

Dr. Ganesan Pandian, Assistant Professor – SAS, VIT

Ph.D. (Energy Systems Engineering): Daegu Gyeongbuk Institute of Science and Technology, South Korea
Post-Doctoral Research Associate: Kyushu University, Japan.

Research Expertise

- Electrochemical Water Splitting
- Zinc Air battery and Aluminum air battery
- Fuel cell assembly
- Vanadium Redox Flow Battery
- Electrochemical CO₂ reduction

Research Achievements

- 24 peer reviewed Journals
- 2950 citations, H-index:20
- Filed 4 patents with Zeon-Nippon Corporation, Japan
- 1 published patent with DGIST and Daegu Corp.

Research Awards

- * Received **A⁺ grade** for receiving the **JSPS- Kakhenki project** worth **5 million yen**.
- * Received **Best Ph. D. Dissertation award** in the year 2018 in the Daegu Gyeongbuk Institute of Science and Technology (DGIST)
- * Received **Best Presentation award** in the Asia Pacific Gas Conference (APGC) which was held on 5-6th October 2016 at Daegu, Korea
- * Awarded for the **Best Researcher** in the year 2015 in the Energy Systems Engineering, DGIST, South Korea.
- * Awarded with prestigious **National Post-doctoral fellowship** by SERB in India on 2017 at Central Electro-Chemical Research Institute (CECRI).

Ph.D. from DGIST, South Korea

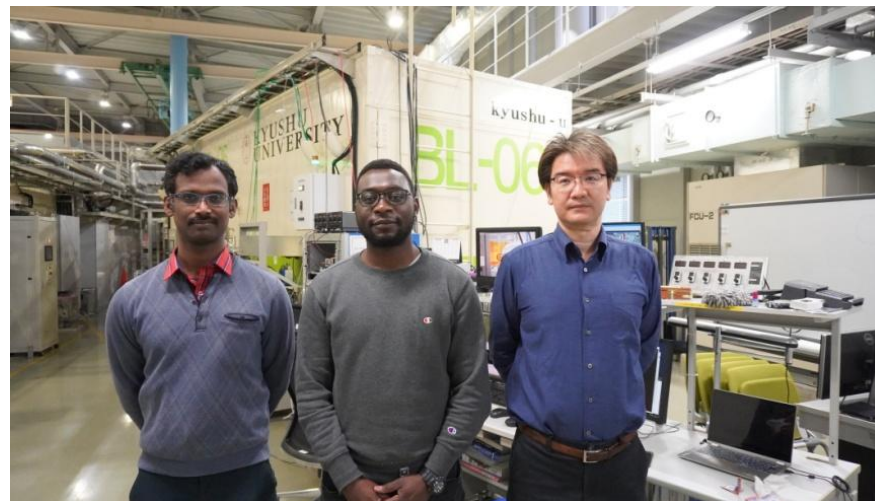


Post-doctoral Research Associate

Kyushu University, Japan



I2CNER, Kyushu University, Japan



Saga [Synchrotron](#)
Center, Kyushu
University, Japan

Engineering Chemistry

Module -1

A. Thermodynamics

Thermodynamics

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

ΔG = Gibbs free energy

ΔH = Heat change

ΔS = Change in disorder

Thermodynamics in

Earth Vs Space Vs Mars

?

Nernst Equation of Electrochemistry

$$\Delta G = -nFE^0$$

ΔG is Gibbs free energy

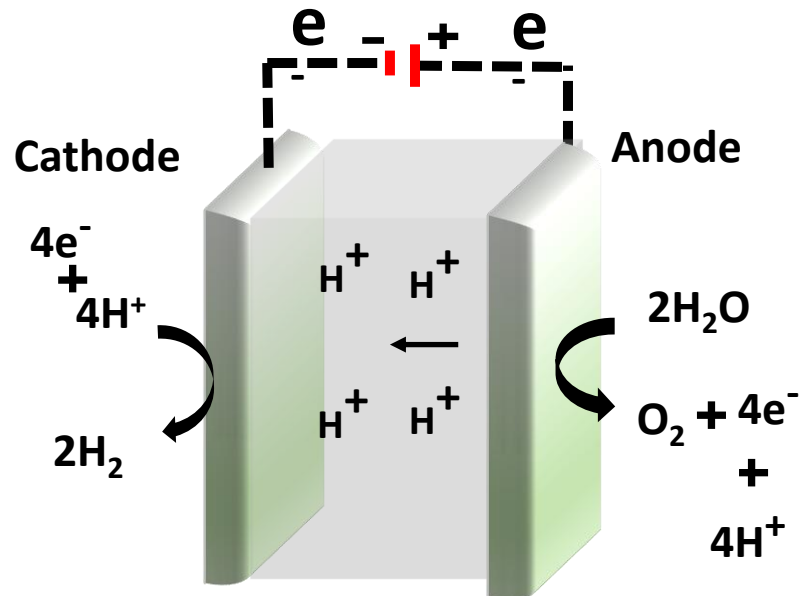
n is no. of electron

F is Faraday Constant

$$E^0 = -\Delta G/(nF)$$

E^0 Standard electrode potential

Proton Exchange Membrane (PEM) Water Electrolyzer

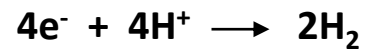


Anode



$$E^0 = -(-237.13)/nF = +1.228 \text{ V}$$

Cathode



$$E^0 = -0/nF = 0 \text{ V}$$

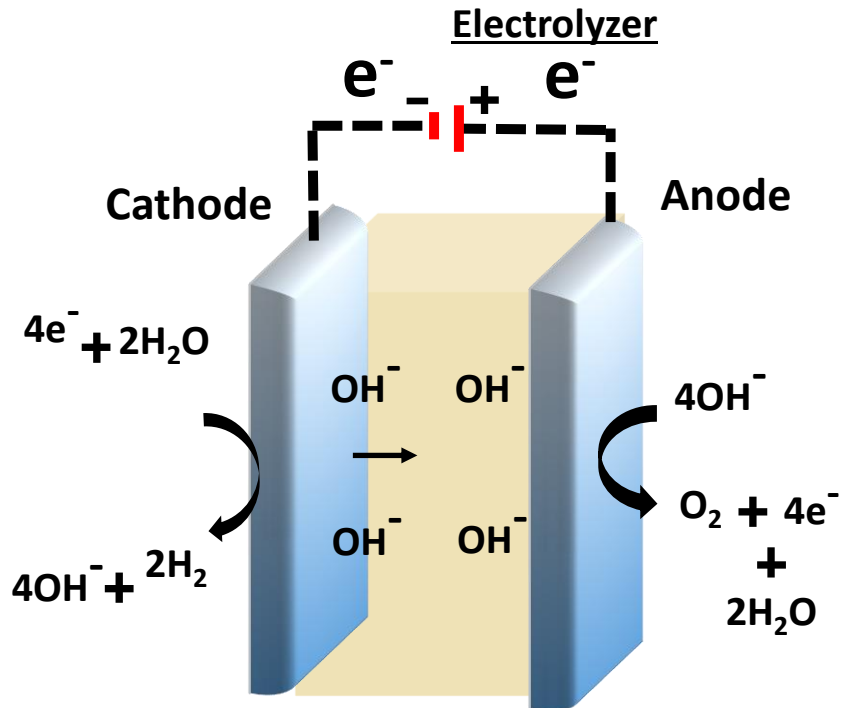
$$\text{Total } E^0 = E^0 (\text{anodic}) - E^0 (\text{cathodic})$$

$$E^0 = +1.23 - (0)$$

$$E^0 = +1.23 \text{ V}$$

Nernst Equation of Electrochemistry

Alkaline Electrolyte Membrane (AEM) Water



Anode



$$\Delta G_{\text{OH}^-} = -157.30 \text{ kJ.mol}^{-1}$$

$$E^0 = - \left(- (4 \cdot -157.30) - (2 \cdot -237.13) \right) / nF$$

$$= +0.4000073 \text{ V}$$

Cathode



$$E^0 = - \left((4 \cdot -237.13) - (4 \cdot -157.30) \right) / nF$$

$$= -0.8284 \text{ V}$$

$$\text{Total } E^0 = E^0 (\text{anodic}) - E^0 (\text{cathodic})$$

$$E^0 = +0.40 - (-0.8284)$$

$$E^0 = +1.23 \text{ V}$$

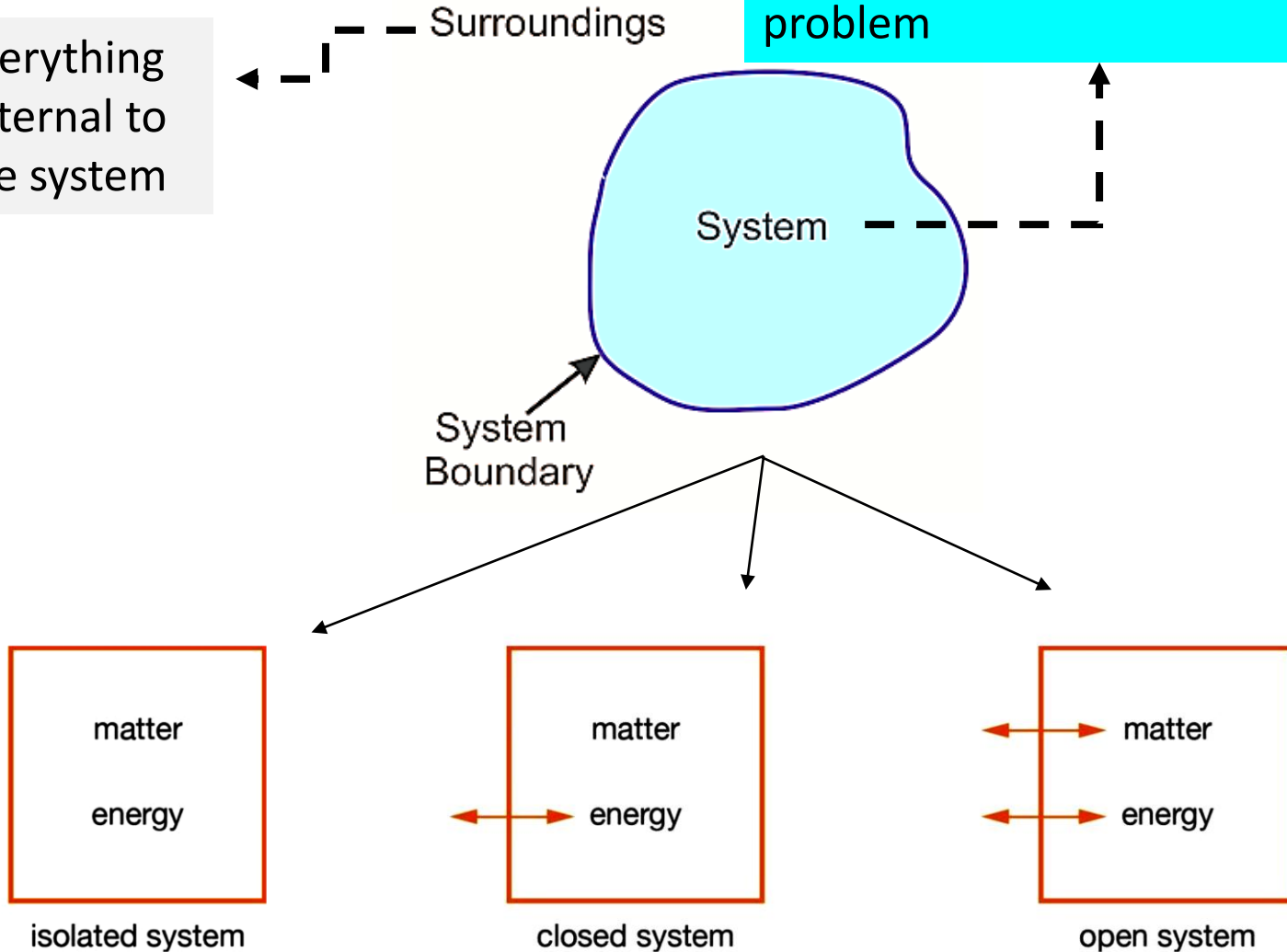
- Nernst Equation is used to solve the real assembly
- To design the new energy devices

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.



Temperature



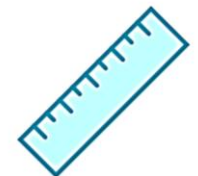
Boiling Point

Extensive Properties

Extensive properties depend on how much matter a sample contains.



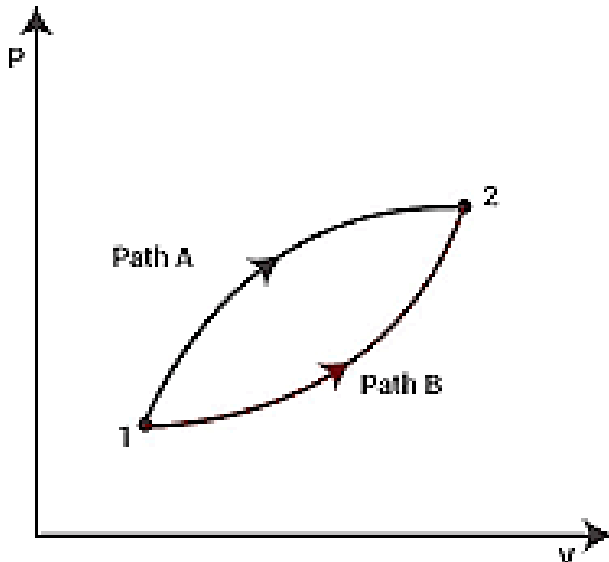
Weight



Length⁸

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.



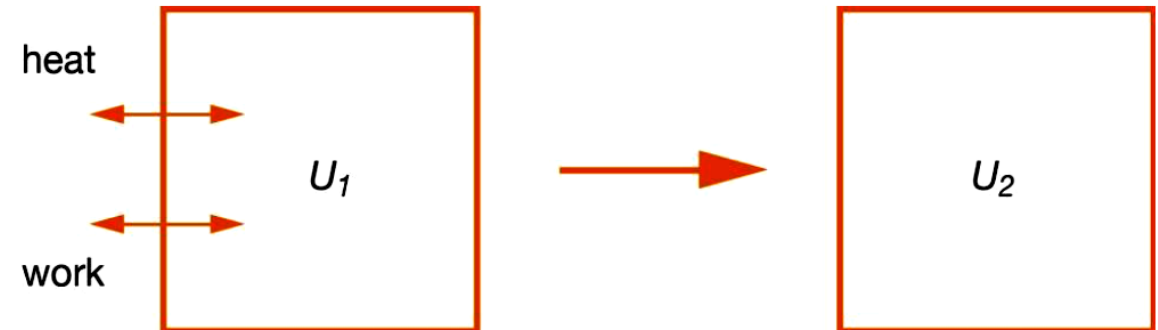
Path function:

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 **heat or work**



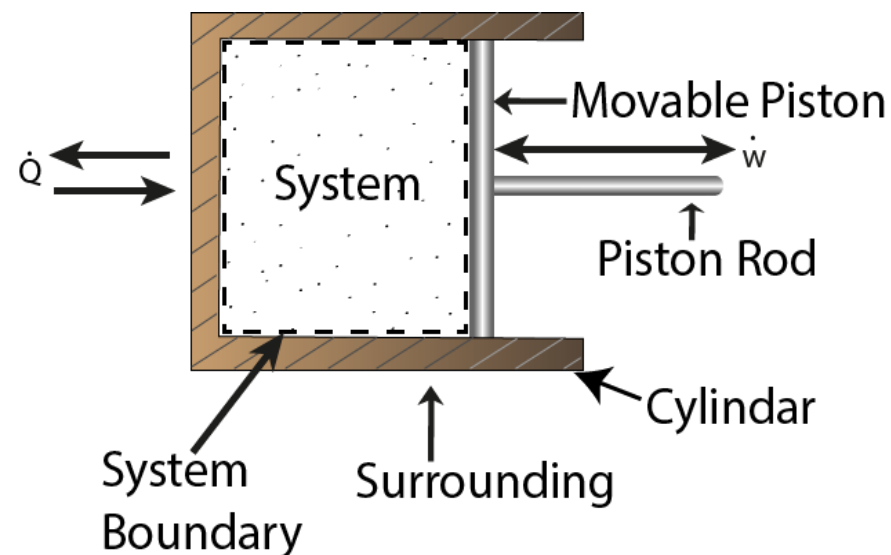
$$\triangleright \Delta U_{\text{system}} = U_{\text{final state}} - U_{\text{initial state}}$$

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 push 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 : $W = -\int_{V_i}^{V_f} P_{ex}dV$

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

□ A thermodynamics 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. Thus, a more appropriate definition is a reversible change in thermodynamics is

A change that can be reversed by an infinitesimal modification of a variable.

Example 1:

Thermal equilibrium of two systems with the same temperature

- 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:

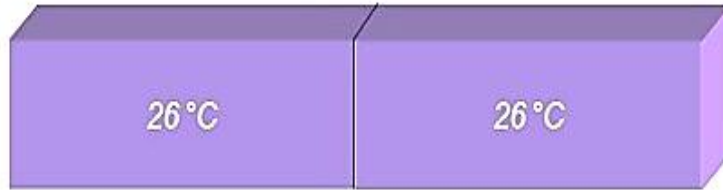
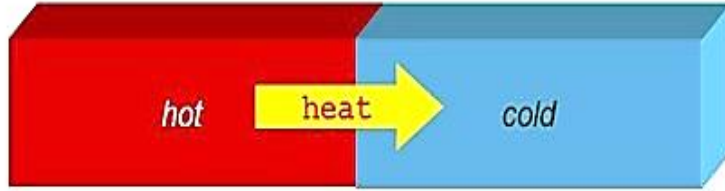
Suppose a gas is confined by a piston.

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.

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

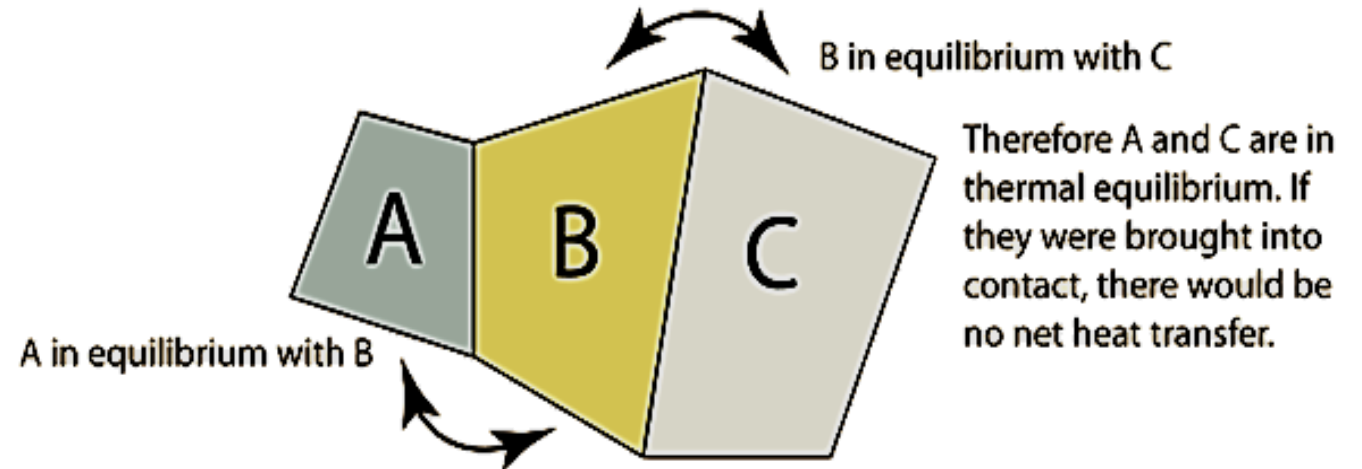
0th Law of Thermodynamics



- 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 has melted in the surroundings, it indicated transfer of energy as heat.

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



$E_1 = E_2$

$$\Delta U = q + w$$

if q :

- ✓ +ve if energy is transferred to the system as work/heat
- ✓ -ve if energy is lost from the system.

$H_2O \rightarrow H_2O + H_2O$

$\Delta G_{H_2O} = \Delta H$

Therefore,

change in internal energy (ΔU) 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

$$\Rightarrow H_f - H_i = q$$

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

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**'

- Molar heat capacity varies with temperature

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

- **Molar heat capacity at constant volume**

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

@ constant volume $w = 0$ & $\Delta U = q$

□ Molar heat capacity at constant pressure (C_p)

$$\Delta U = q + w$$

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

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

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)

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

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

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

$$C_p - C_v = nR \quad n \text{ moles}$$

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

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

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

➤ Isothermal Process (constant temperature)

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

$$P \cdot V \propto T$$

$$P \propto \frac{1}{V}$$

⇒ For an ideal gas,

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

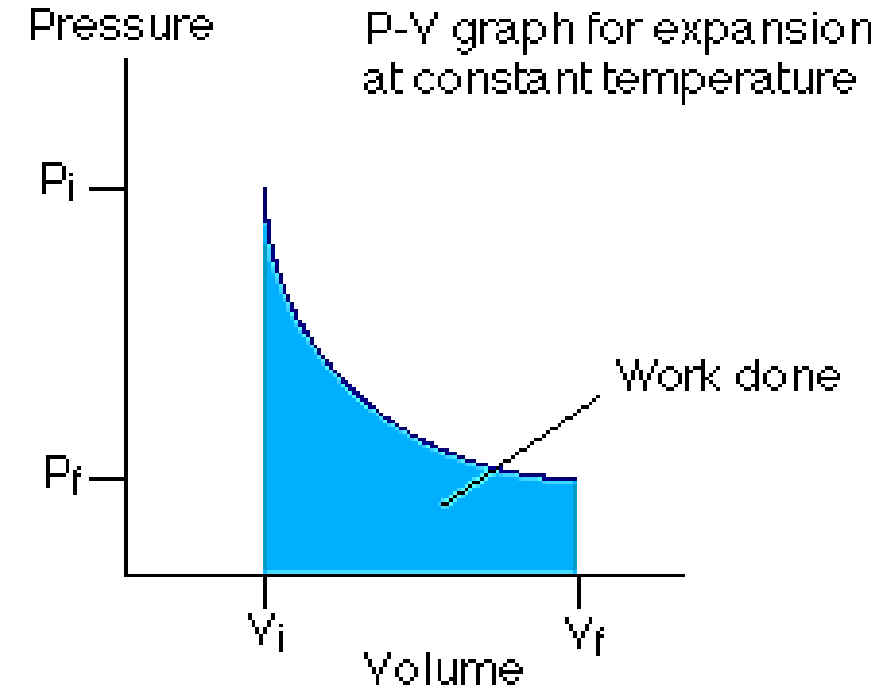
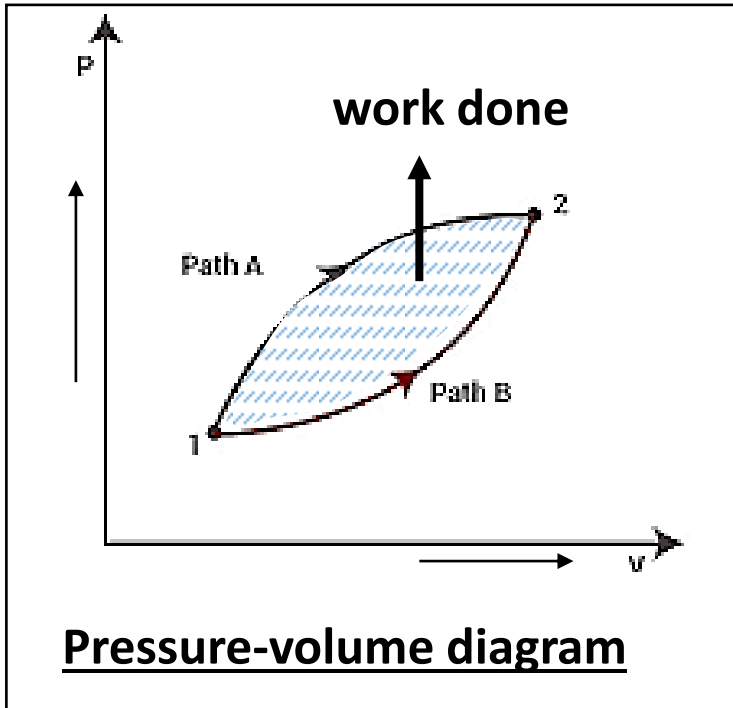
if $T = \text{fixed}$, $\Delta U = 0$ (according to 1st law, which deals with ΔU)

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

$$\Rightarrow q = w$$

- 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**.

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)

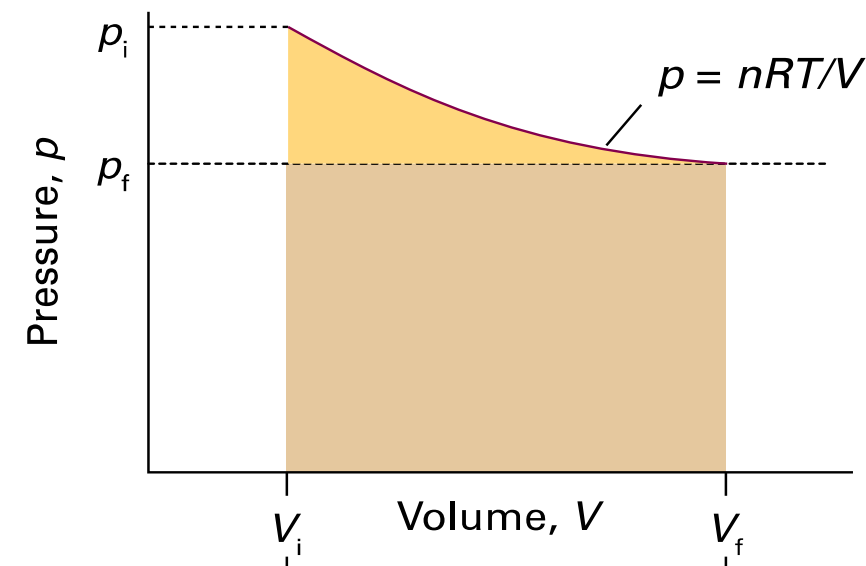
➤ Relations for Irreversible Isothermal expansion

- 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.
- 1st 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 and P

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

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

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

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

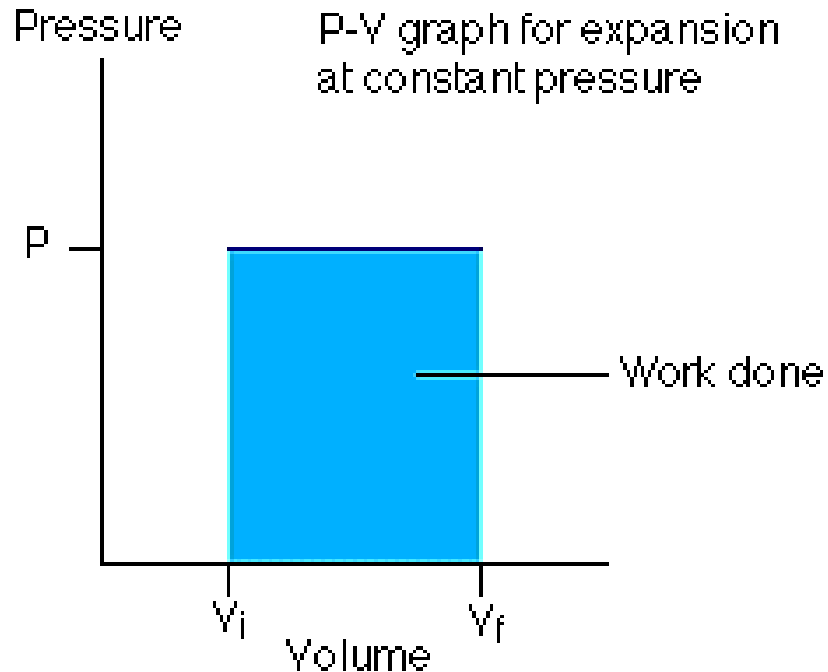
➤ Irreversible adiabatic expansion

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

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

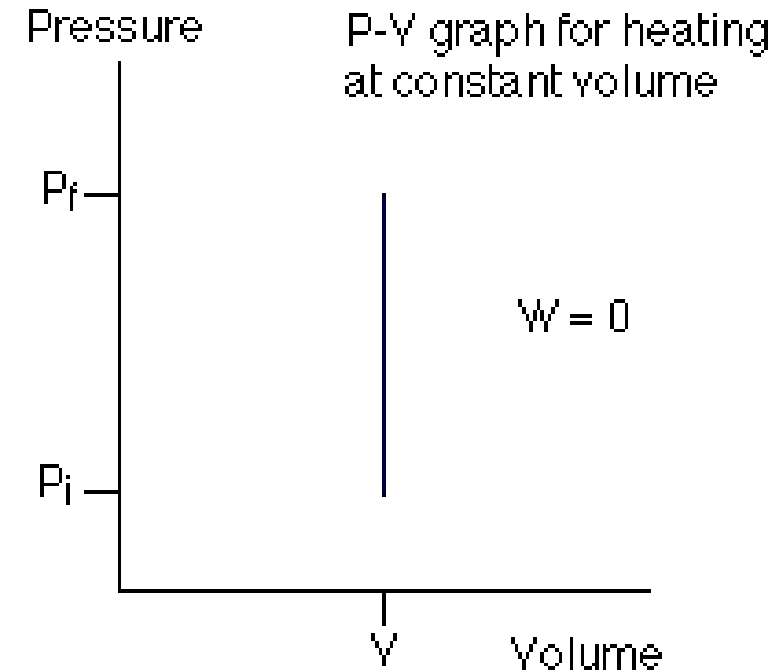
➤ Isobaric process (constant pressure)

- 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



- ❖ **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:

$$P = 1 \text{ atm} = 101325 \text{ Nm}^{-2}$$

$$V_i = \text{vol. of 1 mole of liquid water at 1 atm pressure} \\ = 18 \text{ ml} = 18 \times 10^{-6} \text{ m}^3$$

$$V_f = \text{vol. of 1 mole of steam at 100 °C at 1 atm pressure} \\ = (22.4 \text{ dm}^3 \times 373)/273 = 30.60 \text{ dm}^3 = 0.0306 \text{ m}^3$$

$$w = P (V_f - V_i) \\ = 101325 \text{ Nm}^{-2} [0.0306 \text{ m}^3 - (18 \times 10^{-6}) \text{ m}^3] \\ = 101325 \text{ Nm}^{-2} \times 0.0306 \text{ m}^3 = 3100 \text{ Jmol}^{-1}$$

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

Hence, $w = -3100 \text{ Jmol}^{-1}$

- ❖ **Example 2:** 1 mole of an ideal gas expands against a constant external pressure of 1 atm from a volume of 10 dm³ to a volume of 30 dm³. Calculate the work done by the gas in Joules.

Solution:

$$w = -P_{ex} \Delta V \\ = -(1 \text{ atm})(30 \text{ dm}^3 - 10 \text{ dm}^3) \\ = -20 \text{ dm}^3 \text{ atm}$$

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

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

Therefore,

$$w = -20 \text{ dm}^3 \text{ atm} \\ = -20 \text{ dm}^3 \times \frac{8.314 \text{ J mol}^{-1}\text{K}^{-1}}{0.08206 \text{ dm}^3 \text{ mol}^{-1}\text{K}^{-1}} = -2026 \text{ J}$$

- ❖ **Example 3:** 1 mole of an ideal monoatomic gas at 27 °C expands reversibly and adiabatically from a volume of 10 dm³ to a volume of 20 dm³. Calculate q , ΔU , W and ΔH . Given $\frac{C_v}{R} = \frac{3}{2}$

Solution:

Since the process is adiabatic, $q = 0$

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

$$\Rightarrow \frac{3}{2} \ln \frac{T_f}{300} = \ln \left(\frac{10 \text{ dm}^3}{20 \text{ dm}^3} \right) \Rightarrow T_f = 189 \text{ K}$$

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

For a finite change in n moles,

$$\Delta U = nC_v \Delta T$$

$$= (1 \text{ mol}) \left(\frac{3}{2} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \right) (189 - 300) \text{ K}$$

$$= -1384 \text{ J}$$

Since for an adiabatic process, $q = 0$,

hence $\Delta U = w = -1384 \text{ J}$

$$\Delta H = \Delta U + \Delta PV = \Delta U + \Delta nRT$$

$$= \Delta U + nR(T_f - T_i)$$

$$\rightarrow nR(T_f - T_i)$$

$$\rightarrow = (1 \text{ mol}) (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) (189 - 300)$$

$$= -923 \text{ J}$$

$$\Delta H = -1384 \text{ J} - 923 \text{ J} = -2307 \text{ J}$$

Note: ΔH can also be calculated by using the relation $dH = C_p dT$

- ❖ **Example 4:** 10 moles of an ideal gas expands reversibly and isothermally from a pressure of 10 atm to 2 atm at 300 K. Calculate the work done.

Solution: $w = -nRT \ln \frac{P_i}{P_f} = -(10 \text{ mol}) (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) (300 \text{ K}) \ln \frac{10 \text{ atm}}{2 \text{ atm}} = -40.15 \times 10^3 \text{ J}_{21}$

■ Why we need for the 2nd law of thermodynamics?

→ The 1st 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 2nd law of thermodynamics

□ 2nd 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.

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

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

S = the entropy of the system of interest, &

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 1st law uses the **internal energy** to identify **permissible changes**
- the 2nd 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

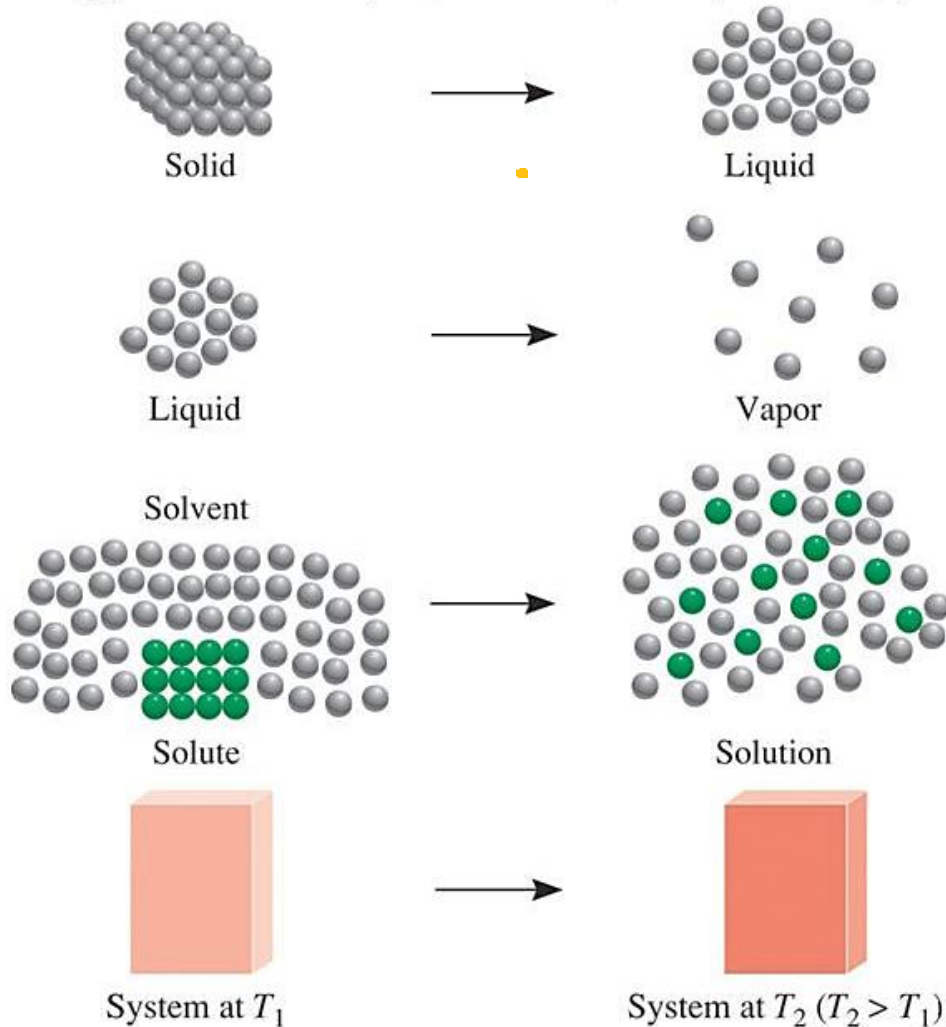
- The thermodynamic definition of entropy concentrates on the change in entropy (**dS**) that occurs as the result of a physical or chemical process.
- if an amount of heat **Q** at zero kelvin flows into a large heat reservoir at temperature **T** above absolute zero, then the entropy increase is

$$\Delta S = Q/T.$$

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

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

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

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

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

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

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

as $dS = dq_{rev}/T$

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

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

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

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

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

➤ Isothermal *Reversible* expansion

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

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

➤ 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 is irreversible, entropy of the universe is increasing continuously**

- The 1st law & the 2nd 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

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

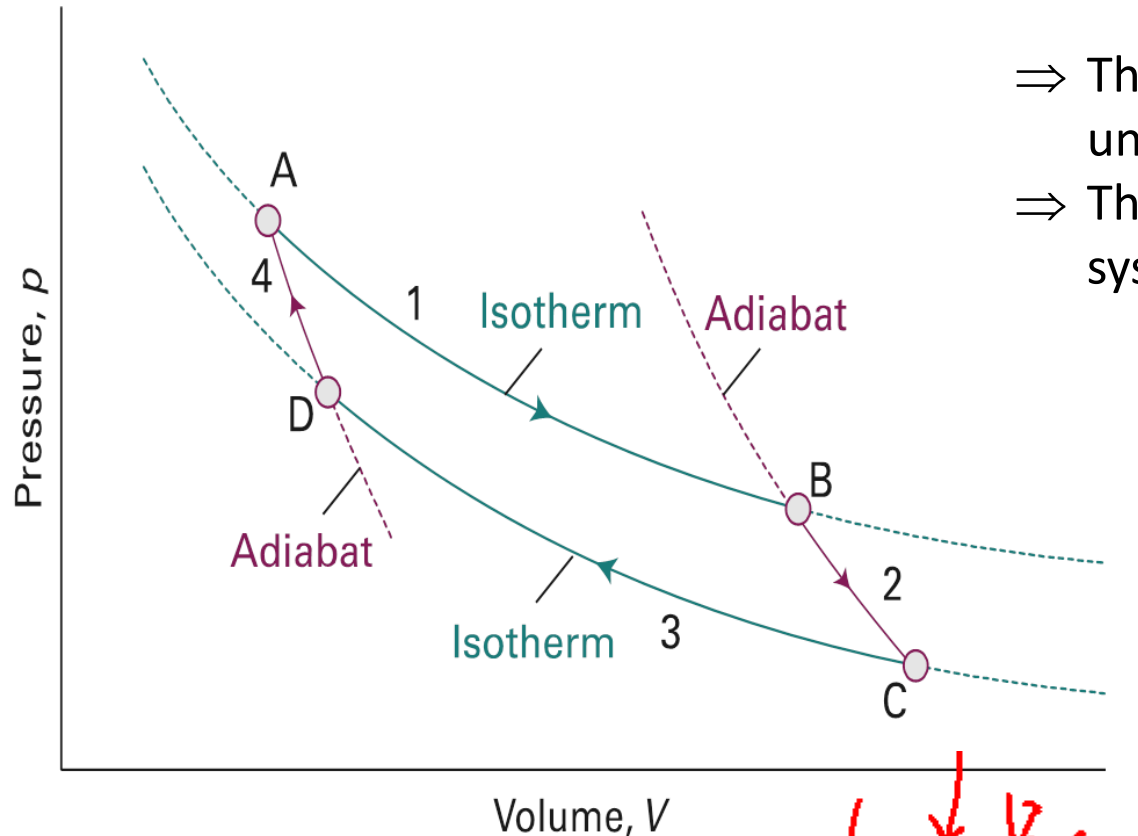
➤ Heat engine

- 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. 1st 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)

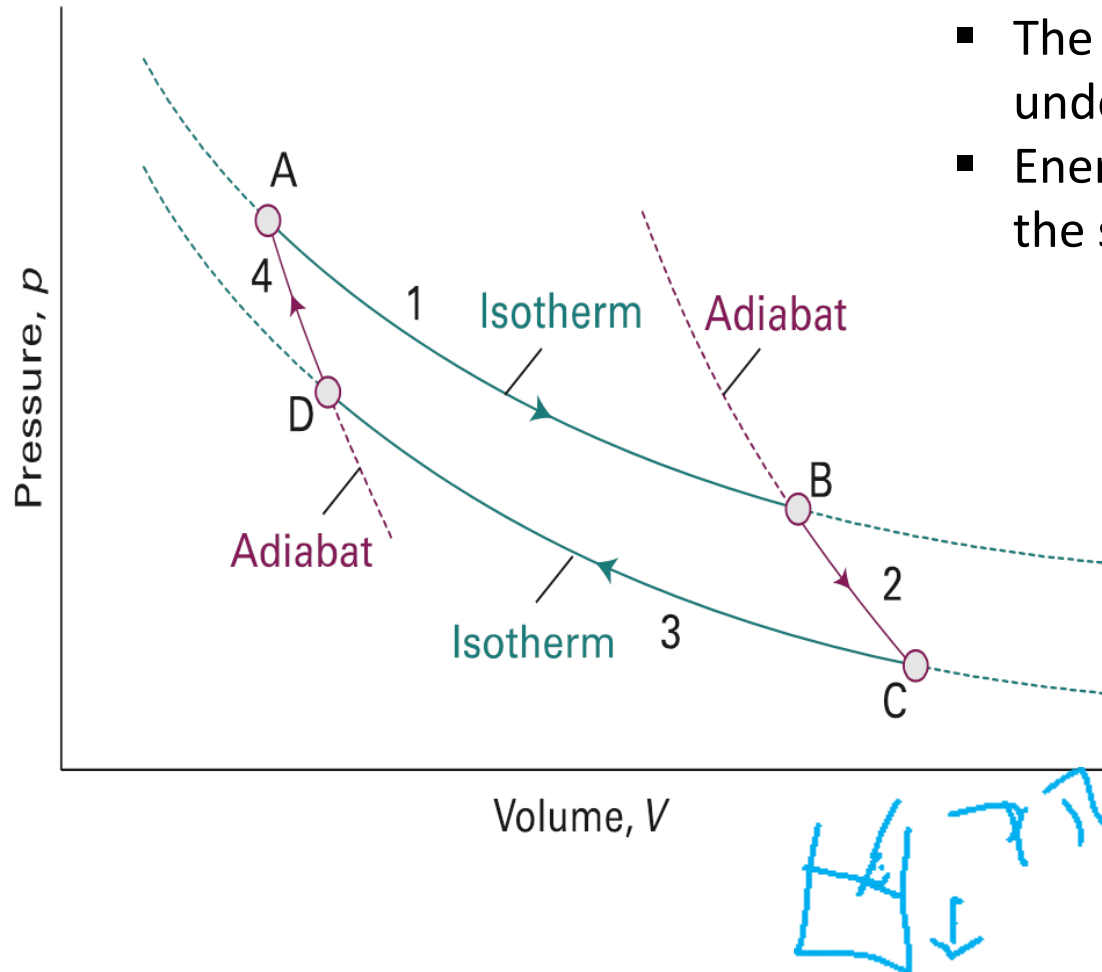
$$q_h = -w_1 = RT_h \ln \frac{V_B}{V_A}$$

B. 2nd 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. 3rd 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. 4th 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.

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

Carnot Cycle

- 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:

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

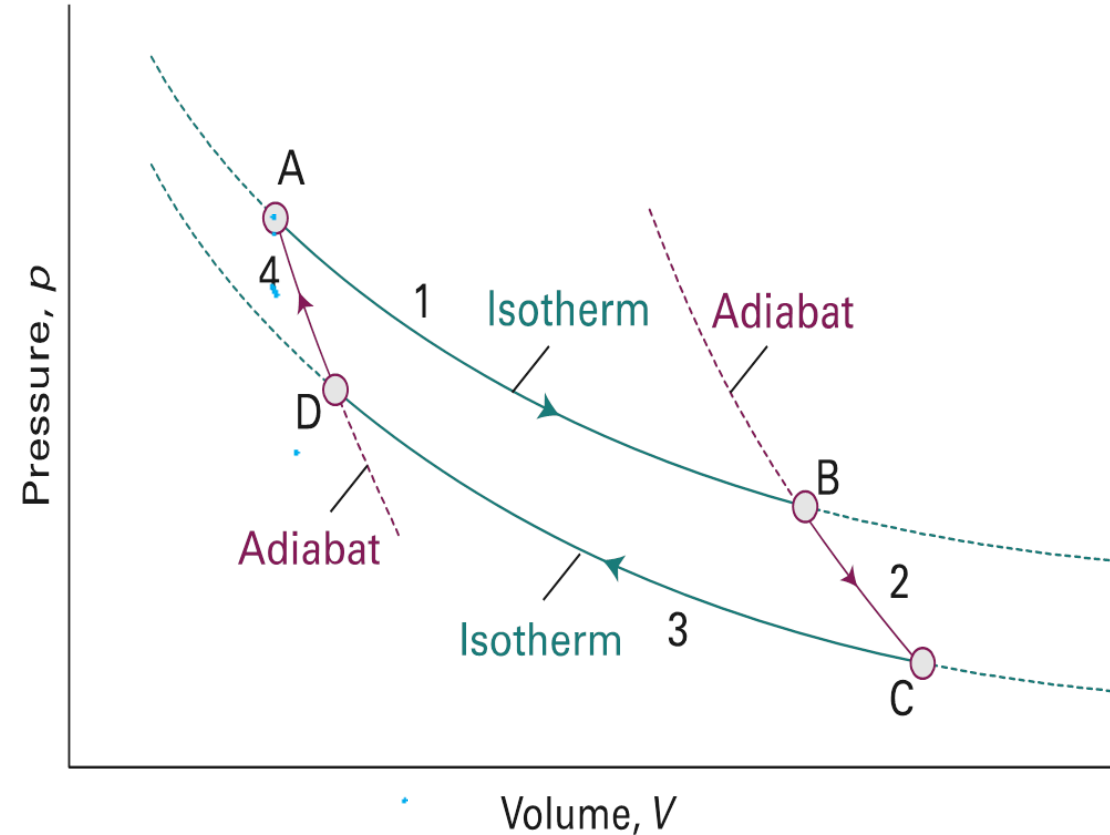
❖ For an ideal gas, $\oint dS = 0$ and $\frac{q_h}{q_c} = -\frac{T_h}{T_c}$

Efficiency of a heat engine

- The thermal efficiency of a heat engine is

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

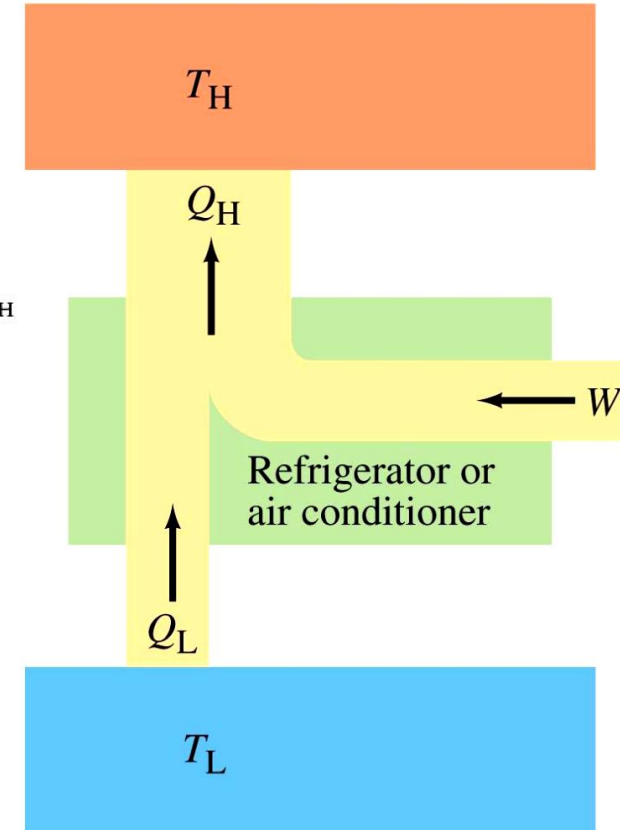
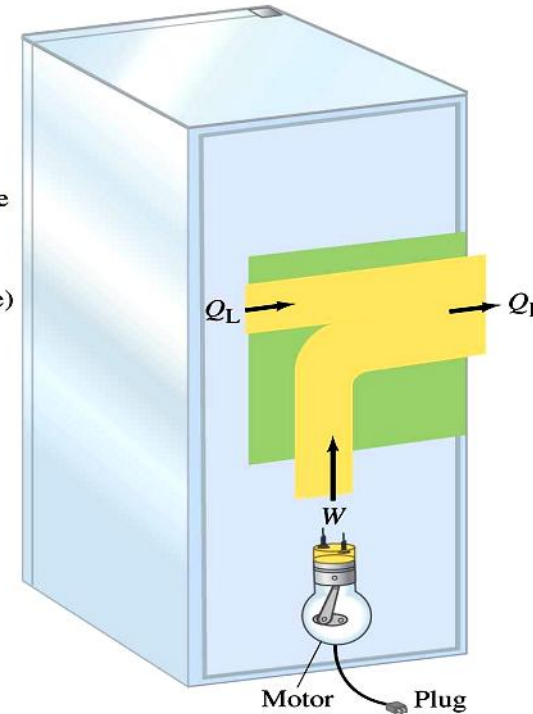
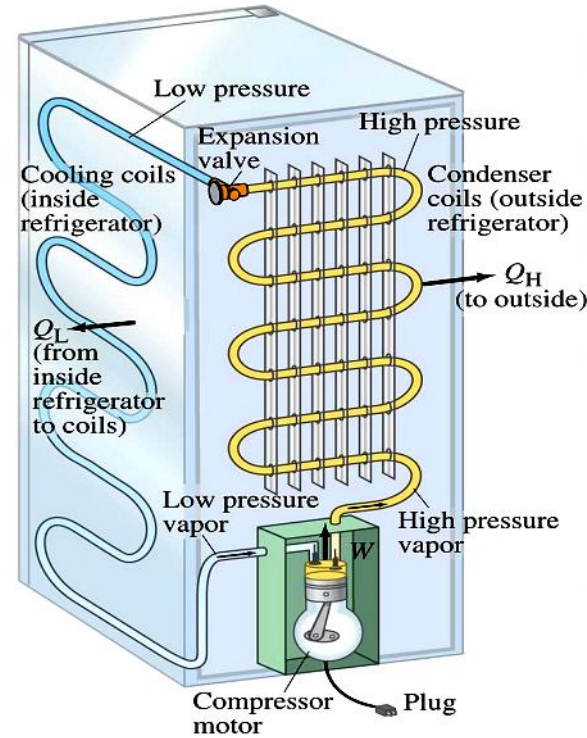
- W.P. 100%
- The “engine” statement of the 2nd Law:
 - it is impossible for any system to have an efficiency of 100% ($\eta = 1$) **[Kelvin’s statement]**



- Another statement of the 2nd 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]**²⁸

Application of the Carnot Cycle

- **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 ΔS_{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** *Gibbs free energy*
- 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: $\Delta G = \Delta H - T\Delta S$
 - **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 1st law & the $d(q_v) = dU$]

$$\Rightarrow TdS \geq dU$$

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

$$\Rightarrow A = U - TS$$

➤ 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]

$$\Rightarrow G = H - TS$$

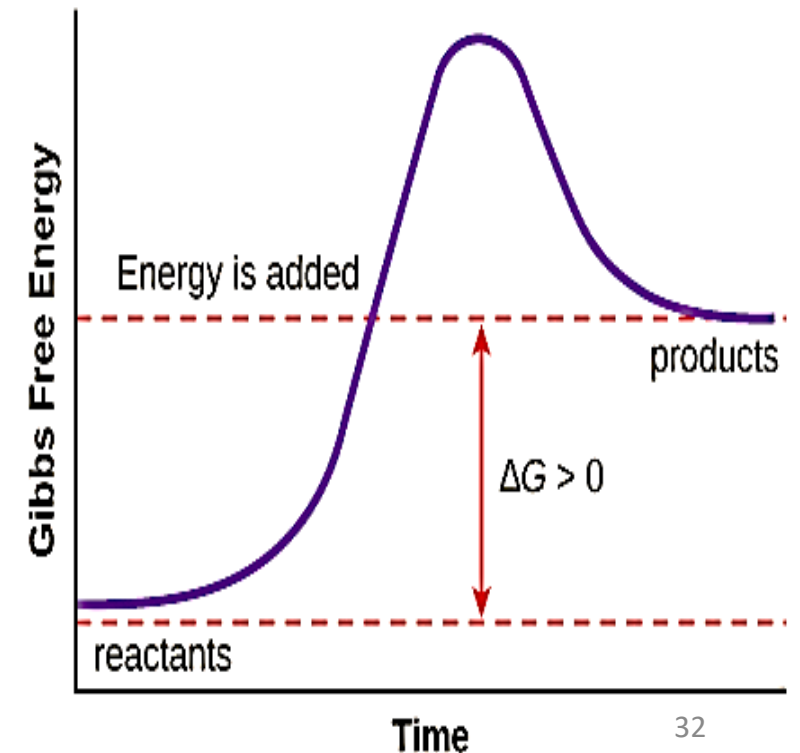
- The criterion of spontaneity in terms of Gibbs Free energy change (dG) and Helmholtz energy (dA)

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

➤ In an endothermic reaction:

- 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 .

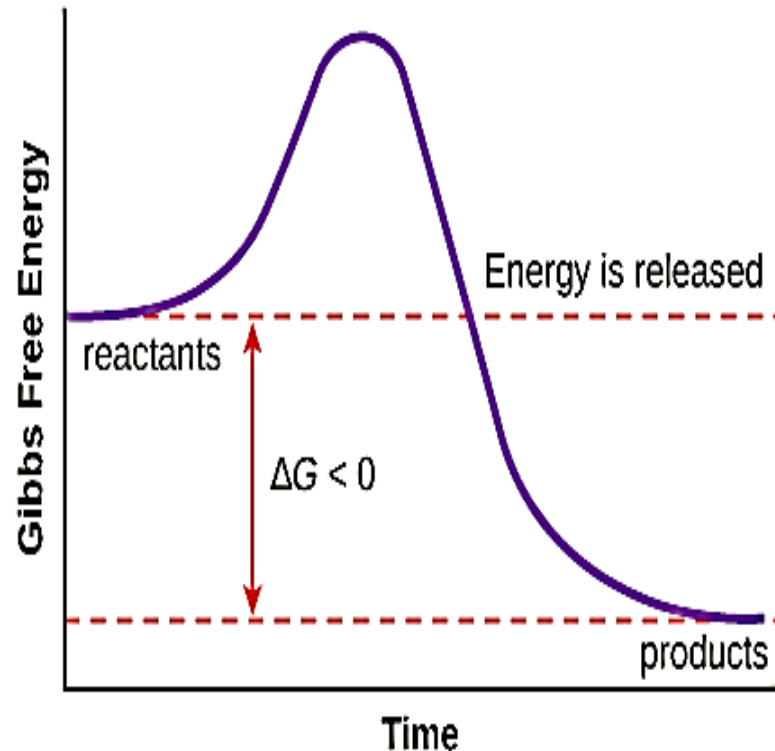
\Rightarrow **Endothermic reactions** are therefore driven by the **increase of entropy** of the system



➤ 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:

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

- ❖ **Example 1:** Calculate the efficiency of a certain power station operates with superheated steam at 300 °C ($T_h = 573$ K) and discharges the waste heat into the environment at 20 °C ($T_c = 293$ K).

Solution:

$$T_c = (1 - \eta)T_h$$
$$\Rightarrow \eta = 1 - (T_c/T_h)$$

$$\begin{aligned} \text{Theoretical efficiency } (\eta) &= 1 - (293\text{K}/573\text{K}) \\ &= 0.489 \\ &= \mathbf{48.9\%} \end{aligned}$$

In practice, there are other losses due to mechanical friction and the fact that turbines do not operate reversibly.

- ❖ **Example 3:** Heat supplied to a Carnot engine is 1897.8 kJ. How much useful work can be done by the engine which works between 0 °C and 100 °C.

Solution:

$$T_c = 0 + 273 = 273 \text{ K}, T_h = 100 + 273 = 373 \text{ K}$$

$$q_h = 1897.8 \text{ kJ}$$

$$\therefore w = q_h \times \left(1 - \frac{T_c}{T_h}\right)$$

$$= 1897.8 \text{ kJ} \times \left(1 - \frac{273 \text{ K}}{373 \text{ K}}\right)$$

$$= 508.7 \text{ kJ}$$

\therefore Work done by the engine is **508.7 kJ**

- ❖ **Example 2:** Calculate the maximum efficiency of a heat engine operating between 100 °C and 25 °C

Solution:

For engines, we have

$$T_c = 25 + 273 = 298\text{K}$$

$$T_h = 100 + 273 = 373 \text{ K}$$

$$T_c = (1 - \eta)T_h$$

$$\Rightarrow \eta = 1 - (T_c/T_h)$$

$$\eta = 1 - (298 \text{ K}/373 \text{ K})$$

$$= 0.201$$

$$= \mathbf{20.1\%}$$

- ❖ **Example 4:** 5 mole of an ideal gas expands reversibly from a volume of 8 dm³ to 80 dm³ at a temperature of 27 °C. Calculate the change in entropy.

Solution:

$$\Delta S = nR \ln(V_f/V_i)$$

Given that $n = 5$, $V_f = 80 \text{ dm}^3$, $V_i = 8 \text{ dm}^3$

$$\begin{aligned}\Delta S &= (5 \text{ mol}) (8.314 \text{ J K}^{-1}\text{mol}^{-1}) \ln(80 \text{ dm}^3/8 \text{ dm}^3) \\ &= \mathbf{95.73 \text{ JK}^{-1}}\end{aligned}$$

- ❖ **Example 6:** 1 mol of an ideal gas expands reversibly from a volume of 10 dm³ and 298 K to a volume of 20 dm³ and temperature 250 K. Assuming $C_v = 3/2 R$, calculate the entropy change for the process.

Solution:

$$\begin{aligned}\Delta S &= C_v \ln \frac{T_f}{T_i} + R \ln \frac{V_f}{V_i} \\ &= 1.5 (8.314 \text{ Jmol}^{-1}\text{K}^{-1}) \ln \left(\frac{250 \text{ K}}{298 \text{ K}} \right) + (8.314 \text{ Jmol}^{-1}\text{K}^{-1}) \ln (20 \text{ dm}^3/10 \text{ dm}^3) \\ &= \mathbf{3.57 \text{ JK}^{-1}\text{mol}^{-1}}\end{aligned}$$

- ❖ **Example 5:** Calculate the change in entropy accompanying the heating of 1 mole of Helium gas (assumed ideal) from a temperature of 298 K to a temperature of 1000 K at constant pressure. Assume $C_v = 3/2 R$

Solution:

$$\text{As } C_p - C_v = R$$

$$\Rightarrow C_p = C_v + R = 2.5 R$$

$$\begin{aligned}\Delta S_p &= C_p \ln \frac{T_f}{T_i} = (2.5 \times 8.314 \text{ Jmol}^{-1}\text{K}^{-1}) \ln \left(\frac{1000 \text{ K}}{298 \text{ K}} \right) \\ &= \mathbf{25.17 \text{ Jmol}^{-1}\text{K}^{-1}}\end{aligned}$$

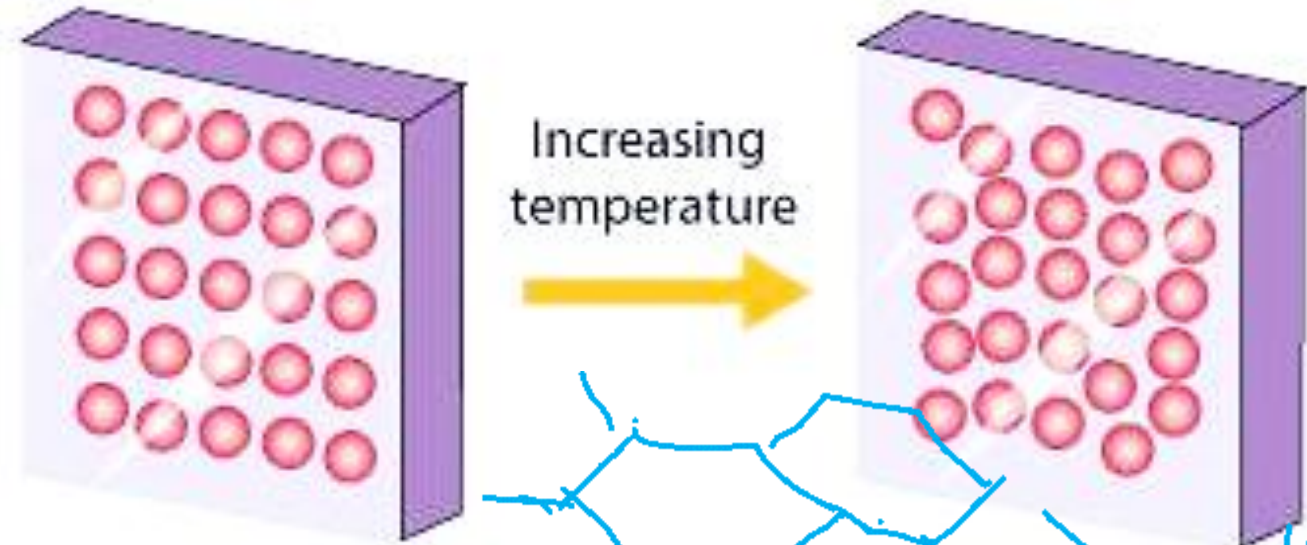
3rd Law of Thermodynamics

- 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:

$$S = k \ln W$$

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.

\Rightarrow 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 $T = 0$



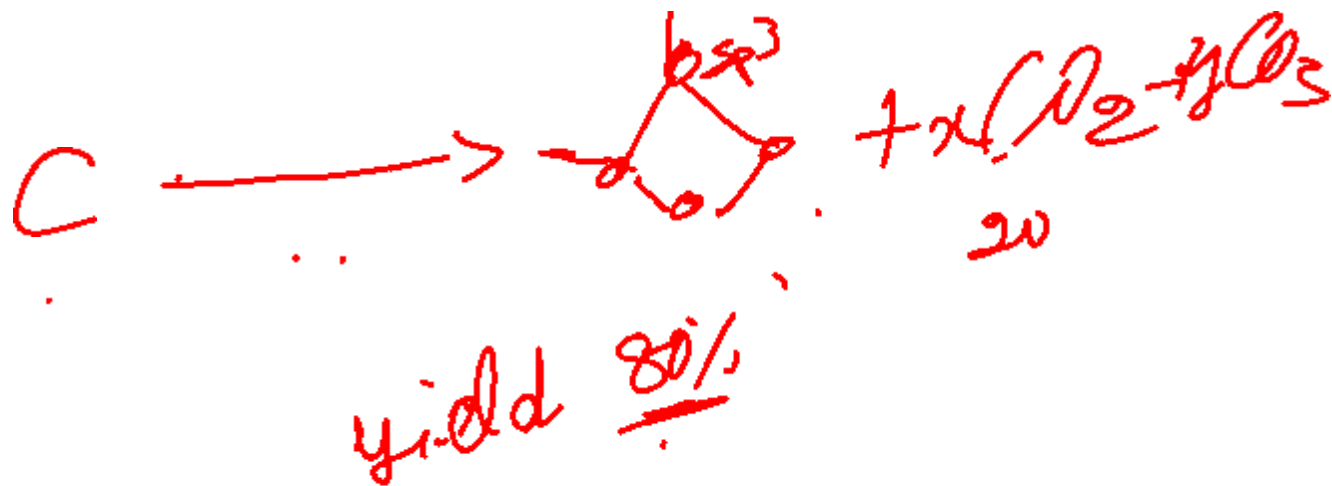
\rightarrow When $T = 0$, $W = 1$
 $\therefore S = k \ln W = 0$

➤ **Third law of thermodynamics:**

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

Module 1

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,

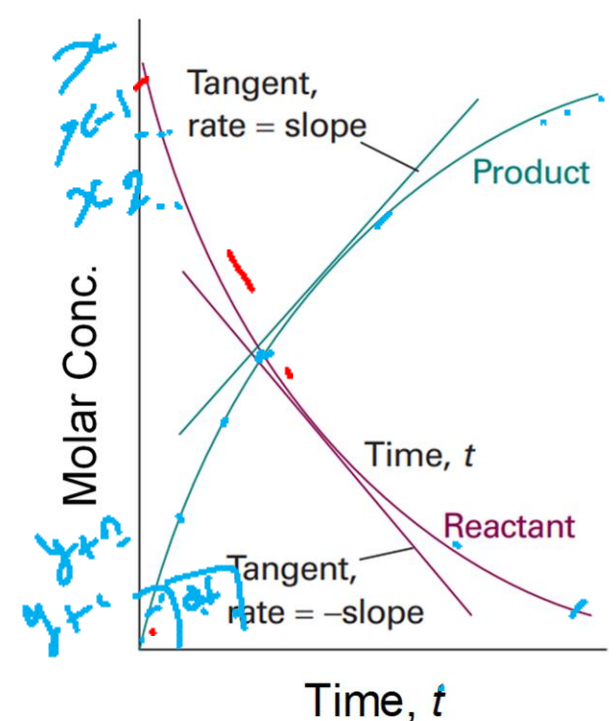
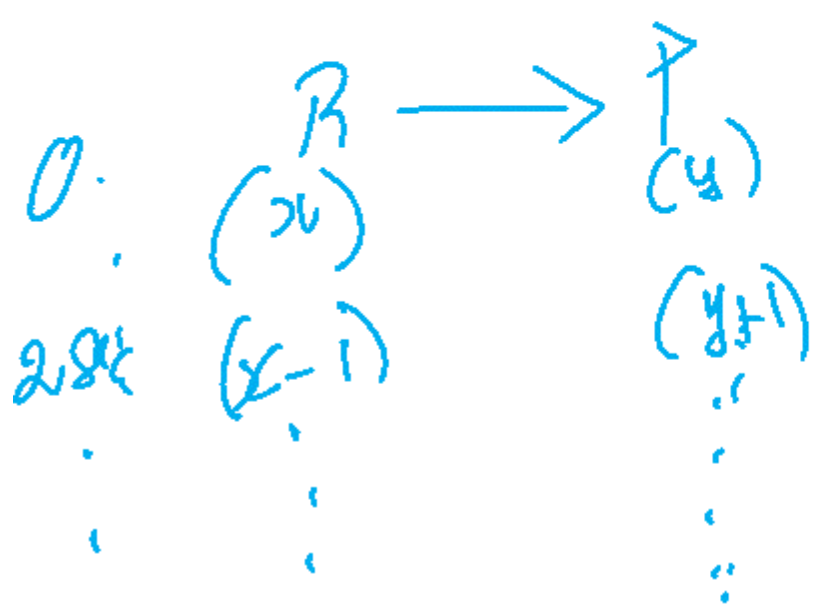
It is to be contrasted with thermodynamics, which deals with the direction in which a process occurs but in itself tells nothing about its rate

Chemical Kinetics deals with the rate of a chemical reaction.

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.

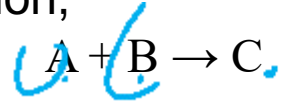
Time & Reactants



$$\frac{d(c)}{dt}$$

The rates of reactions

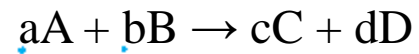
Consider a general reaction,



The rate of reaction will be:

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

Consider another general reaction:



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:

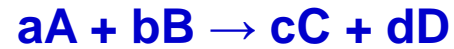
Write rate expressions for the following reactions:

1. $\text{NO}_2 (\text{g}) + \text{CO} (\text{g}) \rightarrow \text{NO} (\text{g}) + \text{CO}_2 (\text{g})$
2. $2\text{HI} (\text{g}) \rightarrow \text{H}_2 (\text{g}) + \text{I}_2 (\text{g})$



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**.




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

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

 - ✓ The rate constant is independent of the concentrations but depends on the temperature. *Order, Conditions*
 - ✓ The units for k vary. Determine units for k by considering units for rate and for concentration.

Order of a reaction



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

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 $k[\text{A}]^0$)
- ✓ $m = 1$ (First order $k[\text{A}]^1$)
- ✓ $m = 2$ (Second order $k[\text{A}]^2$)

Examples:



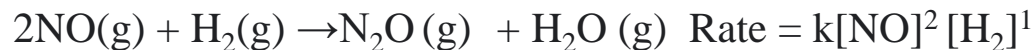
(Zero order)



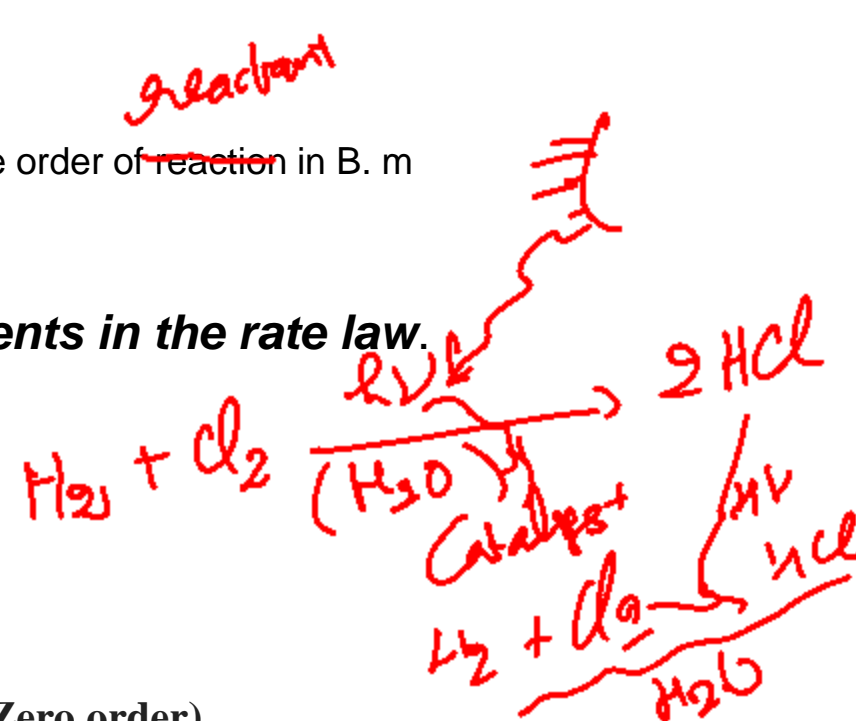
(First order)



(Second order)

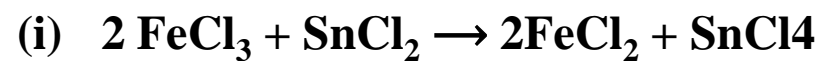


(Third order)



Order of a reaction

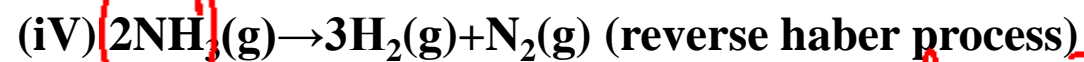
Find the orders for these reactions



3rd order



3rd order

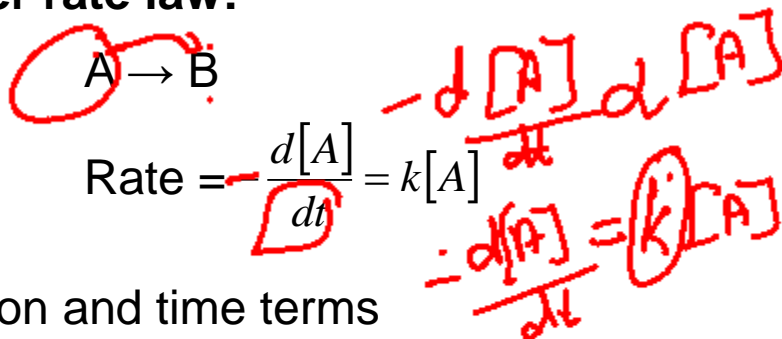


How? zero

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:



Separate concentration and time terms

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

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

$$\int \frac{d[A]}{[A]} = -k \int dt$$
$$\int_{[A]_0}^{[A]^t} \frac{d[A]}{[A]} = -k \int_0^t dt$$

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

Pooja & Sharma
Physical
Chemical

Information - URE
looks
paper

Complications ->
SciFinder
Scopus
ACS

Continue....

Integrated rate laws

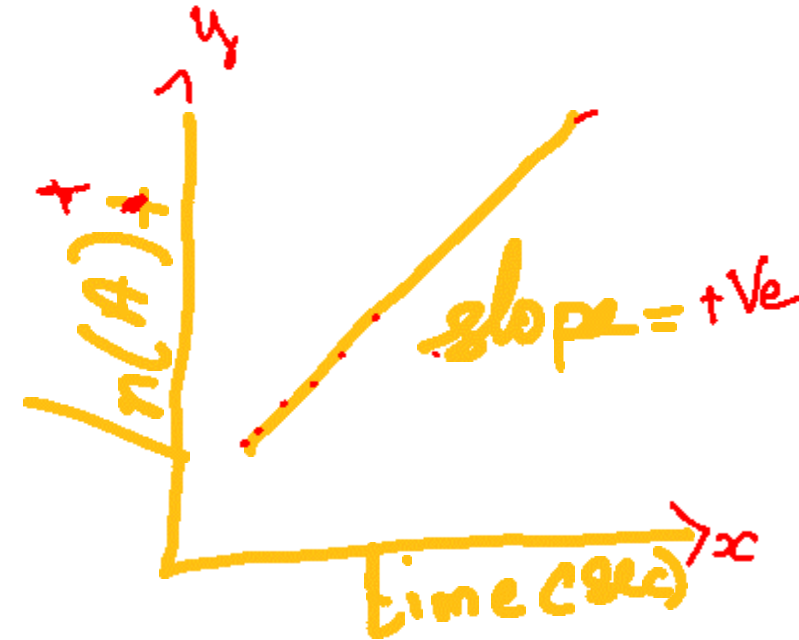
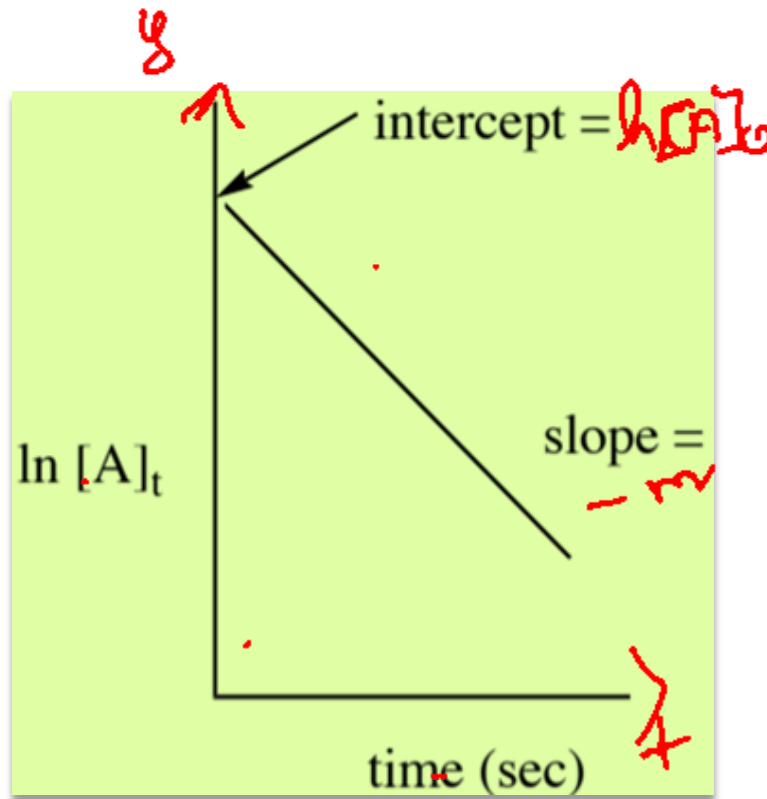
$$\ln[A]_t = -kt + \ln[A]_0$$

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

$$y = -mx + c$$

(Handwritten red annotations: $y = -mx + c$ with m in parentheses and x in parentheses, and a plus sign.)

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.



Integrated rate laws

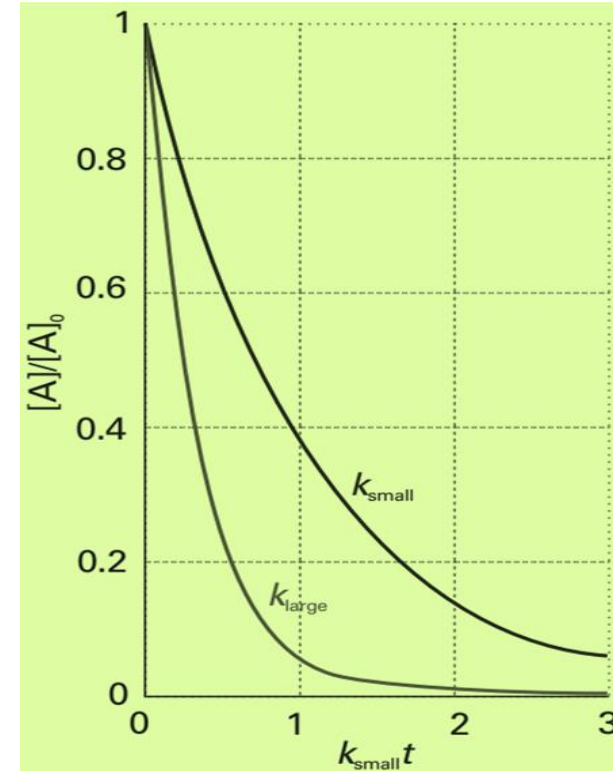
Other forms:

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

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

$$[A]_t = [A]_0 e^{-kt}$$

Integrated first order rate law



The exponential decay of the reactant in a first-order reaction. The larger the rate constant, the more rapid the decay.

Integrated rate laws

Question: The variation in the partial pressure of azomethane with time was followed at 600 K, with the results given below. Confirm that the decomposition is first-order in azomethane, and find the rate constant at 600 K.

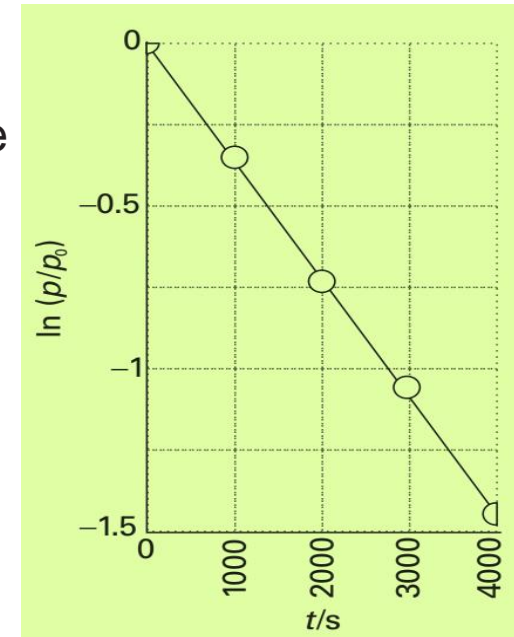


t/s	0	1000	2000	3000	4000
p/Pa	10.9	7.63	5.32	3.71	2.59

Solution: To confirm that a reaction is first-order, plot $\ln([A]_t/[A]_0)$ against time and expect a straight line. Because the partial pressure of a gas is proportional to its concentration, an equivalent procedure is to plot $\ln(p/p_0)$ against t .

First, convert p into $\ln(p/p_0)$ and draw the graph. The plot is straight, confirming a first-order reaction, and its slope is -3.6×10^{-4} .

Therefore, $k = 3.6 \times 10^{-4} \text{ s}^{-1}$.



First-order Half-life

Half-life is the time it takes for the original concentration to be reduced by half.

From above:

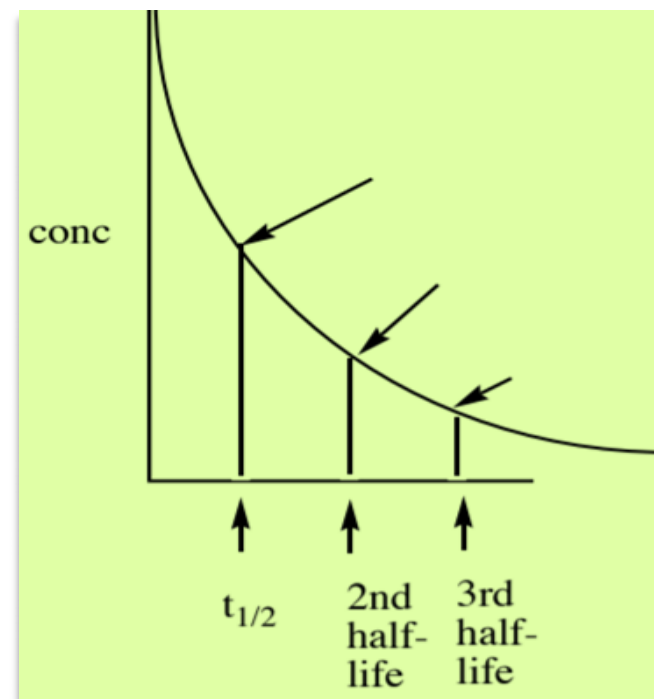
$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln \left(\frac{[A]_0}{2} \right) = -kt_{t/2}$$

$$\ln \frac{1}{2} = -kt_{t/2}$$

$$-0.693 = -kt_{t/2}$$

$$t_{t/2} = 0.693 / k$$



It is clear from the result that the half-life of a reactant is independent of its initial concentration for a first-order reaction. Therefore, if the concentration of A at some *arbitrary* stage of the reaction is [A], then it will have fallen to $1/2[A]$ after a further interval of $(\ln 2)/k$.

First-order Half-life

Another important point to note is the time constant, τ (tau), the time required for the concentration of a reactant to fall to $1/e$ of its initial value.

$$k\tau = -\ln\left(\frac{[A]_0/e}{[A]_0}\right) = -\ln\frac{1}{e} = 1$$

Thus, the time constant of a first-order reaction is the reciprocal of the rate constant, τ .

Question:

1. The half-life of a first-order reaction was found to be 10 min at a certain temperature. What is its rate constant?

Solution: $k = 0.693/600\text{s} = 0.00115\text{s}^{-1}$

First-order Half-life

Question:

2. If 3.0 g of substance A decomposes for 36 minutes the mass of unreacted A remaining is found to be 0.375 g. What is the half-life of this reaction if it follows first-order kinetics?

Solution:

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

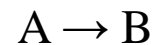
$$\ln \frac{[A]_t}{[A]_0} / t = -k$$

$$k = -\frac{\ln \frac{0.375 \text{ g}}{3 \text{ g}}}{36 \text{ min}}$$

$$k = 0.0578 \text{ min}^{-1}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{0.0578} = 12 \text{ min}$$

Integrated second-order rate law

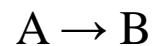


$$-\frac{d[A]}{dt} = k[A]^2$$

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

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

Integrated zero-order rate law



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

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

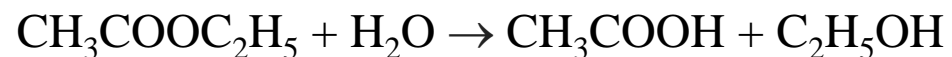
Pseudo First Order Reaction

- 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 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:



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

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

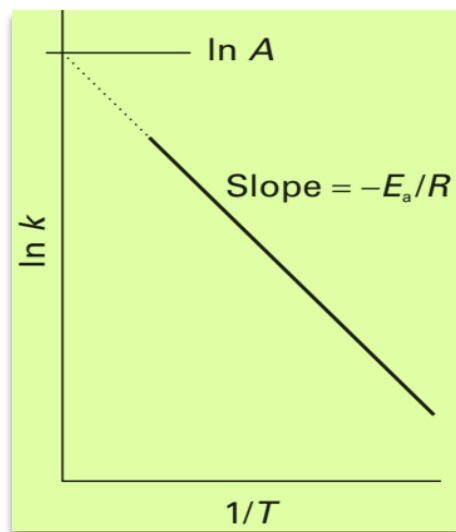
Temperature dependence of reaction rates

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.

Temperature dependence of reaction rates

Questions:

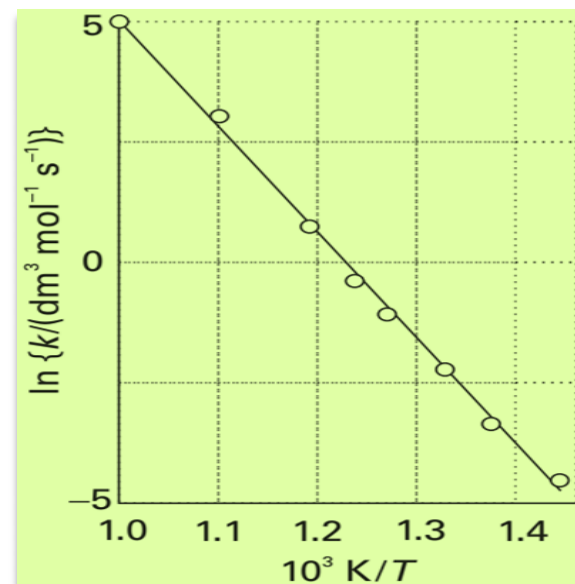
1. The rate of the second-order decomposition of acetaldehyde (CH_3CHO) was measured over the temperature range 700–1000 K, and the rate constants are reported below. Find E_a and A .

T/K	700	730	760	790	810	840	910	1000
$k/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$	0.011	0.035	0.105	0.343	0.789	2.17	20.0	145

Solution: First convert T in (10^3) and k into $\ln k$. Now, plot $\ln k$ against $1/T$. You will obtain the following graph having slope = -22.7 and intercept 27.7.

$$\text{Now, } E_a = 22.7 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times 10^3 \text{ K} = \mathbf{189 \text{ kJ mol}^{-1}}$$

$$A = e^{27.7} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = \mathbf{1.1 \times 10^{12} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$



Temperature dependence of reaction rates

2. The values of rate constants for a reaction are 9.51×10^{-9} L/mol.s and 1.10×10^{-5} L/mol.s at temperatures 500K and 600 K respectively. Calculate the activation energy.

Solution:

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$E_a = -R \ln \frac{k_2}{k_1} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]^{-1}$$

After substituting the given values and calculating,

$$E_a = 176 \text{ kJ/mol}$$

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 , let's consider the collision between molecules of reactants A and B:

Collision theory:

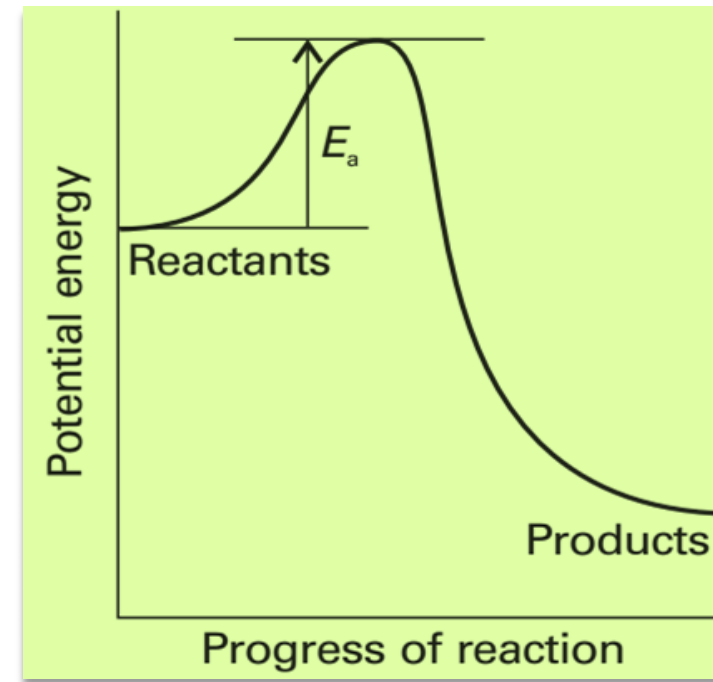
1. The rate of a reaction is proportional to the rate of reactant collisions:
2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.
3. The collision must occur with adequate energy to permit mutual penetration of 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

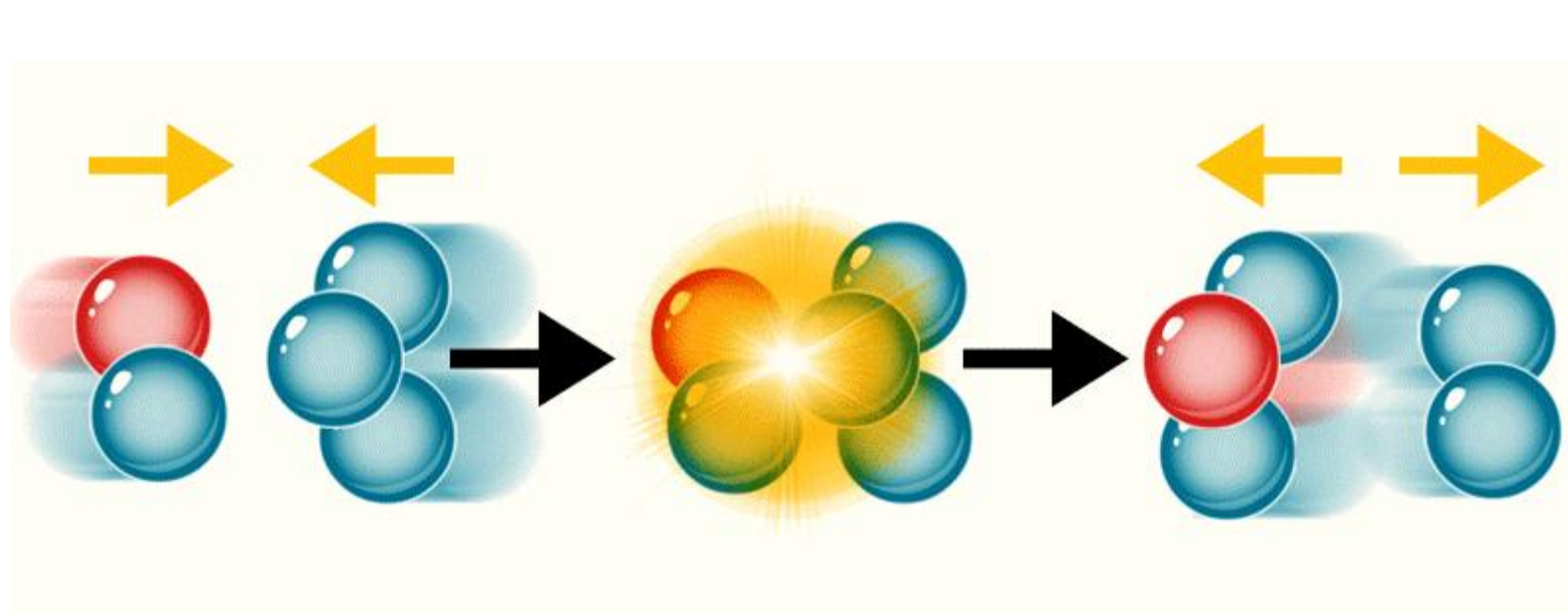
- ❖ The potential energy rises to a maximum and the cluster of atoms that corresponds to the region close to the maximum is called the **activated complex**.
- ❖ After the maximum, the potential energy falls as the atoms rearrange in the cluster and reaches a value characteristic of the products.
- ❖ 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

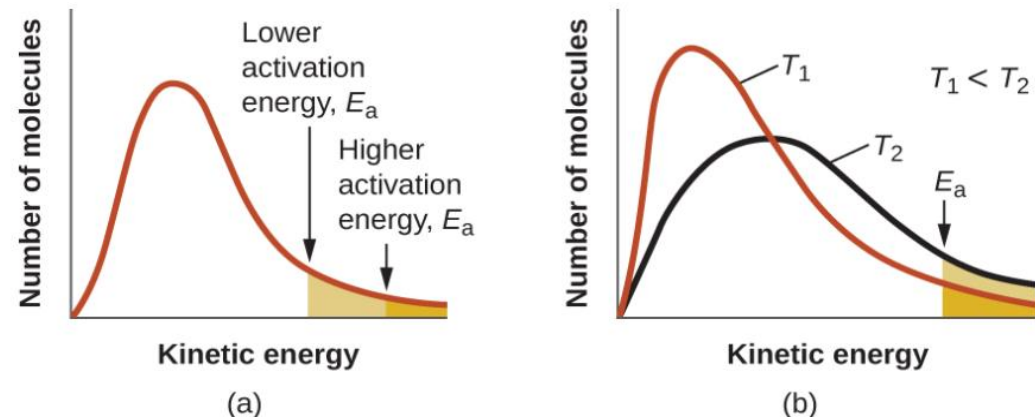
Both postulates of the collision theory of reaction rates are accommodated in the Arrhenius equation. The frequency factor A is related to the rate at which collisions having the correct orientation occur. The exponential term is related to the fraction of collisions providing adequate energy to overcome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

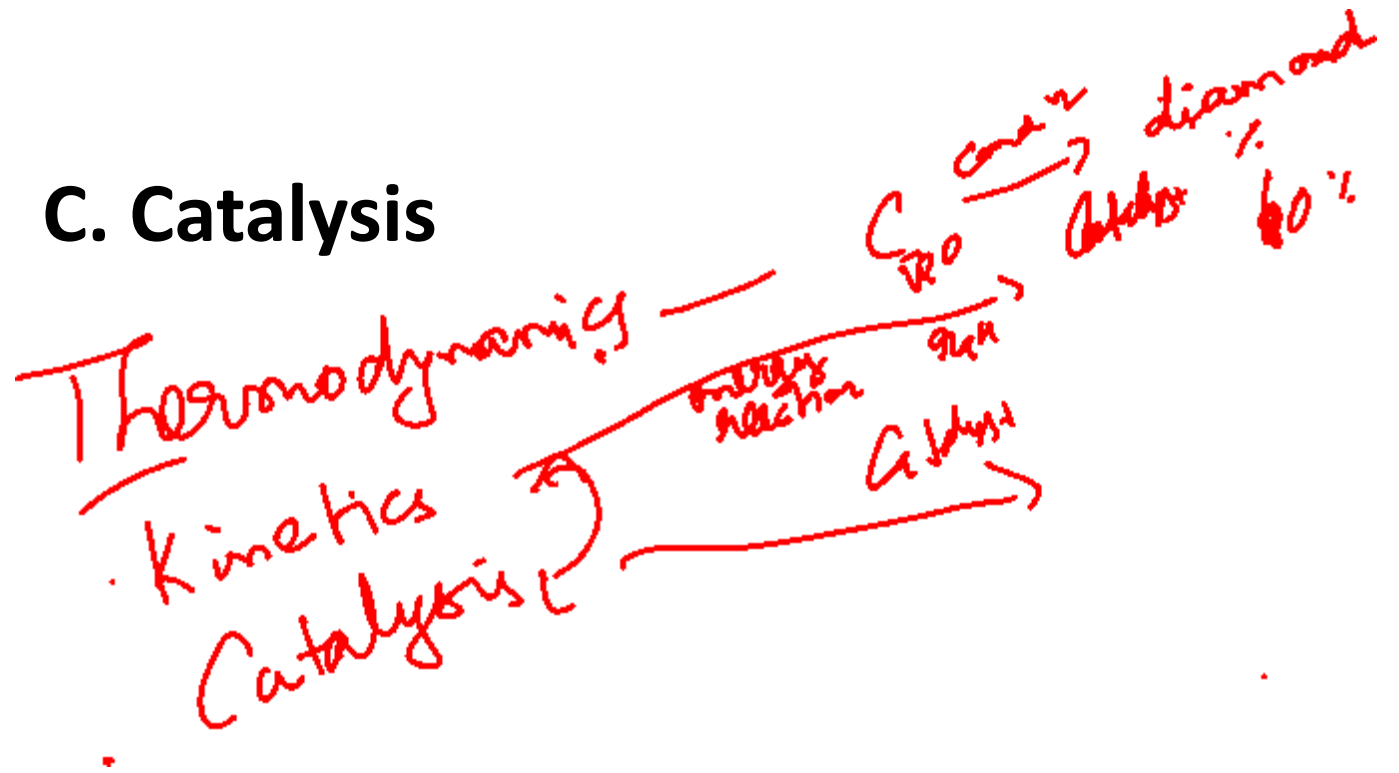


(a) As the activation energy of a reaction decreases, the number of molecules with at least this much energy increases, as shown by the shaded areas.

(b) At a higher temperature, T_2 , more molecules have kinetic energies greater than E_a , as shown by the yellow shaded area.

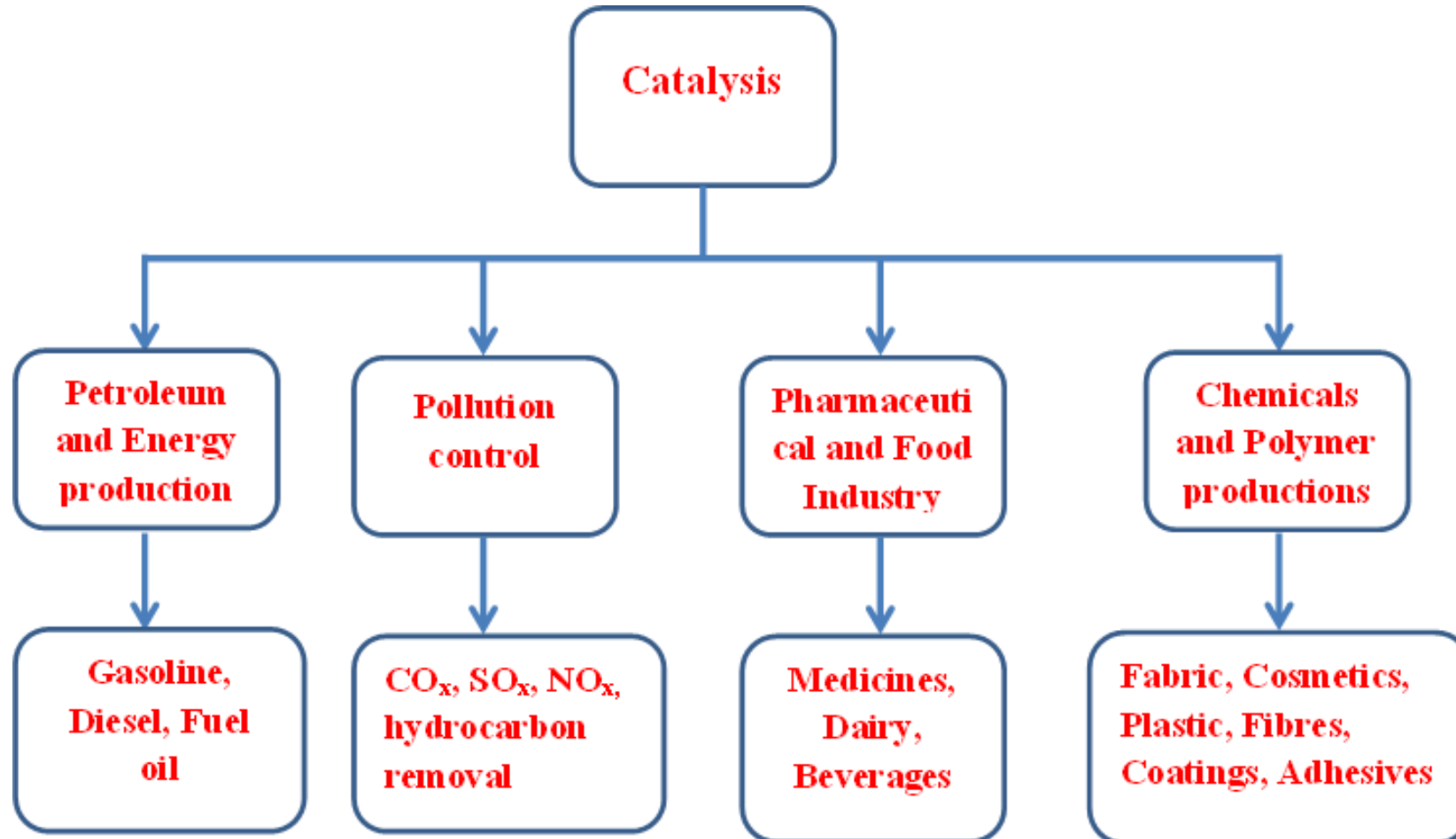
Module 1

C. Catalysis



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.



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**.

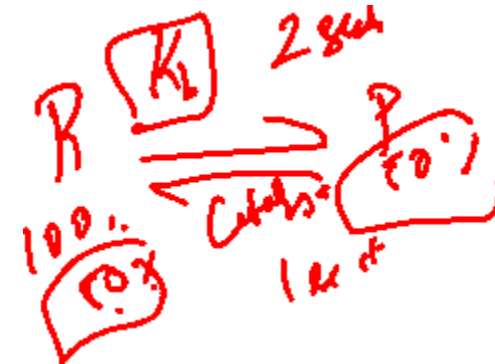
The economic significance of the catalyst industry is enormous. The catalytic processes contribute greater than 30-40% of global GDP. The global catalyst market size was estimated at USD 34.0 billion in 2019 and is expected to reach USD 35.1 billion in 2020.

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:

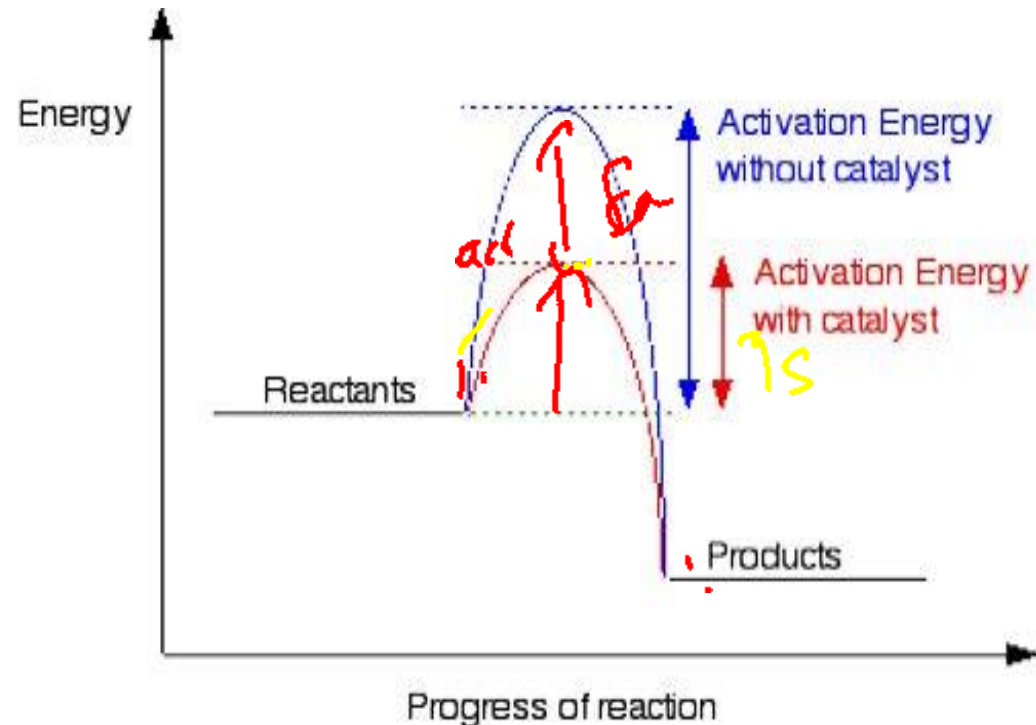


Figure: Schematic diagram to illustrate the effect of catalyst on activation energy of reactions.

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.

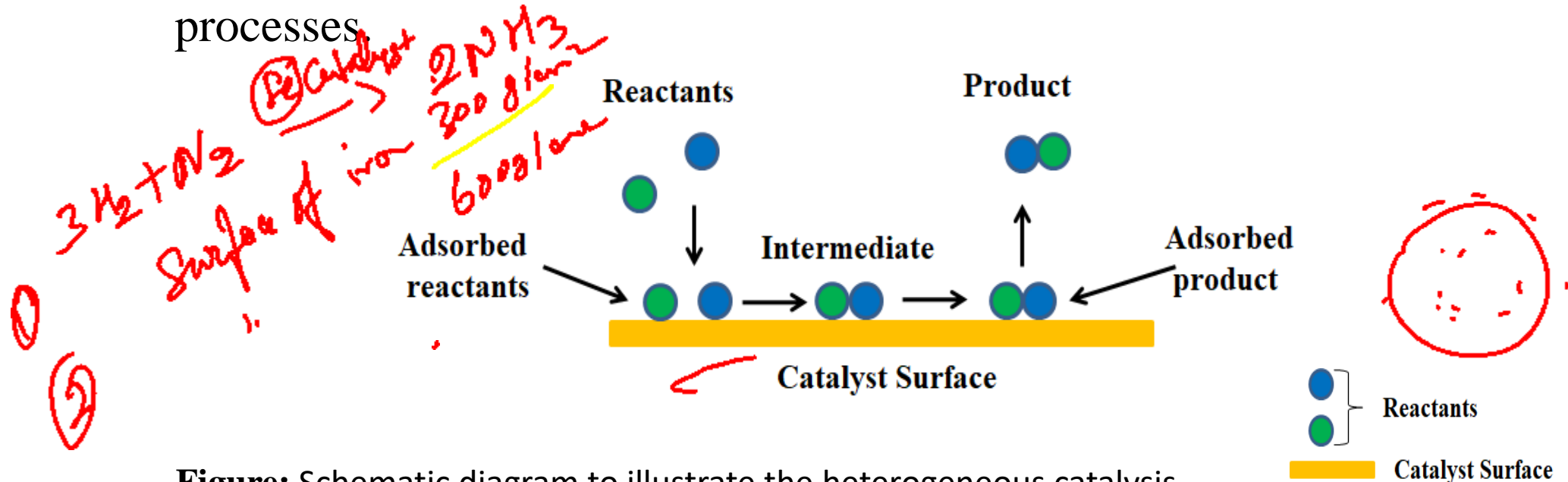
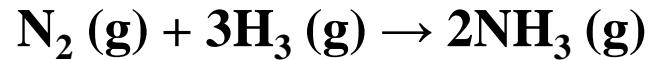


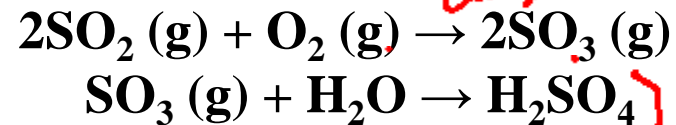
Figure: Schematic diagram to illustrate the heterogeneous catalysis.

Examples of Heterogeneous catalyst

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



(b) Manufacture of sulphuric acid by the Contact process. Vanadium pentoxide (V₂O₅) or platinum are catalysts for the production of SO₃ (g) from SO₂ (g) and O₂ (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 H₂O₂ (aqueous) by MnO₂ (s).



(d) **Examples of reactions in which both the reactant and the catalyst are in the solid phase.** The decomposition of KClO₃ is catalysed by solid MnO₂.



Heterogeneous

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.

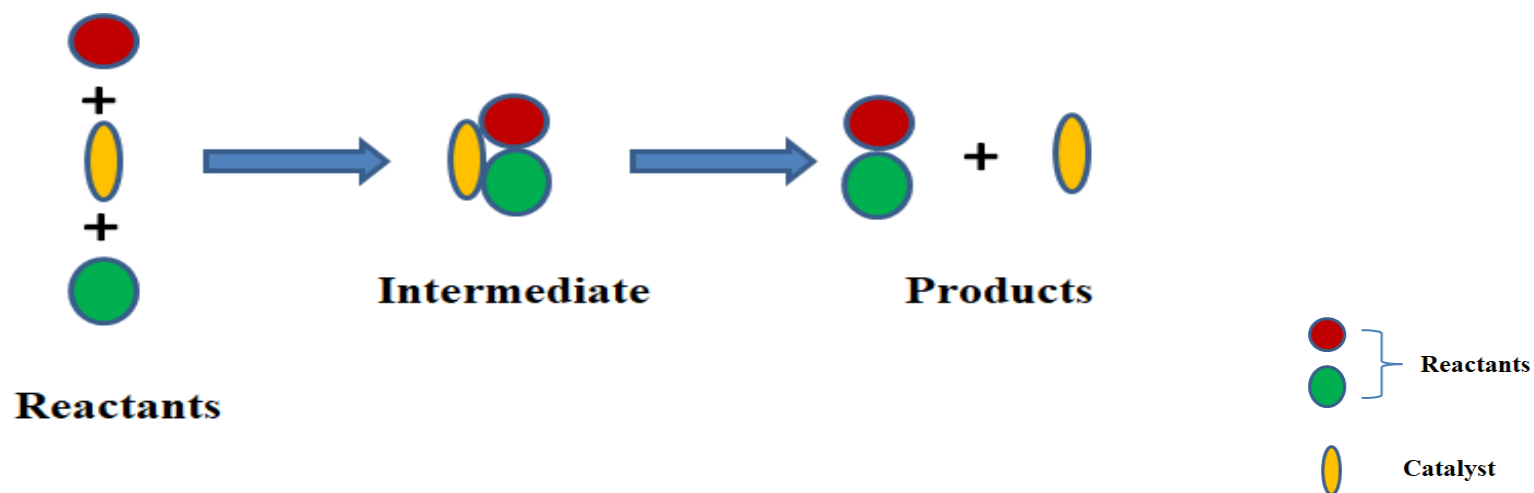
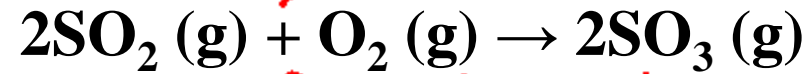


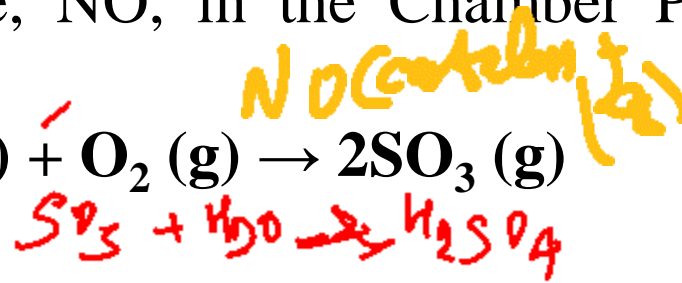
Figure: Schematic diagram to illustrate the homogeneous catalysis.

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.



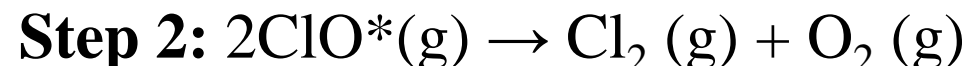
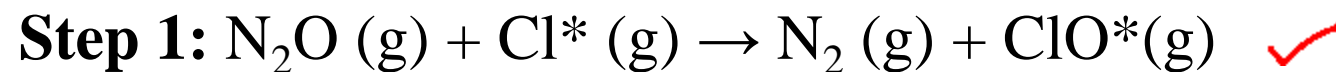
here, NO acts as a catalyst.



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



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



D. Enzyme catalysis

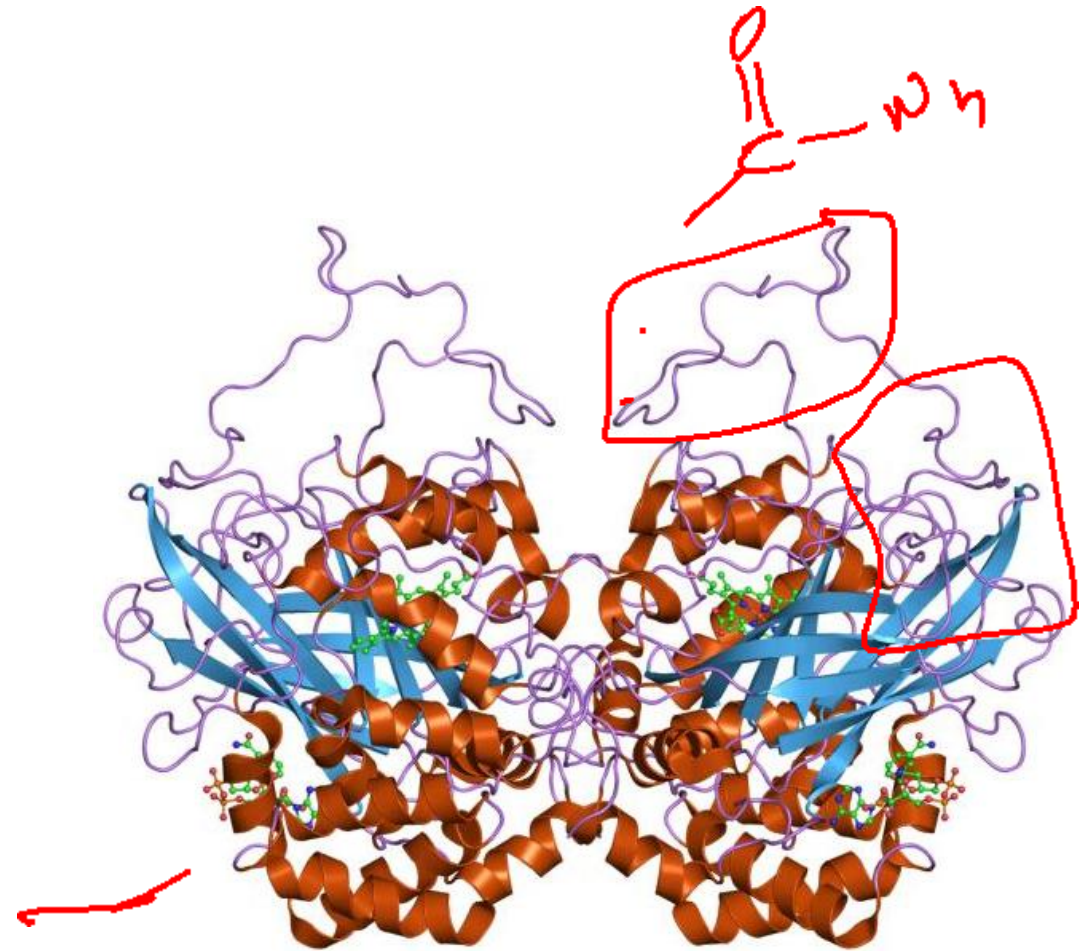
Michaelis-Menton mechanism

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)

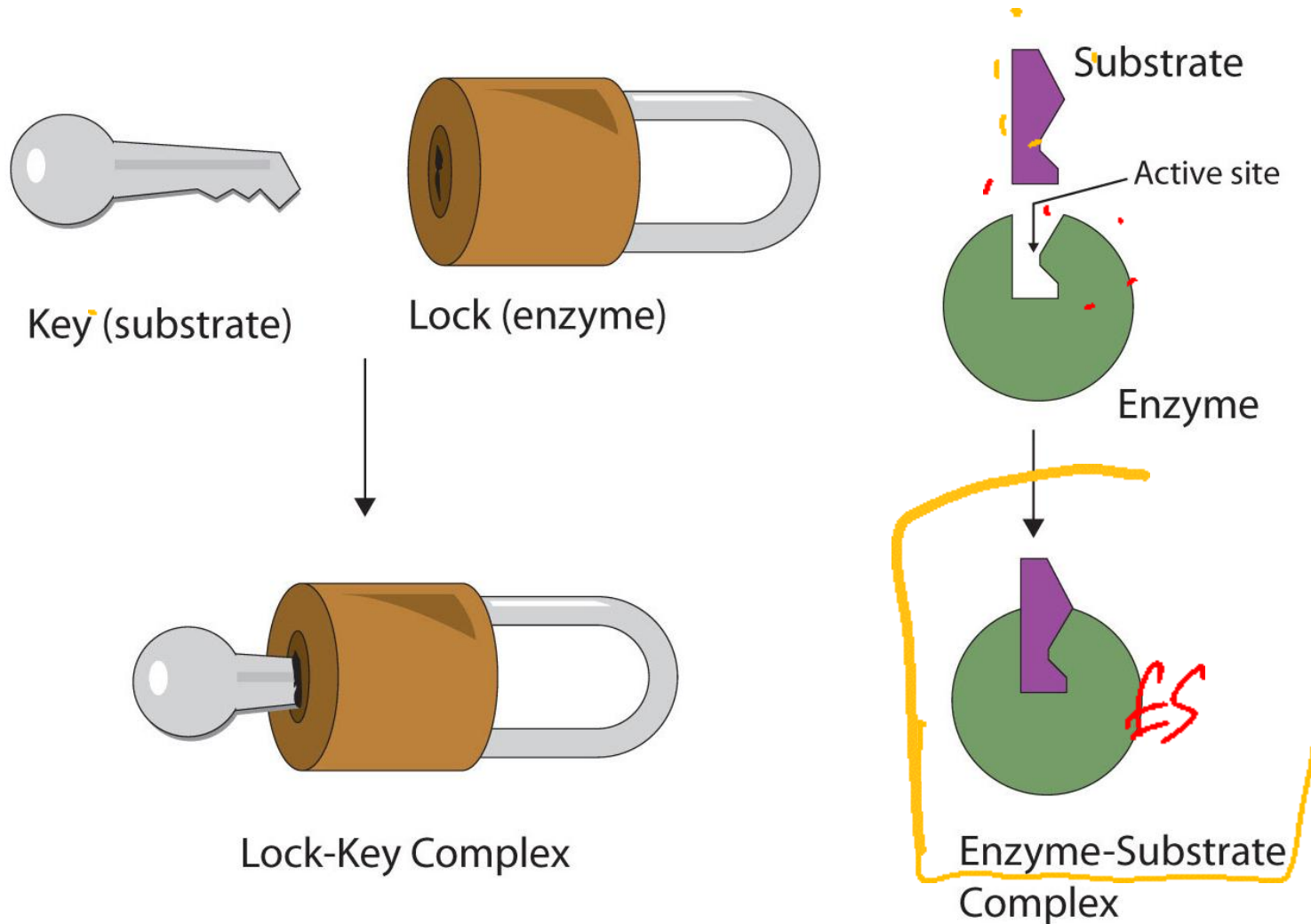


Reaction catalysed by the enzyme, catalase



Molecular structure of **Catalase**

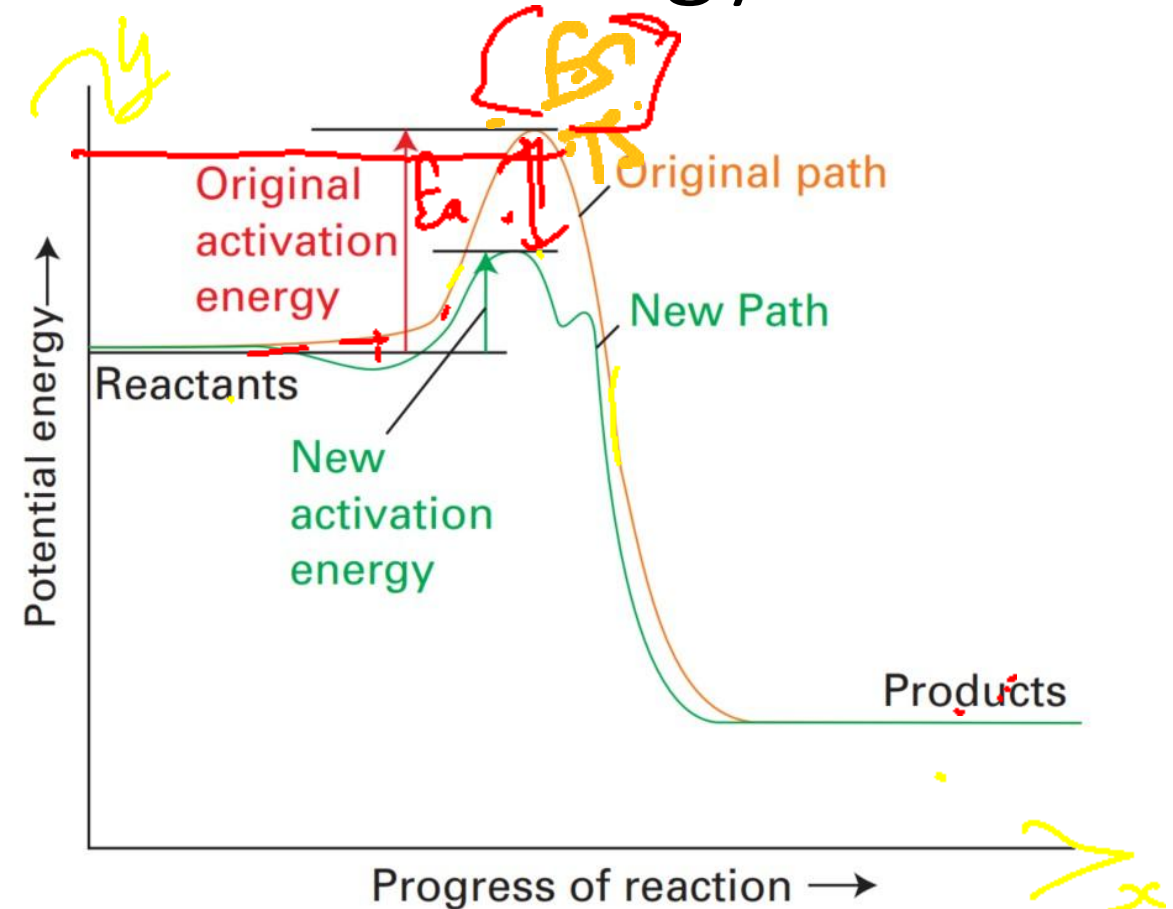
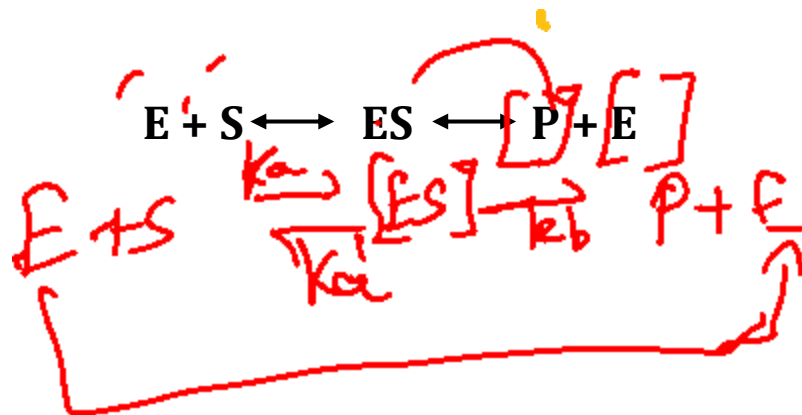
Mechanism of enzyme-catalyzed reactions



- ❑ 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.

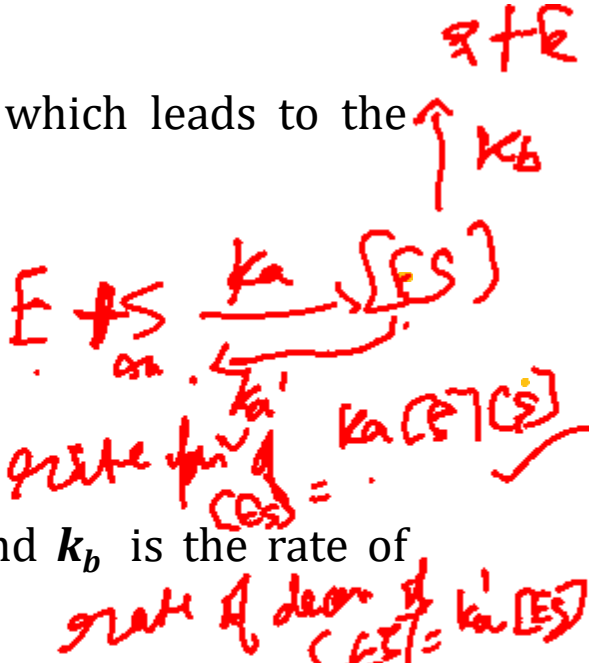
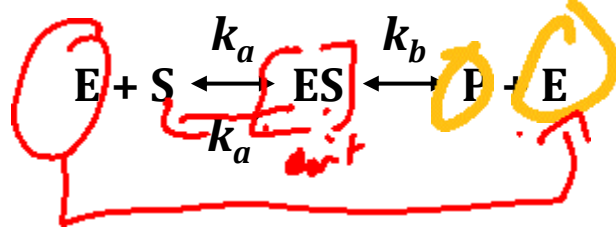
Enzymes' effect on the activation energy

- ❑ 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 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:



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.

Handwritten notes:

$$= \text{rate of formation} - \text{rate of decomposition} \quad \text{rate of formation of } P = k_b [ES]$$

Michaelis-Menten Mechanism

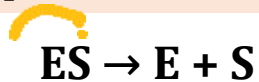
One of the earliest descriptions of the action of enzymes is the **Michaelis-Menten mechanism**. The proposed mechanism, with all species in an aqueous environment, is as follows.

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



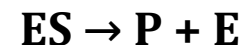
$$\text{Rate of formation of ES} = k_a[E][S]$$

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:



rate of formation of P = $k_b[ES]$

Derivation

Since the product P is formed irreversibly, according to the rate law, the rate of formation of the product P is

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

Since the net rate of formation of [ES] is zero, we can write the following:

$$\text{Net rate of formation of ES} = k_a[\text{E}][\text{S}] - k'_a[\text{ES}] - k_b[\text{ES}] = 0$$

$$\text{So, } [\text{ES}] = \frac{k_a[\text{E}][\text{S}]}{k'_a + k_b}$$

However, [E] and [S] are the molar concentrations of the free enzyme and free substrate. If [E]₀ is the total concentration of enzyme, then [E] + [ES] = [E]₀ and we can replace [E] in this expression by [E]₀ - [ES].

Therefore,

$$[\text{ES}] = \frac{k_a([\text{E}]_0 - [\text{ES}])[\text{S}]}{k'_a + k_b}$$

Derivation

Multiplication by $(k'_a + k_b)$ gives first

$$k'_a[ES] + k_b[ES] = k_a[E]_0[S] - k_a[ES][S]$$

And then,

$$(k'_a + k_b + k_a[S])[ES] = k_a[E]_0[S]$$

Division by k_a turns this expression into

$$\left\{ \frac{k'_a + k_b}{+k_a} + [S] \right\} [ES] = [E]_0[S]$$

K_M

We recognize the first term inside the parentheses as K_M , so this expression rearranges to

$$[ES] = \frac{[E]_0 [S]}{[S] + K_M} \quad \{1.1\}$$

Where K_M is the **Michaelis constant** (having the dimension of concentration), so

$$K_M = \frac{k'_a + k_b}{+k_a} \quad \{1.2\}$$

Derivation

The rate law for the rate of formation of product in terms of the concentrations of enzyme and substrate turns out to be

Rate of formation of P = $k_b[ES] = k_r[ES]$

$$k_r = \frac{k_b [S]}{[S] + K_M}$$

Handwritten notes: {1.3} k_b [S] / K_M =

So, from 1.1, we can say that,

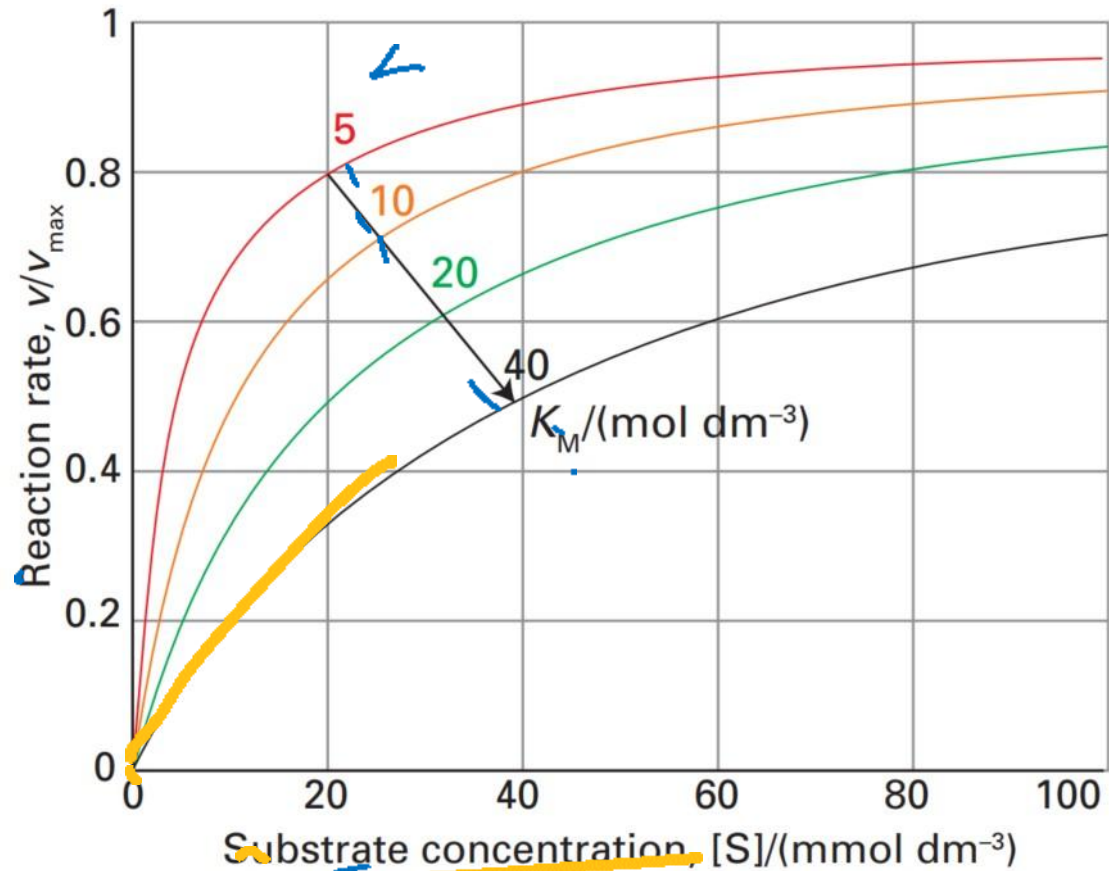
According to eqn 1.3, the rate of enzymolysis is first-order in the added enzyme concentration, but the effective rate constant k depends on the concentration of substrate. We can infer from eqn 1.3 that:

- When $[S] \ll K_M$, the effective rate constant is equal to $k_b[S]/K_M$. Therefore, the rate increases linearly with $[S]$ at low concentrations.
- When $[S] \gg K_M$, the effective rate constant is equal to k_b , and the rate law in eqn 1.3 reduces to

Rate of formation of P = $k_b[E]_0$

Handwritten notes: $k_{eff} = k_b$

Conditions for maximum and minimum velocities



- When $[S] \ll K_M$, the effective rate constant is equal to $k_b[S]/K_M$. Therefore, the rate increases linearly with $[S]$ at low concentrations.
- When $[S] \gg K_M$, the effective rate constant is equal to k_b , and the rate law in eqn 1.3 reduces to

$$\text{Rate of formation of P} = k_b[E]_0$$

Maximum velocity- V_{max}

When $[S] \gg K_M$, the rate is independent of the concentration of S because there is so much substrate present that it remains at effectively the same concentration even though products are being formed.

Under these conditions, the rate of formation of product is a maximum, and $k_b[E]_0$ is called the maximum velocity, v_{max} , of the enzymolysis:

$$v_{max} = k_b[E]_0 \quad \{1.4\} \quad [ES] \rightarrow [P]$$

The rate-determining step is Step 3: the decomposition of ES to form P, because there is ample ES present (because S is so abundant), and the rate is determined by the rate at which ES reacts to form the product.

It follows from eqns 1.1 and 1.4 that the reaction rate v at a general substrate composition is related to the maximum velocity by

$$v = \frac{[S] v_{max}}{[S] + K_M} \quad \{1.5\}$$

$$[ES] = \frac{[E]_0 [S]}{[S] + K_M}$$

Lineweaver-Burk Plot

If we take the reciprocal on both sides of eqn 1.5, it becomes,

$$\frac{1}{v} = \frac{[S] + K_M}{[S]v_{max}} = \frac{1}{v_{max}} + \left\{ \frac{K_M}{v_{max}} \right\} \frac{1}{[S]}$$

Since this expression has the form,

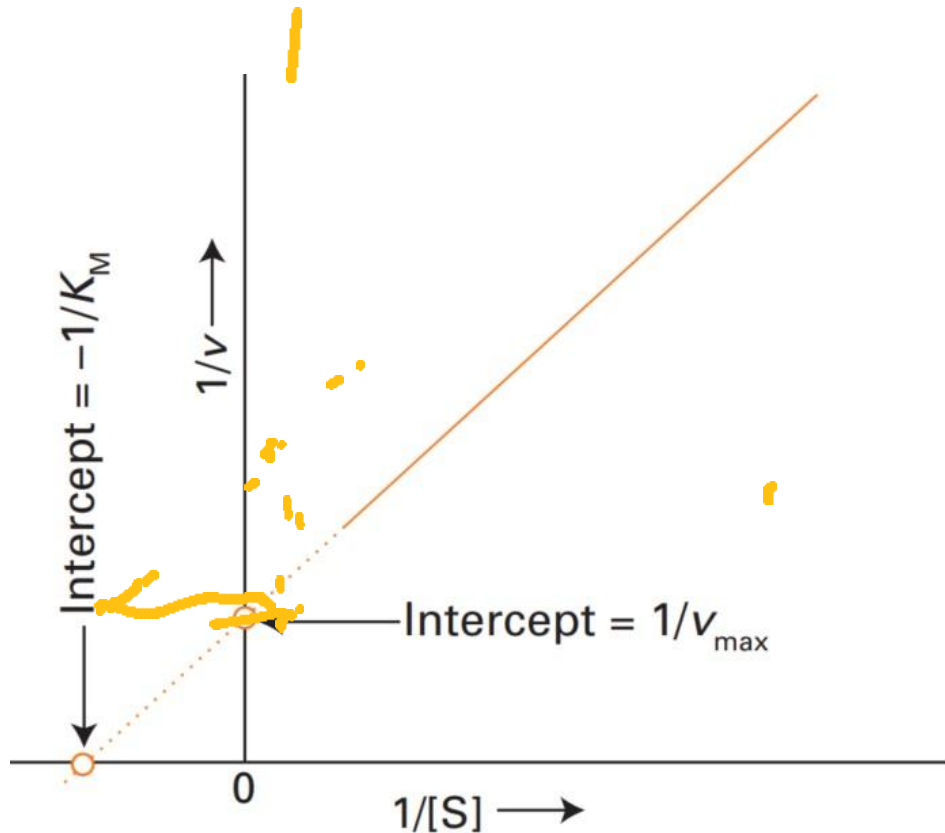
$$\boxed{\frac{1}{v}} = \boxed{\frac{1}{v_{max}}} + \left\{ \frac{K_M}{v_{max}} \right\} x \boxed{\frac{1}{[S]}} \quad \text{✓} \quad \{1.6\}$$

y intercept slope x

y - max

Eqn. 1.6 is the basis for the analysis of enzyme kinetic data using a **Lineweaver-Burk Plot**, a graph of $1/v$ (the reciprocal of the reaction rate) against $1/[S]$ (the reciprocal of the substrate concentration).

Lineweaver-Burk Plot



- ❑ The **intercept** of the extrapolated (dotted) straight line with the horizontal axis is used to obtain the **Michaelis constant, K_M** .
- ❑ The intercept with the vertical axis, is used to determine $v_{max} = k_b[E]_0$, and hence k_b . The **slope** may also be used, as it is equal to K_M/v_{max} .
- ❑ **Alternatively, note that the extrapolated intercept with the horizontal axis (where $1/v = 0$) occurs at $1/[S] = -1/K_M$.**

Catalytic constant & efficiency

The turnover frequency, or catalytic constant, of an enzyme, k_{cat} , is the number of catalytic cycles (turnovers) performed by the active site in a given interval divided by the duration of the interval.

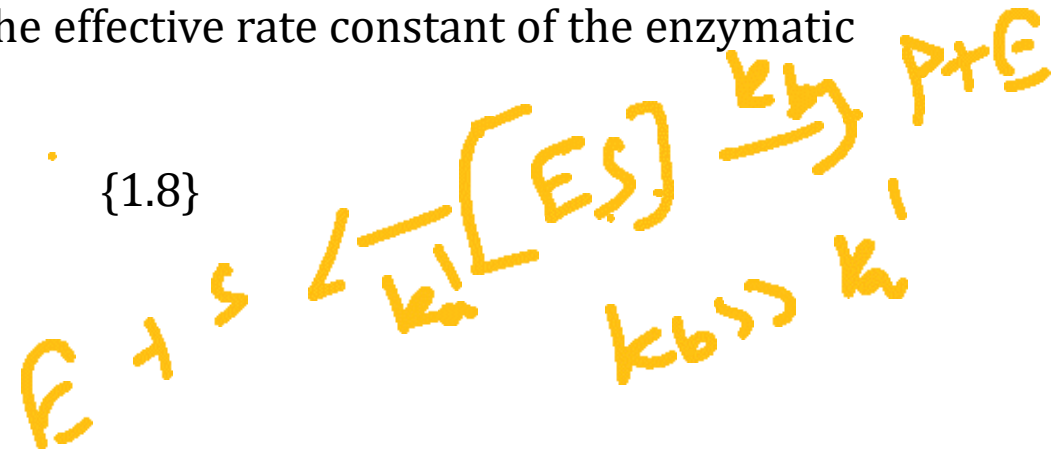
This quantity has units of a first-order rate constant and, in terms of the Michaelis–Menten mechanism, is numerically equivalent to k_b , the rate constant for release of product from the enzyme–substrate complex. So, it follows that,

$$k_{cat} = k_b = \frac{\bar{v}_{max}}{[E]_0} \quad \{1.7\}$$

The catalytic efficiency, η (eta), of an enzyme is the ratio k_{cat}/K_M . The higher the value of η , the more efficient is the enzyme. We can think of the catalytic activity as the effective rate constant of the enzymatic reaction.

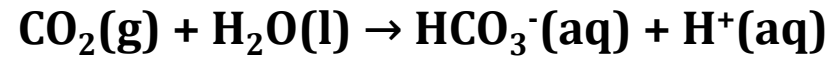
$$\eta = \frac{k_{cat}}{K_M} = \frac{k_a k_b}{k'_a + k_b} \quad \{1.8\}$$

The efficiency reaches its maximum value of k_a when $k_b \gg k'_a$.



Sample problem

The enzyme carbonic anhydrase catalyzes the hydration of CO₂ in red blood cells to give bicarbonate (hydrogen carbonate) ion:



The following data were obtained for the reaction at pH=7.1, 273.5 K and an enzyme concentration of 2.3 nmol dm⁻³

[CO ₂]/(mmol dm ⁻³)	v/(mmol dm ⁻³ s ⁻¹)
1.25	2.78x10 ⁻²
2.5	5.00x10 ⁻²
5	8.33x10 ⁻²
20	1.67x10 ⁻¹

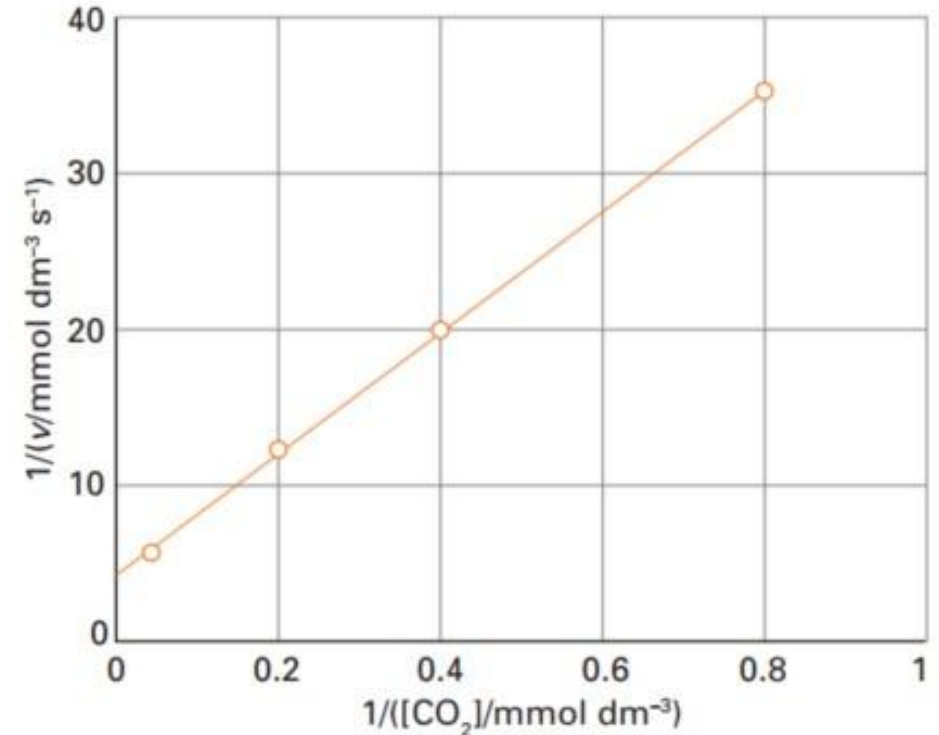
Determine the catalytic efficiency of carbonic anhydrase at 273.5 K

Contd.

We construct a Lineweaver-Burk plot by drawing a table of $1/[S]$ and $1/v$. The intercept at $1/[S]=0$ is v_{max} and the slope of the line through the points is K_M/v_{max} . So, K_M is found from the slope divided by the intercept. From eqn 1.7, and the enzyme concentration, we calculate k_{cat} and the catalytic efficiency from eqn 1.8

$1/[\text{CO}_2]/(\text{mmol dm}^{-3})$	$1/v/(\text{mmol dm}^{-3}\text{s}^{-1})$
0.8	35.97
0.4	20.00
0.2	12.00
0.05	5.99

From the graph, slope is 40 and intercept is 4.



Contd.

$$v_{\max}/(\text{mmol dm}^{-3} \text{ s}^{-1}) = \frac{1}{\text{intercept}} = \frac{1}{4.00} = 0.250$$

and

$$K_{\text{M}}/(\text{mmol dm}^{-3}) = \frac{\text{slope}}{\text{intercept}} = \frac{40.0}{4.00} = 10.0$$

It follows that

$$k_{\text{cat}} = \frac{v_{\max}}{[\text{E}]_0} = \frac{2.5 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}}{2.3 \times 10^{-9} \text{ mol dm}^{-3}} = 1.1 \times 10^5 \text{ s}^{-1}$$

and

$$\eta = \frac{k_{\text{cat}}}{K_{\text{M}}} = \frac{1.1 \times 10^5 \text{ s}^{-1}}{1.0 \times 10^{-2} \text{ mol dm}^{-3}} = 1.1 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$