

# 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).

### **1<sup>st</sup> class**

Thermodynamics: Basic Terminologies

0<sup>th</sup> Law of Thermodynamics

1<sup>st</sup> Law of Thermodynamics

### **2<sup>nd</sup> class**

Enthalpy & Heat Capacity

Application of 1<sup>st</sup> Law to the Expansion Work

Numerical from 1<sup>st</sup> Law

### **3<sup>rd</sup> class**

2<sup>nd</sup> Law of Thermodynamics

Entropy and Carnot Cycle

### **4<sup>th</sup> class**

Free Energy

Numerical from 2<sup>nd</sup> law of Thermodynamics

Spontaneity of a Chemical Reaction

3<sup>rd</sup> Law of Thermodynamics

### **5<sup>th</sup> class**

Chemical kinetics

Factors affecting reaction rates

Rate laws and rate constants

First order reaction

Half-life of first order reaction

### **6<sup>th</sup> class**

Second-order reactions

Zero-order reactions

Pseudo first order reaction

### **7<sup>th</sup> class**

Temperature and rate of reactions

Collision model and activation energy

*Arrhenius equation*

Catalysis

### **8<sup>th</sup> class**

Types of catalysis

Homogeneous and Heterogeneous catalysis

Enzyme catalysis

Michaelis-Menten equation

# **Part-A**

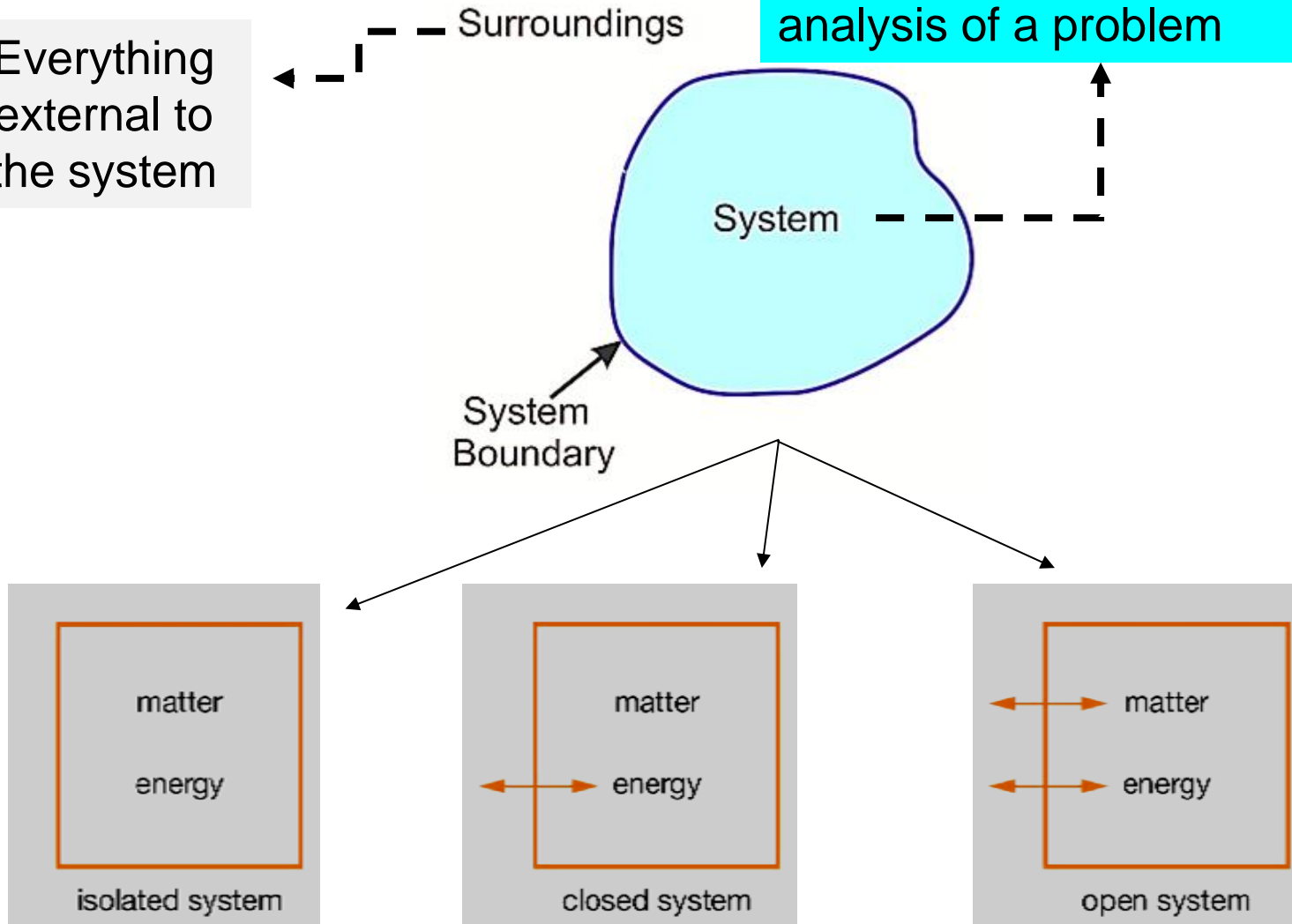
## **Thermodynamics**

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

## Thermodynamic Systems:

Everything  
external to  
the system

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



## Properties of a system:

### # Intensive Properties:

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



Temperature



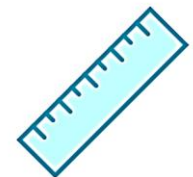
Boiling Point

### # Extensive Properties

Extensive properties depend  
on how much matter a sample  
contains.



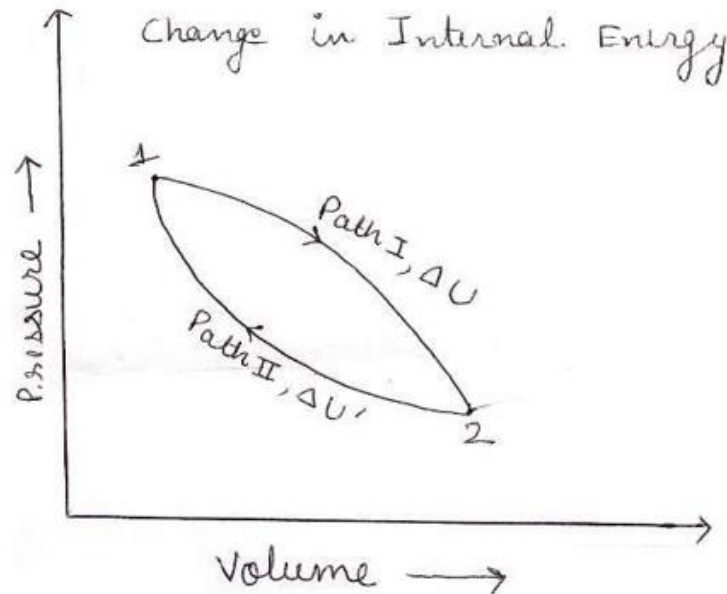
Weight



Length<sup>4</sup>

## # 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.



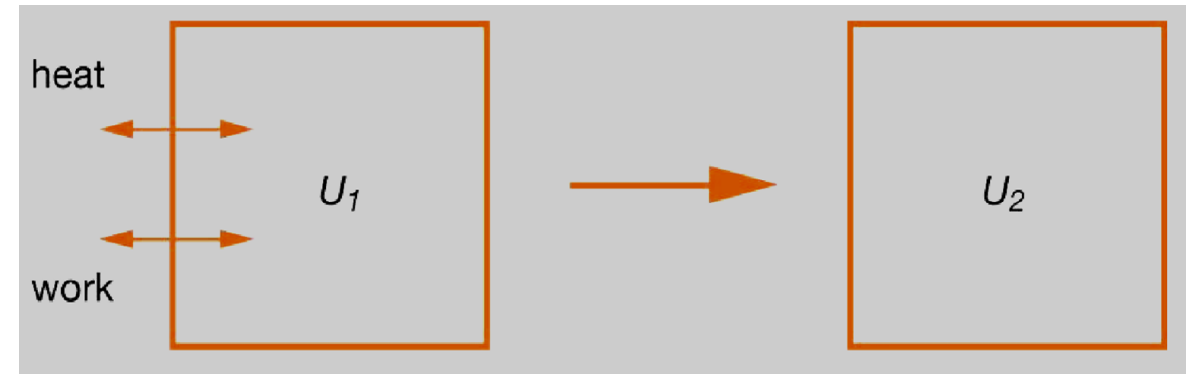
## # Path function:

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**



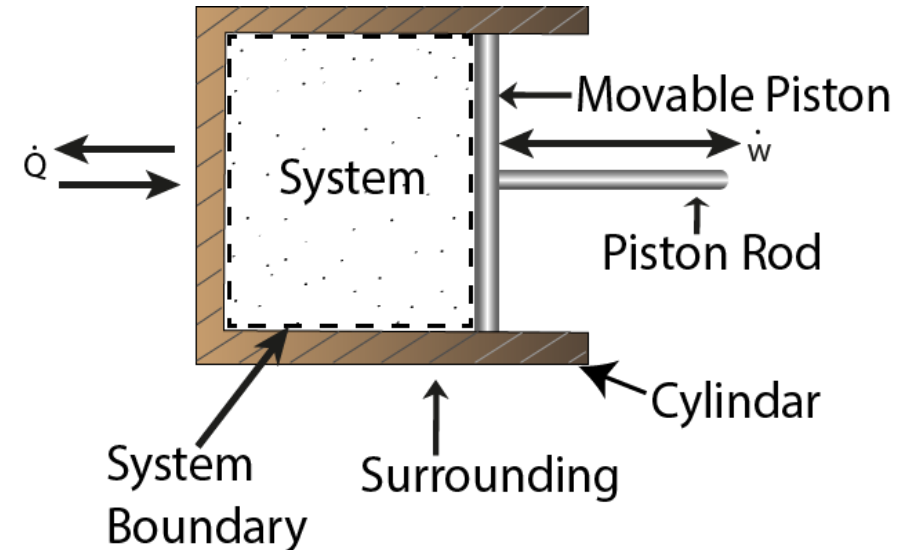
$$\triangleright \Delta U_{\text{system}} = U_{\text{final state}} - U_{\text{initial state}}$$

## 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)  $\times$   $w$  (distance moved in the direction of force)



- **Gas is heated**  $\Rightarrow$  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  $P_{ex}$ :

$$\underline{dw = -P_{ex}dV}$$

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

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

❑ 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:*

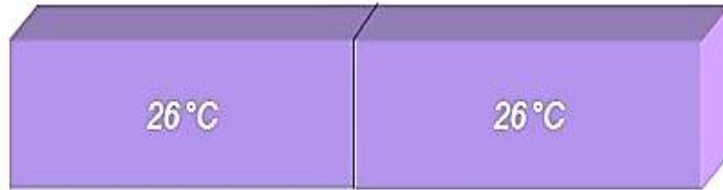
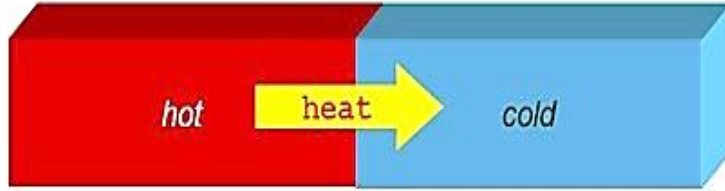
**Reversible expansion:**

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.

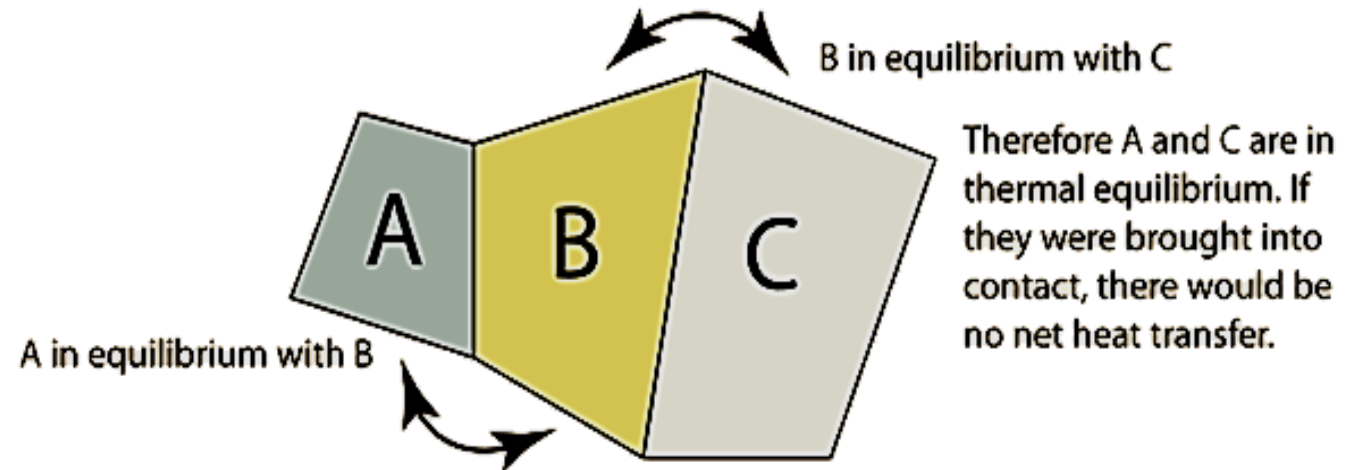
$$dw = -P_{ex}dV = -pdV$$
$$W = - \int_{v_i}^{v_f} p dv$$



- ❑ 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 0<sup>th</sup> law:

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



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



- 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 &  $\Delta U$  = 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* ( $\Delta U$ ) of a system = heat added to the system ( $q$ ) - the work done *by* the system ( $w$ )**

$$\Delta U = q - w$$

- 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

$$\Rightarrow H_f - H_i = q$$

$$\Delta U = \Delta H - P\Delta V$$

$$\text{or } \Delta H = \Delta U + P\Delta V$$

,

- 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.

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

- ☺ 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  $w = 0$  &  $\Delta U = q$

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

## □ 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  $\Rightarrow$

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

## □ Relationship between $C_p$ & $C_v$

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

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

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

- **For ideal gas**,  $PV = RT$  (for 1 mole)  
 $\Delta(PV) = R \Delta T$

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

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

$$C_v = 3/2 R \text{ (For monoatomic ideal gas)}$$

$$C_p = 5/2 R \text{ (For monoatomic ideal gas)}$$

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

## ➤ Isothermal Process (constant temperature)

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

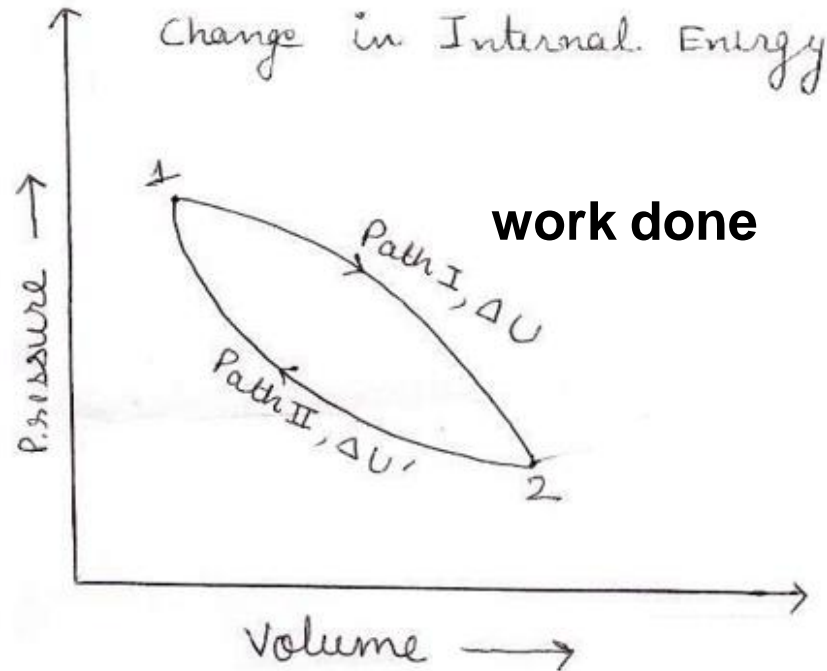
⇒ **For an ideal gas,**

**The internal energy ( $U$ )  $\propto$  Temperature ( $T$ )**

if  $T = \text{fixed}$ ,  $\Delta U = 0$  (according to 1<sup>st</sup> law, which deals with  $\Delta U$ )

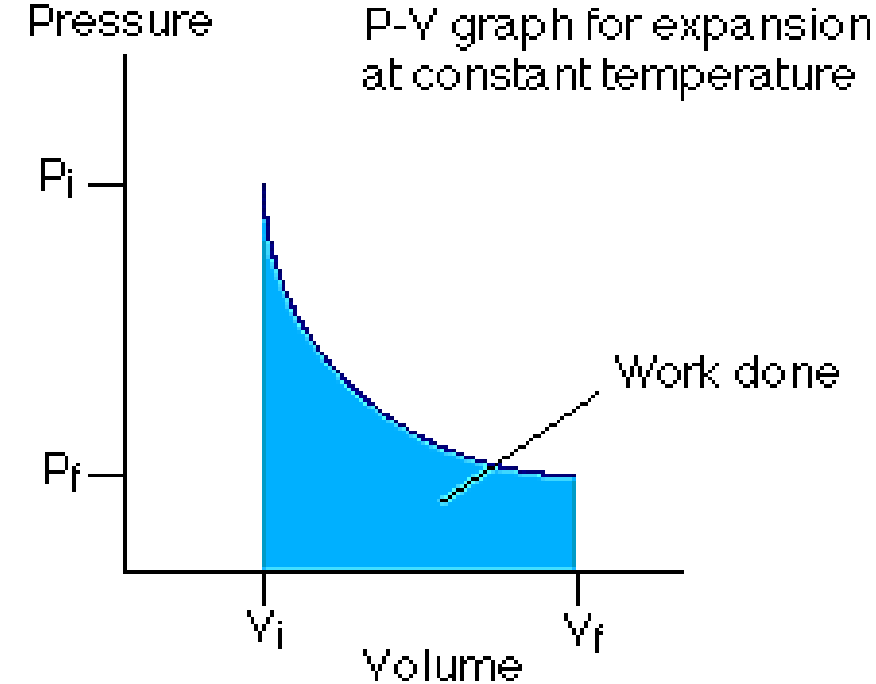
$$\text{As, } \Delta U = q - w = 0 \\ \Rightarrow q = w$$

- 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.**



## Pressure-volume diagram

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



## ➤ Reversible isothermal expansion:

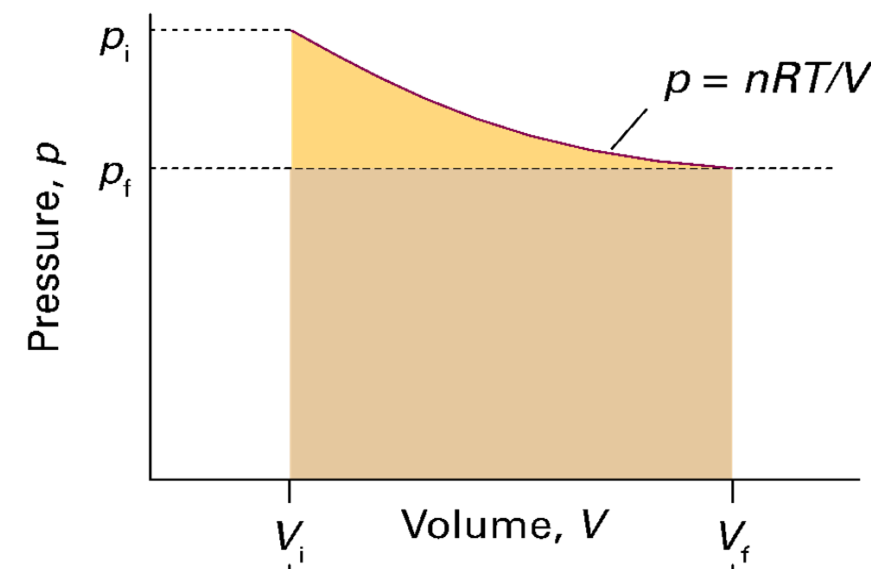
$$w = \int_{v_i}^{v_f} P dv = \int_{v_i}^{v_f} \frac{nRT}{V} dv \quad (\text{as } PV = nRT)$$

(throughout the expansion,  $P_{\text{ex}} = P$  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)



## ➤ Irreversible Isothermal expansion

- a) Free expansion (expansion in vacuum)

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

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

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

- 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.**

## ➤ Adiabatic process (constant

heat)

- no heat is added/ removed from a system.
- 1<sup>st</sup> law of thermodynamics:

$$\Delta U = w$$

(as no heat is allowed to enter/leave the system,  $q = 0$ )

✓ Example: A gas expanding so quickly that no heat can be transferred. Due to the expansion work, temperature drops. **This is exactly what happens with a carbon dioxide fire extinguisher**, with the gas coming out at high pressure and cooling as it expands at atmos. pressure

→ **Expansion:**  $w = -ve$ ,  $\Delta U = -ve$ ;

So, **T** of the system falls

⇒ Work is done by the system at the expense of its internal energy

- $w = \Delta U = C_v \Delta T$  (for 1 mole of gas)
- $\Delta H = C_p \Delta T$  (for 1 mole of gas)

## ➤ Reversible adiabatic

expansion

- Relation between **T**, **V**

$$\left(\frac{T_i}{T_f}\right) = \left(\frac{V_f}{V_i}\right)^{\gamma} \Rightarrow \ln\left(\frac{T_i}{T_f}\right) = (\gamma - 1) \ln\left(\frac{V_f}{V_i}\right)$$

$$\Rightarrow \ln\left(\frac{T_i}{T_f}\right) = \left(\frac{C_p}{C_v} - 1\right) \ln\left(\frac{V_f}{V_i}\right) \quad [as, \gamma = \frac{C_p}{C_v}]$$

$$\Rightarrow \ln\left(\frac{T_i}{T_f}\right) = \left(\frac{R}{C_v}\right) \ln\left(\frac{V_f}{V_i}\right) \quad [as, C_p - C_v = R]$$

$$\Rightarrow \boxed{C_v \ln\left(\frac{T_i}{T_f}\right) = R \ln\left(\frac{V_f}{V_i}\right)}$$

## ➤ Irreversible adiabatic

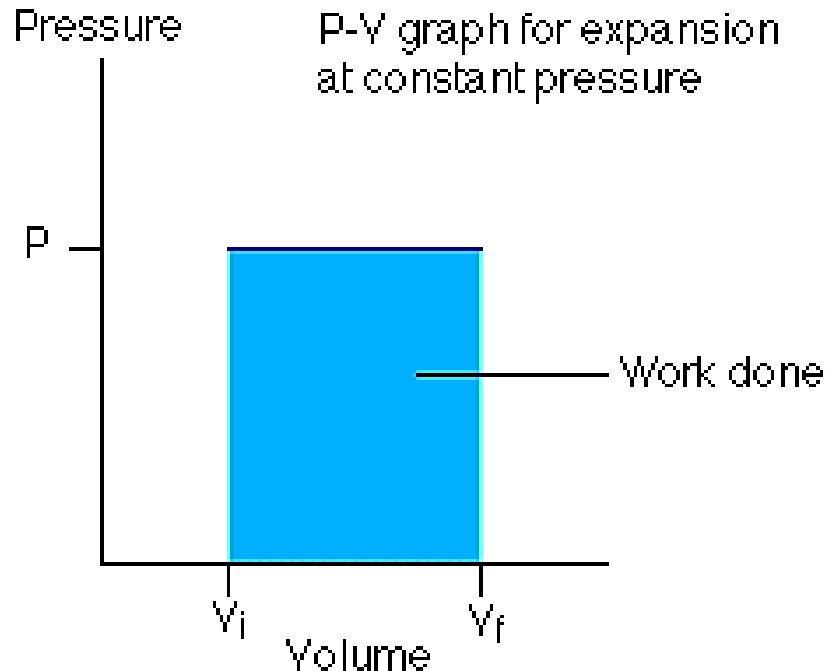
expansion

- Free expansion ( $P_{ex} = 0$ ):  $\Delta T = 0$ ,  $W = 0$ ,  $\Delta H = 0$
- Expansion against a constant pressure:

$$C_v (T_f - T_i) = R P_{ex} \left( \frac{T_i P_f - T_f P_i}{P_i P_f} \right)$$

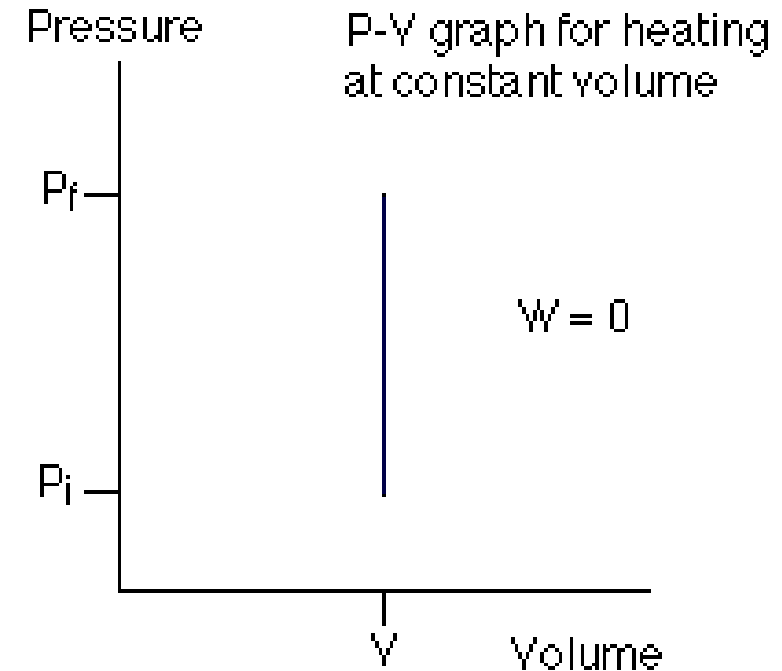
## ➤ Isobaric process (constant pressure)

- the pressure is kept constant.
  - The work done by the system in an isobaric process is simply the pressure multiplied by the change in volume
- ✓ Example of an isobaric system: A gas, being slowly heated or cooled, confined by a piston in a cylinder.



## ➤ Isochoric process (constant volume)

- the volume is kept constant
  - The work done is zero in an isochoric process
- ✓ Example of an isochoric system: A gas in a box with fixed walls





- **Why we need for the 2nd law of thermodynamics?** ➤ The 1<sup>st</sup> law uses the **internal energy** to identify **permissible changes**  
→ The 1<sup>st</sup> 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<sup>nd</sup> law of thermodynamics
- The 2<sup>nd</sup> law uses the **entropy** to identify which of these **permissible changes are spontaneous**.

## □ 2<sup>nd</sup> 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.

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

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

**S** = the entropy of the system of interest, &

**S<sub>sur</sub>** = the entropy of the surroundings

# **Note:** when considering applications of the 2<sup>nd</sup> 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.

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

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

## ➤ Thermodynamic definition of entropy

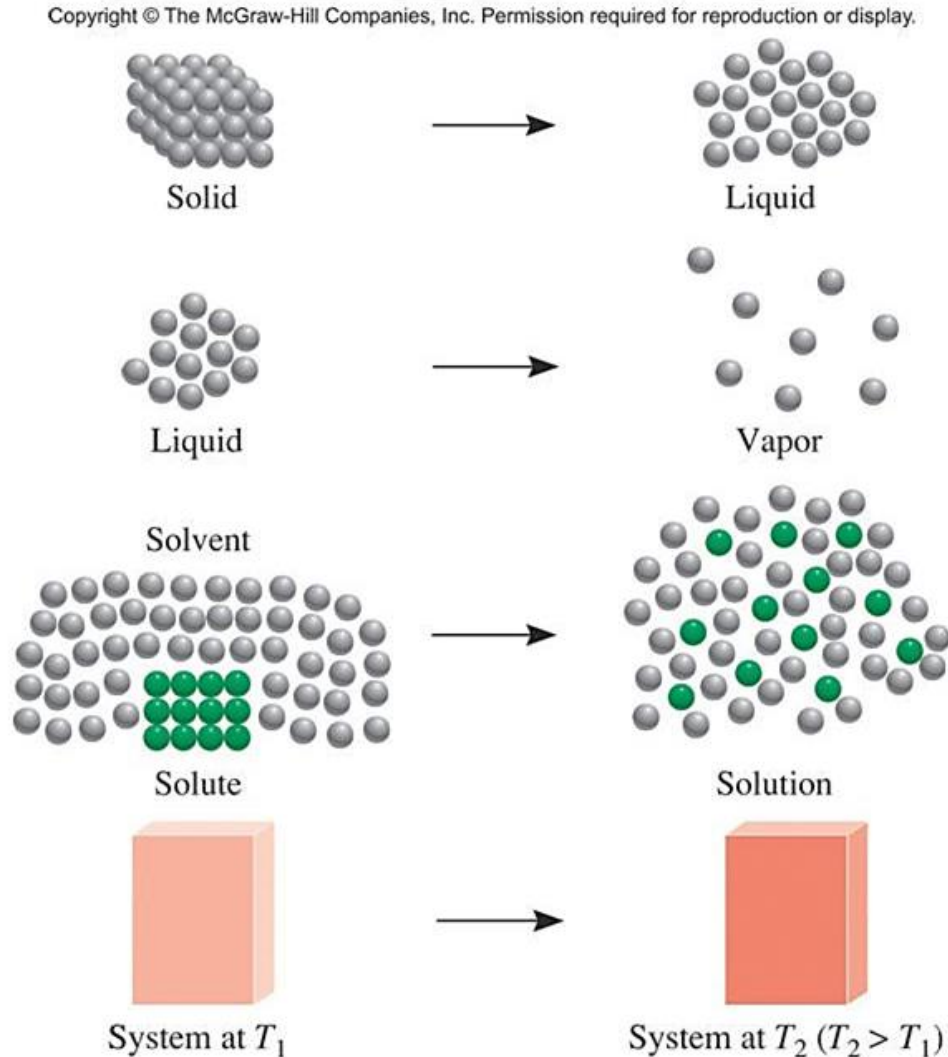
→ The thermodynamic definition of entropy concentrates on the change in entropy (**dS**) that occurs as the result of a physical or chemical process.

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

$$dS = dq_{\text{rev}}/T, \quad \Delta S = \int_i^f \frac{dq_{\text{rev}}}{T}$$



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



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

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

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

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

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

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

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

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

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

## ➤ 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 1<sup>st</sup> law]  
 $\Rightarrow$  no heat is absorbed by or removed from the surrounding,

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

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

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

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

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

## ➤ Isothermal *Reversible* expansion

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

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

## ➤ Clausius inequality

$$dS \geq \frac{dq}{T}$$

▪ 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:

$$dS_{\text{total}} = dS_{\text{system}} + dS_{\text{surrounding}} = 0$$

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

▪ Irreversible process

$$dS_{\text{total}} > dS_{\text{system}} + dS_{\text{surrounding}} > 0$$

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

- The 1<sup>st</sup> law & the 2<sup>nd</sup> law of thermodynamics were summed up by German Physicist Rudolf Clausius as below:  
***The energy of the universe remains constant; the entropy of the universe tends towards a maximum***

## ➤ Entropy change during different processes

- For an ideal gas (1 mole) with variable T & V

$$\Delta S = C_v \ln \frac{T_f}{T_i} + R \ln \frac{V_f}{V_i}$$

- For an ideal gas with variable P & T

$$\Delta S = C_p \ln \frac{T_f}{T_i} - R \ln \frac{P_f}{P_i}$$

- For an ideal gas in an isothermal process

$$\Delta S_T = R \ln \frac{V_f}{V_i} = -R \ln \frac{P_f}{P_i}$$

- For an ideal gas in an isobaric process

$$\Delta S_P = C_p \ln \frac{T_f}{T_i}$$

- For an ideal gas in an isochoric process

$$\Delta S_v = C_v \ln \frac{T_f}{T_i}$$

## ➤ Heat engine

- Its a device which transforms heat into work
- This happens in a cyclic process
- Heat engines require a hot reservoir to supply energy ( $Q_H$ ) and a cold reservoir to take in the excess energy ( $Q_C$ )
  - $Q_H$  is defined as **positive**,  $Q_C$  is defined as **negative**

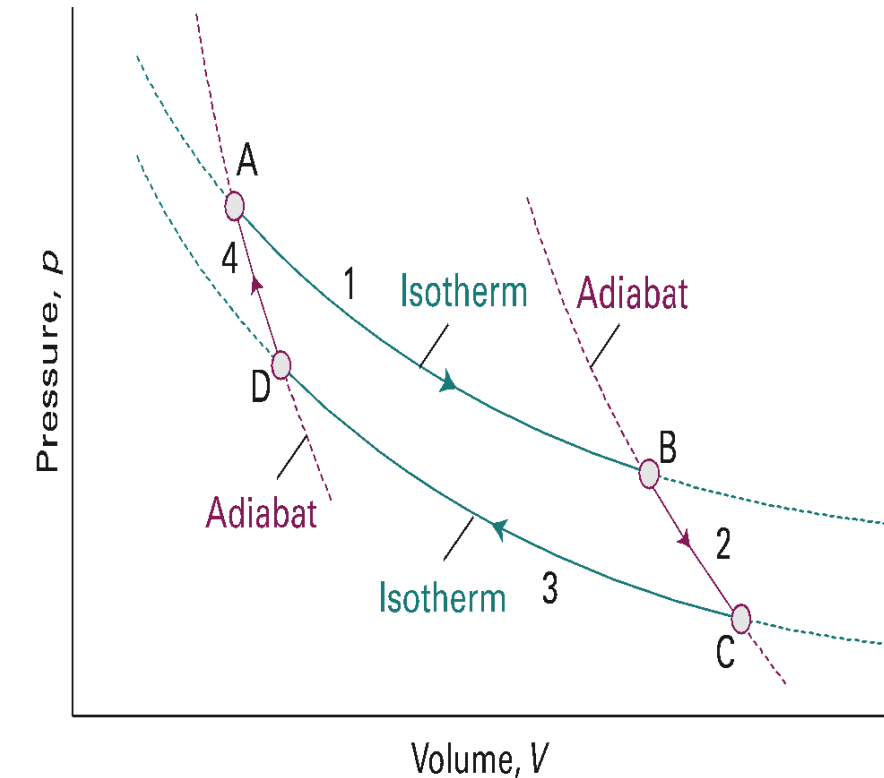
## ➤ Carnot Cycle

- A ***Carnot cycle*** (named after the French engineer Sadi Carnot) consists of **four reversible stages** in which a gas (the working substance) is either **expanded/compressed** in various ways
- To demonstrate the maximum convertibility of heat into work
- The system consists of **1 mole of an ideal gas** which is subjected to **four strokes**

## ➤ Four stages of Carnot Cycle:

### A. 1<sup>st</sup> stroke:

Curve AB: A → B: **Isothermal expansion** at  $T_h$   
Work done *by* the gas



### B. 2<sup>nd</sup> stroke:

Curve BC (B → C): **Adiabatic expansion**,  
Work done *by* the gas

### C. 3<sup>rd</sup> stroke:

Curve CD (C → D): **Isothermal compression** at  $T_c$ ,  
Work done *on* the gas.

### D. 4<sup>th</sup> stroke:

Curve DA (D → A): **Adiabatic compression**  
Work done *on* the gas

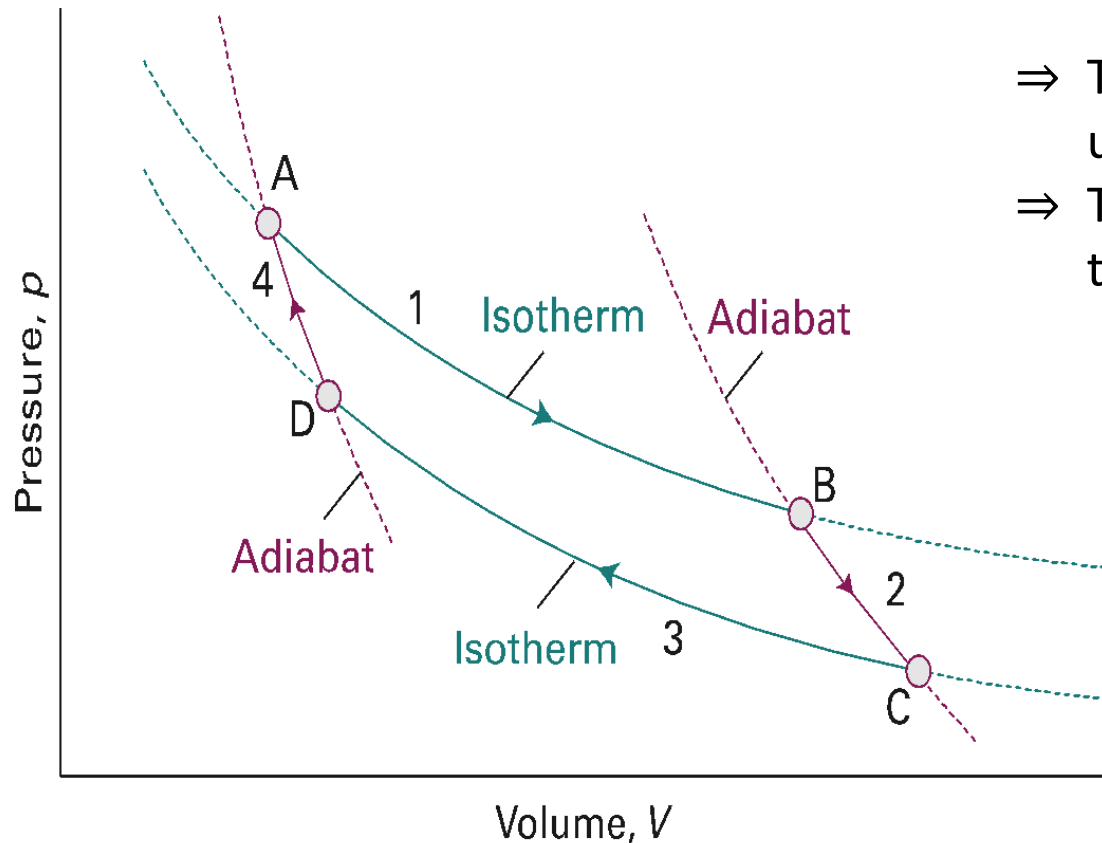
- The thermal efficiency ( $\eta$ ) of a heat engine is

$$\eta = \frac{\text{work performed}}{\text{heat absorbed from the hot source}} = \frac{W}{q_h} \\ = 1 - q_c/q_h = 1 - T_c/T_h$$

- The “**engine**” statement of the 2<sup>nd</sup> Law:
  - it is impossible for any system to have an efficiency of 100% ( $\eta = 1$ )

- Another statement of the 2<sup>nd</sup> Law:
  - It is impossible for any process to have as its sole result the transfer of heat from a cooler object to a warmer object

## ➤ Four stages of Carnot Cycle:



### A. 1<sup>st</sup> stroke:

Curve AB: A → B: **Isothermal expansion** at  $T_h$

Work done *by* the gas

- ⇒ The gas is placed in thermal contact with  $Q_h$  (at  $T_h$ ) and undergoes reversible isothermal expansion from A to B.
- ⇒ The entropy change is  $q_h/T_h$  ( $q_h$  = the energy supplied to the system as heat from the hot source)

$$q_h = -w_1 = RT_h \ln \frac{V_B}{V_A}$$

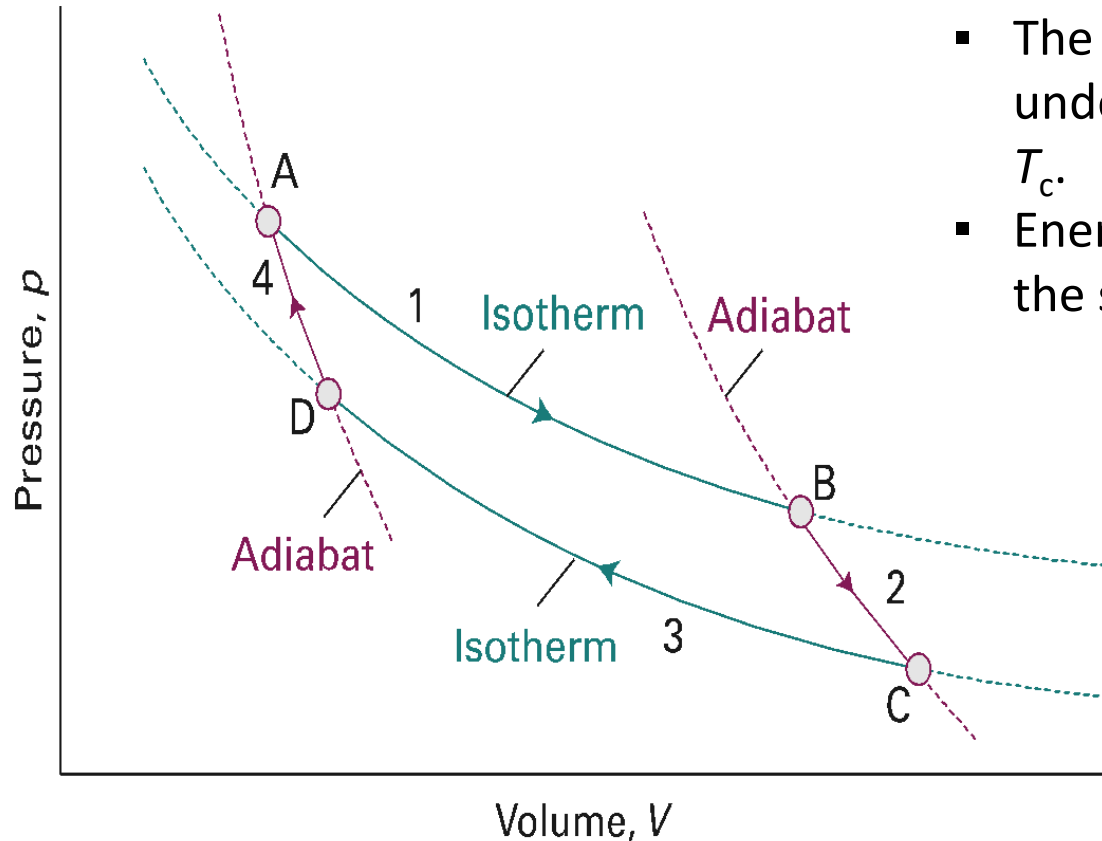
### B. 2<sup>nd</sup> stroke:

Curve BC (B → C): **Adiabatic expansion**,

Work done *by* the gas

- ⇒ Contact with  $Q_h$  is broken & the gas undergoes reversible adiabatic expansion from B to C.
- ⇒ No energy leaves the system as heat,  $\Delta S = 0$
- ⇒ The expansion is carried on until the temperature of the gas falls from  $T_h$  to  $T_c$  (the temperature of  $Q_c$ )

$$-w_2 = -C_v (T_h - T_c)$$



## C. 3<sup>rd</sup> stroke:

Curve CD (C → D): **Isothermal compression** at  $T_c$ ,  
Work done *on* the gas.

- The gas is placed in contact with the cold sink ( $Q_c$ ) and undergoes a reversible isothermal compression from C to D at  $T_c$ .
- Energy is released as heat to the cold sink; the entropy change of the system =  $q_c/T_c$ , where  **$q_c$  is negative**.

$$-q_c = w_3 = RT_c \ln \frac{V_D}{V_C}$$

## D. 4<sup>th</sup> stroke:

Curve DA (D → A): **Adiabatic compression**  
Work done *on* the gas

- Contact with  $Q_c$  is broken and the gas undergoes reversible adiabatic compression from D to A such that the final temperature is  $T_h$ .
- No energy enters the system as heat, so the change in entropy is zero.

$$w_4 = C_v (T_h - T_c)$$

- The area enclosed by the four curves represents the net work done by the engine in one cycle
- The total change in entropy around the cycle is the sum of the changes in each of these four steps:

$$\oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c}$$

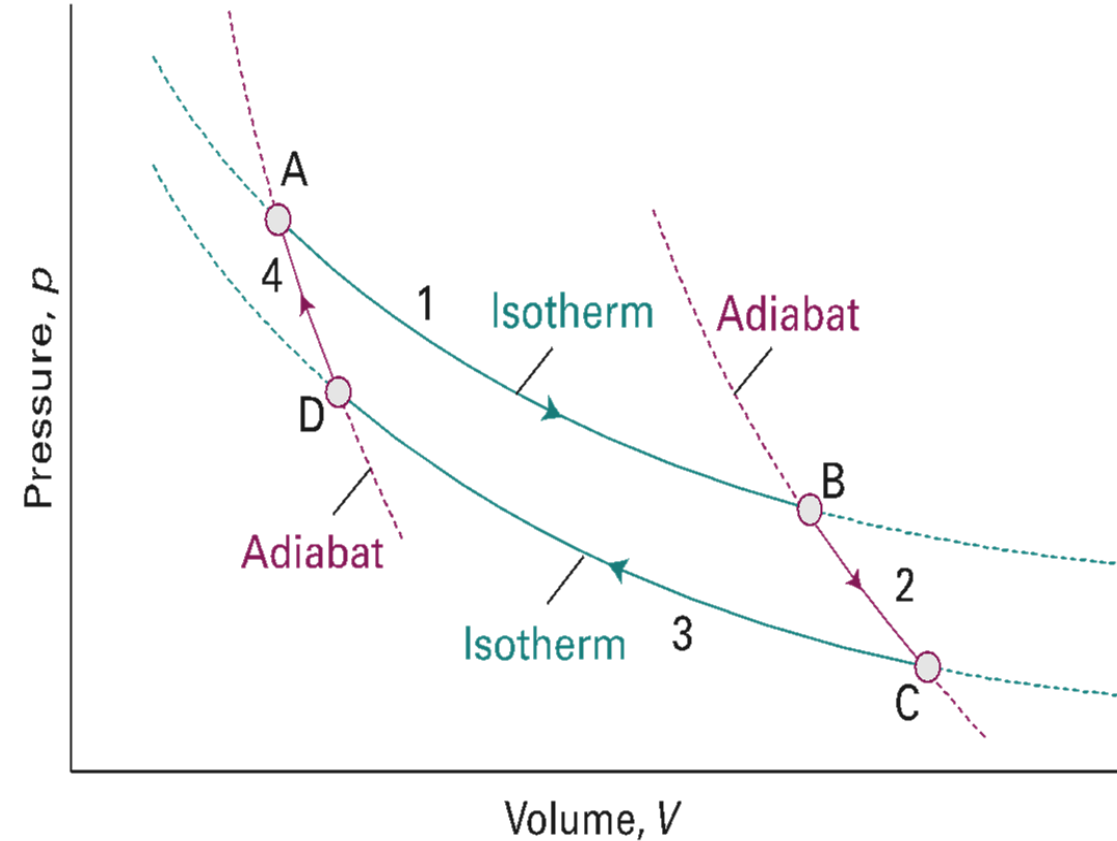
❖ For an ideal gas,  $\oint dS = 0$  and  $\frac{q_h}{q_c} = -\frac{T_h}{T_c}$

## Efficiency of a heat engine

- The thermal efficiency of a heat engine is

$$\eta = \frac{\text{work performed}}{\text{heat absorbed from the hot source}} = \frac{W}{q_h} = 1 - q_c/q_h = 1 - T_c/T_h$$

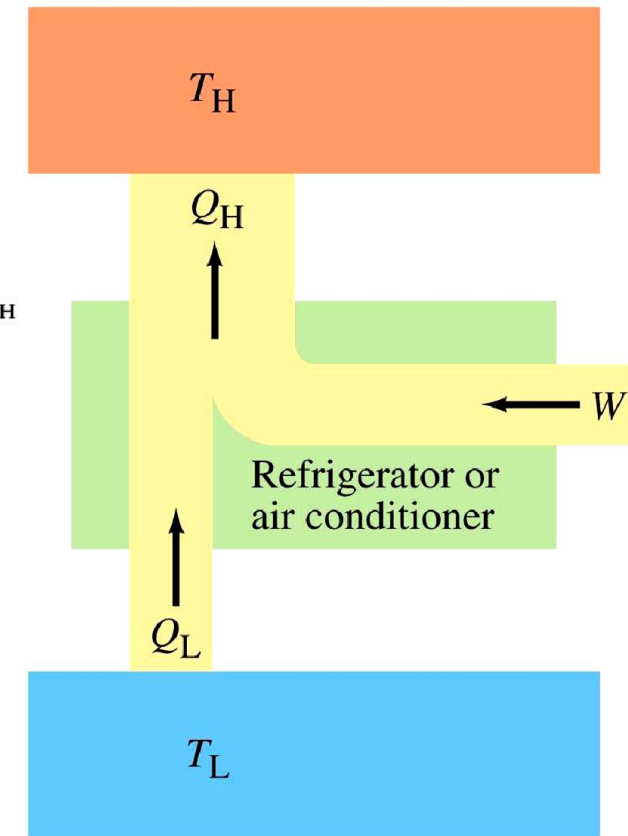
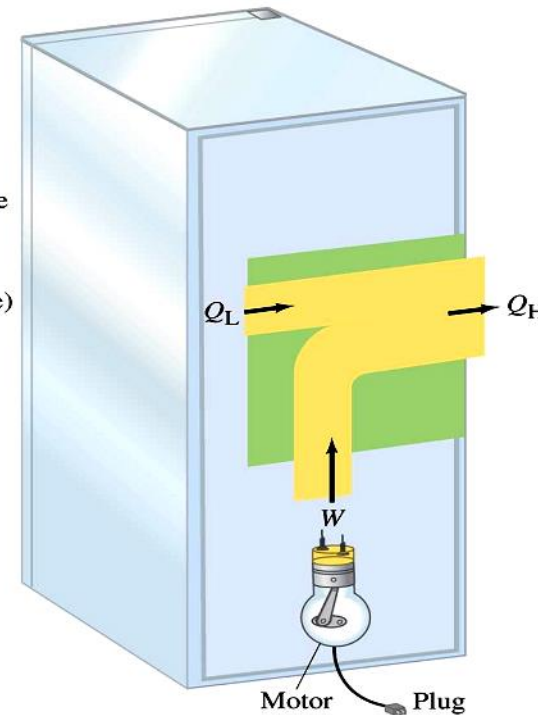
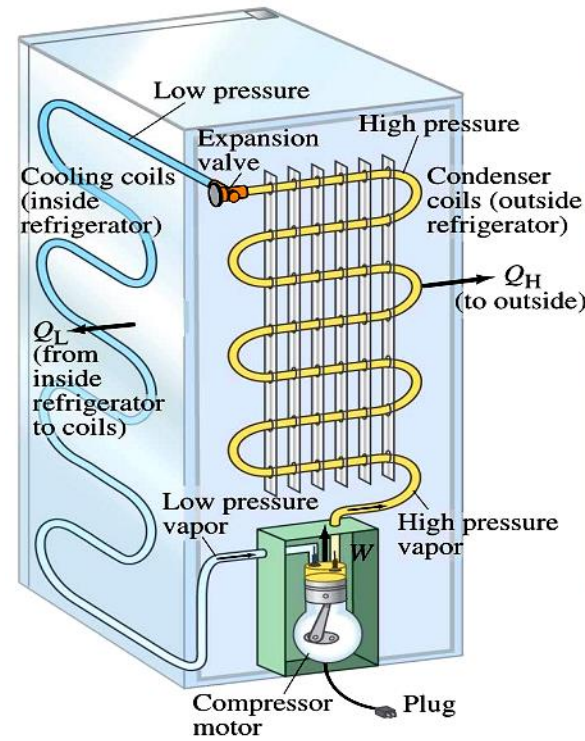
- The “**engine**” statement of the 2<sup>nd</sup> Law:
  - it is impossible for any system to have an efficiency of 100% ( $\eta = 1$ ) **[Kelvin’s statement]**



- Another statement of the 2<sup>nd</sup> Law:
  - It is impossible for any process to have as its sole result the transfer of heat from a cooler object to a warmer object **[Clausius’s statement]**



- **Energy efficiency** of the Carnot cycle is **independent** of its **working substance**.
- Any cyclic process that **absorbs heat** at one temperature and **rejects heat** at another temperature and is **reversible** has the **energy efficiency** of a Carnot cycle.



- Thermal devices or thermal machines are one of the applications of this cycle.
- ✓ The heat pumps to produce heating,
  - ✓ the refrigerators to produce cooling,
  - ✓ the steam turbines used in the ships,
  - ✓ the combustion engines of the combustion vehicles
  - ✓ the reaction turbines of the aircraft

→ **Refrigeration, Air conditioners & Heat pumps**

- These appliances are heat engines operating in reverse.
- By doing work, heat is extracted from the cold reservoir & exhausted to the hot reservoir



## ➤ Thermodynamic Temperature

- Suppose an engine works reversibly between a hot source at a temperature  $T_h$  and a cold sink at a temperature  $T_c$ , then it follows that
$$T_c = (1 - \eta)T_h$$
- Kelvin used this expression to define the **thermodynamic temperature scale** in terms of the efficiency of a heat engine in which the hot source is at a known temperature and the cold sink is the object of interest.
- The **Kelvin scale** (which is a special case of the thermodynamic temperature scale) is currently defined by using **water at its triple point** as the notional **hot source** and defining that temperature as **273.16 K** exactly.

## ➤ Free energy and the spontaneity

- As,  $\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}$  and  $\Delta S_{total}$  is a criterion for the spontaneity/feasibility of a process.
  - It is not always easy to know the entropy change of both system and the surrounding**
  - We can express this in terms of **G** (the free energy function) and thus can devise a criterion of **spontaneity in terms of the state function of the system**.
  - There are few assumptions:
    - **Assumption no 1:**  
The system is in **thermal equilibrium** with its surroundings at a **temperature T**.
    - **Assumption no 2:**  
**Heat transfer** between the system and the surrounding happens at **constant volume**
    - **Assumption no 3:**  
**Heat transfer** between the system and the surrounding happens at **constant pressure**.

## ➤ Under the Assumption 1 & Assumption 2

**Clausius inequality becomes:**  $dS - \frac{dU}{T} \geq 0$

[we get this by applying the 1<sup>st</sup> law & the  $d(q_v) = dU$ ]

$$\Rightarrow TdS \geq dU$$

$dA = dU - TdS$  [ $A$  = Helmholtz free energy]

$$\Rightarrow \boxed{A = U - TS}$$

## ➤ Under the Assumption 1 & Assumption 3

**Clausius inequality becomes:**  $dS - \frac{dH}{T} \geq 0$

[constant P, no additional work]

$$\Rightarrow TdS \geq dH$$

$dG = dH - TdS$  [ $G$  = Gibbs free energy]

$$\Rightarrow \boxed{G = H - TS}$$

- The criterion of spontaneity in terms of Gibbs Free energy change ( $dG$ ) and Helmholtz energy ( $dA$ )

$$\boxed{dG \leq 0 \text{ \& } dA \leq 0}$$

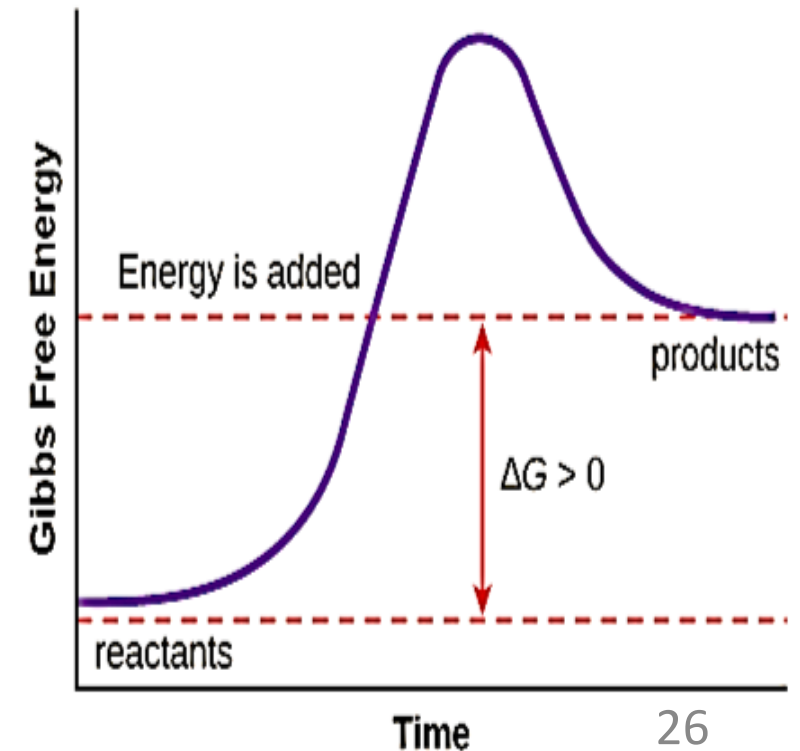
## ➤ In an endothermic reaction:

$$dH > 0$$

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  $dH$ .

$\Rightarrow$  **Endothermic reactions** are therefore driven by the **increase of entropy** of the system

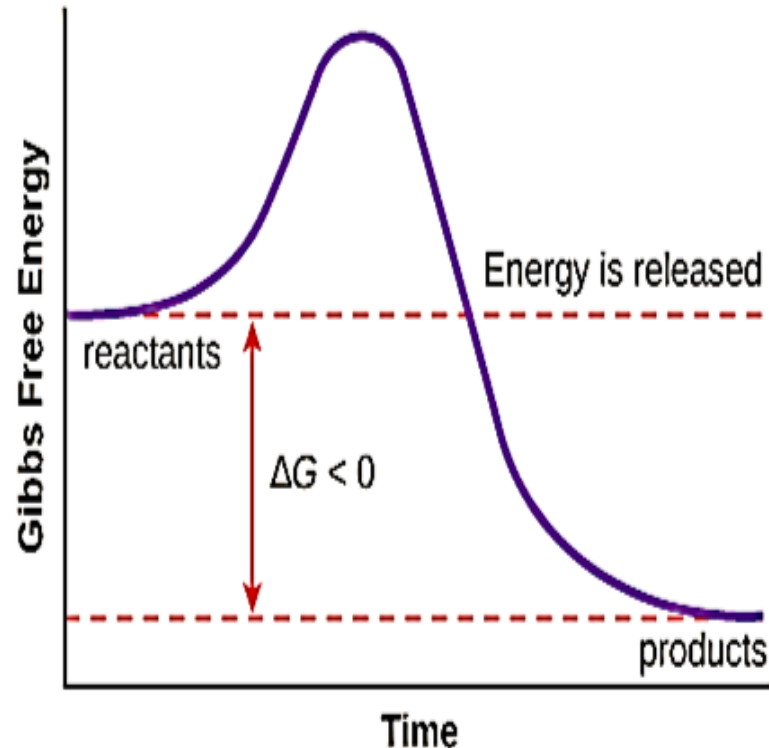


## ➤ In an exothermic

### 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,

### ➤ $dG = 0$

- Free energy change with temperature and pressure:

$$\begin{aligned}\Delta G &= nRT \ln \frac{P_2}{P_1} \\ &= nRT \ln \frac{V_1}{V_2}\end{aligned}$$

# 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,  $\Delta S_{\text{universe}}$  must be positive.

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

## 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.

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

- **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** ( $\Delta H$ ), **Entropy** ( $\Delta S$ ), and **Free Energy** ( $\Delta G$ ))

- A spontaneous reaction is one that releases free energy, and so the sign of  $\Delta G$  must be negative. Since both  $\Delta H$  and  $\Delta S$  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.

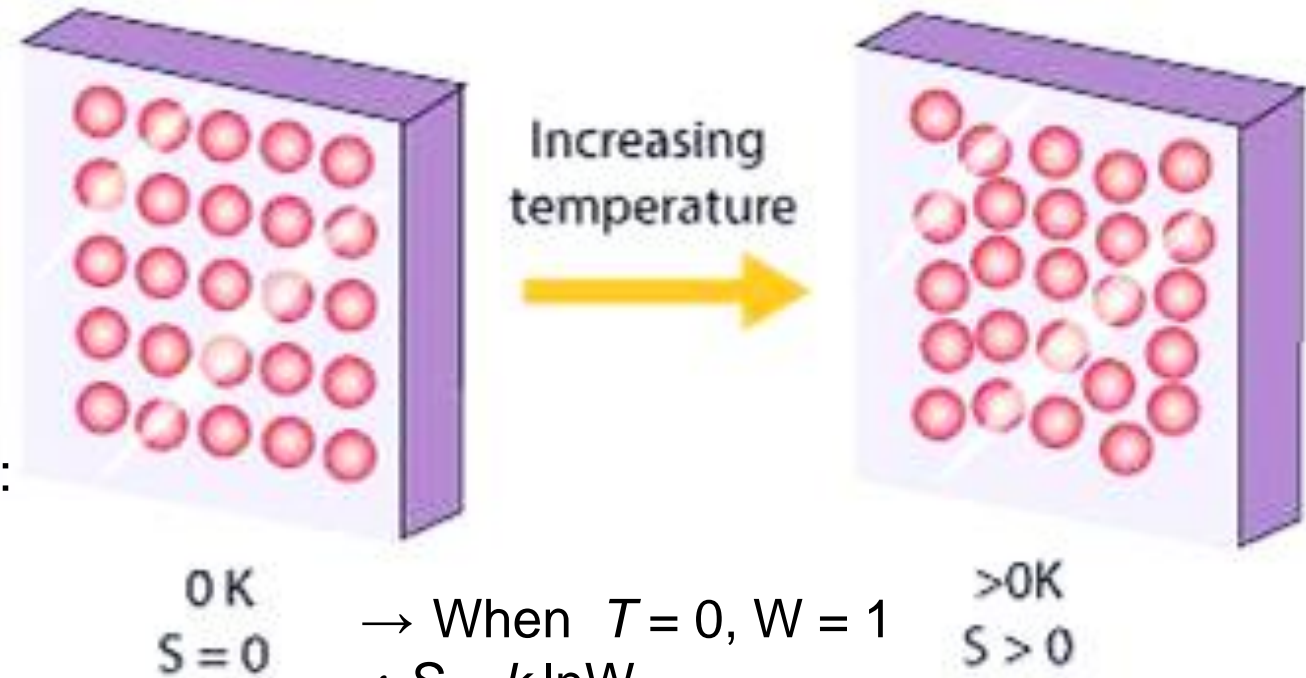
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$\Delta H^\circ$	$\Delta S^\circ$	$\Delta G^\circ$
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

- 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:

$$S = k \ln W$$

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  $T = 0$ .**

# Part-B

## Chemical Kinetics

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

- The chemistry that deals with the reaction rates is known as **chemical kinetics**.
- It plays an important role in the production of chemicals on an industrial scale and the decay of radioactive isotopes used in medicine.
- Chemical kinetics is also useful in providing information about how reactions occur—the order in which chemical bonds are broken and formed during the course of a reaction.
- Experimental information on the rate of a given reaction provides important evidence that helps us formulate a *reaction mechanism*, which is a step-by-step, molecular-level view of the pathway from reactants to products.

*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*

### **Factors That Affect Reaction Rates**

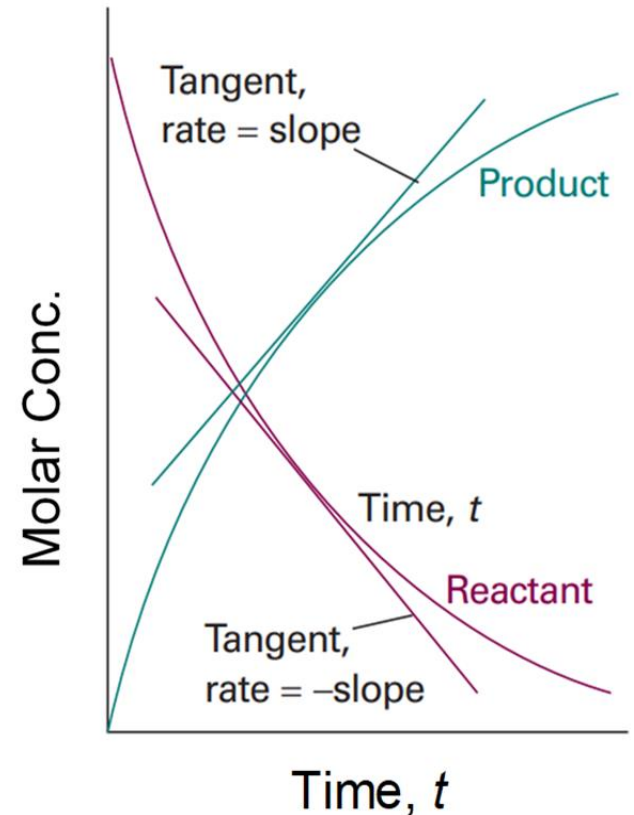
1. ***Physical state of the reactants-*** homogeneous, involving either all gases or all liquids, or as *heterogeneous*, in which reactants are in different phases.
2. ***Reactant concentrations.***
3. ***Reaction temperature.***
4. ***The presence of a catalyst.***



# Reaction Rates

On a molecular level, reaction rates depend on the frequency of collisions between molecules. *The greater the frequency of collisions, the higher the reaction rate.*

- 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.



# Concentration and the rates of reactions

Consider a general reaction,  $A + B \rightarrow C$

- The rate of this reaction can be expressed either as the rate of disappearance of reactant 'A' and 'B' or as the rate of appearance of product 'C'.
- The rate of reaction will be:
- **Average rate of appearance /disappearance of A, B or C = change in concentration of A, B or C**

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} \quad \text{change in time}$$

Now, consider another general reaction:  $aA + bB \rightarrow cC + dD$

where a, b, c & d are stoichiometric coefficients

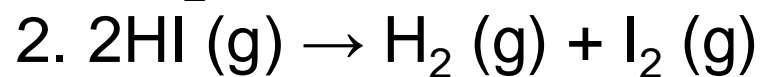
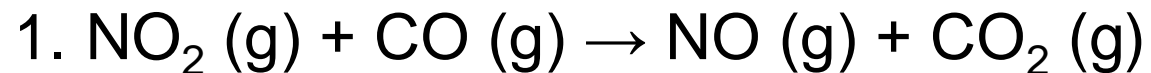
The rate of reaction will be:

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

# The rates of reactions

## Sample Questions:

Write rate expressions for the following reactions:



## Solution:

1. 
$$-\frac{d[\text{NO}_2]}{dt} = -\frac{d[\text{CO}]}{dt} = \frac{d[\text{NO}]}{dt} = \frac{d[\text{CO}_2]}{dt}$$

2. 
$$-\frac{1}{2} \frac{d[\text{HI}]}{dt} = \frac{d[\text{H}_2]}{dt} = \frac{d[\text{I}_2]}{dt}$$



## 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**.

For the general reaction:



the rate law generally has the form

$$\text{rate} = k [A]^m [B]^n$$

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

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

Exponents  $m$  and  $n$  are typically small whole numbers, whose values are not necessarily equal to the coefficients  $a$  and  $b$  from the balanced equation.

# 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:  $\text{rate} = k[\text{A}]^m[\text{B}]^n[\text{C}]^c$
- 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

- *It is the sum of the exponents of the concentrations in the rate law equation*
- *It can be integers, fractions, negative or positive.*
- *It can be determined only experimentally*
- *It may not be equal to the number of molecules of reactants*

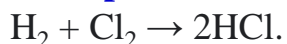
Ex. For the reaction:  $A + B \rightarrow C$

$$\text{rate} = k [A]^m [B]^n$$

- *where,  $m$  is the order of reaction with respect to A,  $n$  is the order of reaction with respect to B.*
- *The overall reaction order is the sum of the exponents in the rate law =  $m + n$*

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

## Examples:



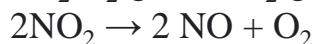
$$\text{Rate} = k [H_2]^0 [Cl_2]^0$$

(Zero order)



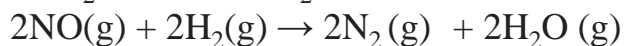
$$\text{Rate} = k [SO_2Cl_2]^1$$

(First order)



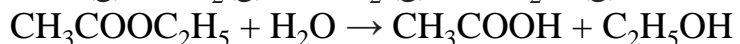
$$\text{Rate} = k [NO_2]^2$$

(Second order)



$$\text{Rate} = k [NO]^2 [H_2]^1$$

(Third order)



$$\text{Rate} = k [CH_3COOC_2H_5]^1 [H_2O]^0$$

(pseudo-first-order)

# Molecularity of a reaction

- *It is the number of molecules or ions that participate in the rate determining step*
- *It is a theoretical concept and it can be determined from rate determining step (slowest step).*
- *It is always an integer between 1 to 3, as it is not possible to colliding of four or more molecules simultaneously.*
- *For elementary reactions (single step reactions):*
  - *It is the sum of stoichiometry coefficients of the reactants*

*Ex.  $H_2 + I_2 \rightarrow 2HI$*

*Molecularity = 1 + 1 = 2*
- *For complex reactions:*
  - *The sum of the number of reactant in the rate determining steps gives the molecularity*

# First-Order Reactions

A **first-order reaction** is one whose rate depends on the concentration of a single reactant raised to the first power.

If a reaction of the type **A → products** is first order, the rate law is:

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

Separate concentration and time terms

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

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

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

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

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

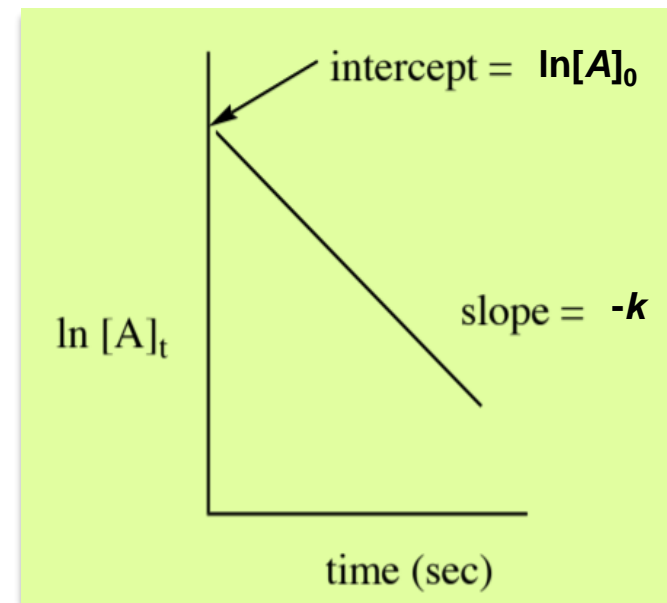
Straight line equation ( $y = mx + c$ )

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

$$y = mx + c$$

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.





# Half-Life of First Order Reaction

The **half-life** of a reaction ( $t_{1/2}$ )

- It is the time required for the concentration of a reactant to reach half its initial value,  $[A]_{t_{1/2}} = \frac{1}{2} [A]_0$ .
- Half-life is a convenient way to describe how fast a reaction occurs, especially if it is a first-order process.
- A fast reaction has a short half-life.
- We can determine the half-life of a first-order reaction by substituting

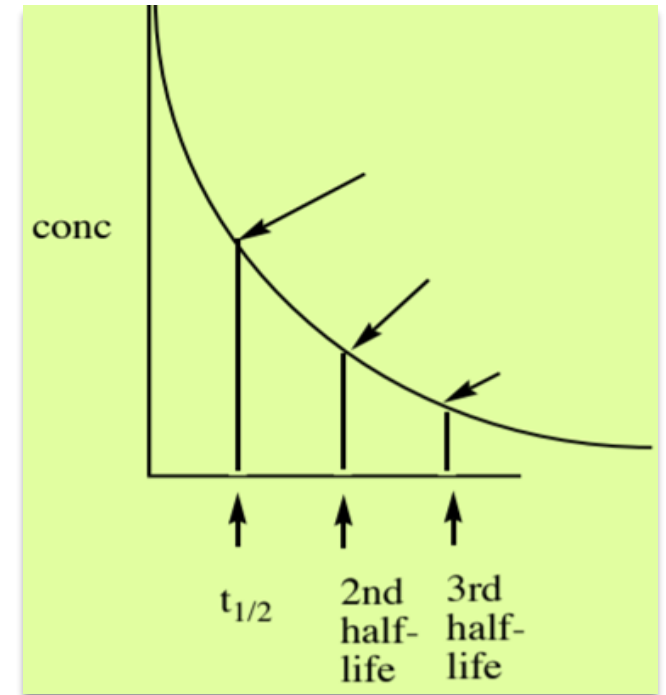
$[A]_{t_{1/2}} = \frac{1}{2} [A]_0$  for  $[A]_t$  and  $t_{1/2}$  for  $t$  in Equation :

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

$$\ln \left[ \frac{\frac{1}{2} [A]_0}{[A]_0} \right] = -k t_{1/2}$$

$$\ln \frac{1}{2} = -k t_{1/2}$$

$$t_{1/2} = -\frac{\ln \frac{1}{2}}{k} = \underline{\underline{0.693}}{k}$$

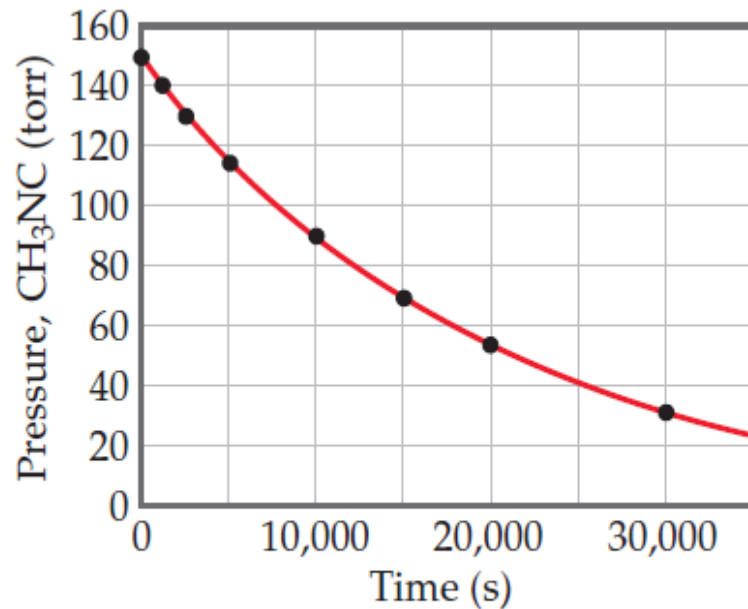


Ex. The conversion of methyl isonitrile ( $\text{CH}_3\text{NC}$ ) to its isomer acetonitrile ( $\text{CH}_3\text{CN}$ ) at  $199^\circ\text{C}$ .

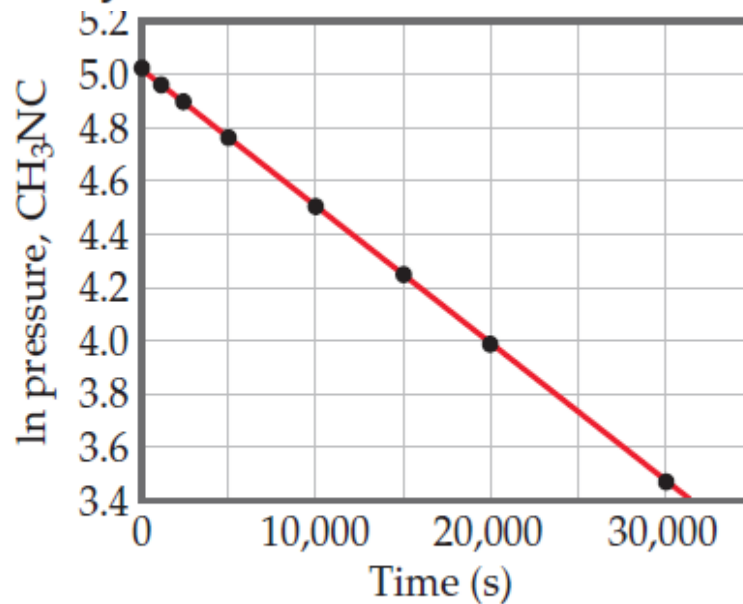


$$\ln[\text{CH}_3\text{NC}]_t = -kt + \ln[\text{CH}_3\text{NC}]_0$$

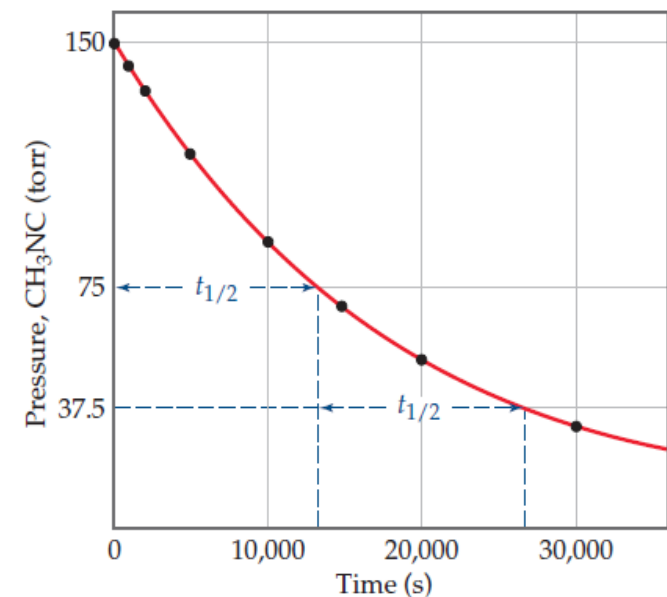
Kinetic data for conversion of methyl isonitrile into acetonitrile.



(a)



(b)



▲ **Figure** Kinetic data for the rearrangement of methyl isonitrile to acetonitrile at  $199^\circ\text{C}$ , showing the half-life of the reaction.

**Figure (a)** shows how the pressure of this gas varies with time.

**Figure (b)** shows that a plot of the natural logarithm of the pressure versus time is a straight line.

The slope of this line is  $-5.1 \times 10^{-5} \text{ s}^{-1}$ .  $\therefore k = 5.1 \times 10^{-5} \text{ s}^{-1}$

# Second-Order Reactions

A **second-order reaction** is one for which the rate depends either on a reactant concentration raised to the second power or on the concentrations of two reactants each raised to the first power.

For Ex: in reactions **A → products** or **A + B → products** that are second order with respect to only one reactant, A:

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^2$$

$$\frac{d[A]}{[A]^2} = -kdt$$

With the use of calculus, this differential rate law can be used to derive the integrated rate law for second-order reactions:

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

- This equation, has four variables,  $k$ ,  $t$ ,  $[A]_0$ , and  $[A]_t$ , and any one of these can be calculated knowing the other three.
- This Equation also has the form of a straight line ( $y = mx + c$ ).
- **If the reaction is second order, a plot of '1/ [A]<sub>t</sub>' versus 't' yields a straight line with slope  $k$  and y-intercept 1/ [A]<sub>0</sub>.**
- **One way to distinguish between first and second-order rate laws is to graph both  $\ln[A]_t$  and 1/ [A]<sub>t</sub> against  $t$ .**
- If the  $\ln[A]_t$  plot is linear, the reaction is first order;
- if the 1/ [A]<sub>t</sub> plot is linear, the reaction is second order.

## Half-Life of Second-Order Reactions

The half-life of a chemical reaction is the time taken for half of the initial amount of reactant to undergo the reaction.

Therefore, while attempting to calculate the half life of a reaction, the following substitutions must be made:

$$[A]_t = \frac{[A]_0}{2} \text{ and, } t = t_{1/2}$$

Now, substituting these values in the integral form of the rate equation of second order reactions, we get:

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \quad \gg \quad \frac{1}{\frac{[A]_0}{2}} - \frac{1}{[A]_0} = k t_{1/2}$$

Therefore, the required equation for the half life of second order reactions can be written as follows.

$$t_{1/2} = \frac{1}{k [A]_0}$$

*This equation for the half life implies that the half life is inversely proportional to the concentration of the reactants.*

# Zero-Order Reactions

- We have seen that in a first-order reaction the concentration of a reactant 'A' decreases nonlinearly, as shown by the red curve in **Figure**.
- As [A] declines, the *rate* at which it disappears declines in proportion.
- A **zero-order reaction** is one in which the rate of disappearance of A is *independent* of [A].
- The rate law for a zero-order reaction is

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^0$$

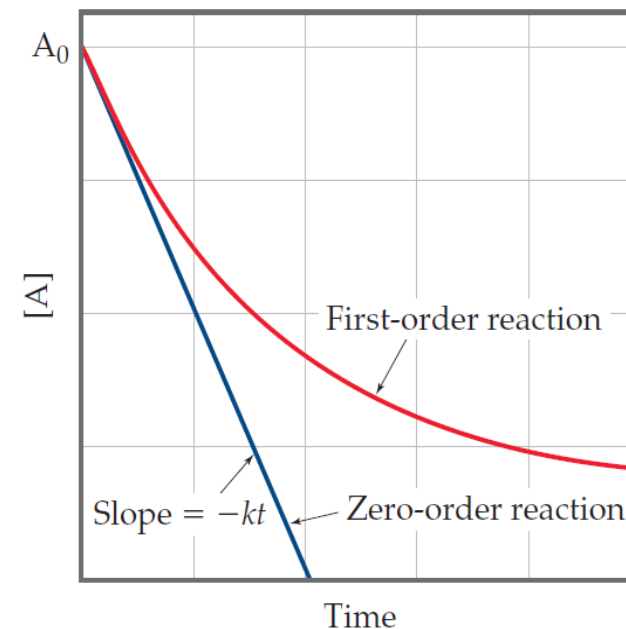
$$[A]_t - [A]_0 = -kt$$

The integrated rate law for a zero-order reaction is

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

where  $[A]_t$  is the concentration of A at time  $t$  and  $[A]_0$  is the initial concentration.

This is the equation for a straight line with vertical intercept  $[A]_0$  and slope  $-kt$ , as shown in the blue curve in Figure.



**Figure.** Comparison of first-order and zeroorder reactions for the disappearance of reactant A with time

Ex. The most common type of zero-order reaction occurs when a gas undergoes decomposition on the surface of a solid.



Photochemical reaction:



## Half-Life of a Zero Order Reaction

The timescale in which there is a 50% reduction in the initial population is referred to as half-life. Half-life is denoted by the symbol ' $t_{1/2}$ '.

- $W = \Delta U = C_v \Delta T$  (for 1 mole of gas)

# 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.



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.

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:



$$\text{Rate} = k [\text{CH}_3\text{COOC}_2\text{H}_5]$$

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



The compounds known as chlorofluorocarbons (CFCs) are well-known agents responsible for the destruction of Earth's protective ozone layer. Another simple molecule that has the potential to destroy the stratospheric ozone layer is methyl bromide,  $\text{CH}_3\text{Br}$  (Figure 14.11). Because this substance has a wide range of uses, including antifungal treatment of plant seeds, it has been produced in large quantities in the past (about 150 million pounds per year worldwide in 1997, at the height of its production). In the stratosphere, the C—Br bond is

broken through absorption of short-wavelength radiation. The resultant Br atoms then catalyze decomposition of  $\text{O}_3$ .

Methyl bromide is removed from the lower atmosphere by a variety of mechanisms, including a slow reaction with ocean water:

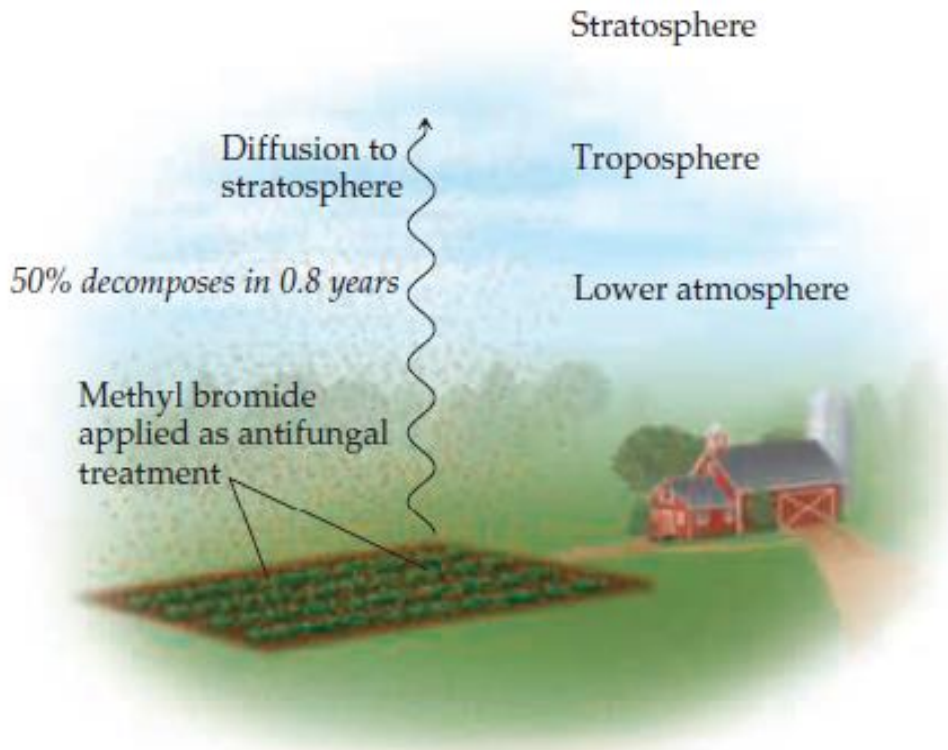


To determine the potential importance of  $\text{CH}_3\text{Br}$  in destruction of the ozone layer, it is important to know how rapidly the reaction in Equation 14.18 and all other reactions remove  $\text{CH}_3\text{Br}$  from the lower atmosphere before it can diffuse into the stratosphere.

The average lifetime of  $\text{CH}_3\text{Br}$  in Earth's lower atmosphere is difficult to measure because the conditions that exist in the atmosphere are too complex to be simulated in the laboratory. Instead, scientists analyzed nearly 4000 atmospheric samples collected above the Pacific Ocean for the presence of several trace organic substances, including methyl bromide. From these measurements, it was possible to estimate the *atmospheric residence time* for  $\text{CH}_3\text{Br}$ .

The atmospheric residence time is related to the half-life for  $\text{CH}_3\text{Br}$  in the lower atmosphere, assuming  $\text{CH}_3\text{Br}$  decomposes by a first-order process. From the experimental data, the half-life for methyl bromide in the lower atmosphere is estimated to be  $0.8 \pm 0.1$  yr. That is, a collection of  $\text{CH}_3\text{Br}$  molecules present at any given time will, on average, be 50% decomposed after 0.8 yr, 75% decomposed after 1.6 yr, and so on. A half-life of 0.8 yr, while comparatively short, is still sufficiently long so that  $\text{CH}_3\text{Br}$  contributes significantly to the destruction of the ozone layer.

In 1997 an international agreement was reached to phase out use of methyl bromide in developed countries by 2005. Although exemptions for critical agricultural use have been granted, global consumption in 2013 was only 3% of the levels seen in the early 1990s.



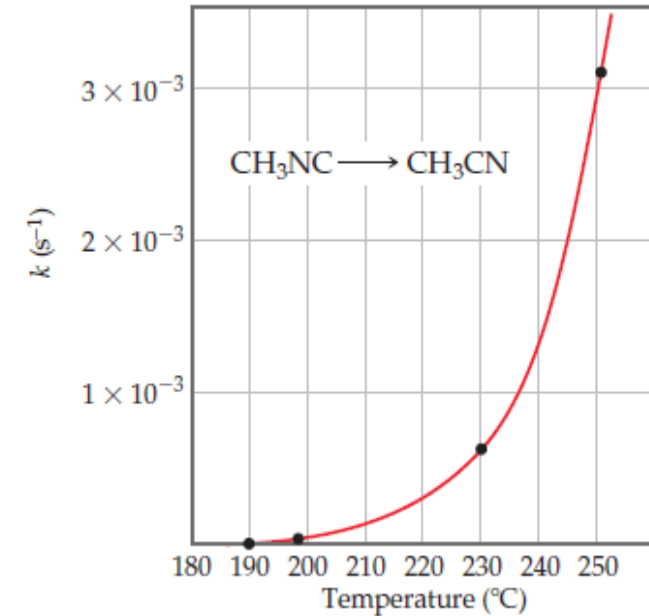
Distribution and fate of methyl bromide in Earth's atmosphere.



# Temperature and Rate

- The rates of most chemical reactions increase as the temperature rises.
- The faster rate at higher temperature is due to an increase in the rate constant with increasing temperature.
- For example,  **$\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$**

The rate constant and, hence, the rate of the reaction increase rapidly with temperature, approximately doubling for each 10 °C rise.



Temperature dependence of the rate constant for methyl isonitrile conversion to acetonitrile

## The Collision Model

- *The greater the number of collisions per second, the greater the reaction rate.*
- *As reactant concentration increases, therefore, the number of collisions increases, leading to an increase in reaction rate.*
- *According to the kinetic-molecular theory of gases, increasing the temperature increases molecular speeds. As molecules move faster, they collide more forcefully (with more energy) and more frequently, both of which increase the reaction rate.*

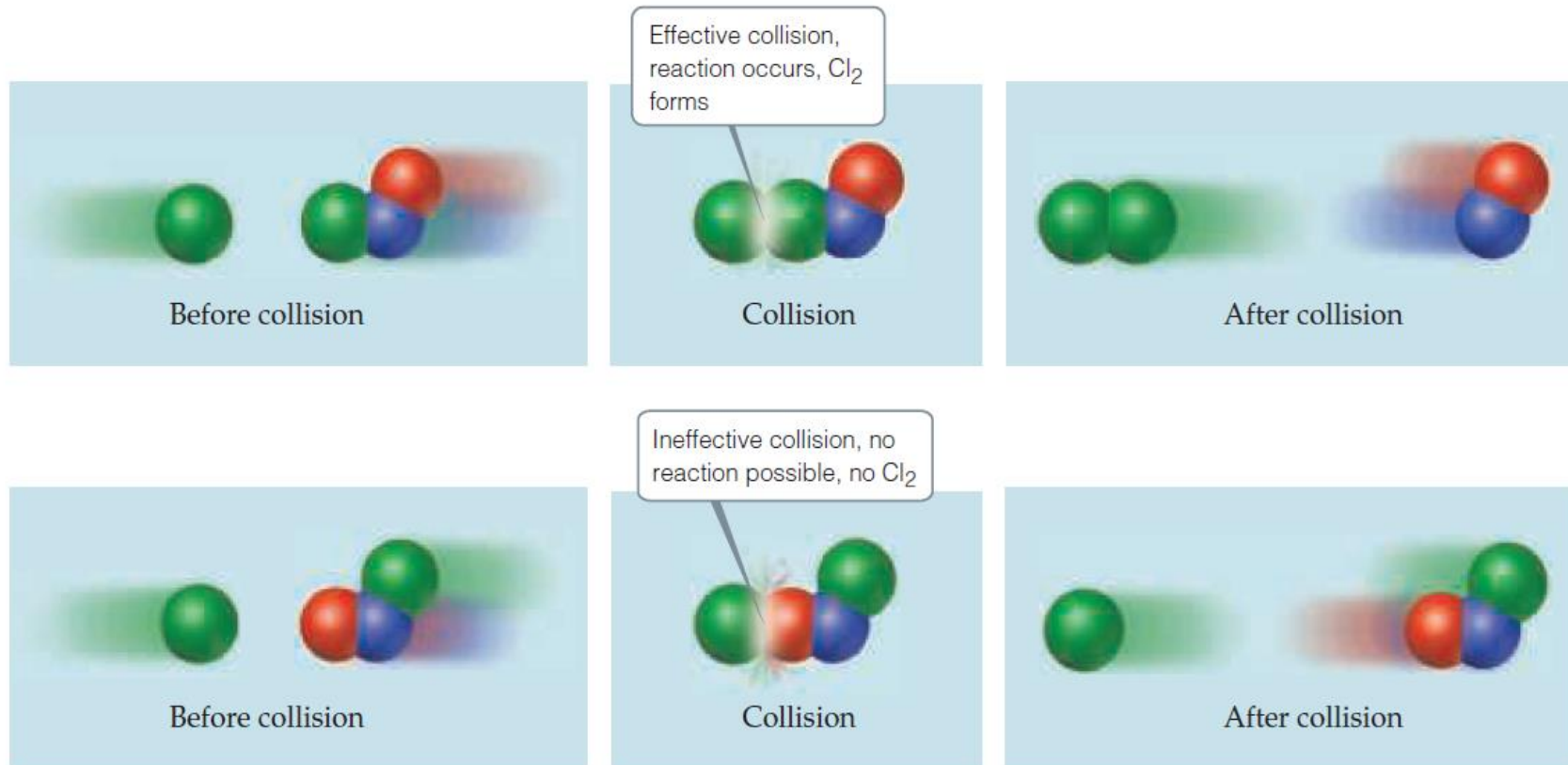
## The Orientation Factor:

- *In most reactions, collisions between molecules result in a chemical reaction only if the molecules are oriented in a certain way when they collide.*
- *The relative orientations of the molecules during collision determine whether the atoms are suitably positioned to form new bonds.*

For example,

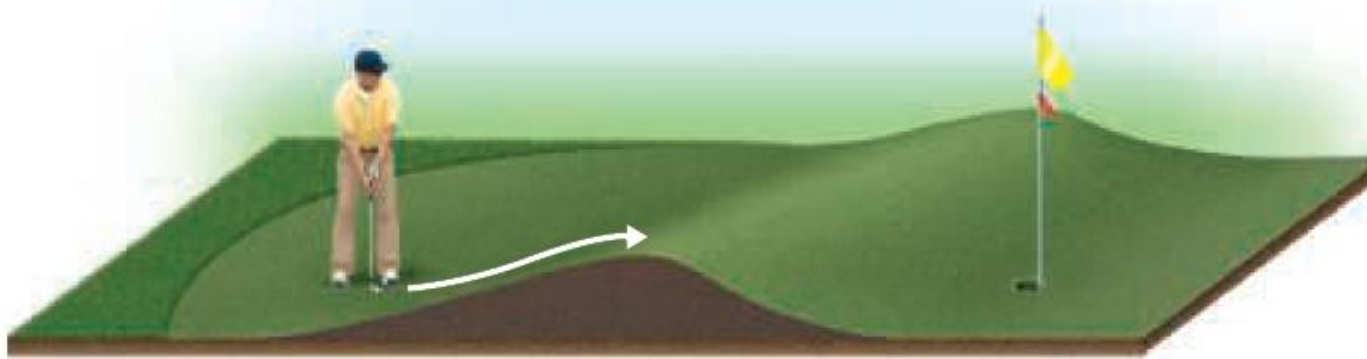


- **Molecular collisions may or may not lead to a chemical reaction between Cl and NOCl.**



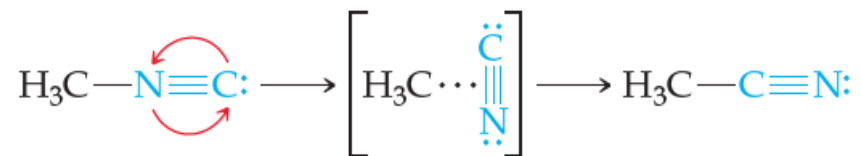
## Activation Energy:

- *In 1888 the Swedish chemist Svante Arrhenius suggested that molecules must possess a certain minimum amount of energy to react.*
- According to the collision model, this energy comes from the kinetic energies of the colliding molecules.
- Upon collision, the kinetic energy of the molecules can be used to stretch, bend, and ultimately break bonds, leading to chemical reactions.
- ***The minimum energy required to initiate a chemical reaction is called the activation energy,  $E_a$ , and is represented by the symbol  $E_a$ .***

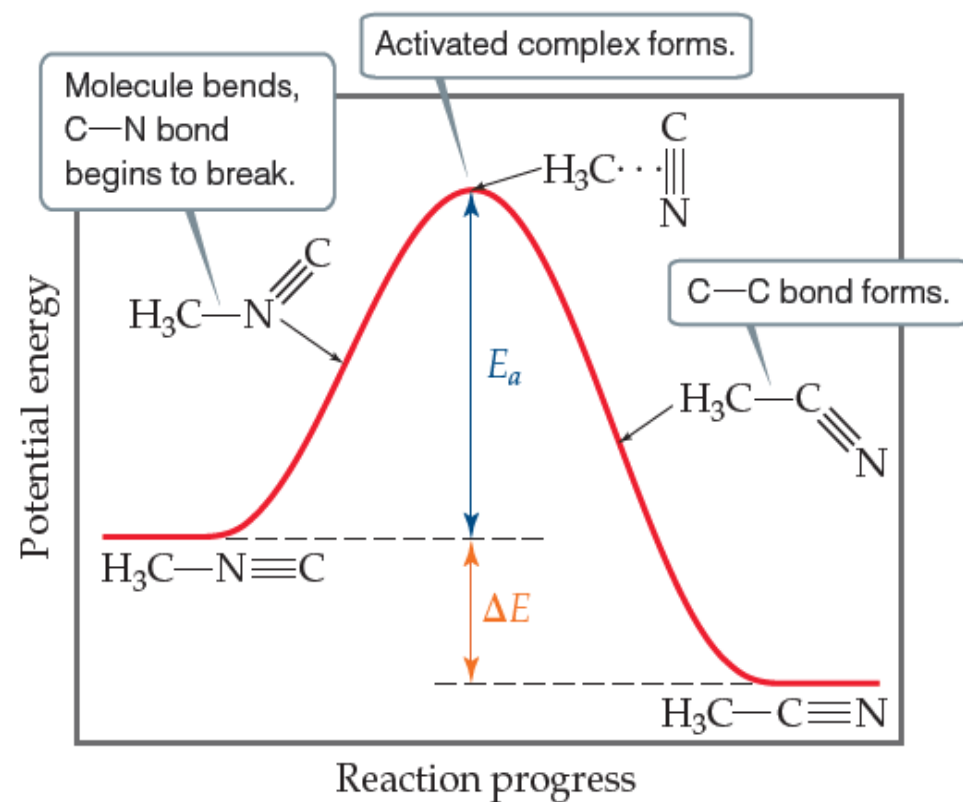


Energy is needed to overcome a barrier between initial and final states.

For example,

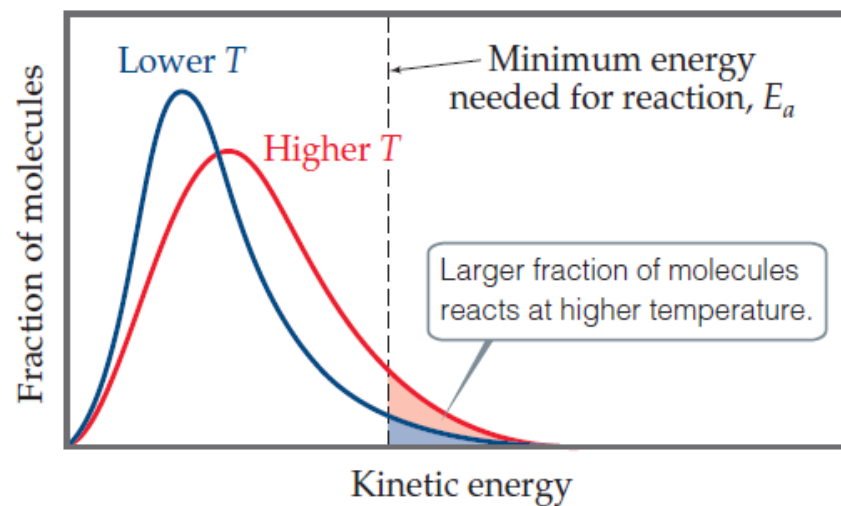


**Energy profile for conversion of methyl isonitrile ( $\text{H}_3\text{CNC}$ ) to its isomer acetonitrile ( $\text{H}_3\text{CCN}$ ).**



- The difference between the energy of the starting molecule and the highest energy along the reaction pathway is the activation energy,  $E_a$ .
- The molecule having the arrangement of atoms shown at the top of the barrier is called either the **activated complex** or the **transition state**.
- *The rate constant depends on the magnitude of  $E_a$*
- *Generally, the lower the value of  $E_a$  is, the larger the rate constant and the faster the reaction.*

**The effect of temperature on the distribution of kinetic energies of molecules in a sample.**



- Figure shows the distribution of kinetic energies for two temperatures, comparing them with the minimum energy needed for reaction,  $E_a$ .
- At the higher temperature a much greater fraction of the molecules have kinetic energy greater than  $E_a$ , which leads to a greater rate of reaction.

## Arrhenius equation

Arrhenius noted that for most reactions the increase in rate with increasing temperature is nonlinear. The Arrhenius equation gives the dependence of the rate constant of a chemical reaction on the absolute temperature as  $k = A e^{-\frac{E_a}{RT}}$ .

**Arrhenius equation** (non exponential form)

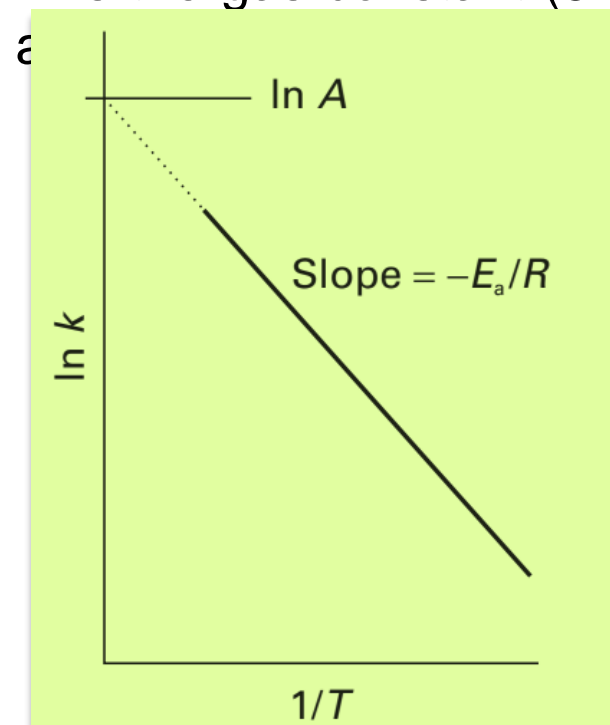
$$\ln k = \ln e^{-\frac{E_a}{RT}} + \ln A$$

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

- ❖ A graph of  $\ln k$  versus  $1/T$  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.

where,  $k$  is rate constant,  $E_a$  is the activation energy,

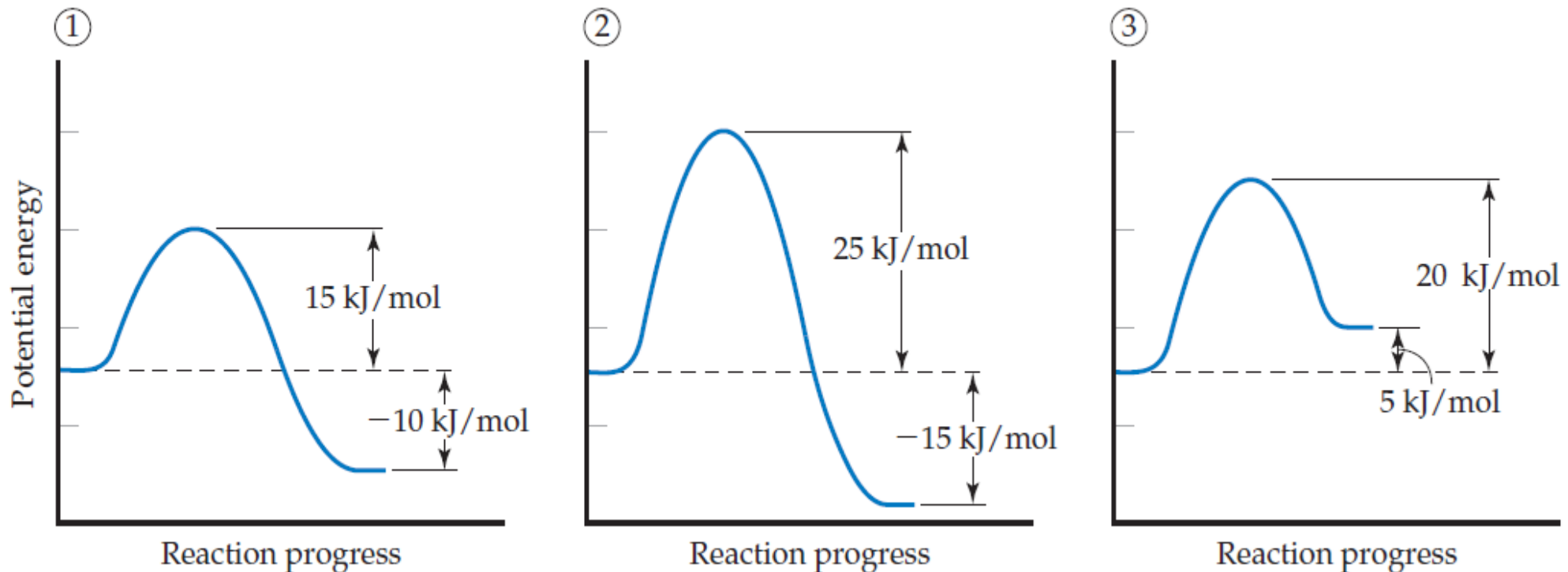
$A$  is the pre-exponential (frequency) factor is constant, and  $RT$  is the average kinetic energy i.e.,  $R$  is the gas constant (8.314 J/mol-K), and  $T$  is the



- value of from intercept at infinite  $T$  (i.e.;  $1/T=0$ )
- value of  $E_a$  from the slope.

**Consider a series of reactions having these energy profiles:**

Rank the forward rate constants from smallest to largest assuming all three reactions have nearly the same value for the frequency factor  $A$ .



### SOLUTION

- The lower the activation energy, the larger the rate constant and the faster the reaction.
- The value of  $\Delta E$  does not affect the value of the rate constant.
- Hence, **the order of the rate constants is  $2 < 3 < 1$ .**

# Catalysis

- A ***catalyst*** is a substance that changes the speed of a chemical reaction without undergoing a permanent chemical change itself.
- Most reactions in the body, the atmosphere, and the oceans occur with the help of catalysts.
- Much industrial chemical research is devoted to the search for more effective catalysts for reactions of commercial importance.
- **The phenomenon of alteration of the rate of a reaction by a catalyst is known catalysis.**
- The science and technology of catalysis is of great significance as it affects our daily life.
- The catalytic processes contribute greater than 30-40% of global GDP
- Four major sectors of the world economy involve catalytic processes.
  - ✓ Petroleum and Energy Production,
  - ✓ Chemicals and Polymer Production,
  - ✓ Food industry and
  - ✓ Pollution control.

# 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 .

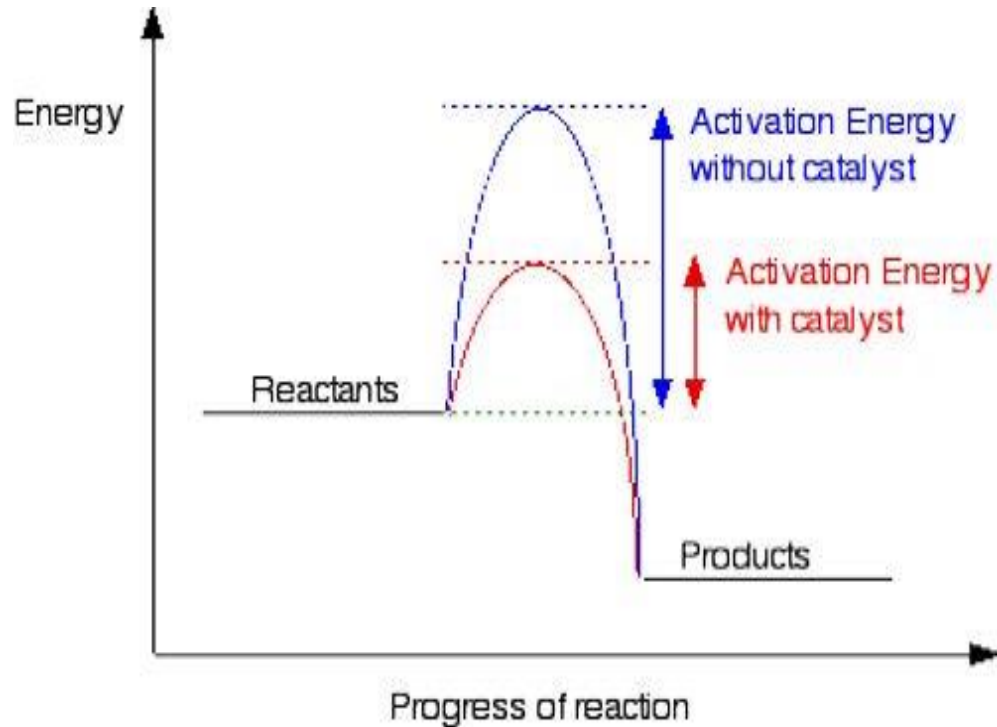


Figure: Schematic diagram to illustrate the effect of catalyst on activation energy of reactions.

# Types of catalysis

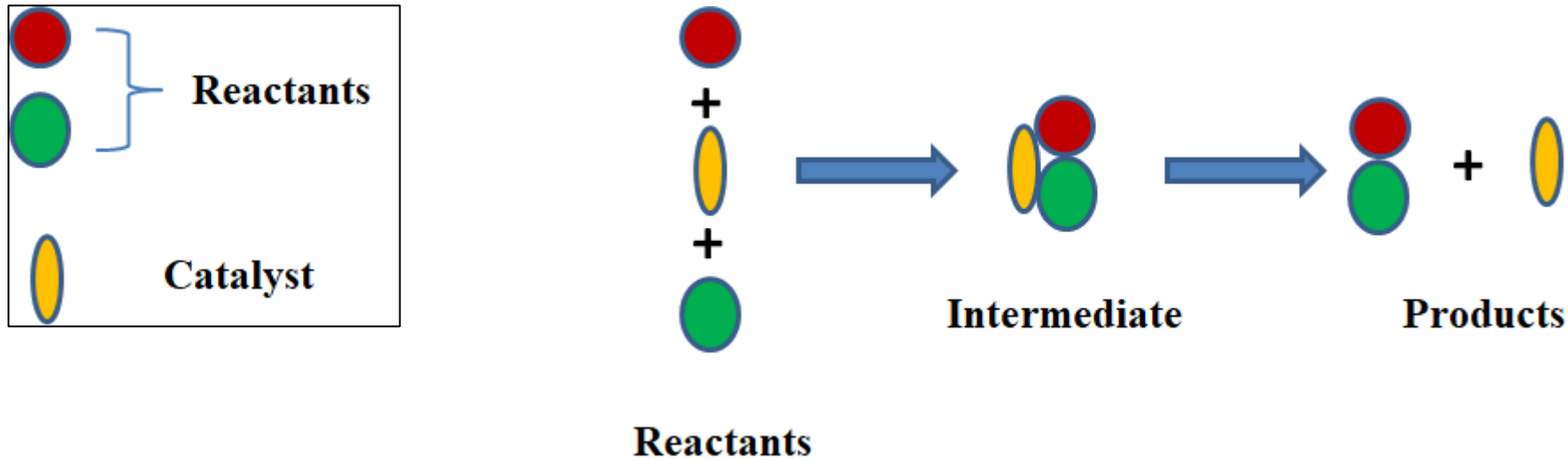
Following are the main types of catalysis:

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



# 1. 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.

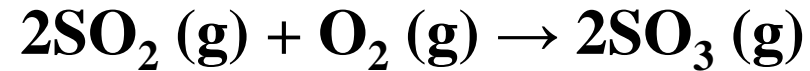


**Figure:** Schematic diagram to illustrate the homogeneous catalysis.

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

## Examples of homogeneous catalysis in the gas phase

(1) Oxidation of sulphur dioxide,  $\text{SO}_2$ , by oxygen to sulphur trioxide,  $\text{SO}_3$ , in presence of nitric oxide,  $\text{NO}$ , in the Chamber Process for sulphuric acid manufacture.



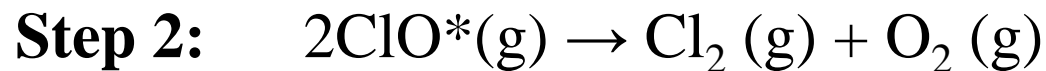
here,  $\text{NO}$  acts as a catalyst.

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



*In presence of light chlorine forms chlorine radicals, which react with  $\text{N}_2\text{O}$  forming the intermediate radical  $\text{ClO}^*$ .*

The proposed mechanism is:

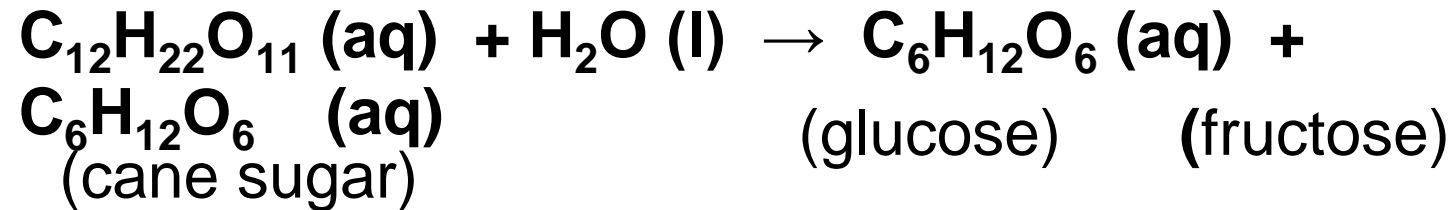


## Examples of homogeneous catalysis in the solution phase

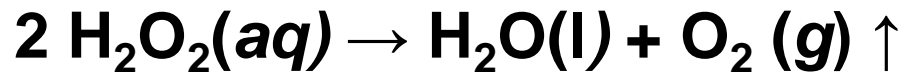
(3) Hydrolysis of ester in the presence of acid and alkali:



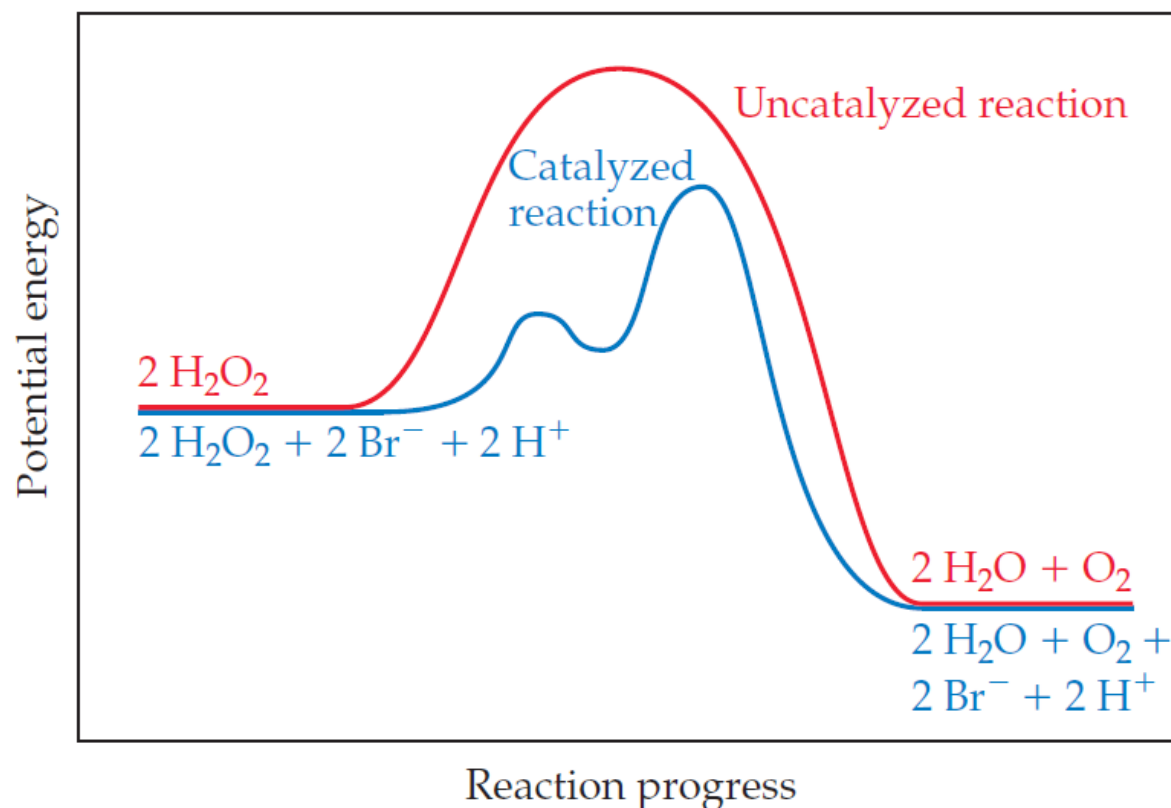
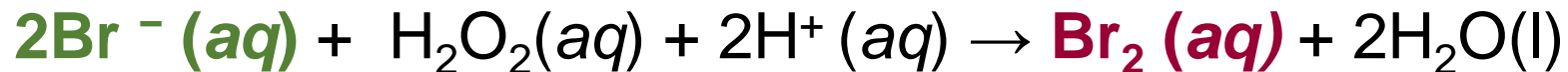
(4) Hydrolysis of sucrose (cane sugar) into glucose and fructose in presence of minerals acids acting as catalysts:



The decomposition of aqueous hydrogen peroxide,  $\text{H}_2\text{O}_2(\text{aq})$ , into water and oxygen:



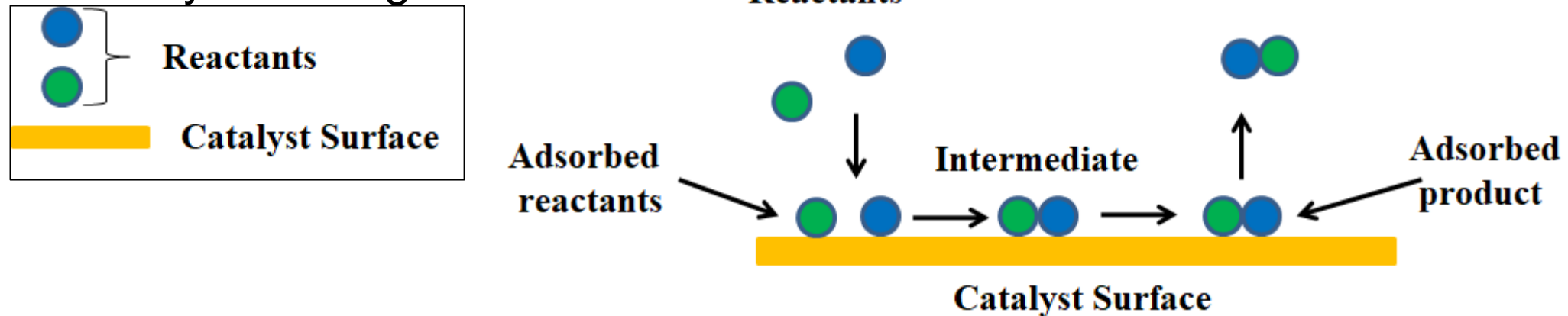
In presence of catalyst:



## 2. 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



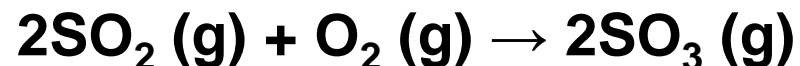
**Figure:** Schematic diagram to illustrate the heterogeneous catalysis.

## Examples of Heterogeneous catalyst

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



(b) Manufacture of sulphuric acid by the Contact process. Vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) or platinum are catalysts for the production of  $\text{SO}_3 (\text{g})$  from  $\text{SO}_2 (\text{g})$  and  $\text{O}_2 (\text{g})$ .



(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  $\text{H}_2\text{O}_2$  (aqueous) by  $\text{MnO}_2 (\text{s})$ .



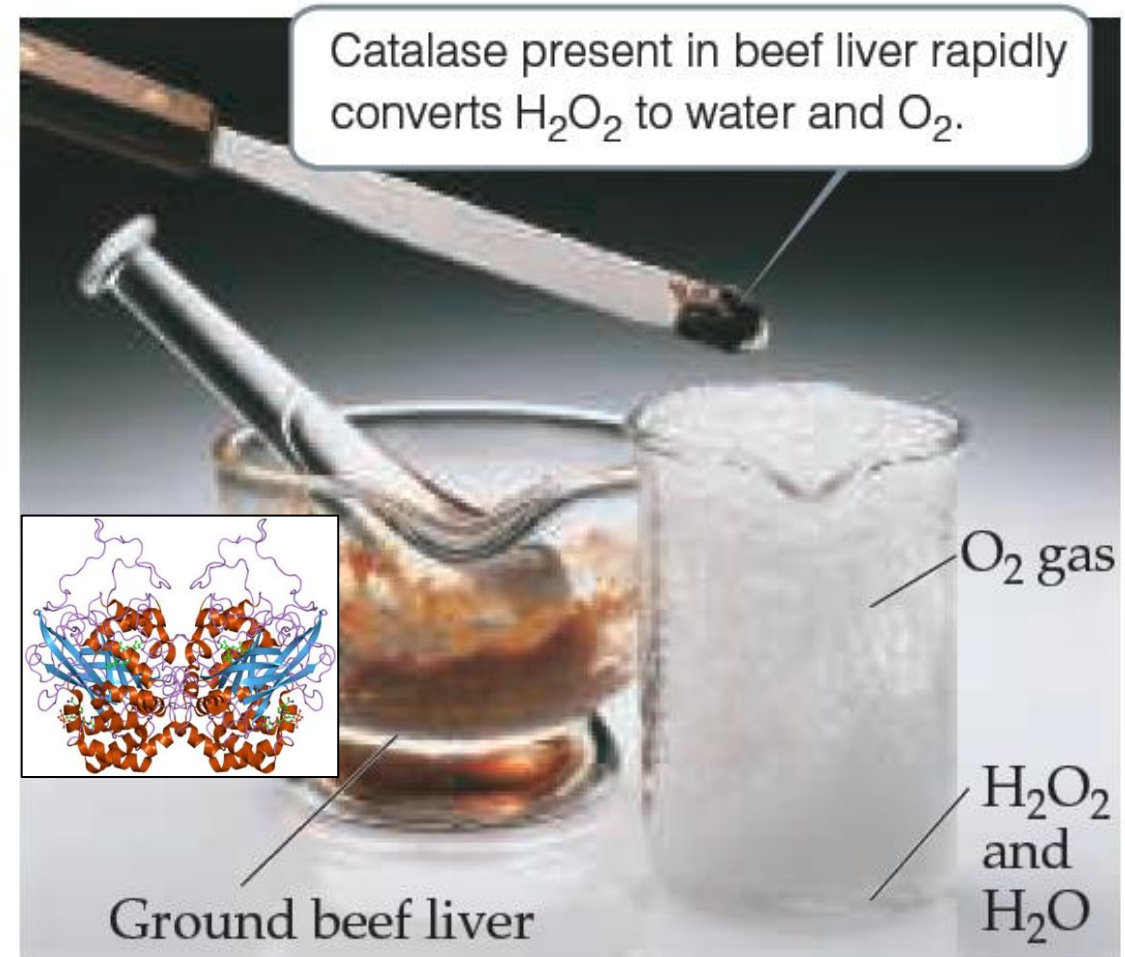
(d) **Examples of reactions in which both the reactant and the catalyst are in the solid phase.** The decomposition of  $\text{KClO}_3$  is catalysed by solid  $\text{MnO}_2$ .



# Enzyme catalysis

- *Biological catalysts known as **enzymes** are necessary for many of the chemical reactions occur in an extremely complex system of the human body.*
- **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)

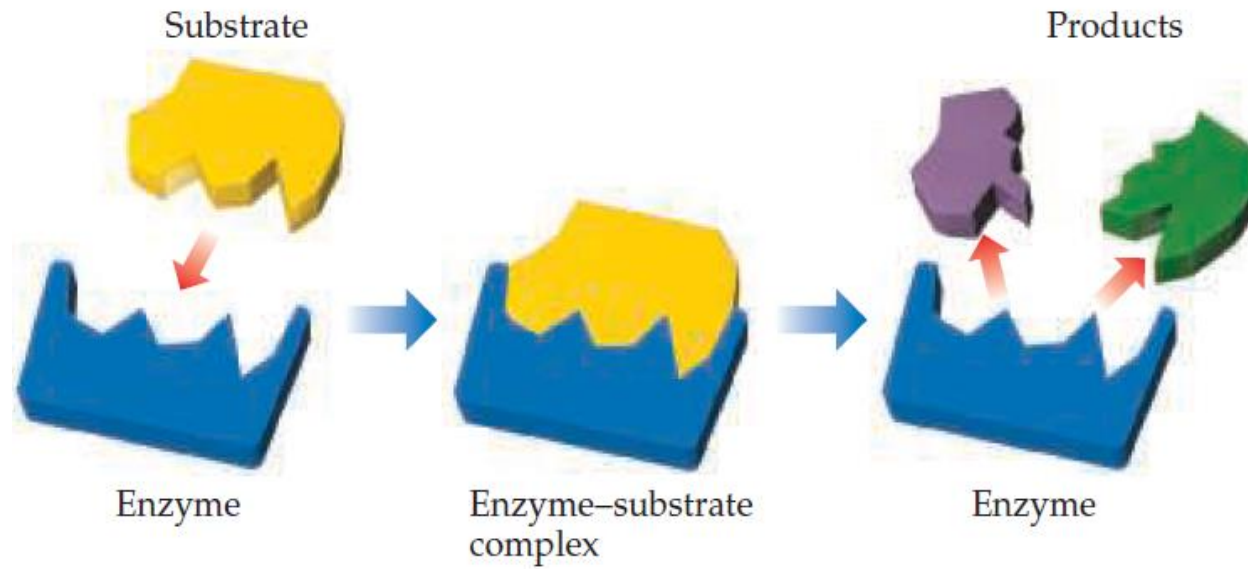
Reaction catalysed by the enzyme, **catalase**



**Enzymes speed up reactions.**

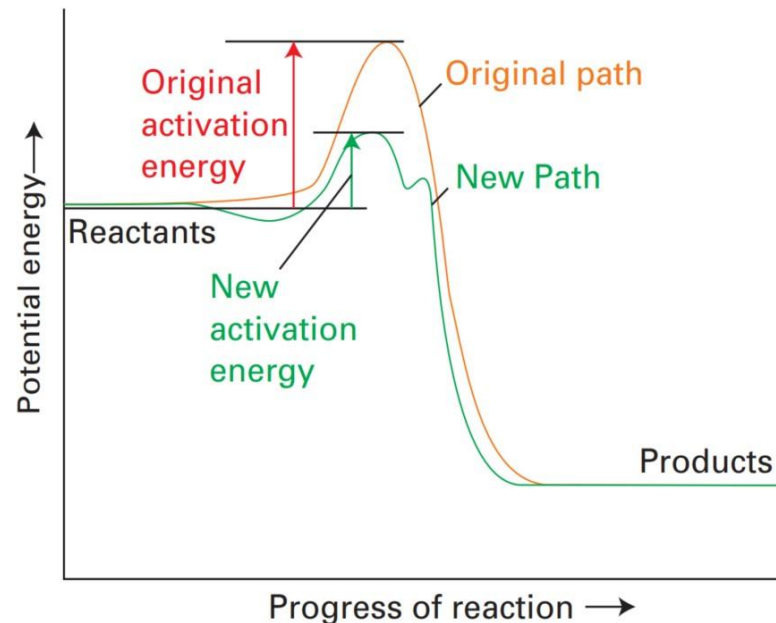


# Mechanism of enzyme-catalyzed reactions



- ❑ 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



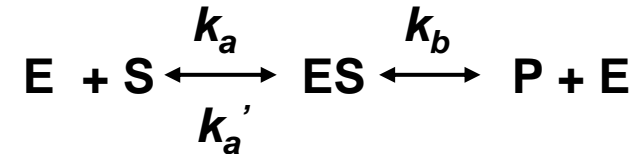
- ❑ Enzymes lower the activation energy for reactions. The lower the activation energy, the faster the rate of the reactions.
- ❑ For example: the **enzyme catalase** reduces the activation energy for the decomposition of hydrogen peroxide to  $8 \text{ kJ mol}^{-1}$ , corresponding to an acceleration of the reaction by a factor of  $10^{15}$  at 298 K.
- ❑ A generic equation for the enzyme-substrate complex formation is as follows:



# 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 to form an enzyme-substrate complex, which leads to the synthesis of the product and the release of the enzyme

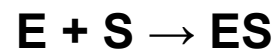


- Where,  $k_a$  is the rate of formation of ES,  $k_a'$  is the rate of dissociation of ES, and  $k_b$  is the rate of formation of P from ES.

# Michaelis-Menten Mechanism

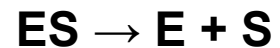
One of the earliest descriptions of the action of enzymes is the **Michaelis-Menten mechanism**. The proposed mechanism, with all species in an aqueous environment, is as follows.

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



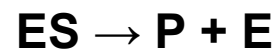
$$\text{Rate of formation of ES} = k_a[E][S]$$

**Step 2:** Unimolecular decomposition of the complex:



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

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



$$\text{Rate of formation of S} = k_b[ES]$$