



STUDY MATERIAL

ENGINEERING CHEMISTRY (BBS00010)

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MODULE IV: INTERMOLECULAR FORCES AND FREE ENERGY IN CHEMICAL EQUILIBRIUM

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INTERMOLECULAR FORCES

The forces holding the molecules together in solids and liquids are called **intermolecular forces**.

Nonbonding (Intermolecular)				
Ion-dipole		Ion charge– dipole charge	40–600	$\text{Na}^+ \cdots \text{O} \begin{array}{l} \text{H} \\ \text{H} \end{array}$
H bond	$\delta^- \quad \delta^+ \quad \delta^-$ $-\text{A}-\text{H} \cdots \cdots \text{:B}-$	Polar bond to H– dipole charge (high EN of N, O, F)	10–40	$\begin{array}{c} \text{:}\ddot{\text{O}}-\text{H} \\ \\ \text{H} \end{array} \cdots \cdots \begin{array}{c} \text{:}\ddot{\text{O}}-\text{H} \\ \\ \text{H} \end{array}$
Dipole-dipole		Dipole charges	5–25	$\text{I}-\text{Cl} \cdots \cdots \text{I}-\text{Cl}$
Dipole–induced dipole		Dipole charge– polarizable e^- cloud	2–10	$\text{H}-\text{Cl} \cdots \cdots \text{Cl}-\text{Cl}$
Dispersion (London)		Polarizable e^- clouds	0.05–40	$\text{F}-\text{F} \cdots \cdots \text{F}-\text{F}$

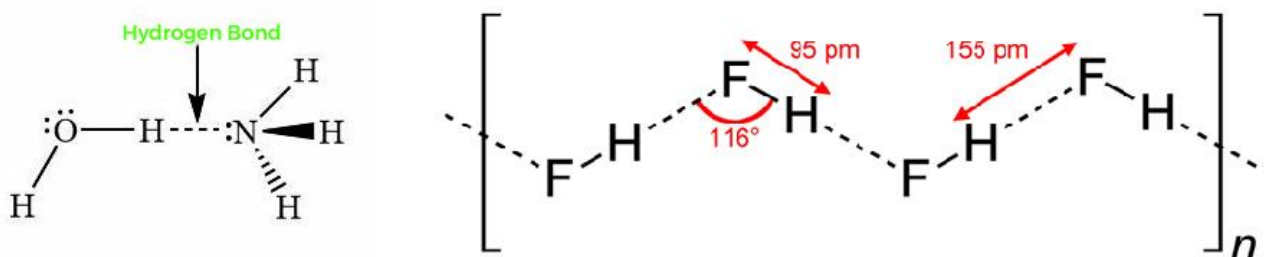
The common intermolecular forces/interactions are

- **Ion-dipole interactions.**
- **H-bonding.**
- **Dipole-dipole interactions.**
- **Dipole-induced dipole interactions.**
- **Instantaneous dipole-induced dipole interactions (London dispersion force).**

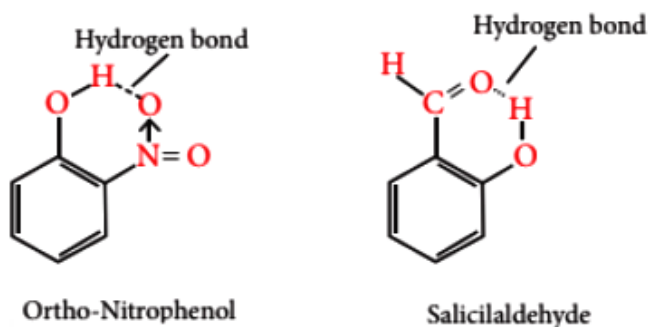
The last two types of forces are collectively known as **Van Der Waals' forces** and are generally very weak.

Hydrogen Bonding (H-bonding)

- It is a weak electrostatic force of attraction between hydrogen (H) and typically electronegative elements such as F, O and N.
- It is of two types: **Intermolecular H-bonding** and **Intramolecular H-bonding**.
- Intermolecular H-bonding**: H-bonding between different molecules. Examples: Water, ammonia, hydrogen fluoride, etc.

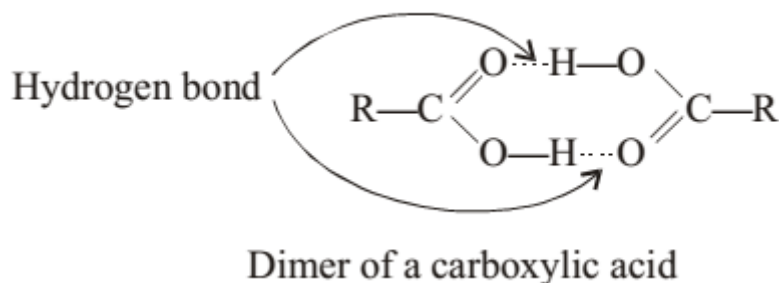


- Intramolecular H-bonding**: H-bonding within a molecule. Examples: o-nitrophenol, salicylic acid, salicylaldehyde, etc.



Q1. Why carboxylic acid exists in dimer form?

Ans: In a pure carboxylic acid, the hydrogen bonding can occur between two molecules of acid to produce a dimer. This immediately doubles the size of the molecule and so increases the Van Der Waals dispersion forces between one of these dimers and its neighbours and resulting in a high boiling point.

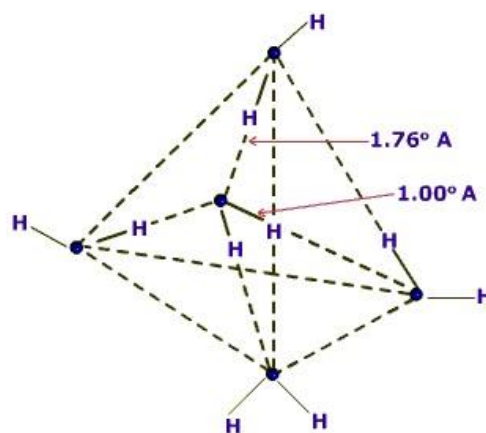
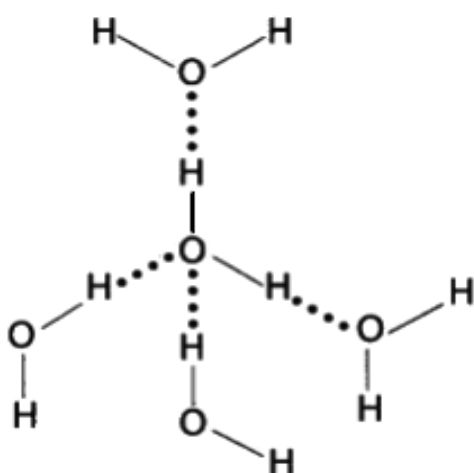


Q2. KHF₂ exists but KCl₂ does not. Why?

Ans. H-bonding is possible in the molecules where N, O or F is present. In KHF₂ molecule H-bonding is present in between electropositive hydrogen atom and more electronegative fluorine atom. As a result, HF₂⁻ is formed and hence, KHF₂ exists. But in KCl₂ molecule no H-bonding is possible in between H and Cl, thus, the molecule does not exist.

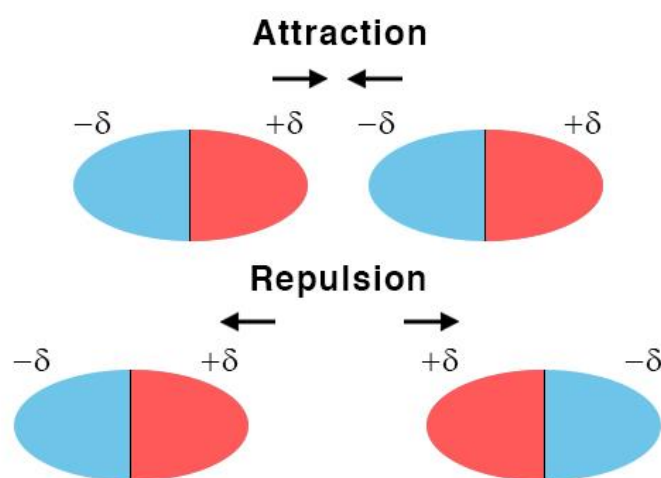
Q3. Why does ice float in water?

Ans. When liquid water is condensed to solid (ice) then four H-bonding are formed and ice has a tetrahedral cage-like structure with a huge voided space. Thus water expands when freezes, i.e., volume of ice becomes higher than water and density decreases. Thus, ice floats in water.



Dipole-dipole interactions

- In the covalent bonding between two atoms with very different electronegativity the bond becomes highly polar due to formation of partial charges and forms dipoles.
- This dipole can interact with other permanent dipoles.
- This interaction is stronger than the dipole-induced dipole interactions.

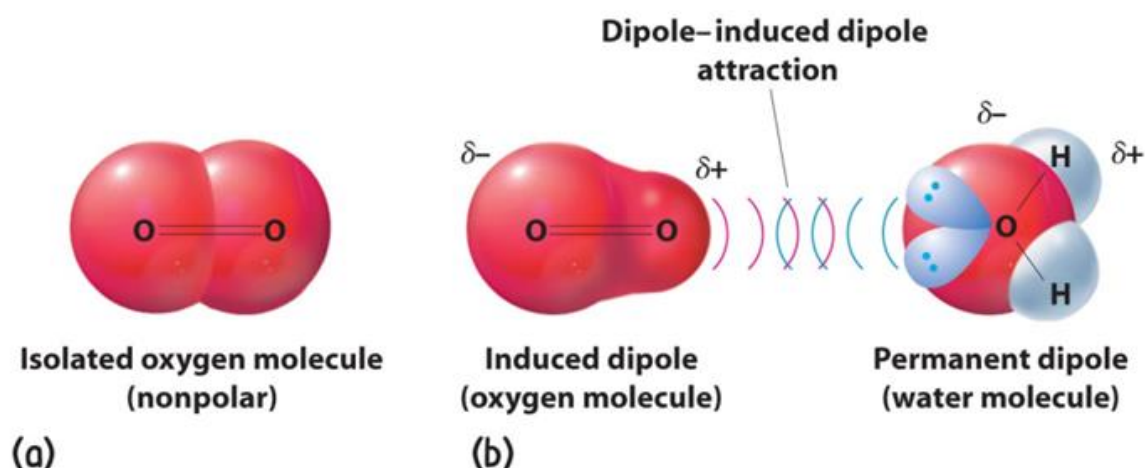


- With increase in the polarity, dipole moment increases. As a result, the boiling point of the molecule also increases.

Molecules	Dipole moment (D)	B.P. (K)
CH ₃ CH ₂ CH ₃ (Propane)	0.1 D	231 K
CH ₃ -O-CH ₃ (Dimethyl ether)	1.3 D	248 K
CH ₃ Cl (Methyl chloride)	1.9 D	249 K
CH ₃ -CHO (Acetaldehyde)	2.7 D	294 K
CH ₃ -CN (Acetonitrile)	3.9 D	355 K

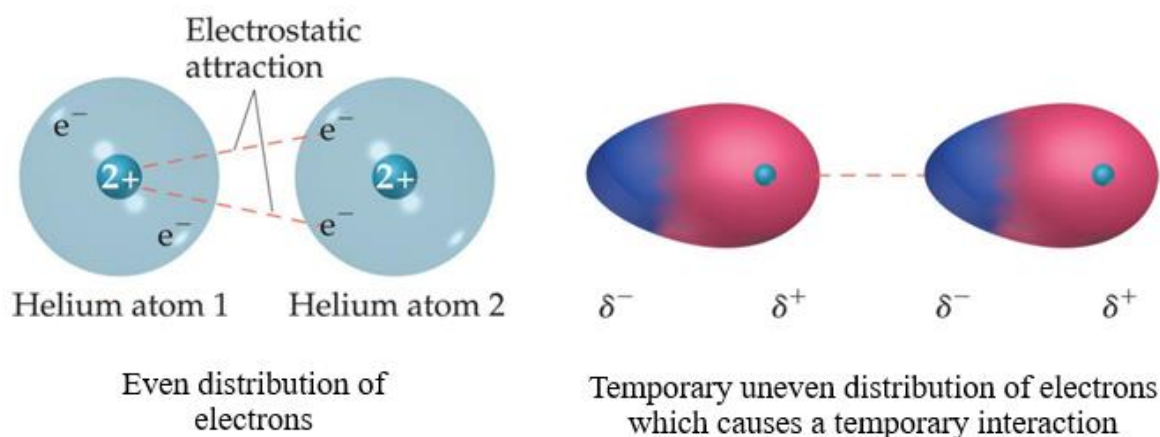
Dipole-induced dipole interactions

This is the interaction between polar molecule having permanent dipole moment and a non-polar molecule with zero dipole moment. This is generally stronger than the dispersion forces but weaker than dipole-dipole interactions.

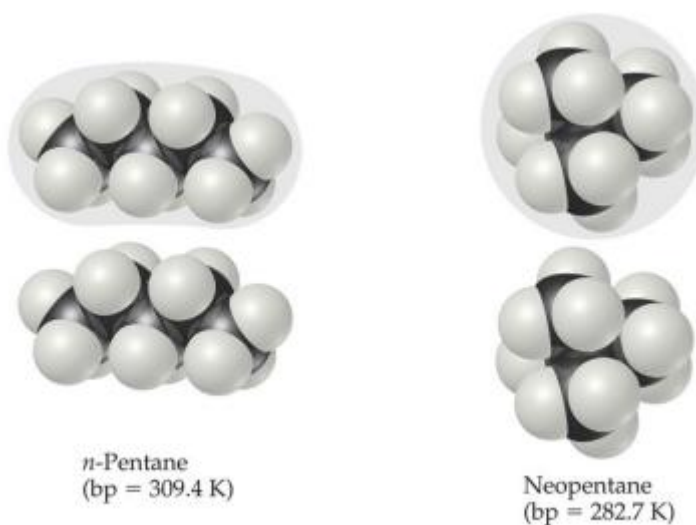


Instantaneous dipole-induced dipole interactions (London Dispersion Force)

- It is the weakest intermolecular force of interactions.
- An uneven distribution of electrons around the nucleus of an atom is known as Instantaneous dipole.

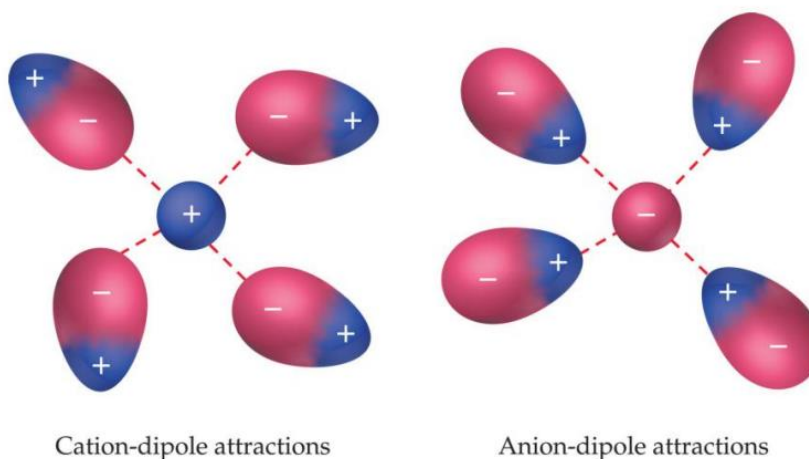


- Instantaneously generated dipole (due to asymmetry in electron charge distribution around the nucleus) on one atom leads to slight polarization of the other neighbour atom.
- This force acts over a short distance and acts between the surfaces of the molecules.
- The molecules having higher surface area has higher dispersion force, for example, n-pentane has higher surface area than neopentane and that's why the boiling point.



Ion-dipole interactions

- It is the strongest intermolecular force of interactions, even stronger than H-bonding.
- Due to this type of forces, ionic substances are dissolved in polar solvents.





EQUATION OF STATE

Early experiments on the variables of state (such as T, P, V, and n) showed that only two of these variables of state need to be known to predict the state of a sample of matter. An equation of state is an equation which relates the variables of state (T, P, V, and n). It's particularly useful when you want to know the effect of a change in one of the variables of state.

- **Solids and Liquids:** If the pressure on a solid or liquid is increased, the volume does not change much. If the temperature is increased, the volume doesn't change much either. Therefore, an appropriate equation of state describing such systems would be: $V_{(T, P, n)} = \text{constant}$.
- **Gases:** In contrast, changing the pressure or temperature of a gas will have an easily observable effect on the volume of that gas. For an ideal gas (no intermolecular interactions and no molecular volume) an appropriate equation of state would be: $V_{(T, P, n)} = (nRT)/P$

Equation of state for real gases: VAN DER WAALS EQUATION

➤ What is the definition of real gas in chemistry?

Ans. A real gas is a gas whose molecules have intermolecular forces of attraction and undergo inelastic collision. Their individual molecules occupy an actual volume and they do not obey the ideal gas law.

➤ What is the difference between a real gas and ideal gas?

Ans. A real gas is an actual gas whose individual molecules take up volume, whose particles exhibit intermolecular forces and the collisions between its particles are inelastic.

An ideal gas is a hypothetical gas whose individual molecules don't take any space, its particles have no intermolecular forces and they collide elastically.

➤ What is Van Der Waals equation and how it is different from the ideal gas law?

Ans. Van der Waals equation is a modification of the original ideal gas equation:

$$PV = nRT$$



The real gas equation takes into consideration the molecular size of the gas particles and the intermolecular forces between them. This equation is designed to describe the behaviour of real gases, but it can still be used for ideal gases as well in certain circumstances.

Pressure correction term:

- The existence of intermolecular forces between the molecules lowers the observed pressure in real gases because the molecules are attracted to each other. So the pressure on the container will be less than ideal gas. Hence, the internal pressure of the real gas (**P'**) is higher than that of ideal gas (**P**). [**P' > P**].
- This depends on the number of molecules per liter.
- Since two molecules interact, the effect must be squared.

Thus, the corrected pressure, $P' = P + a \left(\frac{n}{V} \right)^2$

Where '**a**' is the constant which indicates the intermolecular force of attraction and that differs for each gas.

Volume correction term:

- The actual volume for free movement of real gaseous particles is less than the ideal gas because of particle size (**V > V'**).
- More molecules will have more effect, i.e., this depends on number of molecules.

Thus, the corrected volume, $V' = V - nb$

Where '**b**' is the constant which indicated the molecular volume and that differs for each gas.

So the Van Der Waals equation for real gas is

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

Where, **P** = Pressure, **V** = Volume, **R** = Real gas constant, **T** = Temperature, **n** = no. of moles of gas, '**a**' and '**b**' are Van der Waals constants.



The **pressure correction term** (related with '**a**') is due to the intermolecular force of attraction and the **volume correction term** (related with '**b**') is due to the molecular volume.

Unit of 'a' and 'b'

$$\text{'a'} = \text{atm.lit}^2.\text{mol}^{-2}$$

$$\text{'b'} = \text{lit.mol}^{-1}$$

➤ **When real gas behaves ideally?**

Ans. At low pressure and high temperature, the real gas behaves ideally.

At low pressure and high temperature, the volume of the gas becomes infinite. So the pressure correction term approaches to zero.

$$\frac{an^2}{V^2} \approx 0$$

Also the volume correction term becomes $V - nb \approx V$

So the equation finally becomes $PV = nRT$ (ideal gas equation)

CRITICAL PHENOMENA

- **Critical temperature (T_c):** Every gas has a particular temperature above which the gas cannot be liquefied regardless of the amount of the pressure applied to it. It is the highest temperature at which the substance can exist as a liquid. This temperature is known as critical temperature.
- **Critical pressure (P_c):** The pressure required to liquefy the gas at critical temperature is called critical pressure.
- **Critical volume (V_c):** The volume occupied by one mole of gas at critical temperature and critical pressure is known as critical volume.



Relation between Van Der Waals gas constants and critical phenomena

For n moles of real gas, the Van Der Waals equation is given by

$$\left(P + \frac{an^2}{V^2}\right) (V - nb) = nRT$$

For 1 mole, the above equation becomes

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$\left(\frac{dP}{dV}\right)_T = -\frac{RT}{(V - b)^2} + \frac{2a}{V^3} \quad \dots\dots (i)$$

$$\left(\frac{d^2P}{dV^2}\right)_T = \frac{2RT}{(V - b)^3} - \frac{6a}{V^4} \quad \dots\dots (ii)$$

At critical states, $\left(\frac{dP}{dV}\right)_T = 0$ and $\left(\frac{d^2P}{dV^2}\right)_T = 0$

Thus, equation (i) and (ii) becomes

$$\frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^3} \quad \dots\dots (iii)$$

$$\frac{2RT_c}{(V_c - b)^3} = \frac{6a}{V_c^4} \quad \dots\dots (iv)$$

From the above two equations, we get,

$$V_c = 3b$$

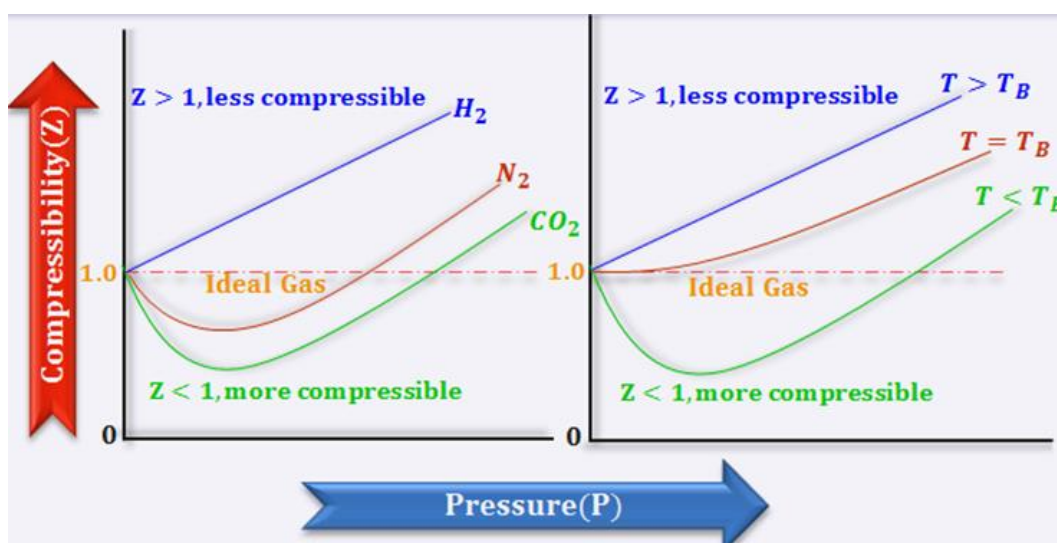
$$T_c = \frac{8a}{27Rb}$$

$$P_c = \frac{a}{27b^2}$$

Critical compressibility factor

$$Z_c = \frac{P_c V_c}{RT_c} = \frac{3}{8} = 0.375$$

For ideal gases, $Z_c = 1$



Model Questions:

1. Define critical constants of a real gas.
2. Using Van Der Waal's equation show that $RT_c/P_c V_c = 8/3$, where the terms have usual meaning.
3. What do you mean by instantaneous dipole-induced dipole interactions? Explain with an example.
4. Write down the Van Der Waal's equation for n mole of a real gas. Write units of Van Der Waal's constant 'a' and 'b'.



THERMODYNAMICS

Thermodynamics is concerned with the flow of heat and it deals with the relationship between **heat** and **work**.

It is applied in studying the energy change associated with all physical and chemical processes and mutual transformation of different kinds of energy.

Thermodynamic laws help us to predict

- i. The feasibility of a particular process i.e. whether the process can occur simultaneously or not under a given set of conditions of temperature, pressure and concentration.
- ii. Maximum efficiency of various types of heat engines.

Limitations of thermodynamics:

- i. It is applicable to macroscopic systems only. The laws are independent of atomic and molecular structure of matter.
- ii. It does not tell us anything about the rate of the reaction.

Properties of a system:

- i. **Intensive properties:** A property which is **independent** of the mass of the substance present in the system. Examples – Temperature (**T**), Pressure (**P**), density (**d**), Boiling point, Melting point, Surface tension (**γ**), Viscosity (**η**), Molar volume (**V_m**), Molar heat capacity (**ĉ**), etc.
- ii. **Extensive properties:** A property which **depends on** the mass of the substance present in the system. Examples – Mass (**m**), Volume (**V**), no. of moles (**n**), Internal energy (**U**), Enthalpy (**H**), Entropy (**S**), Heat capacity (**c**), pH, EMF, etc.

State function: Thermodynamic function or property whose value depends only on the initial and final state of the system. Example – change in temperature, internal energy, enthalpy and entropy, etc.

Path function: Thermodynamic function or property whose value depends on the path of the transformation. Example – heat absorbed, work done, etc.

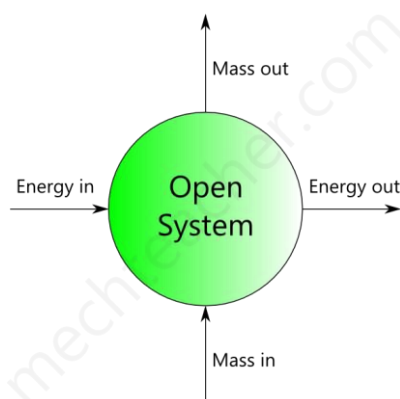
Classification of thermodynamic systems:

- i. **Open system:** In an open system, transfer of mass as well as energy can take place between the system and its surroundings.

Most of the engineering devices are open systems.

Example of open system:

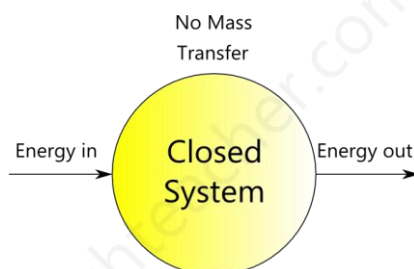
1. Hot liquid in an open pot.
2. Hot tea in a cup.



- ii. **Closed system:** In closed system, the mass within the boundary of the system remains constant and only transfer of energy may take place between the system and its surroundings.

Example of closed system:

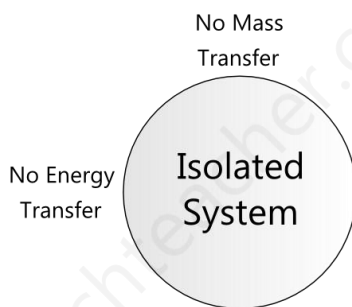
1. Pressure cooker.
2. A rubber balloon filled with air and tightly closed.
3. The gas is confined between a piston and cylinder.





iii. Isolated system: In an isolated system, neither mass nor energy transfer takes place between the system and its surroundings.

Example of isolated systems: Thermo flasks & hotspots.



Thermodynamic processes

Process: A change in the state of the system from one equilibrium state to another is called process.

Reversible process	Irreversible process
i. It occurs at a very slow speed and involves a series of equilibrium states.	i. It takes place very rapidly and does not involve a series of equilibrium states.
ii. The driving force and the opposing force are nearly equal.	ii. The driving force and the opposing force differ widely.
iii. The amount of work done in a reversible process is maximum.	iii. Work obtainable is always less than that of a reversible process.
iv. Reversible process occurs in an infinite number of steps and infinite time is required for its completion.	iv. Irreversible process does not involve many steps and gets completed in a short time.



Different types of process based on thermodynamic functions:

- i. **Isothermal process:** Temperature of the system is kept constant. ($\Delta T = 0$).
- ii. **Isobaric process:** Pressure of the system is kept constant. ($\Delta P = 0$).
- iii. **Isochoric process:** Volume of the system is kept constant. ($\Delta V = 0$).
- iv. **Adiabatic process:** No heat is transferred between the system and the surrounding. ($\Delta q = 0$).

P-V work done in different thermodynamic processes

- **Isothermal reversible expansion:**

$$w_{rev} = -nRT \ln \left(\frac{V_2}{V_1} \right)$$

- **Isothermal irreversible expansion:**

$$w_{irr} = -P_{ext} (V_2 - V_1)$$

- **Adiabatic reversible expansion:**

$$w_{ad} = nC_V (T_2 - T_1) = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$$

- NOTE:**
- i. *Work done on the system = Positive work done (+w).*
 - ii. *Work done by the system = Negative work done (-w).*
 - iii. *Heat adsorbed by the system = Positive (+q).*
 - iv. *Heat released by the system = Negative (-q).*

Thermodynamic functions

I. Internal Energy (U)

- All matters must have a storage of energy for its existence. The total energy stored by a system for its existence is known as '**internal energy**', denoted by '**U**'.



- Total internal energy of a system cannot be calculated but the change in internal energy (ΔU) can easily be calculated.
- Internal energy (U) is **state function** and change in internal energy (ΔU) is an **exact differential**, as it is independent of the path followed.
- Internal energy of any system is an **extensive property** as it depends on the amount of substance present in the system.
- Unit of internal energy: **Joule (J)** in SI.

First law of thermodynamics

- The first law of thermodynamics is an extension of the law of conservation of energy which states that **energy can neither be created nor be destroyed, although it can be converted from one form to another.**
- The change in internal energy of a system is equal to the **heat transferred (added)** to the system **minus the work done by the system.**

ΔU	$=$	Q	$-$	W
Change in internal energy		Heat added to the system		Work done by the system

Change in internal energy for different thermodynamic processes:

- a. In an **adiabatic process**, $q = 0$, thus, $\Delta U = -w$

Where, w is the adiabatic work done by the system $= nC_V (T_2 - T_1) = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$

- b. In an **isothermal process**, any heat flow into or out of the system must be slow enough to maintain the thermal equilibrium.

For ideal gases, if $\Delta T = 0$, then $\Delta U = 0$

Therefore, $q = w$, i.e., any energy entering the system (q) must leave as work (w).



- c. In an **isobaric process**, ΔU , w and q are generally **non-zero**, hence calculating the work done by the system is straightforward, i.e., $w = P \cdot \Delta V$

Water boiling in a saucepan is an example of isobaric process.

- d. In an **isochoric process**, the volume of a system doesn't change ($\Delta V = 0$), thus it will do not work to its surroundings ($w = 0$).

Therefore, $\Delta U = q$, i.e., the change in internal energy is equal to the heat transferred to the system. Hence, $\Delta U = q_v$.

Heating a gas in a closed container is an example of isochoric process.

II. Enthalpy (H)

- It is a thermodynamic function which deal with heat changes at constant pressure particularly for chemical processes.
- Enthalpy (H) is defined as $H = U + PV$, where 'U', 'P' and 'V' all are state functions and exact differentials, thus, 'H' is also a **state function** and **exact differential**.

- Physical significance:** By definition, $H = U + PV$

So, change in enthalpy, $\Delta H = \Delta U + P\Delta V + V\Delta P$

Also from the first law of thermodynamics, $\Delta U = q - P\Delta V$

So, $\Delta H = q + V\Delta P$

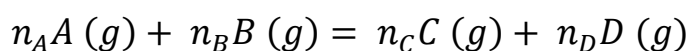
If the process is carried out at constant pressure ($\Delta P = 0$),

Then, $\Delta H = q_p$, i.e., heat change of process/reaction at constant pressure.

- Similar to internal energy, total enthalpy cannot be calculated but the change in enthalpy (ΔH) can easily be calculated.
- Enthalpy (H) is an **extensive property**.

Relationship between ΔH and ΔU in a chemical process

Consider a gaseous reaction,



Here, change of number of mole, $\Delta n = (n_C + n_D) - (n_A + n_B)$



Now at constant pressure, we get,

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

$$\text{So, } \Delta H = \Delta U + \Delta nRT \quad [\text{For any ideal gas, } P\Delta V = \Delta nRT]$$

$$\text{Or, } q_p = q_v + \Delta nRT$$

Now, a. When $\Delta n = 0$, then $\Delta H = \Delta U$

b. When $\Delta n > 0$, then $\Delta H > \Delta U$

c. When $\Delta n < 0$, then $\Delta H < \Delta U$

The Carnot cycle

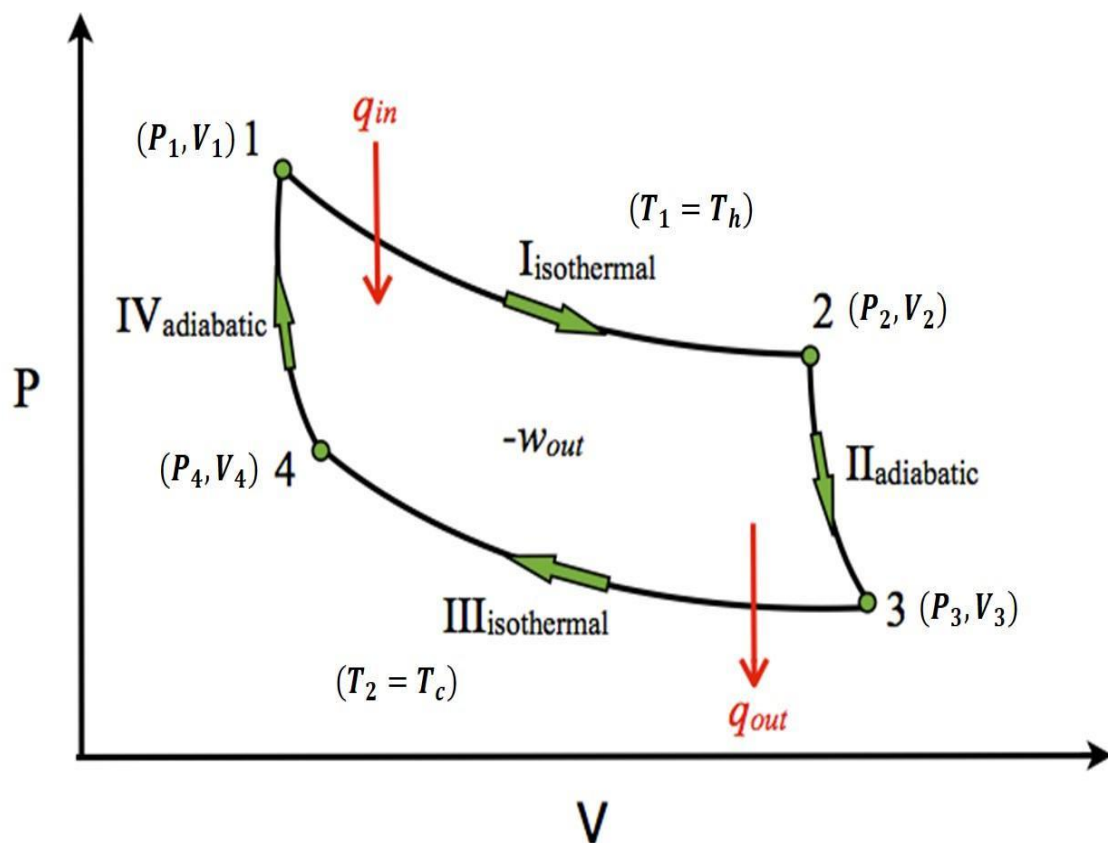
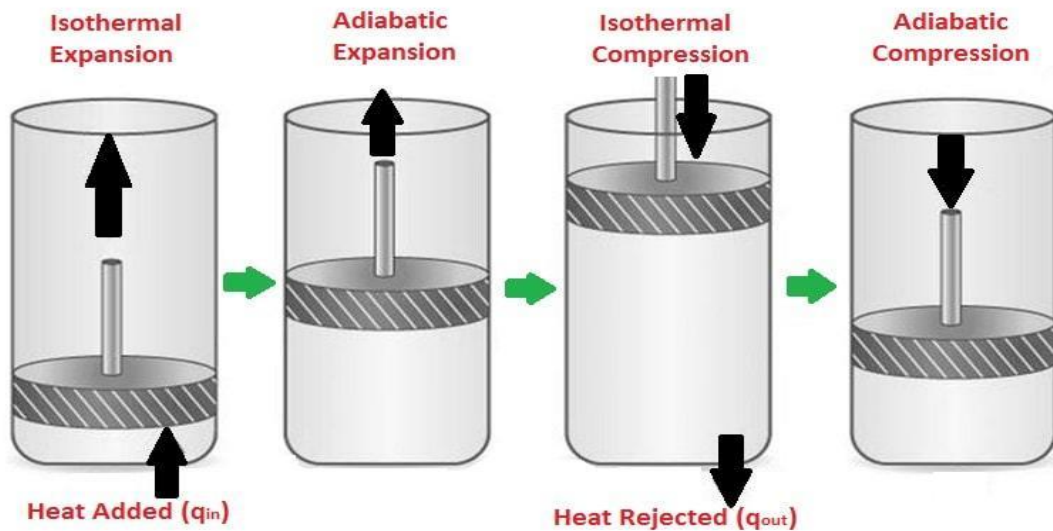
It is the most efficient heat engine ever possible and theoretically developed by Nicholas Carnot. The Carnot engine model was graphically represented by Clapeyron and mathematically proved by Clausius. This heat engine operates on the basis of **Carnot cycle**. The Carnot cycle is one complete cycle consists of four successive reversible processes known as '**four strokes**.' This cycle is employed to demonstrate the maximum conversion of heat into work and the work which leads to the concept of entropy. A heat engine acts by transferring energy from a **warm region (source)** to a **cool region (sink)** of space and, in the process, converting some of that energy to mechanical work.

The four successive reversible processes are

- a. **Isothermal reversible expansion of gas.**
- b. **Adiabatic reversible expansion of gas.**
- c. **Isothermal reversible compression of gas.**
- d. **Adiabatic reversible compression of gas.**

Here, in this cycle, a gas confined in a cylinder with frictionless piston is first placed on the heat source, where it receives some heat and expands isothermally and reversibly. Then the gas is detached from the source and allowed to expand adiabatically and reversibly. Then the gas is again placed on the sink, where it releases the heat and undergoes compression isothermally and reversibly. Then, lastly, the gas is detached from the source and allowed to undergo compression adiabatically and reversibly.

The process and the Carnot cycle is depicted in the following figures:





Calculation of work done in different process of Carnot cycle

i. Step 1 (1 → 2): Isothermal reversible expansion:

$$w_1 = -P\Delta V = -nRT_1 \ln \frac{V_2}{V_1} \dots\dots (i)$$

ii. Step 2 (2 → 3): Adiabatic reversible expansion:

$$w_2 = C_V (T_2 - T_1) \dots\dots (ii)$$

iii. Step 3 (3 → 4): Isothermal reversible compression:

$$w_3 = -P\Delta V = -nRT_2 \ln \frac{V_4}{V_3} = +nRT_2 \ln \frac{V_3}{V_4} \dots\dots (iii)$$

iv. Step 4 (4 → 1): Adiabatic Reversible compression:

$$w_4 = C_V (T_1 - T_2) = -C_V (T_2 - T_1) \dots\dots (iv)$$

Thus, net work done, $w = w_1 + w_2 + w_3 + w_4$

$$\text{or, } w = -nRT_1 \ln \frac{V_2}{V_1} + C_V (T_2 - T_1) + nRT_2 \ln \frac{V_3}{V_4} - C_V (T_2 - T_1)$$

$$\text{or, } w = -nRT_1 \ln \frac{V_2}{V_1} + nRT_2 \ln \frac{V_3}{V_4} \dots\dots (v)$$

Now, from the cycle, for the isothermal processes (step 1 and 3) and for the adiabatic processes (step 2 and 4), we can write that,

$$\left(\frac{V_2}{V_1}\right) = \left(\frac{V_3}{V_4}\right)$$



Thus, the equation (v) becomes

$$w = -nRT_1 \ln \frac{V_2}{V_1} + nRT_2 \ln \frac{V_2}{V_1}$$

$$\text{or, } w = -nR(T_1 - T_2) \ln \frac{V_2}{V_1}$$

- **Efficiency of Carnot cycle:** It can be defined as the ratio of net work done by the system with respect to the amount of heat absorbed by the system. Thus,

$$\eta = \frac{\text{Net work done}}{\text{Heat absorbed}} = \frac{w}{q_{in}}$$

$$\text{or, } \eta = \frac{-(T_1 - T_2) nR \ln \frac{V_2}{V_1}}{-nR T_1 \ln \frac{V_2}{V_1}}$$

$$\text{or, } \eta = \frac{(T_1 - T_2)}{T_1}$$

$$\therefore \eta = 1 - \frac{T_2}{T_1} = 1 - \frac{T_c}{T_h}$$

Thus, it is proved that,

- i. The efficiency of a Carnot engine depends **only** the temperature of the source (T_h) and the temperature of the sink (T_c).
- ii. It is **independent** of the nature the working substance (gas) of the system.
- iii. Efficiency (η) will be **100%** if the **temperature of the source (T_1 or T_h)** is ∞ (infinite) and the **temperature of the sink (T_2 or T_c)** is **0 K** (absolute zero). But, this condition cannot be attained in practical condition, thus, the efficiency of heat engine can **never** be 100%.
- iv. If $T_1 = T_2$ then, $\eta = 0$



III. Entropy

- Entropy is a thermodynamic function which is measured by the change of its value when the system passes from one state to other state.
- For a finite change in the state of the system at a constant temperature T K, $\Delta S = \frac{q_{rev}}{T}$

Thus, change in entropy (ΔS) can be defined as the ratio of the reversible heat change and temperature (K).

- Physical significance:** It is the property of the system which measures the disorder or randomness of the system.

Solid substances are most ordered, liquid are less ordered than solids and gases are most disordered. Thus, $S_{solid} < S_{liquid} < S_{gas}$

- The entropy change (ΔS) is a **state function**, **exact differential**, and **extensive** property.
- Unit of Entropy: **J K⁻¹**

➤ Entropy change during phase change:

We know that, $\Delta S = \frac{q_{rev}}{T}$

During a phase change at constant temperature, $q_{rev} = \text{Latent heat } (\Delta H)$.

Thus, entropy change of fusion, $\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T}$, where T is the melting point.

Also, entropy change of vaporization, $\Delta S_{vap} = \frac{\Delta H_{vap}}{T}$, where T is the boiling point.

➤ Expression for entropy of any system undergoing any change in its state is given by

$$\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$



➤ **Expression for entropy change of mixing of ideal gas.**

$$\Delta S_{mix} = -R (x_A \ln x_A + x_B \ln x_B)$$

Where X_A and X_B are mole fraction of gases A and B, respectively. R is the gas constant.

IV. Helmholtz free energy or Work function (A)

- 'A' is defined as $A = U - TS$
- As 'U', 'T' and 'S' are state functions and exact differentials, thus, 'A' is also a **state function** and **exact differential**.
- It is an **extensive** property.
- **Physical significance:**

Let consider a change in 'A' in an isothermal process, thus, $\Delta A = \Delta U - T\Delta S$

$$\text{Now } \Delta S = \frac{q_{rev}}{T}$$

$$\text{So, } \Delta A = \Delta U - T\left(\frac{q_{rev}}{T}\right) = \Delta U - q_{rev}$$

Also from the first law of thermodynamics, $\Delta U = q_{rev} - w_{rev}$

$$\text{So, } \Delta A = (q_{rev} - w_{rev}) - q_{rev} = -w_{rev}$$

$$\text{Hence, } -\Delta A = w_{rev}$$

Now, for mechanical work done, $w_{rev} = \int PdV$

$$\therefore -\Delta A = \int PdV = w_{max}$$

So, 'A', i.e., Helmholtz free energy function is such a thermodynamic function that its decrease at constant temperature gives the maximum amount of work that can be obtained from the system, i.e., **expansion (P-V) work** or **gross work**.

- Also, mathematically, $A = U - TS$

Differentiating, we get, $dA = dU - TdS - SdT$



Now, from the first law of thermodynamics and from the concept of entropy, we get,

$$dU = q - dw = TdS - PdV$$

$$\text{So, } dA = (TdS - PdV) - TdS - SdT = -PdV - SdT$$

$$\therefore dA = -PdV - SdT$$

V. Gibbs free energy or Free Energy function (G)

- It is denoted by 'G', and is given by $G = H - TS$.
- 'G' is a **state function**, **exact differential** and an **extensive** property.
- **Physical significance:**

Let consider a change in 'G' in an isothermal process, thus, $\Delta G = \Delta H - T\Delta S$

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

$$\text{Hence, } \Delta G = \Delta U + P\Delta V - T\Delta S = (\Delta U - T\Delta S) + P\Delta V = \Delta A + P\Delta V$$

$$\text{Or, } -\Delta G = -\Delta A + (-P\Delta V) = w_{\max} - P\Delta V$$

Hence, the decrease in free energy in an isothermal process is the maximum amount of the useful work obtainable from the system other than the gross work, i.e., **non-expansion work** or **net work**.

- Also, mathematically, $G = H - TS = U + PV - TS$ [Since, $H = U + PV$]

$$\text{Differentiating, we get, } dG = dU + PdV + VdP - TdS - SdT$$

$$\text{Again, from the first law of thermodynamics, } dU = q - dw = TdS - PdV$$

$$\text{Thus, } dG = TdS - PdV + PdV + VdP - TdS - SdT$$

$$\text{Or, } dG = VdP - SdT$$

$$\therefore dG = VdP - SdT$$



Gibbs-Helmholtz equation

The Gibbs free energy is given by $G = H - TS$. Let G_1, H_1, S_1 and G_2, H_2, S_2 be the free energies, enthalpies and entropies of the system in state-1 and state-2, respectively, at constant temperature T .

$$\text{Then, } G_1 = H_1 - TS_1 \text{ and } G_2 = H_2 - TS_2$$

$$\text{So, } (G_2 - G_1) = (H_1 - H_2) - T(S_1 - S_2)$$

Or, $\Delta G = \Delta H - T\Delta S$, where, ΔG , ΔH and ΔS are the free energy change, enthalpy change and entropy change of the process.

We know that, $dG = VdP - SdT$

$$\text{At constant pressure, } dG_P = -SdT$$

$$\text{Or, } \left(\frac{dG}{dT}\right)_P = -S$$

$$\text{So, in initial state, } \left(\frac{dG_1}{dT}\right)_P = -S_1 \quad \text{and,}$$

$$\text{In final state, } \left(\frac{dG_2}{dT}\right)_P = -S_2$$

$$\text{Subtracting, } \left(\frac{dG_2}{dT}\right)_P - \left(\frac{dG_1}{dT}\right)_P = -(S_2 - S_1)$$

$$\text{Or, } \left[\frac{d(G_2 - G_1)}{dT}\right]_P = -\Delta S \Rightarrow \left[\frac{d(\Delta G)}{dT}\right]_P = -\Delta S$$

Substituting this value of ΔS in $\Delta G = \Delta H - T\Delta S$, we get,

$$\Delta G = \Delta H + T \left[\frac{d(\Delta G)}{dT}\right]_P$$

This is the most common form of Gibbs-Helmholtz equation. It has important application in the study of electrochemical cells.



ΔA and ΔG of ideal gas in an isothermal process

We know that, $dA = -PdV - SdT$

For isothermal process, $dT = 0$, so, $dA = -PdV$

$$\text{So, } \Delta A = \int_1^2 dA = - \int_1^2 PdV$$

Now, for ideal gas, $PV = nRT$, or, $P = \frac{nRT}{V}$

$$\therefore \Delta A = - \int_{V_1}^{V_2} nRT \frac{dV}{V} = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1}$$

Again, we know that, $dG = VdP - SdT$

For isothermal process, $dT = 0$, so, $dG = VdP$

$$\text{So, } \Delta G = \int_1^2 dG = \int_1^2 VdP$$

Now, for ideal gas, $PV = nRT$, or, $V = \frac{nRT}{P}$

$$\therefore \Delta G = \int_{P_1}^{P_2} nRT \frac{dP}{P} = nRT \int_{P_1}^{P_2} \frac{dP}{P} = nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2} = -nRT \ln \frac{V_2}{V_1}$$

Thus, in an isothermal process, ΔA and ΔG are equal for an ideal gas.

➤ Criteria of Spontaneity and conditions of equilibrium:

- i. If $\Delta G_{T,P} < 0$, i.e., ΔG for the process is negative, the process will be spontaneous.**
- ii. If $\Delta A_{T,V} < 0$, i.e., ΔA for the process is negative, the process will be spontaneous.**
- iii. If $\Delta S_{P,V} > 0$, i.e., ΔS for the process is positive, the process will be spontaneous.**
- iv. At equilibrium, $\Delta G_{T,P} = 0$, $\Delta A_{T,V} = 0$, $\Delta S_{P,V} = 0$**



ELECTROCHEMISTRY

It is the branch of science that deals with the inter conversion of electrical energy and chemical energy.

$$\text{Electrochemistry} \Rightarrow \text{Electrical energy} \Leftrightarrow \text{Chemical energy}$$

Oxidation and reduction: According to the modern concept,

Oxidation: Loss of electrons $M \rightarrow M^+ + e^-$

Reduction: Gain of electrons $M^+ + e^- \rightarrow M$

Oxidizing agent: The species which **undergo reduction**, i.e., oxidizes other species but gets reduced itself.

Reducing agent: The species which **undergo oxidation**, i.e., reduces other species but gets oxidized itself.

For any reaction, $A + B^{n+} \rightarrow A^{n+} + B$

A is the reducing agent and B^{n+} is the oxidizing agent.

Types of electrochemical cells:

The oxidation and reduction occurs at electrodes confined in an electrochemical cell.

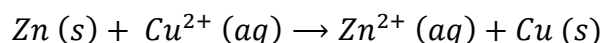
There are two types of electrochemical cells:

- i. **Galvanic Cells (Voltaic/Daniel cells).**
- ii. **Electrolytic cells.**

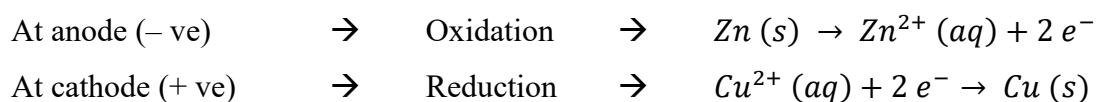
➤ Galvanic cell:

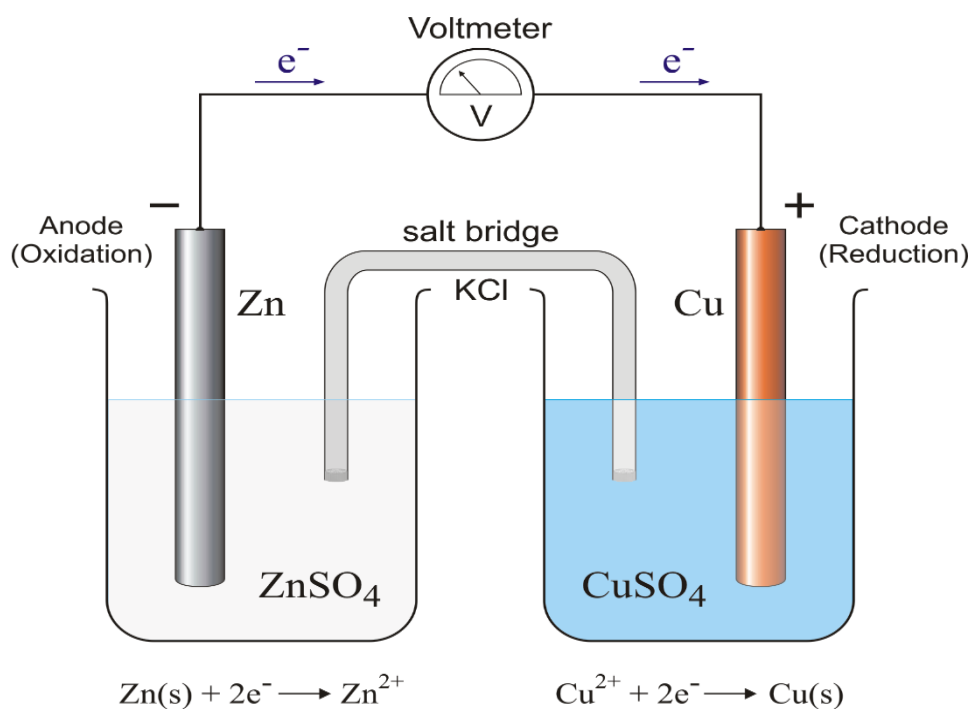
It is such an electrochemical cell which converts the free energy of a spontaneous chemical reaction (chemical energy) into electrical energy.

Let's consider a chemical reaction



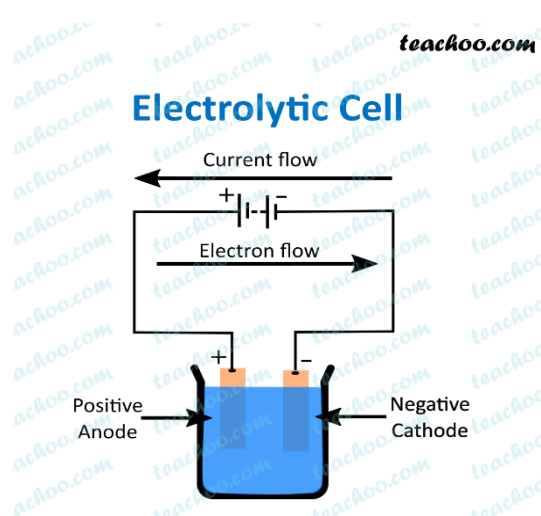
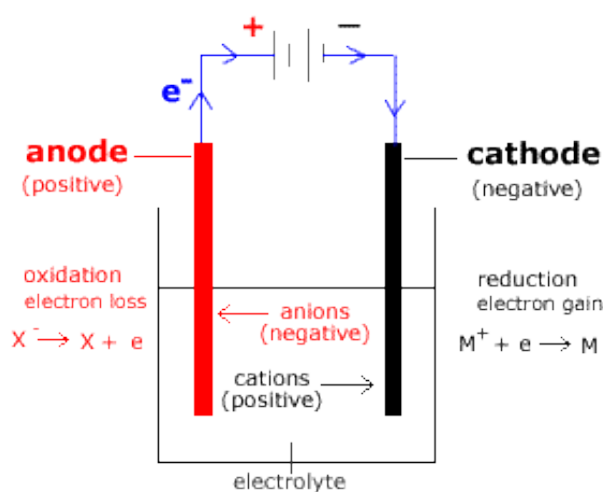
- Cell reactions:



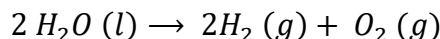


➤ Electrolytic cells:

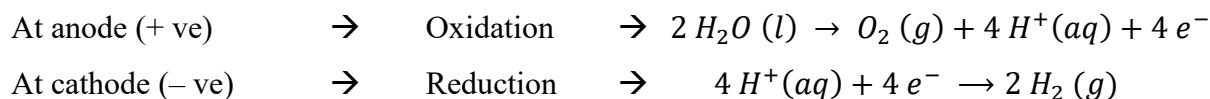
It is such an electrochemical cell which converts the electrical energy into chemical energy which results in progression of a non-spontaneous reaction.



Let's consider a chemical reaction

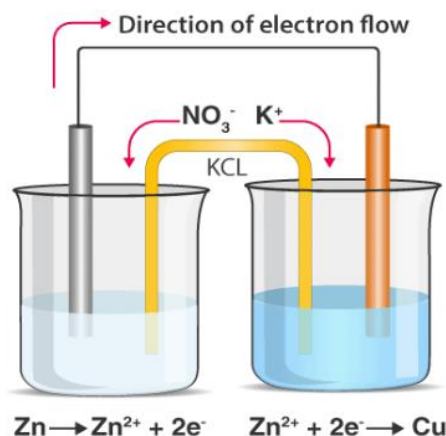


- Cell reactions:



➤ Salt bridge:

- It is a U-shaped glass tube containing suitable strong electrolyte such as **inert KCl, AgNO₃**, etc., that connects the oxidation and reduction half cells.
- If we immerse the two electrodes in one solution in a single container, no salt bridge is necessary, but if we want each electrode in a different solution and in separate containers, we need a salt bridge to complete the circuit of the electrochemical cell.
- It contains mobile ions that act as charge carriers.
- It maintains the electrical neutrality of the cell.
- It minimizes or almost eliminates the formation of liquid junction potential, because the mobility of cation (K⁺) and anion (Cl[–]) are very similar.

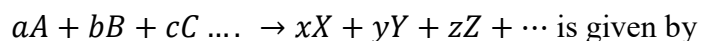


The Nernst Equation

- The equation was introduced by a German chemist named Walther Hermann Nernst.
- The Nernst equation provides a relation between the cell potential of an electrochemical cell, the standard cell potential, temperature, and the reaction quotient.



- The Nernst equation is often used to calculate the cell potential of an electrochemical cell at any given temperature, pressure, and reactant concentration (non-standard conditions).
- The Nernst equation of the following reversible reaction

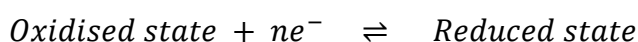


$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln \frac{[X]^x \times [Y]^y \times [Z]^z \times \dots}{[A]^a \times [B]^b \times [C]^c \times \dots}$$

On putting the values of R and F at T = 298 K, we get,

$$E_{cell} = E^0_{cell} - \frac{0.05912}{n} \log \frac{[Products]}{[Reactants]}$$

➤ For half-cell reaction



Thus,

$$E_{half-cell} = E^0_{half-cell} - \frac{0.05912}{n} \log \frac{[reduced\ state]}{[oxidised\ state]}$$

Free energy and EMF

During cell operation, the decrease in free energy appears as electrical energy. This can be represented using the mathematical equation:

$$-\Delta G = nFE_{cell}$$

Where ΔG is the change in Gibbs free energy, n is the number electrons transferred, F is the Faraday constant ($96500\ C\ mol^{-1}$), and E_{cell} is the cell potential.

From the concept of spontaneity, **the working condition of a cell will be spontaneous if the value of ΔG is negative and E_{cell} is positive**. If either of ΔG is positive or E_{cell} is negative then the working condition of a cell will be non-spontaneous.



Application of the Nernst equation

1. To find the electrode and cell potential.

Problem: Find the potential of the following half-cells at 298 K:

- a. FeSO_4 (0.1 M) | Fe (s). (Standard electrode potential of Fe being -0.44 V)
- b. Pt, H_2 (g, 2 atm) | HCl (aq, 0.02 M)

Answer:

- a. The half-cell reaction is given by $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$

Now, applying the Nernst equation,

$$E = E^0 - \frac{0.05912}{n} \log \frac{[\text{Reduced state}]}{[\text{Oxidized state}]}$$

$$\text{or, } E = (-0.44) - \frac{0.05912}{2} \log \frac{[\text{Fe}]}{[\text{Fe}^{2+}]} = (-0.44) + \frac{0.05912}{2} \log [\text{Fe}^{2+}]$$

$$\text{or, } E = (-0.44) + \frac{0.05912}{2} \log (0.1)$$

$$\text{or, } E = (-0.44) - 0.0295 = -0.4695 \text{ V}$$

- b. The half-cell reaction is given by $\frac{1}{2} \text{H}_2(\text{g}) \rightarrow \text{H}^+(\text{aq}) + \text{e}^-$

Now, applying the Nernst equation,

$$E = 0 + \frac{0.05912}{1} \log \frac{\sqrt{p_{\text{H}_2}}}{[\text{H}^+]}$$

$$= 0.05912 \log \left(\frac{\sqrt{2}}{0.02} \right)$$

$$\text{or, } E = 0.109 \text{ V}$$

Problem: Represent the cell in which the following reaction takes place: $\text{Mg}(\text{s}) + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$. Also calculate the cell potential.

Given that: $E^0_{\text{Mg}^{2+}/\text{Mg}} = -2.37 \text{ V}$, $E^0_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}$, $[\text{Ag}^+] = 0.02 \text{ M}$, and $[\text{Mg}^{2+}] = 0.001 \text{ M}$.



Answer: The above cell reaction is represented as

Now, the standard cell potential, $E_{\text{cell}}^0 = 0.80 - (-2.37) \text{ V} = +3.17 \text{ V}$

Hence, according to the Nernst equation,

$$E_{\text{cell}} = 3.17 - \frac{0.05912}{2} \log \frac{[\text{Mg}^{2+}][\text{Ag}]^2}{[\text{Mg}][\text{Ag}^+]^2}$$

$$\text{or, } E_{\text{cell}} = 3.17 - \frac{0.05912}{2} \log \left(\frac{0.001}{(0.02)^2} \right)$$

$$\text{or, } E_{\text{cell}} = (3.17 - 0.0117) \text{ V} = 3.1583 \text{ V}$$

2. To find the equilibrium constant:

Form the Nernst equation,

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{2.303 RT}{nF} \log Q \quad [Q = \text{Reaction Quotient}]$$

At equilibrium, $E_{\text{cell}} = 0$ and $Q = K$

$$\text{So, } E^0 - \frac{2.303 RT}{nF} \log K = 0$$

$$\text{or, } \log K = \frac{nFE^0}{2.303 RT}$$

At $T = 298 \text{ K}$,

$$\log K = \frac{nE^0}{0.05912}$$

$$K = 10^{\left(\frac{nE^0}{0.05912} \right)}$$

Problem: Calculate the equilibrium constant for the reaction, $\text{Fe}^{3+} + 3\text{I}^- \rightarrow \text{Fe}^{2+} + \text{I}_3^-$. The standard reduction potentials for $\text{Fe}^{3+}/\text{Fe}^{2+}$ and I_3^-/I^- are 0.77 and 0.54 V, respectively.

Answer: The standard cell potential for the given reaction is

$$E_{\text{cell}}^0 = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 - E_{\text{I}_3^-/\text{I}^-}^0 = (0.77 - 0.54) \text{ V} = 0.23 \text{ V}$$

Now using the equation,

$$\log K = \frac{nE^0}{0.05912}$$

$$\text{or, } \log K = \frac{1 \times 0.23}{0.05912} = 3.898$$

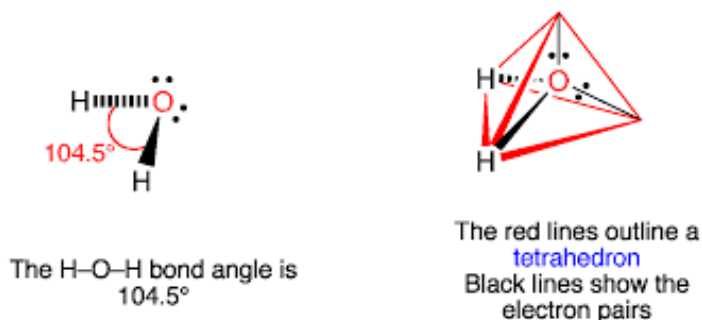
$$\text{or, } K = 10^{3.898} = 7.91 \times 10^3$$

3. To find the pH of an unknown aqueous solution by using different electrodes such as hydrogen electrode, calomel electrode, quinhydrone electrode, glass electrode, etc.

WATER CHEMISTRY

Water (H₂O) is a polar inorganic compound which is colourless, odourless and tasteless liquid at room temperature. It is the most abundant substance on earth and the only common substance to exist as solid, liquid, and gas on earth's surface. Water contains naturally stable elements hydrogen (H) and oxygen (O) with a molecular mass of 18. It may exist as D₂O and known as heavy water. D being one of the isotope of hydrogen, Deuterium (²D), D₂O has a molecular mass of 22.

In water, the central atom oxygen is bound to two hydrogen atoms. Oxygen undergoes sp³ hybridization to give four sp³ hybridized orbitals of equivalent energy in which two contain lone pairs of electrons and other two form two bond pairs with two hydrogen atoms in a tetrahedral geometry.



Physical Properties of water

- **Freezing and boiling point of water:** Water freezes at 0°C and boils at 100°C. These two temperatures are taken as the reference in temperature measurement.



- **Specific heat of water:** The specific heat of water is 1 cal g^{-1} , i.e., 4.18 J g^{-1} . Due to this high specific heat, water is used as boiler industries and as coolant in vehicles.
- **Surface tension and viscosity of water:** Water has a very high surface tension of 72.8 mN/m at 20°C . The viscosity of water is taken as standard and found to be 10.02 mp at 20°C .
- **Polarity and solubility:** Due to presence of two lone pairs of electrons in water it is highly polar in nature. Due to this polar characteristics, ionic compounds such as salts, alcohols, acids, etc., easily dissolve in water and make water as a versatile solvent.
- **Amphoteric nature and pH:** Water is amphoteric in nature. It can act as both acid and base as it can produce both H^+ and OH^- ions by self-ionization. At constant temperature, water always contains equal number of H^+ and OH^- ions and their product is always constant. The pH of pure water is 7.

Sources of water

The main sources of water are as follows:

- i. **Surface water:** It includes both running (streams and rivers) and stagnant (lakes, ponds and reservoirs) water.
- ii. **Underground water:** It includes water from wells and springs.
- iii. **Rainwater.**
- iv. **Seawater.**

Impurities in water

Impurities in water can be broadly classified into the following types:

- i. **Dissolved impurities:** These include dissolved salts such as carbonates, bicarbonates, chlorides and sulfates of sodium, calcium, magnesium and iron. Dissolved gases such as O_2 and CO_2 also come under this category.
- ii. **Suspended impurities:** These include inorganic impurities such as clay, sand or organic impurities such as oil globules, animal and plant matter.
- iii. **Colloidal impurities:** These include finely divided organic matter, silica and clay.



- iv. **Microorganisms:** These include bacteria, fungi, and algae.

Hardness of water

Hardness is the property of water by virtue of which it fails to form lather with soap. This is due to the presence of certain dissolved salts of calcium, magnesium, and other heavy metals such as iron, aluminium and manganese in it.

Water hardness may be of two types: temporary hardness and permanent hardness.

- i. **Temporary hardness:** It is attributed to the presence of dissolved bicarbonates of calcium, magnesium, and other heavy metals. This type of hardness can be removed easily by boiling the water. In this process, the bicarbonate salts decompose into insoluble carbonates or hydroxides which settle down as a crust at the bottom of the vessel. Such hardness is also known as *carbonate hardness*.



- ii. **Permanent hardness:** It is attributed to the presence of chlorides and sulfates of calcium, magnesium, and other heavy metals. It cannot be removed merely by boiling the water. This type of hardness is also known as *non-carbonate hardness*.

Hardness of water is usually expressed in **calcium carbonate equivalent**. The choice of calcium carbonate is because its molecular mass is 100 and it is the most insoluble salt that can be precipitated in water treatment.

Hardness in calcium carbonate equivalent

$$= \text{Mass of hardness imparting substance} \left(\frac{\text{mg}}{\text{l}} \right) \times \left[\frac{\text{Equivalent mass of CaCO}_3}{\text{Equivalent mass of hardness imparting substance}} \right]$$



Units of hardness

Hardness of water is usually measured in milligram per liter (mg l^{-1}) or parts per million (ppm) of calcium carbonate equivalent. It is also expressed in units such as **Degree French ($^{\circ}\text{Fr}$)** and **Degree Clarke ($^{\circ}\text{Cl}$)**. For such units, we use the following conversion formulae: $1^{\circ}\text{Fr} = 10 \text{ ppm}$ and $1^{\circ}\text{Cl} = 0.07 \text{ ppm}$.

Problem: How many milligrams of MgCl_2 dissolved per liter give 60 ppm of hardness?

Answer: According to the equation for hardness measurement,

$$\text{Hardness} = \text{Mass of } \text{MgCl}_2 \left(\frac{\text{mg}}{\text{l}} \right) \times \left[\frac{\text{Equivalent mass of } \text{CaCO}_3}{\text{Equivalent mass of } \text{MgCl}_2} \right]$$

$$\text{or, } \text{Mass of } \text{MgCl}_2 \left(\frac{\text{mg}}{\text{l}} \right) = \frac{\text{Hardness} \times \text{Equivalent mass of } \text{MgCl}_2}{\text{Equivalent mass of } \text{CaCO}_3}$$

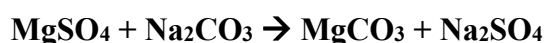
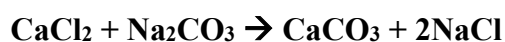
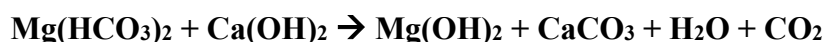
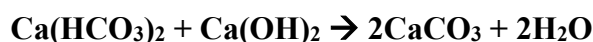
$$\text{or, } \text{Mass of } \text{MgCl}_2 \left(\frac{\text{mg}}{\text{l}} \right) = \frac{60 \times 47.5}{50} = 57 \frac{\text{mg}}{\text{l}}$$

Hence, 57 mg of MgCl_2 dissolved per liter gives 60 ppm of hardness.

Hardness softening methods

- Lime-Soda (L-S) process:**

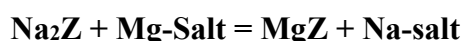
In L-S process, the dissolved hardness-causing salts are converted into insoluble carbonates or hydroxides by adding a calculated amount of lime (Ca(OH)_2) and soda (Na_2CO_3). The insoluble compounds so precipitated are then filtered off. The L-S process can be applied either at room temperature or at an elevated temperature.



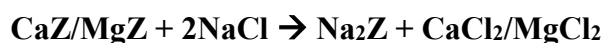


- **Zeolite/Permutit process:**

Zeolite is hydrated sodium aluminosilicate, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$, where $x = 2$ to 10 and $y = 2$ to 6 . The commercially known zeolites are known as permutits. This process involves a reversible exchange of cations between stationary zeolite bed and the external mobile liquid phase.



This process removes both temporary and permanent hardness. The advantage of this process is that after the exhaustion of zeolite bed, the same can be regenerated by simply passing 10% solution of sodium chloride (*brine*) through it.



- **Ion-exchange process:**

This process involves a reversible exchange of ions between stationary ion-exchange resin columns and the external mobile liquid phase. Ion-exchange resins are insoluble, cross-linked, long-chain organic polymers with a micro-porous structure. Based on the active functional group attached to them, ion-exchange resins are of two types:

- Cation-exchange resins:** These contain acidic functional groups such as $-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{OH}$, etc., and capable of exchanging their H^+ ions with the cations responsible for hardness.
- Anion-exchange resins:** These contain basic functional groups such as $-\text{NH}_2$, $[-\text{N}(\text{CH}_3)_4]^+\text{OH}^-$, etc., and capable of exchanging their OH^- ions with the anions responsible for hardness.

Comparison between different hard water softening processes

Characteristics	Lime-Soda process	Permutit process	Ion-exchange process
Requirements	Lime, soda, coagulant	Zeolite	Cation and anion exchange resins
Exchange of ions	No exchange of ions	Cation only	Cations and anions both
Capital cost	Low	High	Very high
Residual hardness	~50 ppm	~10-15 ppm	~0-2 ppm



CORROSION

Corrosion is a process of slow destruction of metal due to chemical or electrochemical attack of environment at their surfaces resulting into the formation of compounds such as oxides, sulfides, sulfates, carbonates, etc. After the extraction of metals from their ores, corrosion facilitates the reverse process, *i.e.*, nature tries to convert them back into the form in which they occur.

The most common example of corrosion is rusting of iron, tarnishing of silver, development of green coating on copper and bronze, etc.

Types of corrosion

There are two types of corrosion:

- a. Dry or Chemical corrosion**
- b. Wet or Electrochemical corrosion**

Dry or Chemical corrosion

It is the direct chemical action of atmospheric gases such as oxygen, halogens, sulfur dioxide, hydrogen sulfide, etc., with metals in absence of moisture. The most common dry corrosion is occurred through the reaction of atmospheric oxygen with metals.

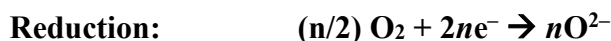
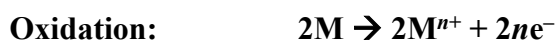
Corrosion by oxygen (Oxidation corrosion)

Atmospheric oxygen reacts with metals in absence of moisture to form their respective oxides. Alkali metals (Li, Na, K, etc.) and alkaline earth metals (Be, Mg, Ca, Sr, etc.) are oxidized at low temperatures, whereas all other metals except Ag, Au, and Pt, are oxidized at elevated temperatures.

The oxidation process starts at the exposed metal surface. The metal undergoes oxidation by losing electrons and form metal cations while oxygen accepts those electrons to form oxide anions.



The general mechanism of oxidation corrosion is given below:



After the formation of the first thin oxide layer (*film*), further oxidation depends upon the nature of the oxide film formed.

- a. **Stable film:** The stable oxide film remains strictly adhered to the metal surface and acts as a physical barrier between the metal and the atmosphere. This prevents the further oxidation, and hence, corrosion, e.g., oxide films of Al, Pb, Cu, Sn, etc.
- b. **Unstable film:** If the oxide film is unstable, it decomposes back into metal and oxygen, and hence, corrosion cannot continue further, e.g., oxide films of Au, Ag, and Pt.
- c. **Volatile film:** This type of oxide film gets volatilized immediately after formation and exposes the new metal surface available for further interaction with oxygen. Therefore, this type of corrosion is rapid and continuous, e.g., oxide film of Mo.
- d. **Porous film:** The porous oxide film has pores or channels through which oxygen slowly diffuses to interact with the metal. Hence, this type of corrosion is slow but continuous, e.g., oxide film of Fe.

Wet or Electrochemical corrosion

Wet corrosion is more common than dry corrosion. It occurs mostly in presence of moisture through the formation of electrochemical cell and is therefore, referred to as electrochemical corrosion.

The mechanism of the electrochemical corrosion involves:

- i. The existence of separate anodic and cathodic areas between which current flows through the conducting medium.

- ii. Oxidation (loss of electrons) takes place at the anodic area and the metal is destroyed by producing metal cations and electrons.



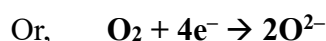
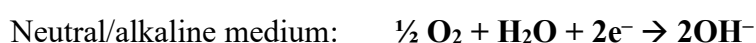
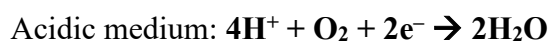
- iii. Reduction (gain of electrons) takes place at cathode. Electrons produced in anode migrate to cathode through the conducting medium and accepted by dissolved oxygen forming ions such as OH^{-} (hydroxides) and O^{2-} (oxides).

The cathodic reactions can happen in two ways:

- a. Through evolution of hydrogen:



- b. Through absorption of oxygen:



- iv. The metallic ions formed at anode and non-metallic ions formed at cathode diffuse through the conducting medium and combine to form the corrosion product somewhere between the anodic and cathodic area.

Rusting of iron

Rusting of iron is an example of electrochemical corrosion. It refers to the formation of a mixture of iron oxides, known as **rust**, on the surface of iron objects or structures. The rusting of iron is characterized by the formation of a layer of a red, flaky substance that easily crumbles into a powder.

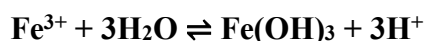
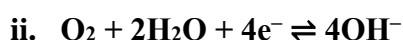
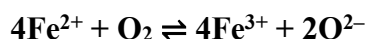




➤ Chemistry behind the rusting of iron:

The exposure of iron (or an alloy of iron) to oxygen in the presence of moisture leads to the formation of rust. This reaction is not instantaneous, it generally proceeds over a considerably large time frame.

The set of chemical reactions involved are given below:



Factors affecting corrosion

- 1. Position of metals in the galvanic series:** Metals present at the top of the series are very reactive and has high tendency to corrode. Also, greater the distance between the metals or alloys in the series, the severe is the corrosion.
- 2. Relative cathodic and anodic area:** Corrosion is severe and highly localized if the anodic area is smaller than that of cathodic area.
- 3. Purity and passivity of metals:** Higher the purity and passivity of metals, lower is the chances of corrosion.
- 4. Environmental factors such as temperature, humidity, pH, conductance of the medium, etc.:** Higher temperature, higher humidity, higher conductance, and lower pH accelerates corrosion.



Measures to prevent corrosion

1. Proper designing of metallic structures and avoiding contact of two dissimilar metals.
2. By using the principle cathodic protection by reducing the size of cathodic area.
3. By using protective coatings which can act as barrier between metal and environment. For example,
 - a. Metallic coating of zinc and tin is applied through galvanizing and tinning process, respectively.
 - b. Inorganic or non-metallic coating of phosphate, chromate, etc., is applied through chemical conversion process.
 - c. Organic coating of paints, varnishes, enamels, etc.

USE OF FREE ENERGY CONSIDERATION IN METALLURGY THROUGH ELLINGHAM DIAGRAM

An Ellingham diagram, first constructed by Harold Ellingham in 1944, is a graph showing the temperature versus standard Gibbs free energy of a reaction involved in extraction of metals from their respective ores. This helps in predicting the equilibrium temperature between a metal, its oxide, and oxygen. These analyses are thermodynamic in nature and thermodynamic predictions are very certain and, therefore, reliable in metallurgical studies.

Construction of Ellingham diagram

Ellingham diagram is a particular graphical form of the principle that the thermodynamic feasibility of a reaction depends on the sign of ΔG , the change in Gibbs free energy, which is equal to $\Delta H - T\Delta S$, where ΔH is the change in enthalpy and ΔS is the change in entropy. For example, if a solid which has an ordered state reacts with a liquid which has somewhat less ordered state to form a gas having highly disordered state, then there is normally a large positive change in entropy for the reaction.

It is certain that change in enthalpy (ΔH) is unaffected by temperature. In this graph ΔG is plotted in relation to temperature. The entropy is represented by the slope of the curve, whereas the enthalpy is represented by the intercept.



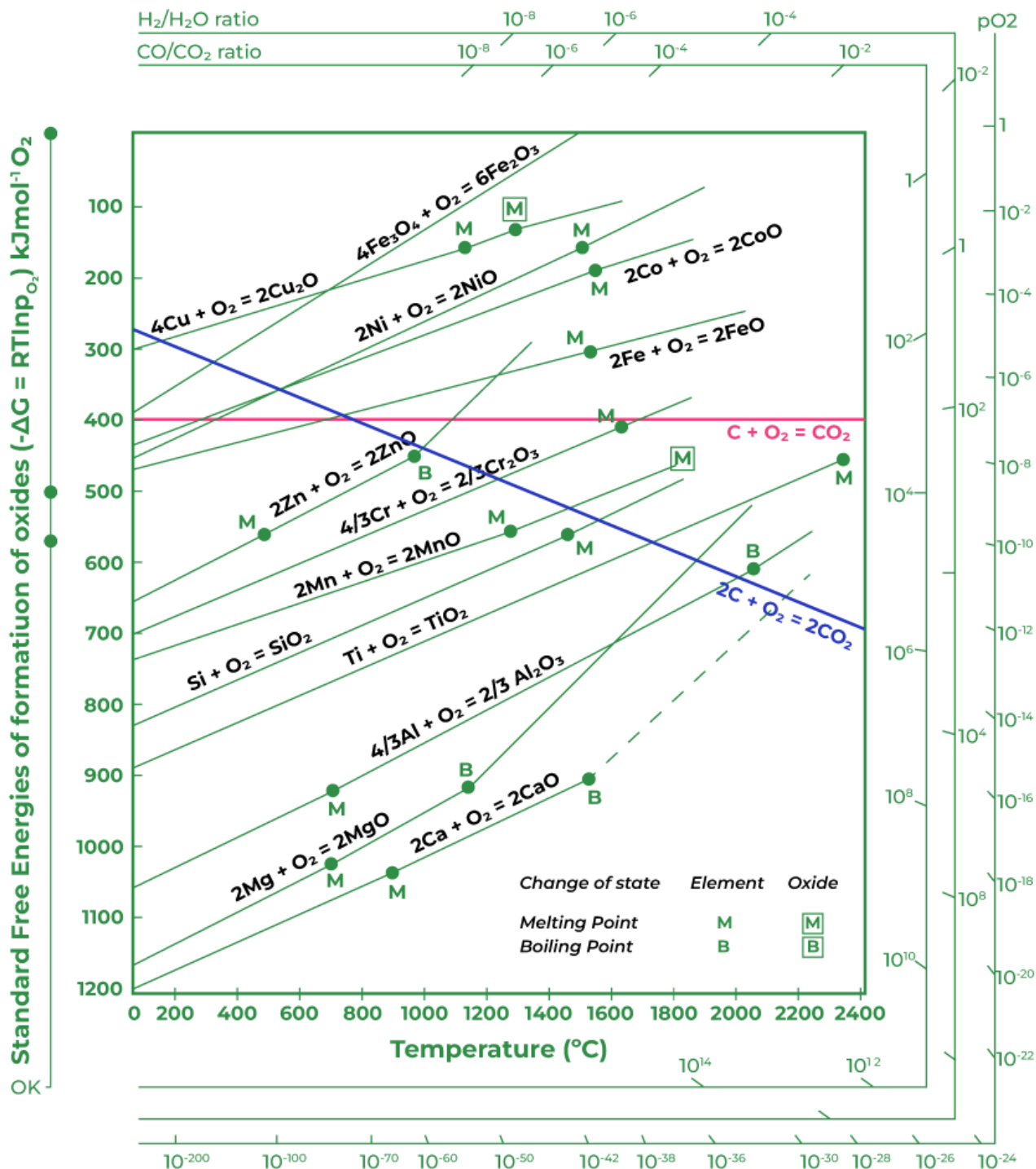
For comparison of different reactions, all values of ΔG refer to the reaction of one mole of O_2 at a partial pressure of 1 atm.

The majority of the lines has slopes upwards, because both the metal and the oxide present as condensed phases, *i.e.*, solid or liquid. All the reactions are, therefore, in between one condensed phase (metal) with a gas (oxygen) to give out another condensed phase (metal oxide).

A notable exception to the above observation is the oxidation of solid carbon in which a solid (carbon) reacts with one mole of oxygen to produce one mole of gas (carbon dioxide), *i.e.*, $C(s) + O_2(g) \rightarrow CO_2(g)$. This leads to a little change in entropy and the line is nearly horizontal. For the reaction, $2C(s) + O_2(g) \rightarrow 2CO(g)$, we have a solid reacting with one mole of oxygen to give two moles of gas (carbon monoxide). Hence there is a substantial increase in entropy and the line slopes rather sharply downward.

Characteristics of Ellingham diagram

- i. Curves in the Ellingham diagram for the formation of metallic oxides are basically straight lines with a positive slope. This slope is proportional to ΔS , which is fairly related with temperature also.
- ii. The lower the position of a metal's line in the Ellingham diagram, the greater is the stability of its oxides. For example, the line for Al is found to be below that of Fe, which shows Al_2O_3 is more stable than Fe_2O_3 .
- iii. If the curves for two metals at a given temperature are compared, the metal with lower Gibbs free energy of oxidation on the diagram will reduce the oxide with higher Gibbs free energy of formation. For example, metallic aluminium can reduce iron oxide to metallic iron, and itself being oxidized to aluminium oxide. This reaction is employed in Thermite process.
- iv. The greater the gap between any two lines, the greater the effectiveness of the reducing agent corresponding to the lower line.
- v. The intersection of two lines means an oxidation-reduction equilibrium. At the point of intersection the free energy change for any of the reaction is zero.
- vi. Below the temperature of intersection, the metallic oxide is more stable than the reductant and cannot be reduced, while above that temperature the oxide can be reduced using any suitable reductant.





Application of Ellingham diagram

- i.** The main application of the Ellingham diagram is in metallurgy, where it helps to select suitable reducing agent for various ores in the extraction process.
- ii.** It is used to determine the relative ease of reducing a given metallic oxide to metal.
- iii.** It helps to guide the purification of metal, especially the removal of trace elements.
- iv.** It helps to determine the partial pressure of oxygen that is in equilibrium with a metal oxide at a given temperature.
- v.** It also helps to determine the ratio of carbon monoxide to carbon dioxide for a smooth reduction of metallic oxide to metal at a given temperature.

Limitation of Ellingham diagram

- i.** Ellingham diagram is built solely on the thermodynamic considerations, hence provides no information regarding the rate of the reaction.
- ii.** It also provides no information about the probability of any side reaction or the probability of simultaneous formation of multiple oxides.
- iii.** The interpretation of ΔG is predicated on the assumption that the reactants and products are in equilibrium, which is not necessarily true.