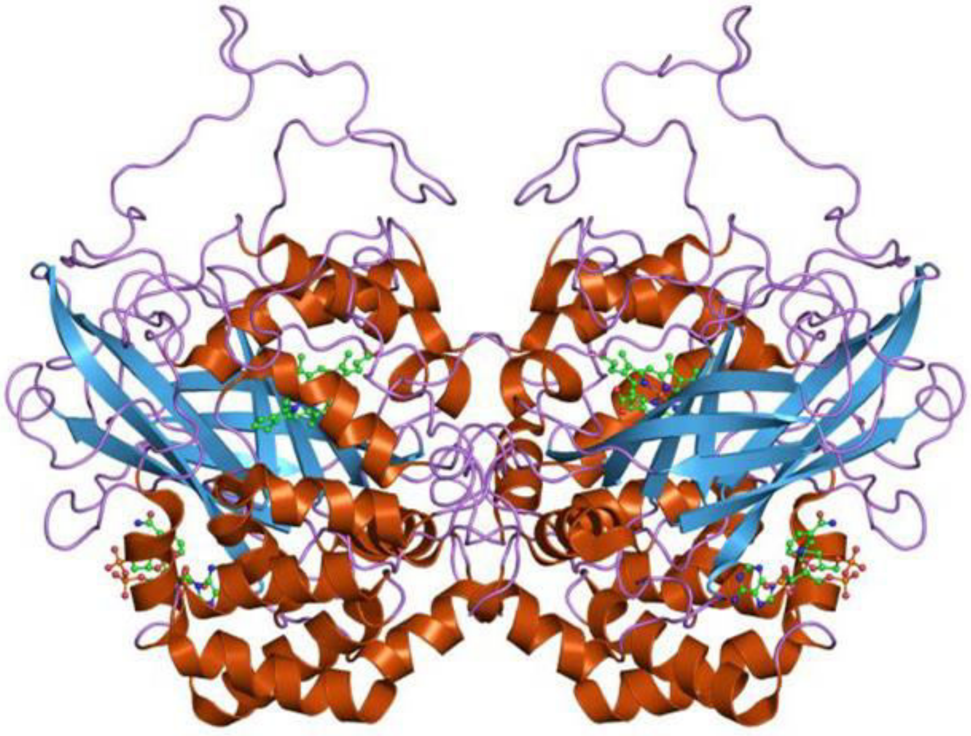
Michaelis-Menton mechanism

Enzymes

- ❑ Enzymes are **protein-based molecules** that can process certain chemical reactions
- ❑ These reactions occur at a **localized site**, called the **active site**, at the rate much faster than a normal chemical reaction.
- ❑ **Substrate** is the molecule that fits into the active site of the enzyme and undergoes transformation to a product.
- ❑ Example of an enzyme catalysed reaction is **catalase** that converts **hydrogen peroxide to water and oxygen**. It is an important enzyme protecting the cell from oxidative damage by reactive oxygen species (ROS)

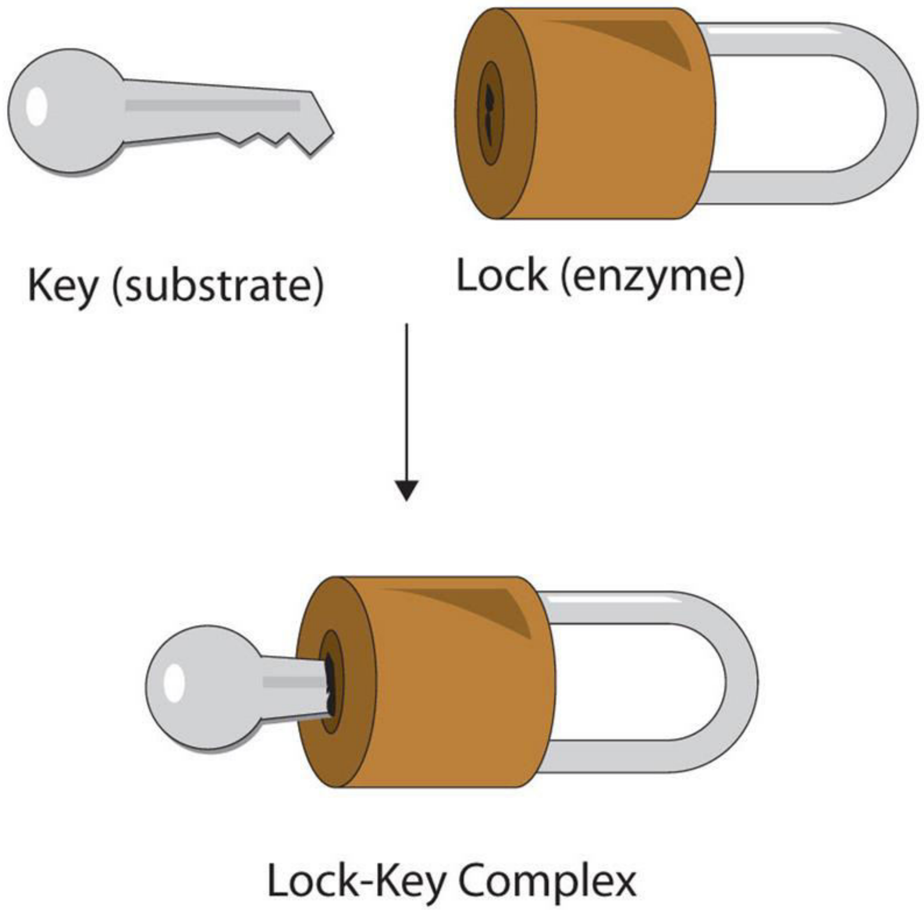
$$\mathbf{H_2O_2 \rightarrow H_2O + O_2}$$

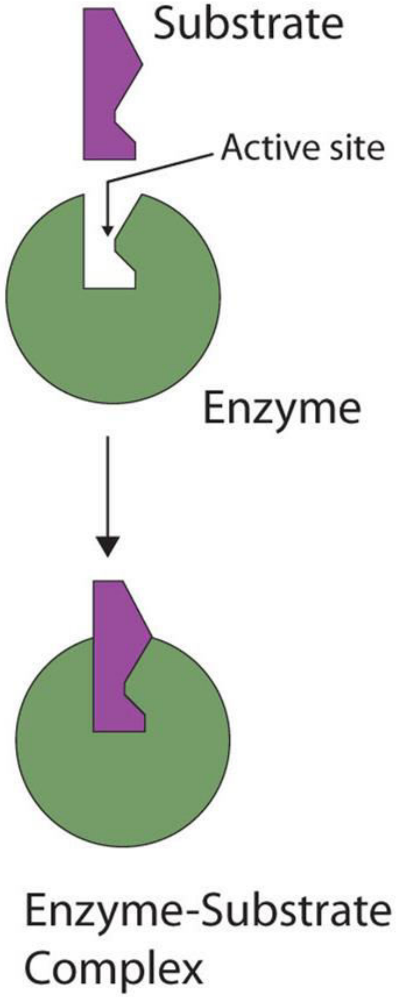
Reaction catalysed by the enzyme, catalase



Molecular structure of **Catalase**

Mechanism of enzyme-catalyzed





- Enzyme-catalyzed reactions work in a **lock and key** fashion.
- The substrate uniquely fits like a key into the active site of the enzyme, forming a **lock-key complex**.
- The substrate is converted into the product by the enzyme at the active site.
- The product is then released from the active site.

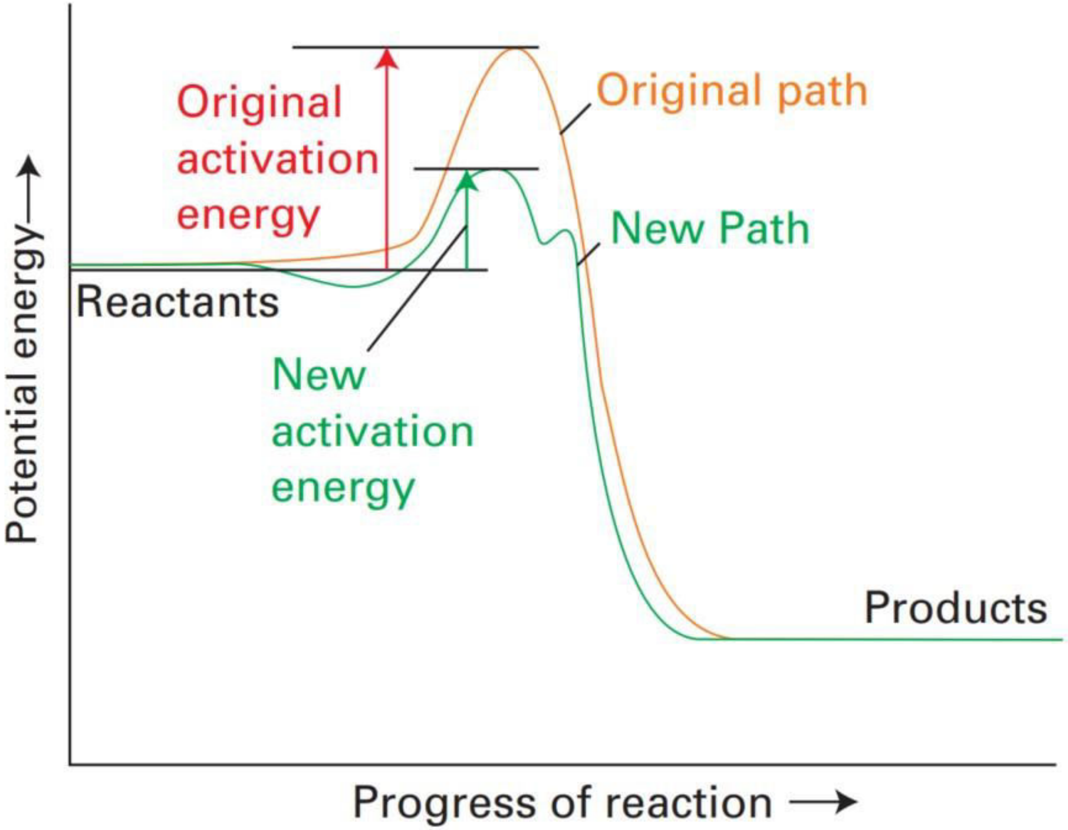
Enzymes’ effect on the activation energy

- Enzymes lower the activation energy for reactions. The lower the activation energy, the faster the rate of the reactions.

- For example: the **enzyme catalase** reduces the activation energy for the decomposition of hydrogen peroxide to 8 kJ mol^{-1}, corresponding to an acceleration of the reaction by a factor of **10^{15}** at 298 K.

- A generic equation for the complex formation is as follows:

$$\mathbf{E + S \longleftrightarrow ES \longleftrightarrow P + E}$$



Michaelis-Menten equation

- Michaelis-Menten equation is a commonly used model that assumes that the concentration of the enzyme remains constant.

- The enzyme reacts with the substrate for form an enzyme-substrate complex, which leads to the synthesis of the product and the release of the enzyme

$$\mathbf{E + S} \underset{k_a'}{\overset{k_a}{\longleftrightarrow}} \mathbf{ES} \overset{k_b}{\longleftrightarrow} \mathbf{P + E}$$

- Where, k_a is the rate of formation of ES, k_a' is the rate of dissociation of ES, and k_b is the rate of formation of P from ES.

Michaelis-Menten Mechanism

One of the earliest descriptions of the action of enzymes is the **Michaelis-Menten mechanism**. The proposed mechanism, with all species in an aqueous environment, is as follows.

Step 1: The bimolecular formation of a combination, ES, of the enzyme E and the substrate S:

$\mathbf{E + S \rightarrow ES}$ **Rate of formation of ES =** $\boldsymbol{k_a}$**[E][S]**

Step 2: Unimolecular decomposition of the complex:

$\mathbf{ES \rightarrow E + S}$ **Rate of decomposition of ES =** $\boldsymbol{k_a'}$**[ES]**

Step 3: The unimolecular formation of products P and the release of the enzyme from its combination with the substrate:

$\mathbf{ES \rightarrow P + E}$ **Rate of decomposition of ES =** $\boldsymbol{k_a'}$**[ES]**

Rate of decomposition of ES = $\boldsymbol{k_a'}$**[ES]**