

Thermodynamic functions: Energy, entropy and free energy

(Internal energy, Helmholtz free energy, Enthalpy, Gibb's free energy- definition, expression and explanation)

Importsants Terms and Types of thermodynamic Systems

Thermodynamics: Thermodynamics is the branch of science or physics that studies various forms of energies and their conversion from one form to the other like electrical energy to mechanical energy, heat to electrical, chemical to mechanical, wind to electrical etc. The study of thermodynamics is comprised of important laws of thermodynamics namely first law of thermodynamics, second law of thermodynamics, third law of thermodynamics and Zeroth law of thermodynamics. Thermodynamics is an important subject area studied under Mechanical Engineering.

System: A quantity of the matter or part of the space which is under thermodynamic study is called as system. There are three types of system: closed system, open system and isolated system.

Surroundings or environment: Everything external to the matter or space, which is under thermodynamic study is called surroundings or environment.

Boundary: The boundary that separates the system and surrounding is called as system boundary. The system boundary may be fixed or moving.

Closed system: The system of fixed mass across the boundary of which no mass transfer can take place is called as closed system. However, across the closed system the energy transfer may take place. An example is fluid being compressed by the piston in cylinder.

Open system: The system across the boundary of which transfer of both mass as well as energy can take place across the boundary is called as open system. An example is an air compressor.

Isolated system: The system in which both the mass as well as energy content remains constant is called an isolated system. In this system no mass or energy transfer takes place across the boundary.

State of the system: The present status of the system described in terms of properties such as pressure, temperature, and volume is called the state of system.

Properties of the system: The characteristics by which the physical condition of the system is described are called as properties of system. Some examples of these characteristics are: temperature, pressure, volume etc and are called as properties of system. The system properties are of two types: extensive and intensive properties.

Extensive properties of system: The properties of the system that depend on the mass or quantity of the system are called extensive properties. Some examples of extensive properties are: mass, volume, enthalpy, internal energy, entropy etc.

Intensive properties of the system: These properties do not depend on the quantity of matter of the system. Some of the examples of intensive properties are: freezing point temperature, boiling point, temperature of the system, density, specific volume etc.

Change of state of system: When one or more properties of the system like pressure, temperature, volume changes, the state of system changes.

Path of change of state: The succession of states through which the system undergoes change to reach the final state is called as the path of change of state of the system.

Homogeneous system: The system that has single or uniform phase such as like solid or liquid or gaseous is called as homogeneous system.

Heterogeneous system: The system that has more than one phase i.e. the combination of solid, liquid and gaseous state is called as heterogeneous system.

Thermodynamics process: When the system changes from one thermodynamic state to the final thermodynamic state due to change in pressure, temperature, volume etc, the system is said to have undergone thermodynamic process. The various types of thermodynamic processes are: isothermal process, adiabatic process, isochoric process, isobaric process and reversible process.

Cyclic process: When the system undergoes a number of changes in states and returns back to the initial state, the system is said to have undergone cyclic process. ($\Delta U_{cyclic} = 0$ and $\Delta H_{cyclic} = 0$).

Isothermal process: The process during which the temperature of the system remains constant is called as isothermal process. ($\Delta T = 0$ and $\Delta U = 0$).

Adiabatic process: The process during which the heat content of the system remains constant i.e. no flow of heat takes place across the boundaries of system, the process is called as adiabatic process. ($\Delta q = 0$).

Isochoric process: In this process the volume of system remains constant. ($\Delta V = 0$).

Isobaric process: The process during which the pressure of the system remains constant, is called as isobaric process. ($\Delta P = 0$).

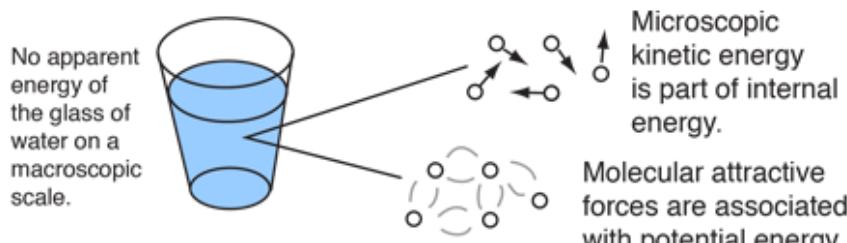
Reversible process: When the system undergoes changes infinitesimally slowly the changes can be reversed back, such a process is called as reversible process. During reversible process the system remains in equilibrium during the change of state of the system.

Entropy of the system: It is the total energy inside the system, which is not available for work during thermodynamic process. It depends on the movement of the molecules inside the system. As the temperature of the system reduces its entropy also reduces. Entropy of the system is never negative.

Internal energy (E/U)

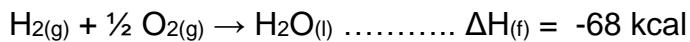
- Internal energy is defined as the energy associated with the random, disordered motion of molecules. It is total energy within the substance and is sum of all the microscopic energies such as (1) translational kinetic energy (2) vibrational and rotational kinetic energy (3) potential energy from intermolecular forces etc.
- It is separated in scale from the macroscopic ordered energy associated with moving objects; it refers to the invisible microscopic energy on the atomic and molecular scale.
- For example, a room temperature glass of water sitting on a table has no apparent energy, either potential or kinetic. But on the microscopic scale it is a seething mass of high speed molecules traveling at hundreds of meters per second. (see below)
- U is the most common symbol used for internal energy.
- It is an extensive property and a state function.
- Its absolute value cannot be determined but change in internal energy can be determined by $\Delta U = U_2 - U_1$ or $\sum U_{\text{products}} - \sum U_{\text{reactants}}$
- For exothermic process (process in which heat is evolved) ΔU is –ve whereas for endothermic process (process in which heat is absorbed, ΔU is +ve).
- Internal energy depends on temperature, pressure, volume and quantity of matter.

Does a glass
of water
sitting on a
table have
any energy?



Enthalpy of the system (H):

- The total heat content of the system is called as enthalpy of the system. The units of enthalpy are same as heat viz. Joules and Calories.
- It is sum of internal energy and PV energy of the system, defined as $H = U + PV$.
- It is a state function and an extensive property.
- Like U, absolute value of H cannot be known but ΔH for a chemical reaction can be determined experimentally by $\Delta H = H_2 - H_1$ or $\sum H_{\text{products}} - \sum H_{\text{reactants}}$
- For exothermic process (process in which heat is evolved) ΔH is -ve whereas for endothermic process (process in which heat is absorbed, ΔH is +ve).
- Enthalpy of a reaction is change in enthalpy that accompanies a chemical reaction represented by a balanced chemical equation i.e. $\Delta H_{(r)} = \sum H_{\text{products}} - \sum H_{\text{reactants}}$
e.g. (1) Enthalpy of formation: it is enthalpy change when one mole of a compound is obtained from its constituent elements.



(2) Enthalpy of combustion: it is enthalpy change taking place when one mole of a compound undergoes complete combustion in presence of O_2 .



Entropy (S):

- **Entropy**, the measure of a system's thermal energy per unit temperature that is unavailable for conversion into mechanical work (doing useful work).
i.e. Entropy = unavailable energy/temperature
- For a reversible process at constant temperature T, change in entropy is equal to heat absorbed or heat evolved divided by the constant temperature in kelvin. i.e.
 $\Delta S = q_{\text{rev}}/T$, where q is the heat absorbed. Unit of entropy is JK/mol
 ΔS is +ve if heat is absorbed
 ΔS is -ve if heat is evolved.
- Because work is obtained from ordered molecular motion, the amount of entropy is also a measure of the molecular disorder, or randomness, of a system.
- The concept of entropy provides deep insight into the direction of spontaneous change for many everyday phenomena. It is the quantity that tells whether a chemical reaction or a physical change can occur spontaneously in an isolated system or not.
- It is an extensive property and a state function
- Its value depends on mass of substance present in system
- $\Delta S = S_{\text{final}} - S_{\text{initial}}$

- At equilibrium $\Delta S = 0$
- For cyclic process, $\Delta S = 0$
- For natural process $\Delta S > 0$, i.e. increasing
- For adiabatic process $\Delta S = 0$.
- The entropy of a system and surrounding taken together increases ($\Delta S > 0$) in a thermodynamically irreversible/natural process, but it remains constant in a thermodynamically reversible process ($\Delta S = 0$).

$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0$ (for reversible process)

$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$ (for irreversible process)

Physical significance of entropy

Physical Significance of Entropy

1. **Entropy as a Measure of the Disorder of the System.** It has already been shown that all spontaneous processes, such as flow of heat from a hot end to a cold end of a conductor, flow of electricity from a point at a higher potential to a point at a lower potential, expansion of a gas in vacuum, diffusion of a solute from a concentrated to a dilute solution, are accompanied by increase in the 'disorder' of the system. Spontaneous processes are accompanied by increase in entropy as well as increase in the disorder of the system.

It has also been shown that melting of a solid or evaporation of a liquid is accompanied by increase of entropy. At the same time, it is known that a solid has a definite crystal lattice, i.e., the atoms or ions or molecules in a solid are arranged in a definite order. The order is much less in a liquid and least in a gas. Thus, increase of entropy implies increase in disorder.

Thus, entropy is regarded as a measure of the disorder of a system. The great thermodynamicist Gibbs described entropy as a measure of the "mixed-up-ness" of a system.

2. **Entropy as a Measure of Probability.** As seen above, all spontaneous processes lead to increase in entropy and also to increase in disorder. A little consideration will show that when a process is spontaneous it means that it is proceeding from a less probable to a more probable state. It appears, therefore, that there is a close relation between entropy S and the thermodynamic probability W of the state of the system both of which increase at the same time. This relationship was expressed by Boltzmann as

$$S = k \ln W + \text{constant} \quad \dots(64)$$

where k is Boltzmann constant, i.e., gas constant per single molecule ($=R/N_A$). Boltzmann defined thermodynamic probability of a system as the ratio of the probability of the actual state to the probability of the state in which there is complete order for the same energy and volume.

According to Planck, the constant in Eq. 64 is zero. Hence,

$$S = k \ln W \quad \dots(65)$$

First Law of Thermodynamics

- The first law of thermodynamics, also known as Law of Conservation of Energy, states that energy can neither be created nor destroyed; energy can only be transferred or changed from one form to another. For example, turning on a light would seem to produce energy; however, it is electrical energy that is converted.
- A way of expressing the first law of thermodynamics is that any change in the internal energy (ΔE) of a system is given by the sum of the heat (q) that flows across its boundaries and the work (w) done on the system by the surroundings:
- The first law of thermodynamics states that the change in internal energy of a system ΔE , equals the net heat transfer into the system Q , plus the net work done on the system W . In equation form, the first law of thermodynamics is,

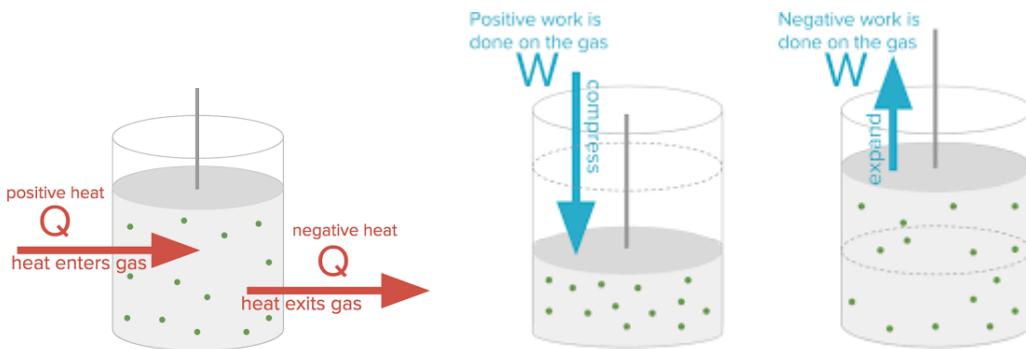
$$\begin{aligned}\Delta E (\text{change in internal energy}) &= q (\text{heat added to the system}) \\ &\quad + w (\text{work done on the system})\end{aligned}$$

OR

$$\Delta E = q + p \Delta V \text{ (since } w = p \Delta V, \text{ where } P = \text{pressure, } \Delta V = \text{change in volume})$$

- This law says that there are two kinds of processes, heat and work, that can lead to a change in the internal energy of a system. Since both heat and work can be measured

and quantified, this is the same as saying that any change in the energy of a system must result in a corresponding change in the energy of the surroundings outside the system. In other words, energy cannot be created or destroyed. If heat flows into a system or the surroundings do work on it, the internal energy increases and the sign of q and w are positive. Conversely, heat flow out of the system or work done by the system (on the surroundings) will be at the expense of the internal energy, and q and w will therefore be negative.



q is +ve if heat absorbed by system

q is -ve if heat evolved by the system

w is +ve if work done on the system

w is -ve if work done by the system

So positive heat q adds energy to the system and positive work W adds energy to the system. This is why the first law takes the form it does, $\Delta E = q + W$. **It simply says that you can add to the internal energy by heating a system, or doing work on the system.**

Thus for adiabatic process, $q = 0$ therefore $w = \Delta E$

for isothermal, cyclic process, $\Delta E = 0$, therefore $q = -w$

for isochoric process, $\Delta V = 0$, therefore $q = \Delta E$

- **Example:** If the gas is heated, it will expand and push the piston up, thereby doing work on the piston. If the piston is pushed down, on the other hand, the piston does work on the gas and the gas does negative work on the piston. This is an example of how work is done by a thermodynamic system. An example with numbers might make this clearer.

Example 1: Nitrogen piston

A container has a sample of nitrogen gas and a tightly fitting movable piston that does not allow any of the gas to escape. During a thermodynamics process, 200 joules of heat enter the gas, and the gas does 300 joules of work in the process.

What was the change in internal energy of the gas during the process described above?

Solution:

We'll start with the first law of thermodynamics.

$$\Delta U = Q + W \quad (\text{start with the first law of thermodynamics})$$

$$\Delta U = (+200 \text{ J}) + W \quad (\text{plug in } Q = +200 \text{ J})$$

[*Why is heat a positive number here?*]

$$\Delta U = (+200 \text{ J}) + (-300 \text{ J}) \quad (\text{plug in } W = -300 \text{ J})$$

[*Why is work a negative number here?*]

$$\Delta U = -100 \text{ J} \quad (\text{calculate and celebrate})$$

Note: Since the internal energy of the gas decreases, the temperature must decrease as well.

Example 2: Heating helium

Four identical containers have equal amounts of helium gas that all start at the same initial temperature. Containers of gas also have a tightly fitting movable piston that does not allow any of the gas to escape. Each sample of gas is taken through a different process as described below:

Sample 1: 500 J of heat exits the gas and the gas does 300 J of work

Sample 2: 500 J of heat enters the gas and the gas does 300 J of work

Sample 3: 500 J of heat exits the gas and 300 J of work is done on the gas

Sample 4: 500 J of heat enters the gas and 300 J of work is done on the gas

Which of the following correctly ranks the final temperatures of the samples of gas after they're taken through the processes described above.

A. $T_4 > T_3 > T_2 > T_1$

B. $T_1 > T_3 > T_2 > T_4$

C. $T_4 > T_2 > T_3 > T_1$

D. $T_1 > T_4 > T_3 > T_2$

Solution:

Whichever gas has the largest increase in internal energy ΔU will also have the greatest increase in temperature ΔT (since temperature and internal energy are proportional). To determine how the internal energy changes, we'll use the first law of thermodynamics for each process.

Process 1:

$$\Delta U = Q + W$$

$$\Delta U = (-500 \text{ J}) + (-300 \text{ J})$$

$$\Delta U = -800 \text{ J}$$

Process 2:

$$\Delta U = Q + W$$

$$\Delta U = (+500 \text{ J}) + (-300 \text{ J})$$

$$\Delta U = +200 \text{ J}$$

Process 3:

$$\Delta U = Q + W$$

$$\Delta U = (-500 \text{ J}) + (300 \text{ J})$$

$$\Delta U = -200 \text{ J}$$

Process 4:

$$\Delta U = Q + W$$

$$\Delta U = (+500 \text{ J}) + (+300 \text{ J})$$

$$\Delta U = +800 \text{ J}$$

The final temperatures of the gas will have the same ranking as the changes in internal energy (i.e. sample 4 has the largest increase in internal energy, so sample 4 will end with the largest temperature).

$$\Delta U_4 > \Delta U_2 > \Delta U_3 > \Delta U_1 \text{ and } T_4 > T_2 > T_3 > T_1$$

Limitations of first law of thermodynamics

1. No restriction on the direction of the flow of heat: the first law establishes definite relationship between the heat absorbed and the work performed by a system. The first law does not indicate whether heat can flow from a cold end to a hot end or not. For example: we cannot extract heat from the ice by cooling it to a low temperature. Some external work has to be done.

2. Does not specify the feasibility of the reaction: first law does not specify that process is feasible or not for example: when a rod is heated at one end then equilibrium has to be obtained which is possible only by some expenditure of energy.
 3. Practically it is not possible to convert the heat energy into an equivalent amount of work. The law does not explain why heat cannot be completely converted into work.
- To overcome these limitations, another law is needed which is known as second law of thermodynamics.

Second Law of Thermodynamics

- The second law of thermodynamics says that the entropy of any isolated system always increases. Isolated systems spontaneously evolve towards thermal equilibrium—the state of maximum entropy of the system. More simply put: the entropy of the universe (the ultimate isolated system) only increases and never decreases ($\Delta S > 0$).
- In other words, “whenever a spontaneous process takes place, it is accompanied by an increase in the total entropy of the universe”. More specifically, the term universe means system and surrounding. Thus,

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

The law tells that when an irreversible spontaneous process occurs the entropy of the system and the surrounding increases. i.e. $\Delta S > 0$. When reversible process occurs, entropy of system remains constant $\Delta S = 0$.

- “Entropy of universe is constantly increasing”
- A simple way to think of the second law of thermodynamics is that a room, if not cleaned and tidied, will invariably become more messy and disorderly with time – regardless of how careful one is to keep it clean. When the room is cleaned, its entropy decreases, but the effort to clean it has resulted in an increase in entropy outside the room that exceeds the entropy lost.

Helmholtz free energy and Gibb's Free energy

- Entropy gives a maximal principle but for the entire universe. It would be useful to find other functions that have similar external properties but for a subsystem of the universe. e.g. One doesn't usually states that ice will freeze at particular temperature, pressure because the entropy of ice plus the freezer plus wires that run to power station plus etc. have total sum entropy that increases.
- Rather it is decidedly more useful to have some other quantity that applies to the water/ice itself as a function of temperature and pressure of its environment.
- Two such quantities are Helmholtz free energy and Gibb's Free energy.
- Helmholtz free energy (ΔA): is the maximum amount of work a system can do at constant volume and temperature.
- Gibbs free energy (ΔG): is the maximum amount of work a system can do at constant pressure and temperature

Work function/Helmhotz function/Helmholtz free energy (ΔA)

Work and Free Energy Functions

We have seen earlier that the sum total of the entropy change of the system and the surroundings (viz., $\Delta S_{\text{sys}} + \Delta S_{\text{sur}}$) serves as a criterion of spontaneity or feasibility of a process. If the total entropy change is positive, the process is feasible. If it is zero, the system remains in a state of equilibrium. However, in order to decide about the feasibility of a process, we shall have to know the entropy change of the system as well as that of the surroundings. This is not always convenient. We, therefore, consider entropy change in terms of other state functions which can be determined more conveniently. Two such functions are the work function and the free energy function represented by A and G , respectively. These are defined by the equations

$$A = U - TS \quad \dots(66)$$

$$G = H - TS \quad \dots(67)$$

Since, U , H and S depend only upon the state of a system (the temperature is included in the three functions in Eq. 66, at constant T , be A_1 , U_1 and S_1 so that

$$A_1 = U_1 - TS_1 \quad \dots(68)$$

Let an appreciable change take place at the same temperature T so that the three functions in another state of the system become A_2 , U_2 and S_2 . Then,

$$A_2 = U_2 - TS_2 \quad \dots(69)$$

Subtracting Eq. 68 from Eq. 69, we have

$$A_2 - A_1 = (U_2 - U_1) - T(S_2 - S_1) \quad \text{or} \quad \Delta A = \Delta U - T\Delta S \quad \dots(70)$$

where ΔA is the change in the function A , ΔU is the corresponding change in internal energy and ΔS is the change in entropy of the system.

Suppose the change under reference is brought about reversibly at the constant temperature T and that the heat absorbed is equal to q_{rev} .

Since from Eq. 28, $\Delta S = q_{\text{rev}}/T$, hence, substituting in Eq. 70, we have

$$\Delta A = \Delta U - q_{\text{rev}} \quad \dots(71)$$

From the equation of the First law of thermodynamics, viz., $\Delta U = q + w$, it follows that

$$w_{\text{rev}} = \Delta U - q_{\text{rev}} \quad \dots(72)$$

If work is done by the system, it is negative so that

$$-w_{\text{rev}} = \Delta U - q_{\text{rev}} \quad \dots(73)$$

Comparing Eq. 71 with Eq. 73,

$$-\Delta A = w_{\text{rev}} \quad \dots(74)$$

Since the process is carried out reversibly, w represents the maximum work. It is thus clear that decrease in the function A (i.e., $-\Delta A$) gives the maximum work that can be done by the system during the given change. The function A is, therefore, termed as the work function. This is also referred to as Helmholtz free energy or Helmholtz function.

Werner Klemm
The scientist who made

Free energy function/Gibb's function/Gibb's free energy (ΔG)

The German physicist Hermann von Helmholtz (1821-1894) was a versatile scientist who made contributions to optics, thermodynamics, acoustics and physiology.

If G_1 , H_1 and S_1 represent the thermodynamic functions in the initial state and G_2 , H_2 and S_2 in the final state, the temperature remaining constant at T , we have from Eq. 67,

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1) \text{ or } \Delta G = \Delta H - T\Delta S \quad \dots(75)$$

But, as already shown in Chapter 13, at constant pressure

$$\begin{aligned} \Delta H &= \Delta U + P\Delta V \\ \therefore \Delta G &= \Delta U + P\Delta V - T\Delta S \end{aligned} \quad \dots(76)$$

Comparing with Eq. 70,

$$\Delta G = \Delta A + P\Delta V \quad \dots(77)$$

Since ΔA is equal to $-w$ (Eq. 74), hence

$$\Delta G = -w + P\Delta V \text{ or } -\Delta G = w - P\Delta V \quad \dots(78)$$

The quantity $P\Delta V$ is the work done by the gas on expansion against the constant external pressure P . Therefore, $-\Delta G$ gives the maximum work obtainable from a system other than that due to change of volume, at constant temperature and pressure. The work other than that due to change of volume is called the **net work**. Thus,

$$\text{Net work} = w - P\Delta V = -\Delta G \quad \dots(79)$$

Hence, $-\Delta G$ is a measure of the net work that can be obtained from a system at constant temperature and pressure. The quantity G is called the **Gibbs function** or **Gibbs free energy** or merely **free energy**. Thus, $-\Delta G$ is a measure of the decrease in free energy. The net work that it measures may be electrical work or chemical work. This quantity is of great importance in physical chemistry ; it is named in honour of the great American physicist, J.W. Gibbs (1839-1903).

Estimation of Entropy and free energy (Gibb's Helmholtz equation of free energy and its application)

Gibbs-Helmholtz Equation

The Gibbs-Helmholtz Equation

Let G_1 represent the free energy of a system in its initial state at temperature T . Suppose the temperature rises to $T+dT$ where dT is infinitesimally small. Let the free energy at the new temperature be G_1+dG_1 .

Now suppose that when the system is in its final state, its free energy is given by G_2 at the temperature T and by G_2+dG_2 at the temperature $T+dT$. If the pressure remains constant all along, Eq. 86 is applicable, i.e.,

$$dG_1 = -S_1dT \quad \dots(106)$$

and $dG_2 = -S_2dT \quad \dots(107)$

where S_1 and S_2 are the entropies of the system in the initial and final states of the system, respectively.

Subtracting Eq. 106, from Eq. 107, we have

$$\begin{aligned} d(G_2 - G_1) &= -(S_2 - S_1) dT \\ d(\Delta G) &= -\Delta SdT \end{aligned} \quad \dots(108)$$

As the pressure is constant, therefore,

$$(\partial(\Delta G)/\partial T)_P = -\Delta S \quad \dots(109)$$

Also, since from Eq. 75, $-\Delta S = (\Delta G - \Delta H)/T$, hence, Eq. 109 becomes

$$(\Delta G - \Delta H)/T = (\partial(\Delta G)/\partial T)_P \quad \dots(110)$$

or $\Delta G = \Delta H + T(\partial(\Delta G)/\partial T)_P \quad \dots(111)$

591

This equation is known as the Gibbs-Helmholtz equation. It is applicable to all processes occurring at constant pressure. It has been used for calculating the enthalpy change ΔH for a process or a reaction provided the values of free energy changes at two different temperatures are known.

For a reaction at constant volume, the corresponding equation will be

$$\Delta A = \Delta U + T(\partial(\Delta A)/\partial T)_V \quad \dots(112)$$

Example 23. The free energy change (ΔG) accompanying a given process is -85.77 kJ at 25°C and -83.68 kJ at 35°C . Calculate the change in enthalpy (ΔH) for the process at 30°C

Solution : ΔG at $25^\circ\text{C} = -85.77 \text{ kJ}$ and at $35^\circ\text{C} = -83.68 \text{ kJ}$

$$\therefore \left(\frac{\partial(\Delta G)}{\partial T} \right)_P = \frac{-83.68 \text{ kJ} - (-85.77 \text{ kJ})}{308 \text{ K} - 298 \text{ K}} = 0.209 \text{ kJ K}^{-1}$$

ΔG at 30°C may be taken as the average of the values at 25°C and 35°C ,

$$\therefore \Delta G \text{ at } 30^\circ\text{C} = -\left(\frac{85.77 \text{ kJ} + 83.68 \text{ kJ}}{2} \right) = -84.725 \text{ kJ}$$

$$-84.725 \text{ kJ} = \Delta H + (303 \text{ K}) (0.209 \text{ kJ K}^{-1}).$$

Hence, $\Delta H = -148.05 \text{ kJ}$

Application of Gibbs-Helmholtz Equation/Relation between emf and Gibbs energy

Applications of G-H Equation /

Calculation of EMF of a reversible cell /

Relation b/w EMF & free energy .

When a cell produces a current,

The current can be used to do work to run a

motor. TD principles can be employed to

derive a relation b/w electrical energy and the
max. amount of work, w_{max} obtainable from
the cell.

$$\therefore w_{max} = nFE$$

n - No. of moles of e^- 's transferred

F - Faraday (96500 coulombs)

E - emf of the cell.

We know

Net electrical work - (nFE) \downarrow see in Free Energy.

$$\therefore -\Delta G = nFE \quad (\text{OK})$$

$$\Delta G = -nFE$$

According to G-H eqn, the free energy of a system @ const P is given by

$$-\Delta G = -\Delta H - T \left(\frac{\partial \Delta G}{\partial T} \right)_P$$

$$\therefore nFE = -\Delta H - T \left(\frac{\partial (-nFE)}{\partial T} \right)_P$$

$$nFE = -\Delta H + nFT \left(\frac{\partial E}{\partial T} \right)_P$$

$$E = \frac{-\Delta H}{nF} + T \left(\frac{\partial E}{\partial T} \right)_P$$

Thus

By knowing E (emf) and $\left(\frac{\partial E}{\partial T} \right)_P$, the value of heat of reaction (ΔH)

occurring in the cell can be calculated.

\therefore

$\left(\frac{\partial E}{\partial T} \right)_P$ determines whether the electrical energy would be equal to, more or less than the heat of the reaction.

CASE-I : When the temp. coefficient is 0

$$\left(\frac{\partial E}{\partial T} \right)_P = 0 \text{ then}$$

$$E = \frac{-\Delta H}{nF} \text{ or } nFE = -\Delta H$$

CASE - 2 When the temp coefficient is +ve

$$\left(\frac{\partial E}{\partial T}\right)_P > 0 \text{ then}$$

$nFE > -\Delta H$ ∵ The additional energy will come either from the surroundings or the temp of the cell would fall.

CASE - 3 When the temp coeff is -ve

$$\left(\frac{\partial E}{\partial T}\right)_P < 0$$

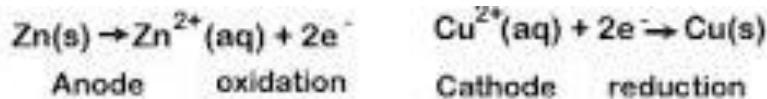
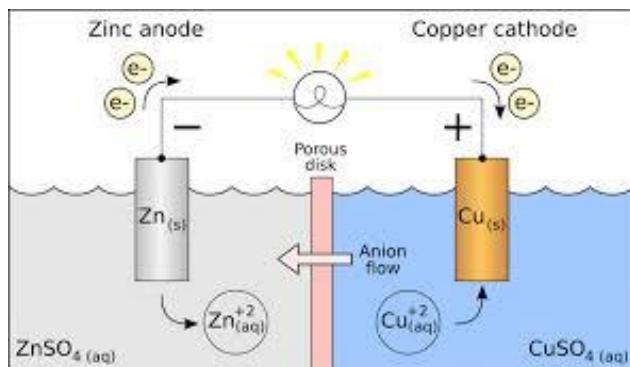
$nFE < -\Delta H$ ∵ The excess energy will be given either to the surroundings or the temp of the cell would rise.

Free energy and EMF of cell (electrochemical cell, galvanic cell, cell representation, cell potential and free energy, Nernst equation and applications)

Electrochemical cell: An **electrochemical cell** is a device capable of either generating electrical energy from chemical reactions or using electrical energy to cause chemical reactions. The electrochemical cells which generate an electric current are called voltaic cells or galvanic cells and those that generate chemical reactions, via electrolysis for example, are called electrolytic cells. A common example of a galvanic cell is a standard 1.5 volt cell meant for consumer use.

An electrolytic is an electrochemical cell that drives a non-spontaneous redox reaction through the application of electrical energy. They are often used to decompose chemical compounds, in a process called electrolysis—the Greek word lysis means *to break up*.

Example: Daniel Cell

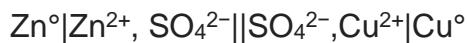


Cell notation or line notation in chemistry is a shorthand way of expressing a certain reaction in an electrochemical cell. The cell anode and cathode (half-cells) are separated by two bars or slashes representing a salt bridge, with the anode on the left and cathode on the right. Individual solid, liquid or aqueous phases within each half-cell are separated by a single bar. Concentrations of dissolved species, in each phase written in parentheses and the state of each phase (usually s (solid), l (liquid), g (gas) or aq. (aqueous solution)) is included in a subscript after the species name.

Some examples of this notation are:



This means that the left electrode (anode) is made of zinc, while the other one (right, cathode) is composed of a silver wire covered by a silver chloride layer which is not soluble. Both of the electrodes are immersed into aqueous media where zinc and chloride ions are present.



This cell is very famous: the Daniell cell. If the electrodes are connected, a spontaneous reaction takes place. Zinc is oxidized, and copper ions are reduced.

Sometimes the state of each species into the cell is written. For example, in the zinc cell (shown above), we can write that zinc, silver and silver chloride are solids, while zinc cation and chloride anion are in aqueous medium. So, the new notation will be:



It is possible to express the ion concentration too. For example, in the Galvanic cell:



In this case, all ions (sulfate, zinc and copper) are in a concentration equal to 1 mol/L.

Nernst equation and applications: (derivation, acid-base titration, redox

titration,

solubility

product)

Date

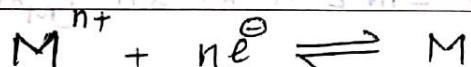
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Nernst Equation +

We know experimentally that the potential of a single electrode or half cell varies with conc. of ions in the cell. In 1889, Walter Nernst derived a mathematical relationship which enable us to calculate the half cell potential or single electrode potential E , from the std electrode potential E° and the temp of the cell.

This relationship is known as Nernst eqn.

Consider the following redox reaction.



For such a redox reaction, the free energy change (ΔG) and its equilibrium const (k) are interrelated as

$$\Delta G = -RT \ln k + RT \ln \frac{[P_{dt}]}{[E_{React}]}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[P_{dt}]}{[E_{React}]} \quad \text{--- (1)}$$

ΔG° = Standard free energy change.

Eqn (1) is known as Van't Hoff Isotherm.

The decrease in free energy of the above reaction will produce electrical energy.

If the reaction involves transfer of 'n' number

of e^- s, then 'n' faraday of electricity will flow.

If E is the emf of the cell, then the total electrical energy (nFE) produced in the cell is

$$\downarrow \text{se in FEC} \quad -\Delta G = nFE \quad (\text{OR})$$

$$\downarrow \text{se in STD} \quad -\Delta G^\circ = nFE^\circ$$

Comparing Eqn ① & ②

$$-nFE = -nFE^\circ + RT \ln \frac{[M]}{[M^{n+}]} \quad \rightarrow ③$$

$$\therefore -nF \quad E = E^\circ - \frac{RT}{nF} \ln \frac{[I]}{[M^{n+}]}$$

Activity of the solid metal $[M] = 1$

~~$$\text{In general} \quad E = E^\circ - \frac{RT}{nF} \ln \frac{[P_{dt}]}{[\text{React}]} \quad (\text{OR})$$~~

~~$$\text{for reduction} \quad E = E^\circ + \frac{RT}{nF} \ln [\text{React}] \quad \because [P_{dt}] = 1$$~~

$$E = E^\circ + \frac{RT}{nF} \ln [M^{n+}]$$

$$E = E^{\circ} + \frac{2.303 RT}{nF} \log [M^{n+}] \quad \text{Date } \boxed{\quad} \boxed{\quad} \boxed{\quad} \quad (4)$$

where

$$R = 8.314 \text{ J K/mole gas const}$$

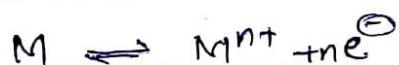
$$F = 96,500 \text{ Coulomb}$$

$$T = 298 \text{ K } (25^\circ\text{C})$$

By substituting the above values in eqn (4)

$$E = E_{\text{red}}^{\circ} + \frac{0.0591}{n} \log [M^{n+}] \quad (5)$$

E° for Oxidation Potential



$$E^{\circ}_{\text{Oxi}} = E_{\text{red}}^{\circ} - \frac{0.0591}{n} \log [M^{n+}] \quad (6)$$

Eqn (5) & (6) are known as Nernst Eqn for single electrode potential.

n = no. of e^- s transferred in the half-cell reaction

Nernst Eqn - Applications

- ① Used to calculate elec: potential of unknown metal
- ② Used to predict corrosion tendency of a metal
- ③ By using electrode potential, conc. of the soln in galvanic cell can be determined.
- ④ Conc. of the reactant "
- ⑤ pH of the soln

①

Measurement of Single Electrode Potential

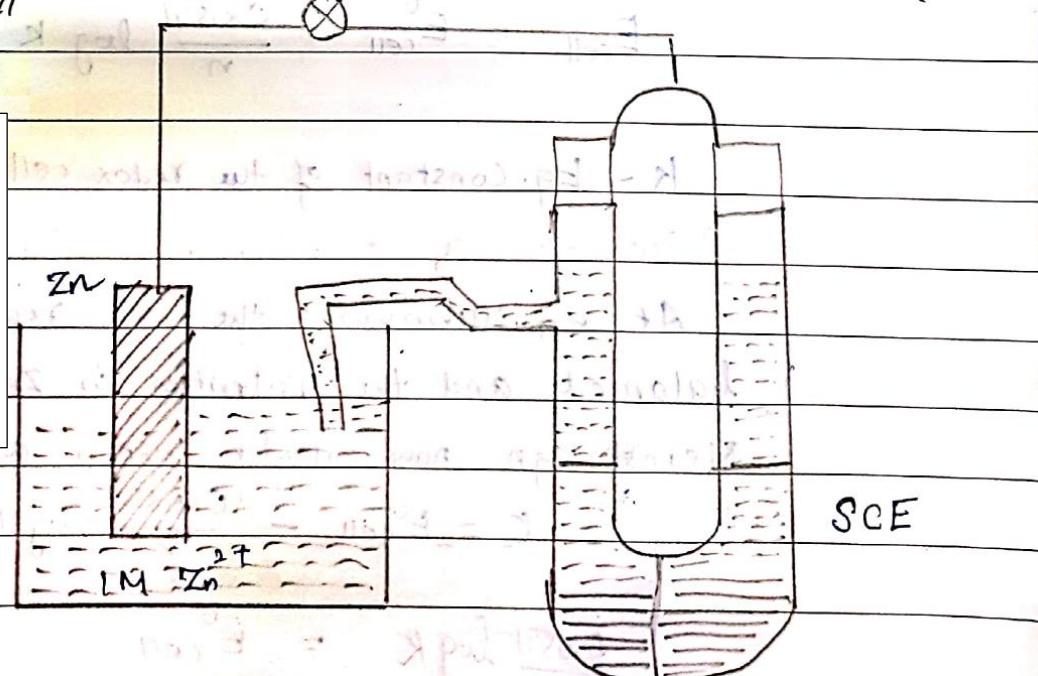
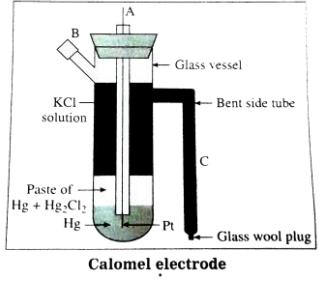
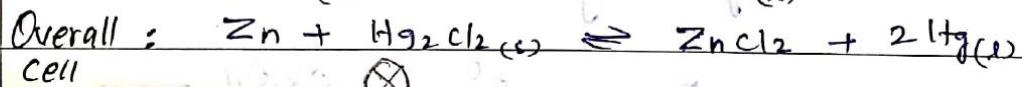
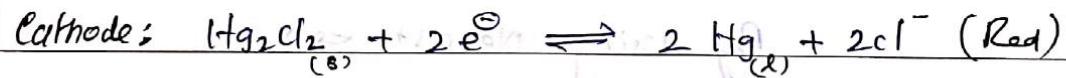
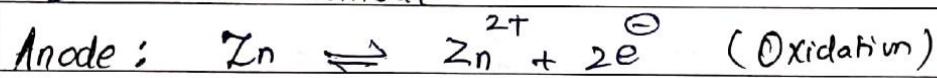
It is impossible to determine the absolute value of a SEP. But we can measure the potential diff b/w two electrodes, combining them to form a complete cell. For this purpose, Reference Electrode is used. Std. H₂ electrode is the commonly used ref. electrode, whose potential has been arbitrarily fixed as zero. The emf of the cell is measured and it is equal to the potential of electrode.

It is very difficult to set-up a H₂ electrode.

Hence, other electrode, called secondary ref. electrode like calomel electrodes are used.

⇒ Measurement of SEP. of Zn Using SCE

To measure the electrode potential of Zn, a cell is made by combining the SCE with Zn electrode. Here Zn electrode acts as Anode; SCE acts as cathode.



The emf of the above cell is measured and the electrode potential is calculated as follows

$$\begin{aligned} E_{\text{cell}} &= E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ} \\ &= E_{\text{cat}}^{\circ} - E_{\text{Zn}}^{\circ} \end{aligned}$$

$$\therefore E_{\text{Zn}}^{\circ} = E_{\text{cat}}^{\circ} - E_{\text{cell}}$$

$$= +0.2422 - 1.0025$$

$$\therefore E_{\text{Zn}}^{\circ} = -0.7603 \text{ Volt. The std. condns are}$$

(i) 1M solns of reactants & products (ii) Temp is 25°C

Calculation of cell potential

By using Nernst eqn

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log K$$

K - Eq. Constant of the redox cell reacn.

Calculation of Eq. constant for cell reacn

At equilibrium, the cell reacn is balanced and the potential is zero. The Nernst eqn now maybe written as

$$0 = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log K$$

$$\frac{0.0591}{n} \log K = E_{\text{cell}}^{\circ}$$

What makes you happy?

$$\therefore \log K_c = \frac{nE_{cell}^{\circ}}{0.0591}$$

Potentiometric Titration :

(i) Acid - Base

Indicator Electrode :

The electrode which responds to the conc. of the reactant or products is called.

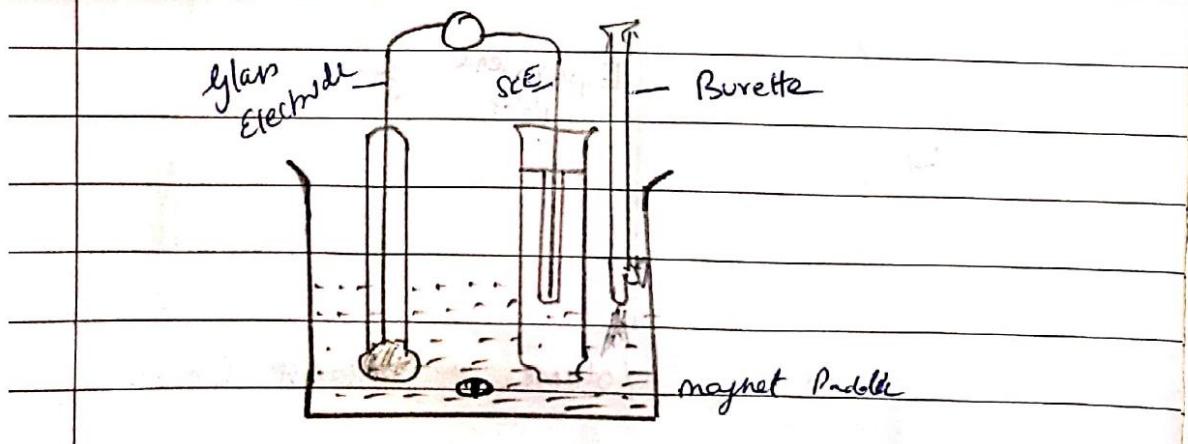
Eg.: Pt

Reference Electrode :

The electrode Potential of the electrode is already known, then this is called. Ref. Elec. (or) Std. Electrode

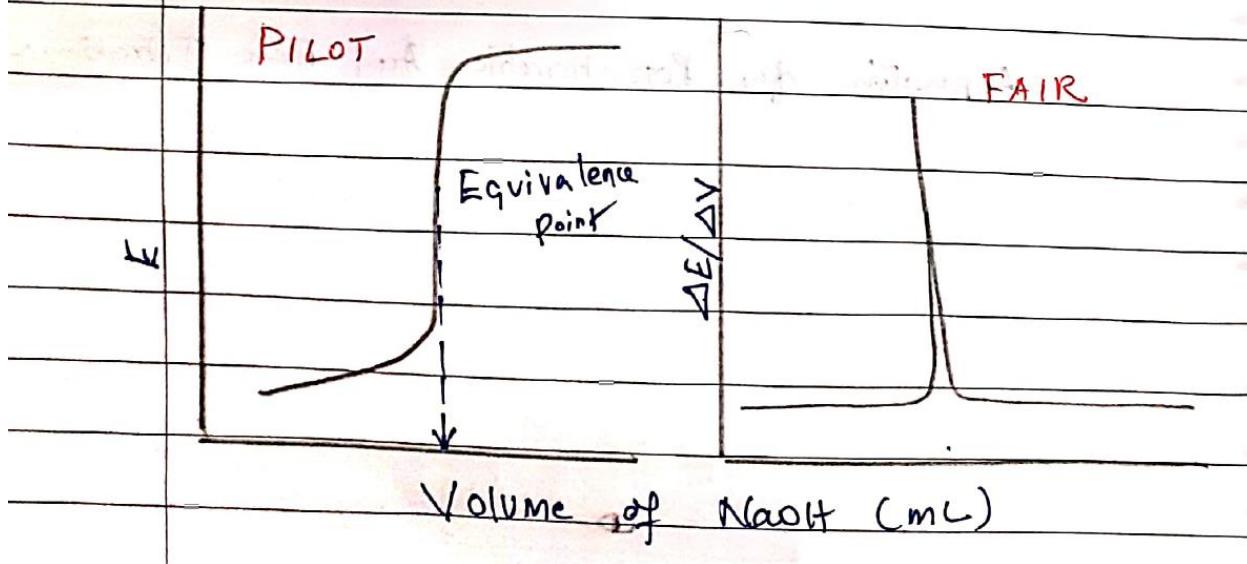
Eg.: H₂, Calomel (SCE)

Apparatus for Potentiometric Acid - Base Titration:-



A H_2 electrode or glass electrode (made up of cerium oxide...) is immersed in soln of the acid whose potential strength is to be determined. The glass electrode is coupled with SCE. The cell thus formed is connected to the potentiometer. When alkali ($NaOH$) is added, pH of the soln changes. The emf of the cell is also changes with pH of the soln.

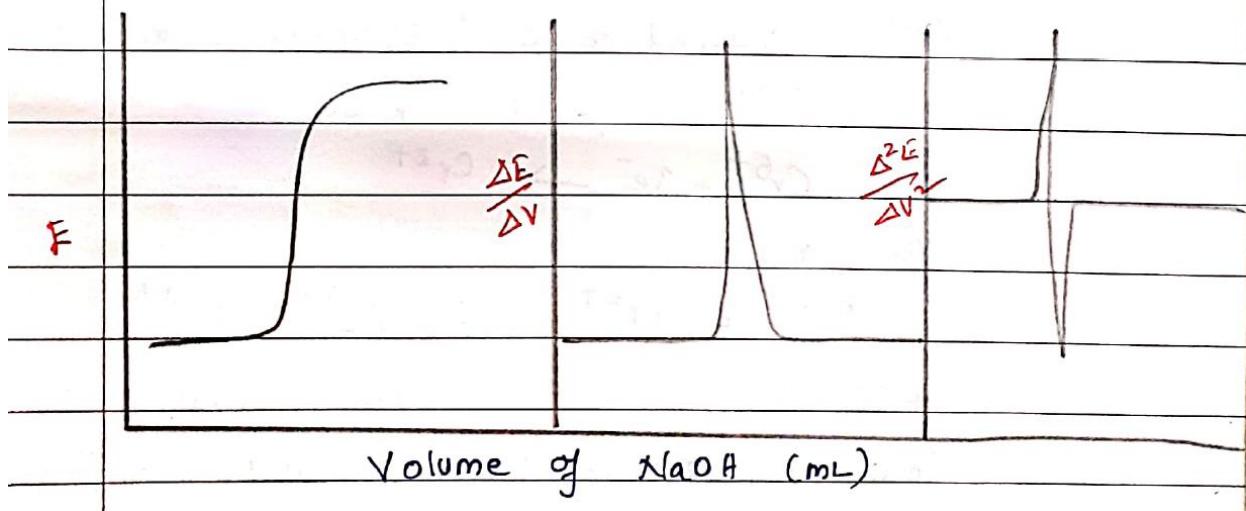
The std alkali soln is added from the burette in small interval. After each addition, the emf of the cell is recorded. The emf is then plotted against $NaOH$. The shape of the curve for the pilot titration is given below



The steepest portion of the curve indicates the equivalence point. However, when the solns are very dilute, or weak acid / bases, the steepness of the curve is less marked and it is difficult to judge the end pt. In such case, graph is drawn b/w $\Delta E/\Delta V$ and Volume of alkali. The max. of the curve is End pt.

★

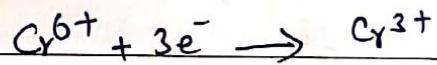
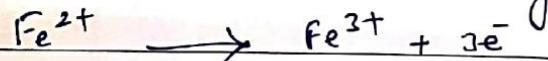
Suppose the cell is connected with pH meter. The following types of graph may obtained.



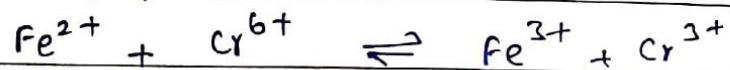
(2)

REDOX TITRATIONS

The titration of Fe^{2+} with $\text{K}_2\text{Cr}_2\text{O}_7$ is an example of redox reaction. A known volume of PAs with a little H_2SO_4 is taken in a beaker. Both the ref (SCE) and indicator (Pt) electrodes are immersed. The initial emf of the cell is noted. Then $\text{K}_2\text{Cr}_2\text{O}_7$ is added in a regular interval of 1.0 mL each time. While adding $\text{K}_2\text{Cr}_2\text{O}_7$, the Fe^{2+} present in the soln is oxidised to give Fe^{3+} ; at the same time Cr^{6+} is reduced to Cr^{3+} according to the following eqn



Overall reaction



According to Nernst's eqn, the potential of the indicator electrode @ the beginning of the titration depends on the ratio $\frac{\text{Fe}^{2+}}{\text{Fe}^{2+}} \cdot \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$

$$E = E^0 + \frac{0.0591}{n} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

At the end pt, where there are no more Fe^{2+} in the soln, since Fe^{2+} is converted to Fe^{3+} by Cr^{6+} , the potential of electrode solely depends upon Cr^{6+} & Cr^{3+} and the Nernst eqn ~~become~~^{be} will

$$E = E^\circ + \frac{0.0591}{n} \log \frac{[\text{Cr}^{6+}]}{[\text{Cr}^{3+}]}$$

So a sharp and appreciable jump of potential is observed @ the equivalence point, when the emf is plotted against the volume of keroz.

Potentiometric titrations of this type are particularly useful for colored solns in which an indicator can not be employed.

Determination of K_{sp}

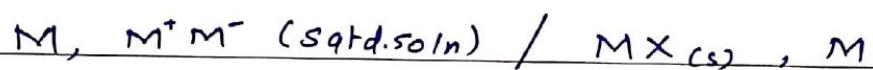
The solubility product of a sparingly soluble salt is a kind of equilibrium constant. Consider the salt MX is eq. with ions in a saturated soln.



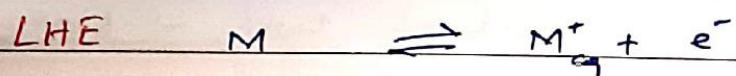
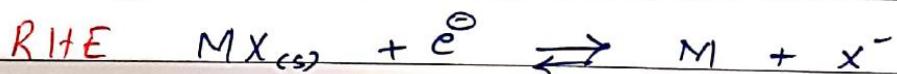
The solubility pdt of the salt is given by

$$K_{sp} = a_{M^+} \times a_{X^-} \quad (\text{or}) \quad [M^+] [X^-]$$

The cell reaction is



The half cell reactions are



$$E^\circ = E_R^\circ - E_L^\circ$$

We know

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

$$-\Delta G^\circ = 2.303 RT \log K_{sp}$$

$$\therefore \log K_{sp} = \frac{nFE^\circ}{2.303RT}$$

Corrosion: (Definition, types and mechanism for -dry, wet, hydrogen evolution and oxygen absorption)

What is Corrosion?

- Corrosion is defined as the **destructive and unintentional degradation** of a material **caused by its environment** which results in **deterioration of its properties**.
- This can be a **weakening of the material** due to a loss of cross-sectional area, it can be the **shattering of a metal** due to **hydrogen embrittlement**, or it can be the **cracking of a polymer** due to sunlight exposure.



- A **common type** of corrosion is **rust**, which is found on iron and steel structures. In this type of corrosion, the iron is reacting with oxygen to form **iron oxide** compounds.

- The **oxygen** can come **from air or water**. Iron oxide is actually more stable than pure iron or steel and therefore rusting is very common.

Cause of corrosion

- Metals corrode because we use them in environments where they are **chemically unstable**.
- Only **copper** and the precious metals (**gold, silver, platinum**, etc.) are found in nature in their **metallic state**.
- All **other metals, to include iron**-the metal most commonly used-are processed from minerals or ores into metals which are **inherently unstable in their environments**.
- This golden statue in Bangkok, Thailand, is made of the only metal which is thermodynamically stable in room temperature air.
- All other metals are unstable and have a tendency to revert to their more stable mineral forms.
- Some metals form protective ceramic films (passive films) on their surfaces and these prevent, or slow down, their corrosion process.
- We can prevent corrosion by using metals that form naturally protective passive films, but these alloys are usually expensive.
- Unfortunately for metals almost all environments can cause corrosion to some degree, since the corroded state is the more stable state.



- Prevention of rust is actually a means of retaining a less stable, or higher energy, state.

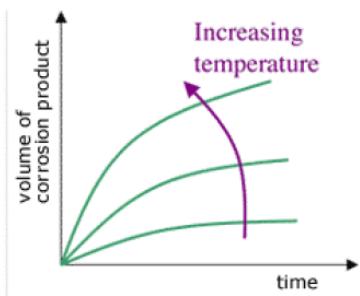
Types of corrosion

- **Dry corrosion**/direct chemical corrosion/ Atmospheric corrosion
 - Metals react with **gaseous** environment
 - (a) Corrosion due to O₂
 - (b) Corrosion due to other gases

- **Wet corrosion**/ electrochemical corrosion/ Immersed corrosion
 - Metals react with **aqueous** environment
 - (a) Evolution of H₂ type corrosion
 - (b) Absorption of O₂ type corrosion
 - (c) Bimetallic/galvanic corrosion

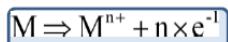
Dry corrosion

- Dry corrosion or oxidation occurs when **oxygen** in the air **reacts** with metal **without the presence of a liquid**.
- Typically, **dry corrosion is not as detrimental as wet corrosion**, but it is very **sensitive to temperature**. If you hold a piece of clean iron in a flame, you will soon see the formation of an oxide layer!
- **Most** engineering metals have a **slow oxidation rate** in the atmosphere **at ambient temperature**.
- **Thickness** of oxide film formed at a given temperature will **vary linearly with time**.
- Oxidation will continue till complete cross section of metal will be oxidized.
- Oxidation occurs much more **rapidly as temperature increases** because the **mobility of ions within the oxide layer increases**.



Dry Corrosion (cont.)

- The basic reaction involved in dry corrosion is:



where M is a metal element.

- The metal loses electrons to form an ion and some free electrons.
- The ionic metal can then **react with oxygen to form a metal oxide**.
- In **dry corrosion**, the **oxygen comes from the air**, in **wet corrosion**, the oxygen is supplied by **aerated water**.

Nature of Metal oxide layer :

(1) **Stable (Non porous, protective)** : It **acts as a barrier between metal and O₂**, So prevents further corrosion. e.g. aluminum (Al), tungsten (W) and molybdenum (Mo), chromium (Cr)

(2) **Porous (Non protective)** : Corrosion occur through pores and **continues till entire metal gets corroded**. e.g. alkali and alkaline earth metals.

(3) **Unstable**: It **decomposes back to metal and O₂**. Ag, Au, Pt are protected by this manner.

(4) **Volatile**: Layer **volatiles** and metal exposed for further corrosion. e.g. stannic chloride on tin is volatile

Pilling Bedworth Rule

- It determines the **protective or non-protective** nature of the oxide layer
- The **ratio of the volume** of the oxide formed to the volume of the metal consumed is called Pilling-Bedworth rule.
- Mathematical expression:

$$\text{Ratio, } R = (M/D) \times (d/m)$$

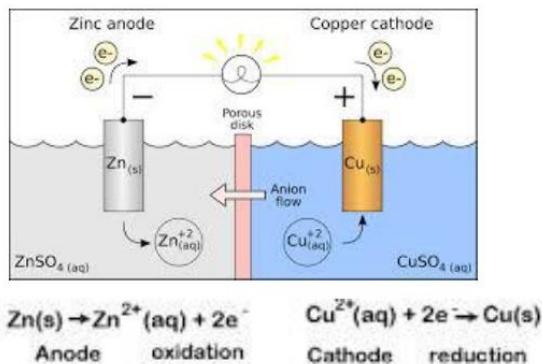
M, D = molecular weight and density of the metal oxide

m, d = atomic weight and density of metal

- If the volume of oxide layer formed is **equal or greater** than the volume of the metal, the oxide layer is protective. However if the oxide layer formed has volume **lesser** than that of the metal, then the oxide layer is non-protective.
- e.g. R (Ca) = 0.64, hence oxide layer is non protective.

R (Al, Fe, Ni, Zn) > 1, hence oxide layer is protective.

Electrochemical cell



Electrochemical series

Corroded end (anodic)	Magnesium Zinc Aluminium 2017 Steel or iron Cast iron Lead-tin solders Lead Tin Brass Copper Bronzes
Protected end (cathodic)	Silver Gold

- Zn and Cu are connected to each other then Zn having lower reduction potential i.e. **-0.76V** acts as anode and is corroded while **Cu** with more reduction potential i.e **0.34V** acts as cathode and remains protected.

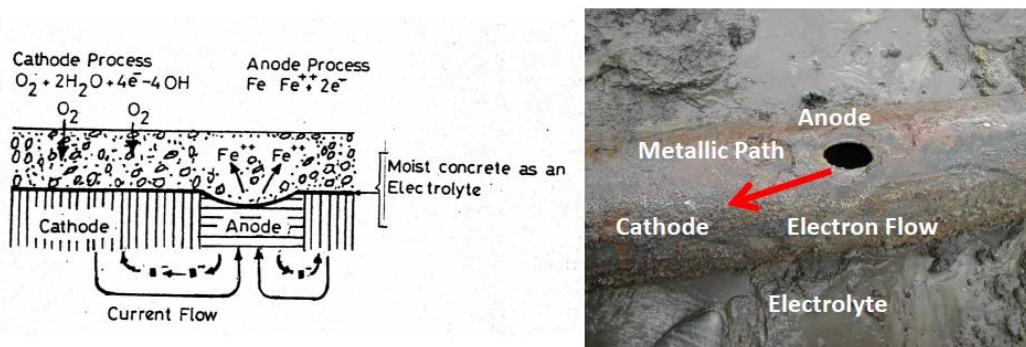
WET CORROSION/ ELECTROCHEMICAL CORROSION

- This type of corrosion occurs when a **electrochemical cell** is set up.

Essential requirements of electrochemical corrosion:

- Anode** (location where corrosion takes place)
Oxidation Half-Reaction
- Cathode** (no corrosion)
Reduction Half-Reaction
- Electrolyte** (Soil, Water, Moisture, etc.)
- Electrical Connection** between anode and cathode (wire, metal wall, etc.)

WET CORROSION/ ELECTROCHEMICAL CORROSION



- One part behaves as **anode and undergoes oxidation** and other part acts as **cathode and undergoes reduction**
- Liquid medium involved acts as **electrolyte**.

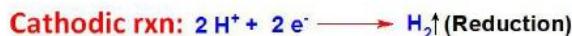
Electrochemical corrosion can be stopped by eliminating any one of the 4 components

Cathodic rxn.: Consumes electrons with either by

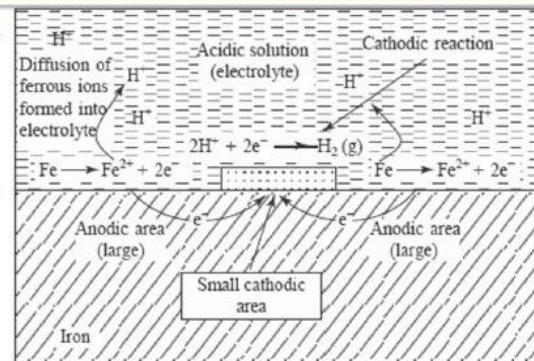
- (a) Evolution of hydrogen
- (b) Absorption of oxygen

(a) Evolution of hydrogen

- Occurs usually in acidic environment
- Eg. IRON

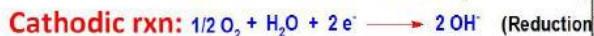


Mechanism of wet corrosion by H₂ evolution

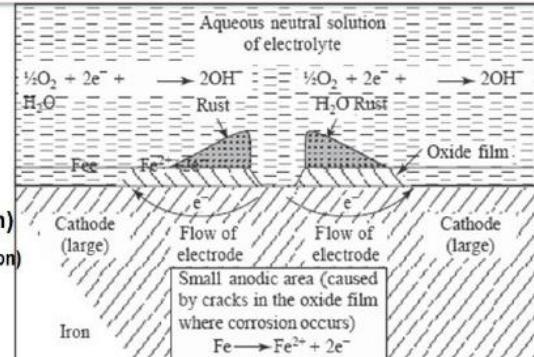


(b) Absorption of O₂

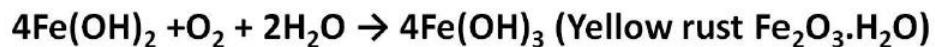
- Rusting of Fe in neutral aq. soln of electrolytes (like NaCl soln.) in the presence of atm. O₂



Mechanism of wet corrosion by O₂ absorption



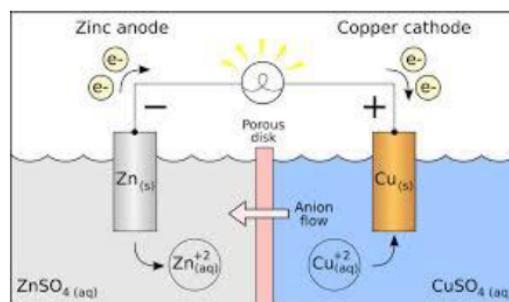
- (a) If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide.



- (b) If the supply of oxygen is limited, the corrosion product may be even black anhydrous magnetite, Fe₃O₄.

(C) Galvanic Corrosion

- A **common type** of corrosion is known as galvanic corrosion.
 - *This type of corrosion occurs when two dis-similar metals are connected to each other in the presence of an electrolyte.*
 - This constitutes a galvanic cell in which **a metal with lower reduction potential undergoes corrosion**.
 - e.g. when Zn and Cu are connected to each other then Zn having lower reduction potential i.e. -0.76V acts as anode and is corroded while Cu with more reduction potential i.e 0.34V acts as cathode and remains protected.
 - Galvanic corrosion occurs when two different metals are connected in an electrolyte and **one metal corrodes in protection of the other**.
 - One metal is corroding in the same manner as we saw in wet corrosion ($M \rightarrow Mn^{++} ne^-$) while the other metal is reacting ($Mn^{++} ne^- \rightarrow M$).
 - From these two reactions we can see that the **anodic electrode corrodes** and the **cathodic electrode is protected**. The corroded metal is called the **sacrificial anode**.
-
- Galvanic corrosion can cause **unwanted accelerated corrosion** when it is not considered during design or construction, however it can also be used to advantage.
 - When considering **which metal will corrode** we can look at the galvanic series. Metals **closer** to one another generally do not have a strong effect on each other, but the **further** apart two metals are, the stronger the corroding effect on the one higher in the list.
 - Anodes and cathodes arise in many ways. As well as connection between two different metals, a plain metal surface can have anodic and cathodic areas.
 - e.g. 1) Grain boundaries can be anodic with respect to grain interiors.
2) Cold worked regions are anodic to regions not cold worked.



Chemical/Dry corrosion	Electrochemical/Wet corrosion
<ul style="list-style-type: none"> It occurs in the dry state 	<ul style="list-style-type: none"> It occurs in the presence of moisture or electrolyte
<ul style="list-style-type: none"> It involves the direct chemical attack by the environment 	<ul style="list-style-type: none"> It involves the setting up of a huge number of tiny galvanic cells
<ul style="list-style-type: none"> It follows adsorption mechanism 	<ul style="list-style-type: none"> It follows mechanism of electrochemical reactions
<ul style="list-style-type: none"> Even a homogeneous metal surface is corroded 	<ul style="list-style-type: none"> Only heterogeneous metal surface or homogeneous metal surface with bimetallic contact is an important condition for this type of corrosion
<ul style="list-style-type: none"> Corrosion products accumulate in the same spot where corrosion occurs 	<ul style="list-style-type: none"> Corrosion occurs at the anode, where products gather at the cathode
<ul style="list-style-type: none"> Uniform corrosion takes place 	<ul style="list-style-type: none"> Pitting is more frequent, especially when anodic area is small.

Corrosion (Pourbaix diagram for iron)

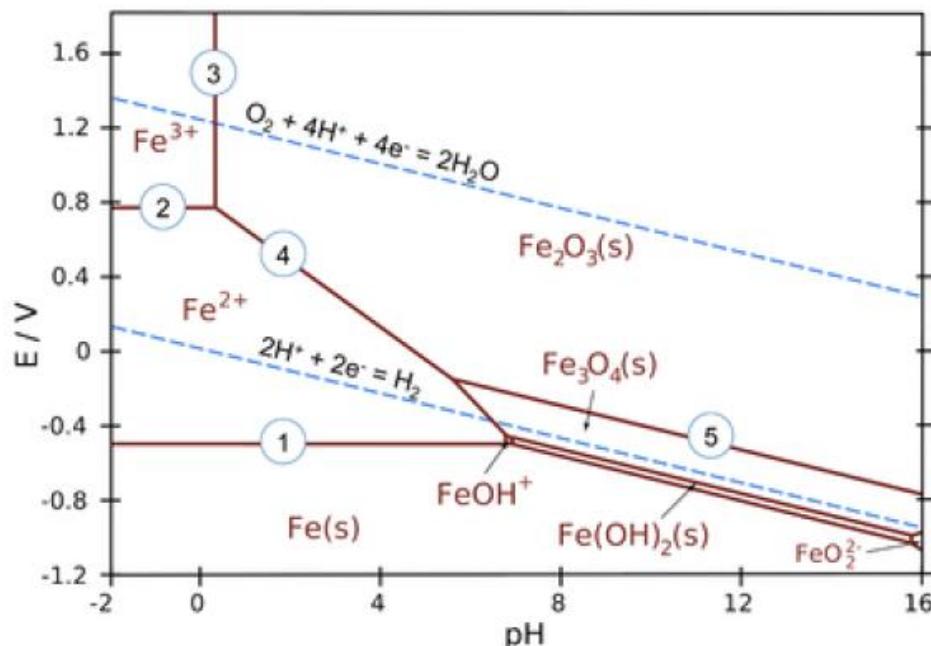
Pourbaix Diagram

What does Pourbaix Diagram mean?

- A Pourbaix diagram provides information about the **stability** of a metal as a function of **pH** and **potential**.
- These diagrams are available for over **70 different metals**.
- Pourbaix diagrams have several uses, including in **corrosion** studies.
- A Pourbaix diagram is also known as a potential/pH diagram, equilibrium diagram, EH-pH diagram, a pE/pH diagram on an E-pH diagram.
- Pourbaix diagrams are **plotted by using the Nernst equation** (an equation used to calculate electrode potential).

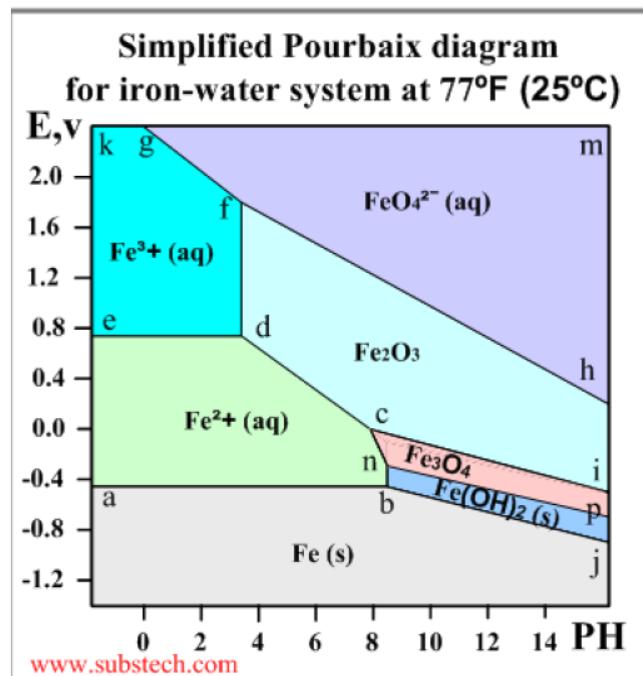
- As the Nernst equation is derived entirely from **thermodynamics**, the Pourbaix diagram can be used to determine which species (metals or alloys) is thermodynamically stable at a given electrode potential (E) and pH.
- Nernst equation: $E = E_0 - (0.059/n) \times \ln (C_{ion})$
- Where: E = electrode potential V; E_0 = standard electrode potential, V; n = number of electrons transferred; C_{ion} = molar activity (concentration) of ions

Pourbaix diagram for iron at ionic concentrations of 1.0 mM



- | | |
|--|---|
| 1) $Fe^{2+} + 2e^- \rightarrow Fe_{(s)}$ | (pure redox reaction - no pH dependence) |
| 2) $Fe^{3+} + e^- \rightarrow Fe^{2+}$ | (pure redox reaction - no pH dependence) |
| 3) $2 Fe^{3+} + 3 H_2O \rightarrow Fe_2O_{3(s)} + 6H^+$ | (pure acid-base, no redox) |
| 4) $2 Fe^{2+} + 3 H_2O \rightarrow Fe_2O_{3(s)} + 6H^+ + 2e^-$ | (slope = $-59.2 \times 6/2 = -178 \text{ mV/pH}$) |
| 5) $2 Fe_3O_{4(s)} + H_2O \rightarrow 3Fe_2O_{3(s)} + 2H^+ + 2e^-$ | (slope = $-59.2 \times 2/2 = -59.2 \text{ mV/pH}$) |

The diagram defines the following zones of the equilibrium states:



below the line a-b-j: Solid iron (**immunity zone**). The electrochemical reactions in this zone proceed in the direction of reduction of iron ions. No corrosion occurs in this zone.

a-b-n-c-d-e: Aqueous solution of ion Fe^{2+} (**corrosion zone**). Metallic iron oxidizes in this zone.

e-d-f-g-k: Aqueous solution of ion Fe^{3+} (**corrosion zone**). Metallic iron oxidizes (corrodes) in this zone.

h-f-g-m: Aqueous solution of ion FeO_4^{2-} (**corrosion zone**).

c-d-f-h-i: Solid ferrous oxide Fe_2O_3 (**passivation zone**). Iron oxidizes (corrodes) in this zone however the resulted oxide film depresses the oxidation process causing passivation (corrosion protection of the metal due to formation of a film of a solid product of the oxidation reaction).

n-c-i-p: Solid oxide Fe_3O_4 ($\text{Fe}_2\text{O}_3 \cdot \text{FeO}$) (**passivation zone**). The oxide film causes passivation.

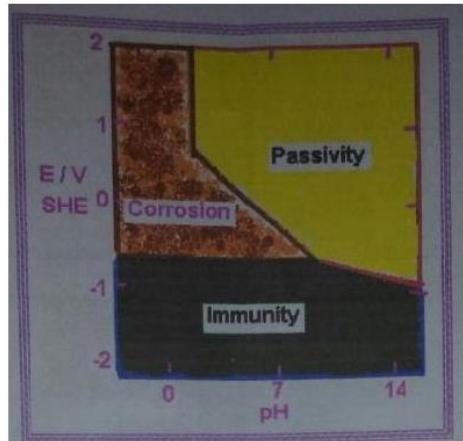
b-n-p-j: Solid hydroxide (II) $\text{Fe}(\text{OH})_2$ / $\text{FeO} \cdot \text{nH}_2\text{O}$ / green rust (**passivation zone**).

Characteristics of Pourbaix diagram:

- **Horizontal lines** represent electron transfer reactions. They are pH-independent, but potential-dependent.
- **Vertical lines** are potential-independent but pH-dependent and not accompanied by any electron transfer.
- **Sloping, straight lines** give the redox potentials of a solution in equilibrium. This equilibrium indicates electron transfer as well as pH.
- The diagram is computed for the equilibrium conditions at 77°F (25°C).

Objectives of the Pourbaix diagrams:

- To show the **directions of the various reactions** at given pH and potential
- To make a basis for **estimation of the corrosion product** compositions at various pH and potential combinations
- To show which environmental pH and potential changes will reduce or prevent corrosion



Pourbaix diagrams provide information on three states of metals:

- **Corrosion:** active state
- **Passivity:** forming passive layers inhibiting the corrosion process on the surface of the metal
- **Immunity:** thermodynamic stability

Limitations of Pourbaix diagram

- The validity of the diagrams is **limited to reactions** between pure metals, pure water and the species that can be formed from these.
- Small amounts of **impurities** and alloying elements may change the diagram.
- These diagrams are purely based on thermodynamic data and do not provide any information on the reactions and not possible to measure the **corrosion rates**.
- Consideration is given only to equilibrium conditions in specified environment, and factors such as temperature and velocity are not considered, which may seriously affect the corrosion rate.

MCQ

1. If an alloy of Au and Zn is immersed in HCl, which among the following will be feasible?

- H₂ evolution
- Zn dissolution
- Formation of nanoporous Au
- All of the above

2. Which of the following statements is not true for Pourbaix diagram?

- It represents the stability of a metal as a function of potential and pH

- (b)The horizontal lines represent electron transfer reactions and are pH independent
- (c)The vertical lines are potential independent
- (d)It considers both thermodynamic and kinetic parameters

3. Which of the following reactions is only pH dependent?

- (a) $\text{Al}^{3+} + 3\text{e}^- = \text{Al}$
- (b) $\text{Zn} + 2\text{H}_2\text{O} = \text{Zn}(\text{OH})_2 + 2\text{H}^+ + 2\text{e}^-$
- (c) $\text{Zn}^{2+} + 2\text{H}_2\text{O} = \text{Zn}(\text{OH})_2 + 2\text{H}^+$
- (c) $\text{H}_2\text{CO}_3 = \text{H}_2\text{O} + \text{CO}_2$

4. Dry corrosion is also called as _____

- a) Chemical corrosion
- b) Electrochemical corrosion
- c) Wet corrosion
- d) Oxidation corrosion

5. Anhydrous inorganic liquid metal surface in absence of moisture undergoes _____

- a) Wet corrosion
- b) Dry corrosion
- c) Galvanic corrosion
- d) Pitting corrosion

6. The rusting iron is the _____

- a) Oxidation corrosion
- b) Liquid metal corrosion
- c) Wet corrosion
- d) Corrosion by other gases

7. Corrosion between the dissimilar metals is called as _____

- a) Galvanic corrosion
- b) Dry corrosion
- c) Oxidation corrosion
- d) Concentration cell corrosion

8. Wet corrosion is also called as _____

- a) Chemical cell
- b) Electro chemical cell
- c) Oxidation reaction
- d) Liquid metal corrosion

9. Corrosion due to the formation of cavities around the metal is called as the _____

- a) Pitting corrosion
- b) Soil corrosion
- c) Water line corrosion
- d) Galvanic corrosion

10. Corrosion due to the flow of the _____ between the cathodic and anodic areas is called as the electro chemical corrosion by evolution of hydrogen ad absorption of oxygen.
- a) Electron current
 - b) Proton current
 - c) Ion current
 - d) Neutron current
11. Corrosion due to difference in water level is _____
- a) Soil corrosion
 - b) Oxidation corrosion
 - c) Pitting corrosion
 - d) Water line corrosion
12. Corrosion is uniform in _____
- a) Dry corrosion
 - b) Wet corrosion
 - c) Pitting corrosion
 - d) Water line corrosion
13. Dry corrosion takes place in _____
- a) Homogeneous solutions
 - b) Heterogeneous solutions
 - c) Neither homogeneous nor heterogeneous
 - d) Both homogeneous and heterogeneous solutions
14. Concentration cell corrosion occurs when a metallic surface is partially immersed in an electrolyte and partially exposed to air.
- a) True
 - b) False
15. Poorly oxygenated part becomes cathode whereas well oxygenated part becomes anode in the differential aeration corrosion.
- a) True
 - b) False