Department of Chemistry, BIT, Mesra
CH101R1: Chemistry

Module V: Phase and Chemical equilibrium **[8 Lectures]**
Phase rule: terms involved, Phase diagram of one component (Water) & two component (Pb/Ag) system & their applications; Gibbs Free energy, Van't Hoff equation and Chemical Equilibrium; Nernst Equation, Standard electrode potential, EMF measurement and its application, Batteries and Fuel Cells.

Phase Rule

The phase rule is a generalization given by Williard Gibbs (1876) which seeks to explain the equilibria existing in heterogeneous systems. It is well known that, in homogeneous systems the reactants and the products are in same or one phase, while in heterogeneous systems the reactants and the products are in different or two phase. With the application of phase rule it is possible to predict qualitatively by means of a diagram the effect of changing pressure, temperature and concentration on a heterogeneous system in equilibrium. Before starting the rule the involved terms like phase, component and degree of freedom need to be explained.

Terms involved

Phase is defined as any homogenous and uniform in composition, physical distinct portions of matter, which is mechanically separated from other such parts of the system by definite boundary surfaces. Following are the examples;

- Water consists of three phases

Ice (S) ↔ Water (L) ↔ Water vapour (g)

- A pure substance (solid, liquid or gas) made of one chemical species , is considered as one phase. Thus oxygen(O_2), benzene(C_6H_6) and ice (H_2O) are all one-phase system.
- A gaseous mixture, miscible in all proportions, will constitute only one phase, e.g., mixture of hydrogen and oxygen or air etc.
- The two immiscible liquids (benzene and water) will form two liquid phases.
- The two miscible liquids (i.e. alcohol and water) will form one separate phase.
- A solution of a substance in a solvent consists of one phase only e.g.: Sugar solution in water.
- A heterogeneous mixture like

$$CaCO_3\,(S) \rightarrow CaO(S) + CO_2\,(g)$$

Consists of three phases (i.e. two solids and one gaseous).

- Mixture of solids: Sulphur is a mixture of rhombic and monoclinc sulphur. These allotropes of sulphur consists of same chemical species but differ in physical properties. Thus a mixture of two allotropes is a two-phase system.

Component is defined as the smallest number of independent variable constituents, in terms of which the composition of each phase can be expressed in the form of chemical equation. The concept of component can be explained with the help of following examples;

- In the water system, the chemical composition of all the three phases is H_2O. Hence, it is one component system.

Ice (S) ↔ Water (L) ↔ Water vapour (g)

- A solution of a salt in a solvent consists of two component system, e.g, NaCl in water.
- A saturated solution of NaCl consists of solid NaCl, NaCl solution, and water vapour. The chemical composition of all the three phases is NaCl & H2O. Hence, it is a two component system.
- Consider the thermal decomposition of MgCO3 in closed vessel

$$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g).$$

There are three phase and two component system (two solid and one gases) but two components, since any two of the three substances are sufficient to express the composition of each of three phases. For example if we choose CO2 and MgO as two component, then;
The composition of MgO phase can be expressed as nMgO

The composition of CO2 phase can be expressed as nCO2
The composition of MgCO3 can be expressed as xMgO+xCO2
Similarly, if we choose MgO and MgCO3 as two component, then;
The composition of MgO phase can be expressed as nMgO
The composition of CO2 phase can be expressed as nMgCO3+nCO2
The composition of MgCO3 can be expressed as xMgCO3

- Suppose a solid dissociate into number of gaseous substances in a closed vessel, e.g.,

$$NH_4Cl(s) \rightleftharpoons NH_4Cl(g) \rightleftharpoons NH_3(g) + HCl(g)$$

The overall composition of the dissociate vapor (NH3, HCl) is exactly the same with the udissociate substances (NH4Cl). Thus the number of component is one with three phases. However, if NH3 or HCl is introduced into the system then it should be a two component system, i.e., NH4Cl and the excess NH3 or HCl.

NH_4Cl (s) ⇔ NH_3 (g) + HCl (g)
$[NH_3] = [HCl]$
Keq = $[NH_3]$ [HCl] / $[NH_4Cl]$ = $[NH_3]$ [HCl]
[Because the active mass of NH_4Cl (s) is constant]
Now, the number of components = No. of constituents – no. of equation relating to concentration of constituents = 3(NH_4Cl, NH_3, HCl) – 2
= 1 i.e, it is a single component system.

When NH_4Cl is heated in a closed vessel along with NH_3 or HCl then :
$[NH_3] \neq [HCl]$
Keq = $[NH_3]$ [HCl]
Therefore, only one equation relates the concentration of constituents

Hence, no. of components (C) = 3 – 1 = 2
Therefore it is a two component system.

- The sulphur system consists of four phases, rhombic, monoclinic, liquid and vapour, the chemical composition of all the phases is 'S'. Hence, it is also one component system.

Degree of freedom is defined as the minimum number of independently variable factors, such as pressure temperature and composition (concentration or volume), which can completely define the equilibrium of a system. The least number of variable factors (concentration, pressure & temperature) which must be specified so that the remaining variables are fixed automatically and the system is completely defined.

- A system with F=0, is known as nonvariant or having no degree of freedom.
- A system with F=1, is known as univariant (having one degree of freedom)
- A system with F=2, is known as bivariant (having 2 degrees of freedom).

For examples;

- A system consisting of pure gas or gas mixture, is a one phase system. If the temperature and pressure are specified, then volume can be known. So, the degree of freedom for the system is two. For a gaseous mixture of N_2 and H_2, we must state both the temperature and pressure. Hence, the system is bivariant (degree of freedom is two).

- In the water system

Ice (S) ↔ Water (l)↔ Vapour (g)

Three phases will be in equilibrium only at particular temperature and pressure. If any of the variable, i.e., temp & pressure is altered, three phases will not remain in equilibrium and one of the phases disappears. Therefore the system is nonvariant (F=0) The system is, zero variant, or non-variant or invariant and has no degree of freedom.

 For a system consisting of water in contact with its vapour.

Water (l)↔ Vapour (g)

We must state either temperature or pressure to define the system completely. Hence; the degree of freedom is one (or) the system is univariant.

 For a system consisting of

NaCl (S) ↔ NaCl – Water (aq) ↔ Water vapour (g)

We must state either temperature or pressure. Hence the system is univariant (degree of freedom is one).

 For pure gas: From gas law, PV = RT, if the values of Pressure (P) and Temperature (T) be specified, Volume (V), the third variable is fixed automatically. Hence degree of freedom (F) = 2

Phase rule

Phase rule can be stated as, in heterogeneous systems, if equilibrium between phases are not influenced by gravity, magnetic & electrical forces, but are influenced only by pressure, temperature and concentration, then the number of degree of freedom (F) of the system is related to number of components (C) and number of phases (P) by the following phase rule equation

$$\boxed{F = C - P + 2}$$

Merits of phase rule

1. It is applicable to both physical and chemical equilibria.
2. It is a convenient method of classifying the equilibrium states in terms of phases, components and degree of freedom.
3. It indicates different system with same degree of freedom behave similarly.
4. It helps us to predict the behaviours of a system, under different sets of variables.
5. It helps in deciding whether the number of substances remains in equilibrium or not.

Limitations of phase rule

1. Phase rule is applicable only for those systems which are in equilibrium. It is not of much use for those systems which attains the equilibrium state very slow.
2. Only three variables like P, T, & C are considered, but not electrical, magnetic and gravitational forces.
3. It is applied only to a single equilibrium system.
4. It requires utmost care in deciding the number of phases existing in equilibrium.
5. Solid and liquid phases must not be in finely – divided state; otherwise deviations occur.

Derivation of phase Rule

Consider a heterogeneous system in equilibrium , having **C** components in which **P** phases are present. According to the definition of the degree of freedom, **F-** is the minimum number of independent variables which must be fixed arbitrarily to define the system completely.

No. of independent variables = Total no. of variables – no. of relations between them at equilibrium

Now let us calculate total no. of independent variables:

(1) **Temperature:** At equilibrium ,temperature of every phase is same, so there is only one temperature variable of the entire system.

(2) **Pressure**: At equilibrium , each phase has the same pressure, so there is only one pressure variable of the entire system.

(3) **Concentration:** Concentration of each components is generally expressed in terms of mole fractions

For example, if there are two components A & B in one phase and if we know the concentration of one (say A), the concentration of other (i.e.,B) can be automatically found because sum is unity. Similarly, if we have three components and if the composition of two is known, then the composition of third can be easily found out. Thus , if we have C components , we must know the concentrations of C – I components . So for P phases the total composition variables are P(C – I).

Hence, total number of variables

= 1 (for temperature) + 1(for pressure) + P(C - 1) (for composition)

= P(C – 1) + 2

When P phases are present , (P – 1) equations are available for each component & for C component , the total no. of equations are C(P – 1).

[If there is one component in two phases, it is possible to write one equation amongst the variables and if there is one component in three phases , it may be represented with the help of two equations.

Therefore in general when P phases are present , (P – 1) equations are available for each components and for C components , the total no. of equations are C(P – 1).]

F = total no. of variables – no.of equations between them at equilibrium

$F = [P(C-1) + 2] – [C (P-1)]$

Hence, F (Degree of freedom) = C – P + 2

Phase diagram

Phase diagram is a graph obtained by plotting one degree of freedom against another. If temperature is plotted against pressure, the diagram is called P-T diagram. Similarly, a plot of temperature against composition is known as T-C diagram. By the phase diagram, we may understand the behaviour of the system, stability and equilibrium between phases. Systems are classified, on the basis of number of components, into three types.

1. One component systems
2. Two component systems
3. Three component systems

Phase diagram of one component system

In any system, the minimum number of phases is one. It is evident from the phase rule equation

$$F=C-P+2 =1-1+2=2$$

For one component system the maximum number of degree of freedom is two. The maximum number of phases in any system is three, from the phase rule equation

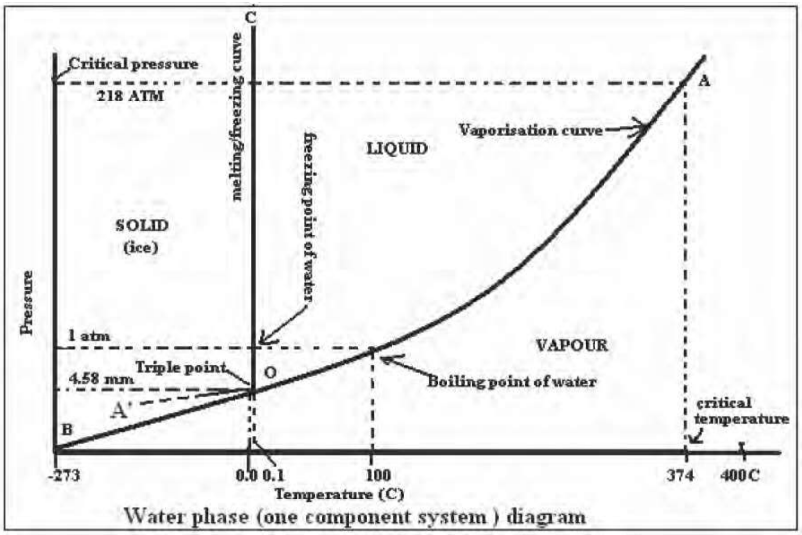
$$F=C-P+2 =1-3+2=0$$

The minimum number of degree of freedom is zero for one component system. From the above calculations, it is clear that for any one-component system the maximum number of degree of freedom is two. Therefore, such a system can be presented completely by a two dimensional diagram. Hence, we may draw the phase diagram by taking pressure and temperature as the two axes. These are known as pressure-temperature (P-T) diagrams, concentration (or) composition remains constant.

The Water system:

Water can exist in three possible phases, namely, solid, liquid and vapour. Hence, there can be three equilibriums with two phases for each equilibrium:

1. Liquid ↔ vapour
2. Solid ↔ Vapour
3. Solid ↔ Liquid



Water phase (one component system) diagram

The curve OA is called the vapourization curve of water; it represents the equilibrium between liquid water and vapour. At any point on the curve the following equilibrium will exist.

Liquid water ↔ vapour

The degree of freedom of the system is one, i.e., univariant. This is predicted by the phase rule.

$$F=1-2+2; F=1$$

This equilibrium will extend up to the critical temperature ($374^{O}C$). Beyond the critical temperature, the equilibrium will disappear only water vapour will exist.

The curve OB is called the sublimation curve of ice; it represents the equilibrium between ice and vapour. At any point on the curve the following equilibrium will exist.

Ice ↔ Vapour.

The degree of freedom of the system is one i.e., univariant. This is predicted by the phase rule.

$$F=C-P+2; F=1-2+2; F=1$$

This equilibrium will extend up to the absolute zero.

Triple point: The vaporization curve (OA) and the sublimation curve (OB) meet at point O, where three phases, namely solid, liquid and vapour will coexist. Such a point is known as the "triple point". Temperature and pressure at the triple point of water are 0.0098 ^{O}C and 4.58 mm respectively, according to phase rule, the degree of freedom is zero i.e., invariant.

$$F=C-P+2; F=1-3+2; F=0$$

The curve OC is called the fusion curve of ice; it represents the equilibrium between ice and water. At any point, on the curve the following equilibrium will exist.

Ice ↔ water

The curve OC shows how is the melting point of ice increased by increasing pressure. The degree of freedom of the system is one, i.e., univariant.

The curve OA' is called vapour pressure curve of the super-cool water (or) metastable equilibrium. Some times water can be cooled below $0^{O}C$ without the formation of ice; this water is known as super-cool water. The super-cool water can be preserved if the system is not subjected to stirring (or) "Seeding" by solid. At any point on the curve the following equilibrium will exist.

Super-cool water ↔ vapour

The degree of freedom of the system is one i.e., univariant.

Area AOB, AOC and BOC contain vapour, liquid and ice phases respectively, with in these single-phase areas, the system is bivariant. This is predicted by the phase rule.

$$F=C-P+2; F=1-1+2; F=2$$

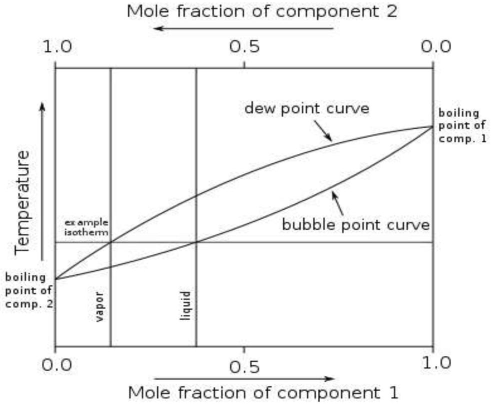
To locate any point in an area, temperature and pressure needs to be known.

Phase diagram of Two-component systems

For binary mixtures of two chemically independent components,

$$C = 2 \text{ so that } F = 4 - P$$

In addition to temperature and pressure, other variables are the composition of each phase, often expressed as mole fraction or mass fraction of one component. As an example, consider the system of two completely miscible liquids such as toluene and benzene, in equilibrium with their vapours. This system may be described by a boiling-point diagram which shows the composition (mole fraction) of the two phases in equilibrium as functions of temperature (at a fixed pressure). Four thermodynamic variables which may describe the system include temperature (T), pressure (p), mole fraction of component 1 (toluene) in the liquid phase (x_{1L}), and mole fraction of component 1 in the vapour phase (x_{1V}). However since two phases are in equilibrium, only two of these variables can be independent (F = 2). This is because the four variables are constrained by two relations: the equality of the chemical potentials of liquid toluene and toluene vapour, and the corresponding equality for benzene. For given T and p, there will be two phases at equilibrium when the overall composition of the system (system point) lies in between the two curves. A horizontal line (isotherm or tie line) can be drawn through any such system point, and intersects the curve for each phase at its equilibrium composition. The quantity of each phase is given by the lever rule (expressed in the variable corresponding to the x-axis, here mole fraction). For the analysis of fractional distillation, the two independent variables are instead considered to be liquid-phase composition (x_{1L}) and pressure. In that case the phase rule implies that the equilibrium temperature (boiling point) and vapour-phase composition are determined. Liquid-vapour phase diagrams for other systems may have azeotropes (maxima or minima) in the composition curves, but the application of the phase rule is unchanged. The only difference is that the compositions of the two phases are equal exactly at the azeotropic composition.



Phase diagram of two component: reduced phase rule (or) condensed phase rule

In a two – component system, minimum number of phases is one, i.e., P = 1, according to the phase rule equation, the maximum degree of freedom is three

$$F = C - P + 2; F = 2 - 1; F = 3$$

So, the phase diagram of a binary system should be represented by a three dimensional diagram of temperatures, pressure and composition, which can not be drawn on paper. Generally solid-liquid equilibrium of an alloy has "no gas phase" and the effect of pressure is small. Therefore, experiments are conducted under atmospheric pressure. Thus, the system in which the pressure is constant (vapour phase is not considered) is known as condensed system. The phase rule becomes.

$$F' = C - P + 1$$

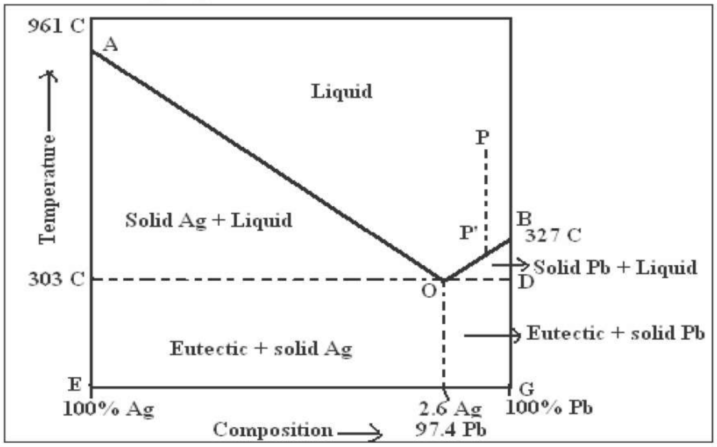
This is known as ***reduced phase rule (or) condensed phase rule***. The phase diagram can be drawn by taking temperature and composition as the two axis. This is known as (T-C) diagram. The reduced phase rule is used only when atmospheric pressure is larger than actual vapour pressure of the component. Depending upon the solubility of the two components and their reactive ability, two component systems are classified into three types

1. *Simple Eutectic formation:* If two substances are completely miscible in the liquid state, but completely immiscible in the solid state, form a simple eutectic. Of the various mixture, one mixture has the lowest melting point such a mixture is known as a eutectic mixture (eutectic means easy melting).

2. *Solid solution formation:* When two substances, especially metals, are completely miscible in both the solid and liquid states, they form solid solutions, where mixing takes place in the atomic levels. A condition for the formation of solid solution is, the two metals should not differ in atomic radius by more than 15%.

3. *Compound formation:* Under some conditions, two metals chemically react to give one or more compounds with definite proportions. Of the compounds, a compound is said to possess congruent (constant) melting point, if it melts exactly at a constant temperature into liquid, having the same composition as that of solid.

Pb-Ag system:
It is a two-component Simple Eutectic system. Here four possible phases are solid Ag, Solid Pb, solution of Ag-Pb and vapor. However, at the constant atmospheric pressure, the vapor phase is absent and reduced phase rule is applicable as F=C-P+1. The phase diagram of the Pb-Ag system is shown in the figure below;



Curve AO: Point A is the melting point of pure Silver. Curve AO shows melting point depression of silver by the addition of lead. At any point in this curve there is equilibrium between solid Ag and liquids part. According to reduced phase rule equation. The system is univarient.

$$F' = C - P + 1;\ F' = 2 - 2 + 1;\ F' = 1$$

Curve BO: Point B is the melting point of pure lead, (327^{O}C), curve BO shows the melting point depression of lead on gradual addition of silver to it. Along this curve solid lead and solution co – exist and hence the system is univariant.

Point O: The two curves AO & BO meet at point O, where three phases solid pb, solid Ag and their solution co-exist, according to condensed phase rule the system is invariant.

$$F' = C - P + 1;\ F' = 2 - 1 + 1;\ F' = 2$$

The point 'O' is known as eutectic point, its composition (Ag=2.6%; Pb=97.4%) and temperature (303OC) is known as eutectic composition and eutectic temperature respectively. Further cooling below the eutectic temperature respectively. Further cooling below the eutectic temperature will cause simultaneous crystallization of a mixture of lead and silver.

Area AOB: Consists of only one phases namely pb-Ag solution. According to reduced phase rule equation.

$$F' = C - P + 1;\ F' = 2 - 1 + 1;\ F' = 2$$

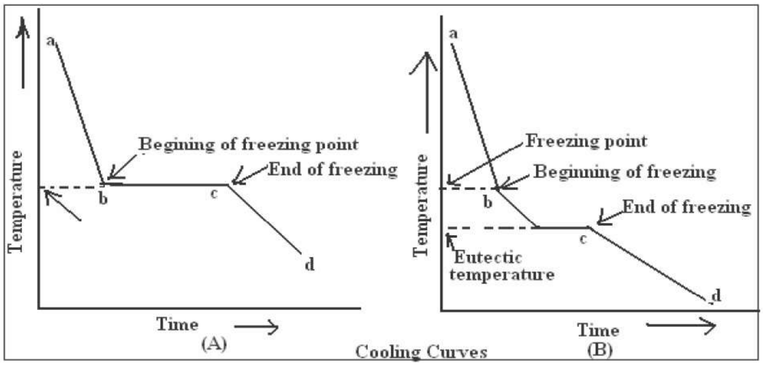
The system is bivarient i.e., both T & composition has to be specified to define the system.

Let us consider a point p, which represents a sample of lead containing less than 2.6% silver. On cooling the temperature falls gradually till point p'. On further cooling lead begins to separate and the concentration of Ag increase in the solution till the point O is reached, after that whole mass solidifies (2.6% Ag; 97.4% pb). This process is utilized in the pattinson's process of desilverization of lead. Below the eutectic point (O), area COEF consists of solid and eutectic compound, where crystalline silver and eutectic compounds are stable. Similarly the area ODFG consists of solid Pb and eutectic compound, where crystalline lead eutectic compounds are stable.

Applications

Pattinson's process: If a sample of argent ferrous lead, containing less than 2.6% Ag is allowed to cool gradually, lead will separate out and the solution will become progressively richer in Ag, till the percentage 2.6 of Ag is reached; and on further cooling, the whole mass will solidify as such. On the other hand, if lead-silver allow containing Ag greater than 2.6% is allowed to cool, and then pure silver separates along the curve AO, till the eutectic composition at O is reached.

Thermal analysis or cooling curve: The shape of the cooling curve can be determined by thermal analysis. Thermal analysis is a method involving a study of cooling curves of the various compositions of a system during solidification. The cooling curve is obtained by plotting fall of temperature with time. The principle of the method can be understood from the following examples. In that addition, a compound is said to possess ***incongruent melting point***, if it decomposes completely at a temperature below its melting point yielding a new solid phase with a composition different from that of the original.



Cooling Curves

1. When a pure substance in the liquid state is allowed to cool slowly and the temperature is noted at definite times. The cooling curve (fig) shows the rate of cooling is continuous up to the point 'b' the solid begins to separate, and the temperature will remain constant, until the liquid is completely solidified (indicated by the line 'b'). Thereafter, the fall in temperature will again become continuous (indicated by the line 'cd').

2. If a mixture of two solids in the liquid state is cooled slowly and the cooling curve is obtained in a similar manner (fig). The cooling curve shows the rate of cooling is continuous up to the point 'b'. At the point 'b' one of the solids begins to separate, this separation will extent up to the point 'c'. At the point 'c' the eutectic compound begins to separate. The temperature remains constant along cd until the solidification completes. Thereafter the fall of temperature becomes uniform, but the rate of fall is quite different from the previous one.

Uses

1. Melting point and eutectic temperature can be noted from the cooling curve.
2. Percentage purity of the compounds can be known.
3. The behaviour of the compounds can be clearly understood from the cooling curves.
4. The procedure of thermal analysis can also be used to derive the phase diagram of any two component system.

Heat treatment of steel: Heat treatment involves the combination of heating and cooling of a metal or alloy in one or more temperature cycles to confer desirable physical properties to the metal or alloy. Heat treatment of steel may be carried out under near equilibrium conditions to improve the ductility or under non equilibrium conditions to enhance the hardness. During heat treatment the size and shape of the grains or the composition of the phase undergoes changes with respect to the micro constituents and also in addition, the internal stresses will be relieved.

Hardening: Hardening involves the transformation of austenite to martensite or the bainite phase, making the steel hard. If steel is quenched by plunging into water or oil to 204°C or lower temperature the carbon atoms do not have sufficient time to form cementite but remain trapped in the lattice. The excess carbon precipitates out in hot metal and prevents the slipping of the planes. Thus quenched steel is quite hard and strong but has lower ductility. This heat treatment is called transformation hardening. Further the quenched steel is not useful for construction purposes, because of its brittleness. Therefore quenching is always followed by another heat treatment process called tempering. The quenched steel is tempered by reheating to below α–iron or γ–iron transition temperature. Normally on tempering, the steel becomes tougher and ductile. Tempering is carried out at about 200°C to make hard steel resistant to abrasion or at higher temperature (~ 540°C) to make tough steel capable of withstanding shock loads.

Case hardening: is a surface treatment by which the inside soft core of steel is hardened on the surface. Low carbon steels are case hardened because they cannot be hardened by quenching.

Cyaniding: also produces case hardened, medium carbon steel articles. Here the article is immersed in a molten bath of sodium or potassium cyanide at about 850°C for some times to facilitate the adsorption of both carbon and nitrogen and then quenched in oil or water.

Nitriding: produces a hard surface on alloy steels. The process involves heating the alloy in the presence of ammonia to about 550°C. Ammonia decomposes and nitrogen formed combines with alloying elements to form hard nitrides on the surface of the alloy.

Annealing: Annealing involves heating and holding the steel at a suitable temperature for some times to facilitate the dissolution of carbon in γ–iron followed by a slow cooling in a controlled manner in a furnace. Steel is softened and becomes ductile and machineable. However annealing decreases the hardness and strength of steel. Annealed hypereutectoid steels contain cementite. They are not soft but can be machined easily. In contrast annealed hypo eutectoid steels contain ferrite and are relatively soft and malleable.

Chemical equilibrium

When reactants are mixed in exact stoichiometric proportion to perform a chemical reaction, it is believed that all the reactants would be converted into products with the release or absorption of energy. This is not true in all cases. Chemical reactions can be classified as: Irreversible and Reversible reactions.

Most of the reactions occur only in one direction. They are called irreversible reactions. For example;

Carbon is burnt in air: $C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$

Neutralisation reaction: $HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)$

Precipitation rectaion: $NaCl\,(aq) + AgNO_3\,(aq) \longrightarrow AgCl\,(s) + NaNO_3\,(aq)$

Strictly speaking all reactions are considered to be reversible. But the rate of reaction in one particular direction is extremely small compared to the other. Thus the reaction proceeds practically in one direction to near completion, leaving a negligibly small amount of reactant at the end.

A reaction is said to be reversible if under certain conditions of temperature and pressure, the forward and reverse reactions occur simultaneously.

Forward reaction: $C_2H_5OH(l) + CH_3COOH\ (l) \xrightarrow{H^+} CH_3COO\ C_2H_5(l) + H_2O(l)$

Backward recation: $CH_3COOC_2H_5(l) + H_2O(l) \xrightarrow{H^+} CH_3COOH(l) + C_2H_5OH(l)$

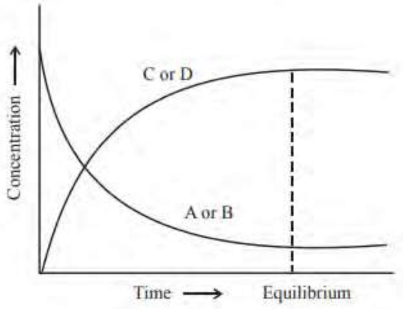
Total rectaion: $CH_3COOH\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O(l)$

Many chemical reactions proceed only to a certain extent and stop. When analysed, the resulting mixture contains both the reactants and products. It is because when reactants combine to form products, the products also start combining to give back the reactants. When such opposing processes take place at equal rates, no reaction appears to take place and it is said that a state of equilibrium has reached.

A reversible reaction is said to be in the equilibrium state when the forward and backward reaction occur simultaneously at the same rate in a closed system and the concentrations of reactants and products do not change with time. In a chemical reaction, chemical equilibrium is the state in which both reactants and products are present in concentrations which have no further tendency to change with time. The chemical equilibrium is achieved when the rate of forward reaction is same as the reverse reaction. Since the rates are equal, there are no net changes in the concentrations of the reactant(s) and product(s). This state is known as dynamic equilibrium. The entire process can be graphically represented by this diagram.

A common example of reversible reactions of the type $A + B \rightleftharpoons C + D$

$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOH + H_2O$



Characteristics of equilibrium state. The state of equilibrium has following characteristics properties:

(i) Chemical Equilibrium is dynamic in nature. The chemical equalibrium is the result of two equal but opposite processes occurring in the forward and reverse directions and there is no “net” change occurring in the system.

(ii) Equilibrium can be attained from either side. The same state of equilibrium (characterized by its equilibrium constant which is discussed later can be reached whether the reaction is started from the reactants or products side. For example, the same equilibrium.

$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$ established whether we start the reaction with N_2O_4 or NO_2.

(iii) Equilibrium can be attained only in a closed system. Equilibrium can be attained only if no substance among, reactants or products, is allowed to escape i.e. the system is a closed one. Any system consisting of gaseous phase or volatile liquids must be kept in a closed container.

Gaseous phase or volatile liquids must be kept in a closed container: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Non-volatile liquid and solid phases even in an open container: $FeCl_3(aq) + 3\ NH_4SCN(aq) \rightleftharpoons Fe\ (SCN)_3\ (s) + 3\ NH_4Cl(aq)$

(iv) A catalyst can not change the equilibrium state. Addition of a catalyst speeds up the forward and reverse reactions by same extent and help in attaining the equilibrium faster. However, the equilibrium concentrations of reactants and products are not affected in any manner.

Law of chemical equilibrium

Chemical Equilibrium can easily be understood by understanding Chemical Kinetics. It is the study of the rate of the reactions under various conditions. Another concept that forms the basis is the Law of mass action. Law of mass action states that the ‘Rate of a chemical reaction is directly proportional to the product of the concentrations of the reactants raised to their respective stoichiometric coefficients'. At equilibrium forward and backward rates are equal and the ratio of the rate constants is a constant and is known as an equilibrium constant. In a reaction mixture at equilibrium, the concentrations of the reactants and products are related by an equilibrium constant. So, Given a reaction:

$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$

Using the **Law of mass action,**

Forward reaction rate $= k_+ [A]^a[B]^b$

Backward reaction rate $= k_- [C]^c[D]^d$

where, [A], [B], [C] and [D] being the active masses and k_+ and k_- are rate constants.

Forward reaction rate = **Backward reaction rate**

$k_+ [A]^a[B]^b = k_- [C]^c[D]^d$

We have,

$K_c = k_+ / k_-$

$\mathbf{K_c} = [C]^c \cdot [D]^d / [A]^a \cdot [B]^b$

The Law of Chemical Equilibrium is defined as, the ratio of product of concentration of the products to the product of concentration of the reactants, with each concentration term is raised to the power by its coefficient in overall balanced chemical equation, is a constant quantity at a given temperature and it is called equilibrium constant.

Equilibrium constants and their significance

The concentrations values in the law of equilibrium are the equilibrium concentrations of reactants and products. Kc is called the concentration equilibrium constant. In case of gases their partial pressures can also be used in place of molar concentrations (since the two are directly proportional to each other) in the law of equilibrium. The new equilibrium constant, Kp , is called the pressure equilibrium constant. For the reaction between H_2 and I_2

$$H_2(g) + I_2(g) \rightleftharpoons 2HI\,(g) \qquad K_c = \frac{[HI]^2}{[H_2][I_2]} \qquad K_p = \frac{p^2_{HI}}{p_{H_2} \times p_{I_2}}$$

Here all are the equilibrium partial pressures of H2 , I2 and HI respectively. For the general gas phase reaction:

$$a\,A\,(g) + b\,B\,(g) \rightleftharpoons c\,C\,(g) + d\,D\,(g) \qquad K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \qquad k_p = \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b}$$

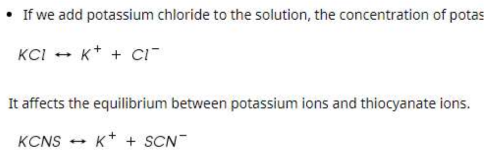
The equilibrium constant of a reaction has a constant and characteristic value at a given temperature. The changes in starting concentration, pressure and the presence of a catalyst do not change the value of the equilibrium constant. However if the temperature is changed. The value of the equilibrium constant also changes. The magnitude of the equilibrium constant is a measure of the extent upto which a reaction proceeds before the equilibrium is reached. The magnitude of K is large when the products are present in larger amounts than the reactants in the equilibrium mixture. For example;

$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)$ $\quad K_c = 90$ at 298 K $\quad$ and for $2CO\,(g) + O_2\,(g) \rightleftharpoons 2\,CO_2\,(g)$ $\quad K_c = 2.2 \times 10^{22}$ at 1000 K.

A large value of Kc for the second reaction indicates that amount of products is much more than the reactants present at the time of equilibrium. Thus the magnitude of equilibrium constant tells us about the position of the equilibrium.

If a system is subjected to a change in concentration of one or more reactants, or a change in temperature or pressure, the equilibrium condition of the system is altered. In 1884, a French Chemist and Engineer, Le Chatelier, showed that in every such case, the new equilibrium state partially reduces the effect of change that brought it about. This principle is known as Le Chatelier's Principle. The principle states that, if a system at equilibrium is subjected to a change of pressure or temperature or number of moles of the component, there will be a tendency for a net reaction in the direction that reduces the effect of this change. Generally we can say that;

An increase in the concentration of the reactants shifts the equilibrium in the forward direction and a decrease in the concentration of the reactants shifts the equilibrium in the backward direction. Similarly, an increase in concentration of the products shifts the equilibrium in the backward direction and a decrease in the concentration of the products shifts the equilibrium in the forward direction.



- If we add potassium chloride to the solution, the concentration of potas

$KCl \leftrightarrow K^+ + Cl^-$

It affects the equilibrium between potassium ions and thiocyanate ions.

$KCNS \leftrightarrow K^+ + SCN^-$

$$Fe^{3+}(aq) + SCN^-(aq) \leftrightarrow [Fe(SCN)^{2+}] \qquad K_c = \frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]}$$

The pressure dependence of the equilibrium constant is usually weak in the range of pressures normally encountered in industry, and therefore, it is usually neglected in practice. This is true for condensed reactant/products (i.e., when reactants and products are solids or liquid) as well as gaseous ones. In gas phase reaction the Change in pressure affects equilibrium involving gaseous phase either in a homogeneous or hetrogeneons system.

Case I: When the number of moles of products is more than the total number of moles. Increase in total pressure keeping the temperature constant, will cause a decrease in volume. This means that the number of moles per unit volume will increase. A net change will take place in the equilibrium in the direction where the number of moles decrease i.e. backward direction.

Case II: When the number of moles of products is less than reactants. Increase in total pressure will bring a net change to the equilibrium in the direction where the total number of moles is decreasing. Decrease in total pressure will bring the net change to equilibrium in the direction where the total number of moles is increasing i.e. backward direction.

Case III: When there is no change in the total number of moles of reactant and product as in the following state of equilibrium. There is no net change in equilibrium state when pressure is changed.

Case I	Case II	Case III
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	$H_2(g) + I_2(g) \rightleftharpoons 2HI$	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Equilibrium Constant & Gibbs Free energy:

The Equilibrium constant is related to the standard Gibbs free energy change for the reaction. The relation is given by the equation:

$$\Delta G^\ominus = -RT \ln K_{eq}$$

Where, R is the universal gas constant, T is the temperature and Keq is the equilibrium constant. Using the definition of Gibbs free energy & Gibbs free energy Isotherm equation, we have:

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus,$$

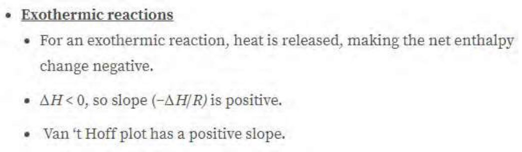
$$\Delta G^\ominus = -RT \ln K_{eq},$$

$$\ln K_{eq} = -\frac{\Delta H^\ominus}{RT} + \frac{\Delta S^\ominus}{R}.$$

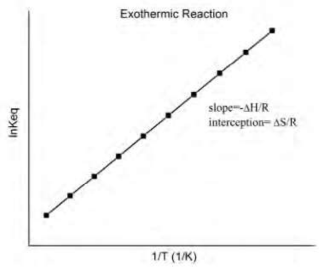
Where, K_{eq} is the equilibrium constant at temperature T, $\Delta H^\ominus$ and $\Delta S^\ominus$ are constants and are enthalpy and entropy of the system respectively. This graph of this equation is called the Van‘t Hoff plot. The plot is used to estimate the enthalpy and entropy of a chemical reaction. From the plot between “ln K_{eq}” & “1/T“, we have $-\Delta H/R$ as the slope, and $\Delta S/R$ as the intercept of the linear fit. Equilibrium constant **K_c** depends on the temperature of the reaction and the relation is given by Van’t Hoff equation**.**

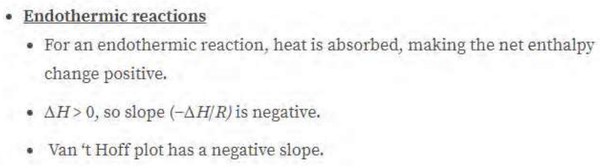
$$\ln \frac{K_2}{K_1} = \frac{-\Delta H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

K_1 is the equilibrium constant at absolute temperature T_1, K_2 is the equilibrium constant at absolute temperature T_2, R is the ideal gas constant, ΔH reaction enthalpy assumed to be constant over the temperature range. This equation can be used to estimate a new equilibrium constant at a new absolute temperature assuming a constant standard enthalpy change over the temperature range. Let’s understand the change in the equilibrium constant for two different kinds of reactions: Endothermic & Exothermic.

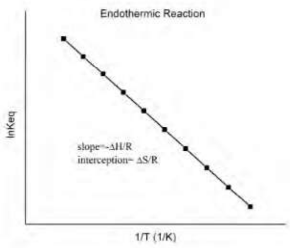


- Exothermic reactions
  - For an exothermic reaction, heat is released, making the net enthalpy change negative.
  - $\Delta H < 0$, so slope $(-\Delta H/R)$ is positive.
  - Van 't Hoff plot has a positive slope.





- Endothermic reactions
  - For an endothermic reaction, heat is absorbed, making the net enthalpy change positive.
  - $\Delta H > 0$, so slope $(-\Delta H/R)$ is negative.
  - Van 't Hoff plot has a negative slope.

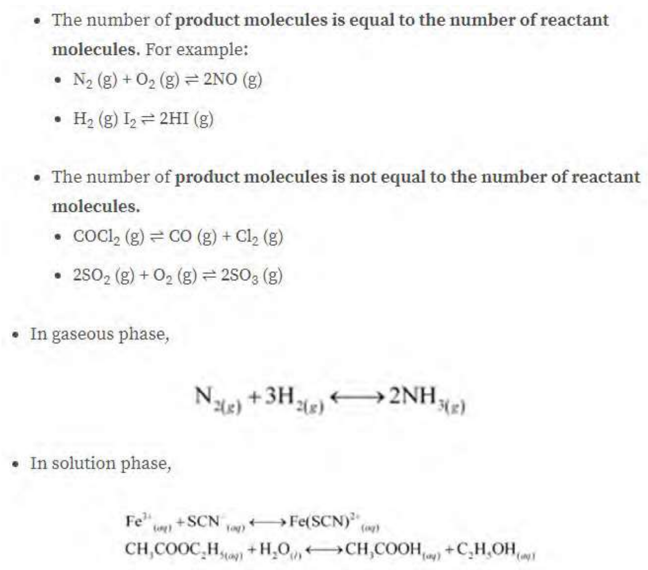


Types of Chemical Equilibria

There are two types of chemical equilibria: Homogeneous equilibria and Heterogeneous equilibria

Homogeneous Equilibria. The equilibrium reactions in which all the reactants and the products are in the same phase are known as homogeneous equilibrium reactions. These are divided into two categories:

The number of product molecules is equal to the number of reactant molecules. For example:

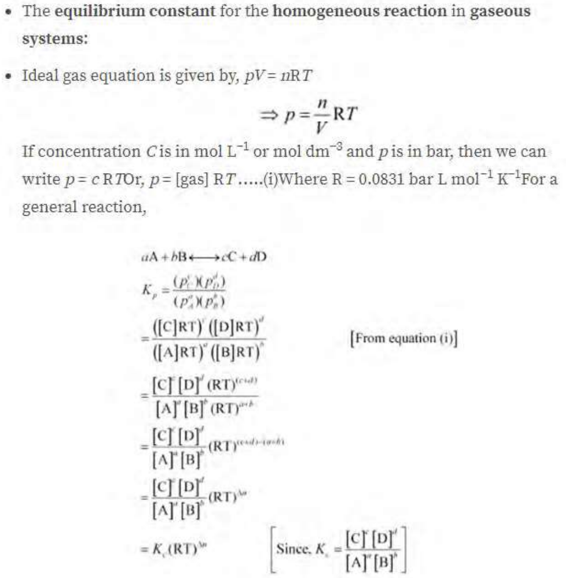


- The number of **product molecules is equal to the number of reactant molecules.** For example:
  - N_2 (g) + O_2 (g) ⇌ 2NO (g)
  - H_2 (g) I_2 ⇌ 2HI (g)
- The number of **product molecules is not equal to the number of reactant molecules.**
  - $COCl_2$ (g) ⇌ CO (g) + Cl_2 (g)
  - $2SO_2$ (g) + O_2 (g) ⇌ $2SO_3$ (g)
- In gaseous phase,

$$N_{2(g)} + 3H_{2(g)} \longleftrightarrow 2NH_{3(g)}$$

- In solution phase,

$$Fe^{3+}{}_{(aq)} + SCN^{-}{}_{(aq)} \longleftrightarrow Fe(SCN)^{2+}{}_{(aq)}$$
$$CH_3COOC_2H_{5(aq)} + H_2O_{(l)} \longleftrightarrow CH_3COOH_{(aq)} + C_2H_5OH_{(aq)}$$



- The **equilibrium constant** for the **homogeneous reaction** in **gaseous systems:**
- Ideal gas equation is given by, $pV = nRT$

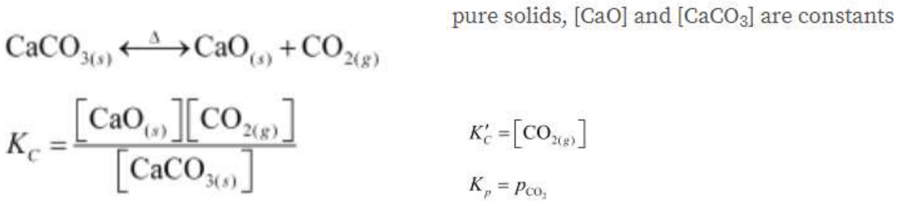
$$\Rightarrow p = \frac{n}{V}RT$$

If concentration C is in mol L^{-1} or mol dm^{-3} and p is in bar, then we can write $p = cRT$Or, p = [gas] RT.....(i)Where R = 0.0831 bar L mol^{-1} K^{-1}For a general reaction,

$$aA + bB \longleftrightarrow cC + dD$$
$$K_p = \frac{(p_C^c)(p_D^d)}{(p_A^a)(p_B^b)}$$
$$= \frac{([C]RT)^c([D]RT)^d}{([A]RT)^a([B]RT)^b} \qquad \text{[From equation (i)]}$$
$$= \frac{[C]^c[D]^d(RT)^{(c+d)}}{[A]^a[B]^b(RT)^{a+b}}$$
$$= \frac{[C]^c[D]^d}{[A]^a[B]^b}(RT)^{(c+d)-(a+b)}$$
$$= \frac{[C]^c[D]^d}{[A]^a[B]^b}(RT)^{\Delta n}$$
$$= K_c(RT)^{\Delta n} \qquad \left[\text{Since, } K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}\right]$$

In the above equation, Δn = (number of moles of gaseous products)− (number of moles of gaseous reactants) in the balanced chemical equation and while calculating K_p, pressure should be expressed in bar (1 bar = 10^5 Pa = 10^5 Nm^{-2})

Heterogeneous Equilibria. The equilibrium reactions in which the reactants and the products are present in different phases are known as heterogeneous equilibrium reactions. For example;



$$CaCO_{3(s)} \overset{\Delta}{\longleftrightarrow} CaO_{(s)} + CO_{2(g)}$$

pure solids, [CaO] and [$CaCO_3$] are constants

$$K_C = \frac{[CaO_{(s)}][CO_{2(g)}]}{[CaCO_{3(s)}]}$$

$$K'_C = [CO_{2(g)}]$$

$$K_p = p_{CO_2}$$

The concentrations of pure solids like [CaO] and [$CaCO_3$] in the above case or the pure liquids to be considered as constant and do not appear in Kp expression.

Weak and strong electrolytes

A redox reaction involves the transfer of electrons from one chemical species to another. Amount (moles) of the salt that has made the solution saturated per liter of solution is called the solubility of the salt. For salt AB.

$$AB \leftrightarrow A^+ + B^-$$

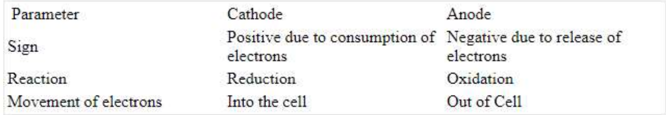
Those substances which allow the passage of electricity by way of the aqueous solution or the fused state and undergo chemical decomposition are called electrolytic conductors. Some examples are the aqueous solution of acids. bases and salts. Following are the two types of electrolytes;

- **Strong electrolytes:** Those electrolytes which completely ionise or dissociate into ions are known as strong electrolytes. Some of the examples of strong electrolytes are HCl, NaOH, K_2SO_4.
- **Weak electrolytes:** Those electrolytes that dissociate partially (ex < 1) are known as weak electrolytes. Some of the examples of weak electrolytes are CH_3COOH, H_2CO_3, NH_4OHH_2S, etc.

The energy from a redox reaction can be used to accomplish work by constructing an electrochemical cell. In an electrochemical cell, the oxidation process and the reduction process are separated into two half-cells connected by an external wire. The half-cell with the oxidation process is losing negative charge (e− loss) while the half-cell with the reduction process is gaining negative charge (e− gain). To maintain electrical neutrality in both half-cells, a salt bridge (or semipermeable membrane) must connect the two half-cells to permit the transfer of ions between the two solutions. Thus, the salt bridge completes the electrical circuit between the half cells.

The transfer of electrons through the external wire create a current that can do work. The driving force pushing the electrons through the wire is the difference in the attraction for electrons in the two half-cells. This voltage difference is called the cell potential (Ecell) and is measured in volts. The cell potential (Ecell) is directly related to the magnitude of the equilibrium constant for the overall oxidation-reduction reaction occurring in the cell. A reaction that more strongly favors product formation (larger Keq) will have a higher cell potential (larger Ecell) than a reaction which only moderately favors product formation.

General Representation of Electrochemical Cells



Parameter	Cathode	Anode
Sign	Positive due to consumption of electrons	Negative due to release of electrons
Reaction	Reduction	Oxidation
Movement of electrons	Into the cell	Out of Cell

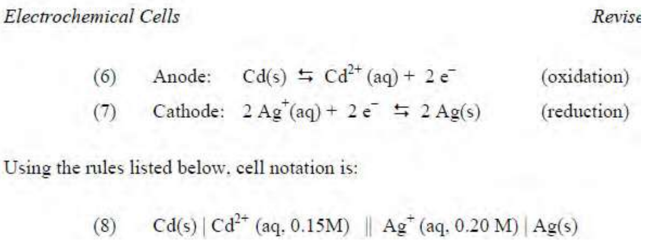
Standard electrode potential and its application to different kinds of half cells

Standard cell potentials (E°cell) can be calculated from potentials (E°) for oxidation and reductions reactions measured under standard conditions (1.00 M solutions, 1.00 atm pressure, 298 K). A positive cell potential means the reaction proceeds spontaneously in the direction the reaction is written; a reaction with a negative cell potential proceeds spontaneously in the reverse direction.

$$E^\circ_{cell} = E^\circ_{reduction} + E^\circ_{oxidation}$$

A galvanic cell is constructed from solutions in two beakers connected by a salt bridge and an external wire. One beaker contains 0.15 M Cd(NO3)2 and a Cd metal electrode. The other beaker contains 0.20 M AgNO3 and Ag metal electrode. In the reaction, cadmium metal is oxidized (loses electrons) and is, therefore, the anode. The silver ion is reduced (gains electrons) to form Ag0 (the cathode).

$$2\,Ag^+(aq) + Cd(s) \leftrightarrows Cd^{2+}(aq) + 2\,Ag(s)$$



Electrochemical Cells *Revise*

(6) Anode: $Cd(s) \leftrightarrows Cd^{2+}(aq) + 2\,e^-$ (oxidation)

(7) Cathode: $2\,Ag^+(aq) + 2\,e^- \leftrightarrows 2\,Ag(s)$ (reduction)

Using the rules listed below, cell notation is:

(8) $Cd(s)\,|\,Cd^{2+}\,(aq, 0.15M)\ \|\ Ag^+\,(aq, 0.20\ M)\,|\,Ag(s)$

Cell Notation Rules:

1. The anode half-cell is described first; the cathode half-cell follows. Within a given half-cell, the reactants are specified first and products last. As the reader's eye proceeds from left to right s/he is reading a description of the oxidation reaction first and the reduction reaction last (in other words - the direction of electron flow). Spectator ions are not included.
2. A single vertical line indicates that species are in different phases (*e.g.* solid electrode |liquid with electrolyte), but in physical contact with each other. A double vertical line indicates a salt bridge or porous membrane separating the individual half-cells.
3. The phase of the species (s, l, g, aq) is always shown in parentheses. If the electrolytes in the cells are not at standard conditions, concentrations and/or pressure should be included with phase in parentheses as shown in equation (8). If no concentration or pressure is noted, the electrolytes in the cells are assumed at standard conditions (1.00 M or 1.00 atm and 298K).

Although many applications of electrochemical cells involve a flow of current between the two electrodes, the most fundamental kind of measurement we can make is of the voltage, or electromotive force (EMF) between the electrodes in the absence of any cell current. This voltage, which we usually refer to as the *cell potential*, is the potential difference between the electrodes, and is the difference between the *half-cell potentials* of the right and left sides. Each of the half-cell potentials is in turn a potential difference between the electrode and the solution, so for our example cell the above relation can be expanded as follows;

$$E_{\text{cell}} = \Delta V = V_{\text{right}} - V_{\text{left}} \qquad E_{\text{cell}} = V_{\text{Cu}} - V_{\text{soln}} + V_{\text{soln}} - V_{\text{Zn}}$$

It is important to understand that individual half-cell potentials are not directly measurable; there is no way you can determine the potential difference between a piece of metal and a solution. Attaching one lead of a voltmeter to the metal and dipping the other in the solution would simply create a new half-cell involving the immersed metallic conductor.

<u>EMF and its measurement and application</u>

When the concentrations of solutes or partial pressures of gases are not at standard conditions, the cell potential (Ecell) can be determined with the Nernst equation. For the general cell reaction occurring at 298 K, the Nernst equation can be rewritten as shown as follows;

$$E_{cell} = E^\circ_{cell} - (0.059\,/\,n)\log Q \qquad \text{(Nernst equation)} \qquad aA + bB \leftrightarrows cC + dD$$

Q: reaction quotient

n: moles of e- transferred

$$(E_{cell} = E^\circ_{cell} - (0.059\,/\,n)\ \log\,([C]^c\,[D]^d\,/\,[A]^a\,[B]^b\,))$$

The Standard Potential Table in your textbook lists many half-cell reactions and their voltages. These potentials are measured relative to a selected standard half-reaction (usually the Standard Hydrogen Electrode (SHE).

The fact that individual half-cell potentials are not directly measurable does not prevent us from defining and working with them. If we cannot determine the absolute value of a half-cell potential, we can still measure its value in relation to the potentials of other half cells. In particular, if we adopt a reference halfcell whose potential is arbitrarily defined as zero, and measure the potentials of various other electrode systems against this reference cell, we are in effect measuring the half-cell potentials on a scale that is relative to the potential of the reference cell. As a reference cell we use the half cell whose reaction is;

$$\tfrac{1}{2}\,H_2(g) \longrightarrow H^+ + e^-$$

This is the hydrogen electrode, an example of a gas electrode as was discussed above. When this electrode is set up under standardized conditions, it becomes the standard hydrogen electrode, sometimes abbreviated SHE. In order to measure the relative potential of some other electrode M2+/M, we can set up a cell

$$\mathrm{Pt}\,|\,\mathrm{H_2}(g)\,|\,\mathrm{H^+}(aq)\,||\,\mathrm{M^{2+}}(aq)\,|\,\mathrm{M}(s) \qquad (5)$$

$$\mathrm{H_2}(g) + \mathrm{M^{2+}} \longrightarrow 2\,\mathrm{H^+} + \mathrm{M}(s)$$

, the potential difference between the platinum and M

$$E_{\mathrm{cell}} = V_{\mathrm{M}} - V_{\mathrm{soln}} + V_{\mathrm{soln}} - V_{\mathrm{Pt}}$$

But since the difference *V*soln-*V*Pt is by definition zero for the hydrogen half-cell, the cell potential we measure corresponds to

$$E_{\mathrm{cell}} = V_{\mathrm{M}} - V_{\mathrm{soln}}$$

which is just the potential of the half-cell

$$\mathrm{M^{2+}} + 2\,\mathrm{e^-} \longrightarrow \mathrm{M}(s)$$

By carrying out a series of measurements in which various other systems are substituted for the M2+/M couple, we can construct a table in which the various half-cell reactions are arranged in order of their potentials. The conventional way of doing this, as shown in Table , is to write the half-cell reactions as reductions, and to place them in the order of increasing (more positive) potentials. The resulting values are known as the *standard half-cell potentials*, denoted byE^0.

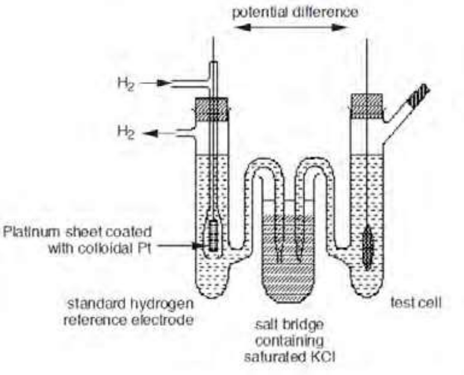


Figure 4: Cell for measurement of standard potentials

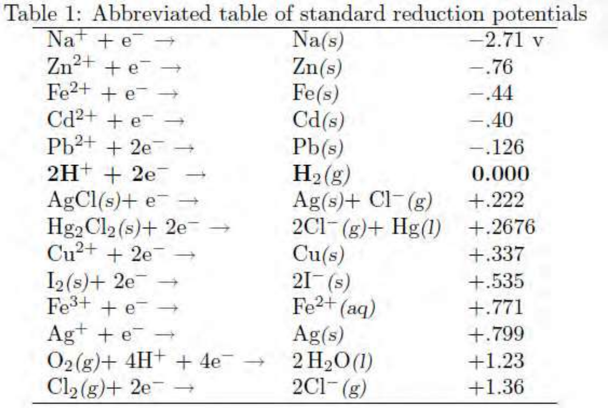


Table 1: Abbreviated table of standard reduction potentials

$\mathrm{Na^+ + e^-} \rightarrow$	$\mathrm{Na}(s)$	−2.71 v
$\mathrm{Zn^{2+} + e^-} \rightarrow$	$\mathrm{Zn}(s)$	−.76
$\mathrm{Fe^{2+} + e^-} \rightarrow$	$\mathrm{Fe}(s)$	−.44
$\mathrm{Cd^{2+} + e^-} \rightarrow$	$\mathrm{Cd}(s)$	−.40
$\mathrm{Pb^{2+} + 2e^-} \rightarrow$	$\mathrm{Pb}(s)$	−.126
$\mathrm{2H^+ + 2e^-} \rightarrow$	**$\mathrm{H_2}(g)$**	**0.000**
$\mathrm{AgCl}(s)\mathrm{+\ e^-} \rightarrow$	$\mathrm{Ag}(s)\mathrm{+\ Cl^-}(g)$	+.222
$\mathrm{Hg_2Cl_2}(s)\mathrm{+\ 2e^-} \rightarrow$	$\mathrm{2Cl^-}(g)\mathrm{+\ Hg}(l)$	+.2676
$\mathrm{Cu^{2+} + 2e^-} \rightarrow$	$\mathrm{Cu}(s)$	+.337
$\mathrm{I_2}(s)\mathrm{+\ 2e^-} \rightarrow$	$\mathrm{2I^-}(s)$	+.535
$\mathrm{Fe^{3+} + e^-} \rightarrow$	$\mathrm{Fe^{2+}}(aq)$	+.771
$\mathrm{Ag^+ + e^-} \rightarrow$	$\mathrm{Ag}(s)$	+.799
$\mathrm{O_2}(g)\mathrm{+\ 4H^+ + 4e^-} \rightarrow$	$\mathrm{2\,H_2O}(l)$	+1.23
$\mathrm{Cl_2}(g)\mathrm{+\ 2e^-} \rightarrow$	$\mathrm{2Cl^-}(g)$	+1.36

Batteries

A **battery** is an electrochemical cell or series of cells that produces an electric current. In principle, any galvanic cell could be used as a battery. An ideal battery would never run down, produce an unchanging voltage, and be capable of withstanding environmental extremes of heat and humidity. Real batteries strike a balance between ideal characteristics and practical limitations. For example, the mass of a car battery is about 18 kg or about 1% of the mass of an average car or light-duty truck. This type of battery would supply nearly unlimited energy if used in a smartphone, but would be rejected for this application because of its mass. Thus, no single battery is "best" and batteries are selected for a particular application, keeping things like the mass of the battery, its cost, reliability, and current capacity in mind. There are two basic types of batteries: primary and secondary. A few batteries of each type are described next.

Primary batteries are single-use batteries because they cannot be recharged. A common primary battery is the dry cell (Figure). The dry cell is a zinc-carbon battery. The zinc can serves as both a container and the negative electrode. The positive electrode is a rod made of carbon that is surrounded by a paste of manganese(IV) oxide, zinc chloride, ammonium chloride, carbon powder, and a small amount of water. The reaction at the anode can be represented as the ordinary oxidation of zinc:

$$\mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) + 2\mathrm{e}^- \qquad E^\circ_{\mathrm{Zn}^{2+}/\mathrm{Zn}} = -0.7618\ \mathrm{V}$$

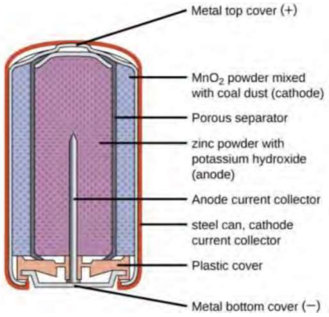
The reaction at the cathode is more complicated, in part because more than one reaction occurs. The series of reactions that occurs at the cathode is approximately

$$2\mathrm{MnO_2}(s) + 2\mathrm{NH_4Cl}(aq) + 2\mathrm{e}^- \longrightarrow \mathrm{Mn_2O_3}(s) + 2\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) + 2\mathrm{Cl}^-$$

The overall reaction for the zinc–carbon battery can be represented as
$2\mathrm{MnO_2}(s) + 2\mathrm{NH_4Cl}(aq) + \mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Mn_2O_3}(s) + 2\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) + 2\mathrm{Cl}^-$ with an overall cell

Alkaline batteries (Figure) were developed in the 1950s partly to address some of the performance issues with zinc–carbon dry cells. They are manufactured to be exact replacements for zinc-carbon dry cells. As their name suggests, these types of batteries use alkaline electrolytes, often potassium hydroxide. The reactions are;

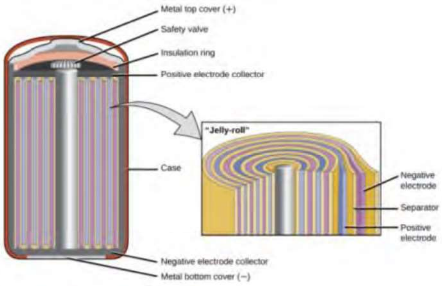
$$\begin{array}{lll}
\text{anode:} & \mathrm{Zn}(s) + 2\mathrm{OH}^-(aq) \longrightarrow \mathrm{ZnO}(s) + \mathrm{H_2O}(l) + 2\mathrm{e}^- & E^\circ_{\text{anode}} = -1.28\ \mathrm{V} \\
\text{cathode:} & 2\mathrm{MnO_2}(s) + \mathrm{H_2O}(l) + 2\mathrm{e}^- \longrightarrow \mathrm{Mn_2O_3}(s) + 2\mathrm{OH}^-(aq) & E^\circ_{\text{cathode}} = +0.15\ \mathrm{V} \\
\hline
\text{overall:} & \mathrm{Zn}(s) + 2\mathrm{MnO_2}(s) \longrightarrow \mathrm{ZnO}(s) + \mathrm{Mn_2O_3}(s) & E^\circ_{\text{cell}} = +1.43\ \mathrm{V}
\end{array}$$



Secondary batteries are rechargeable. These are the types of batteries found in devices such as smartphones, electronic tablets, and automobiles.

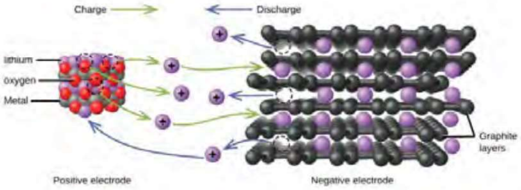
Nickel-cadmium, or NiCd, batteries (Figure) consist of a nickel-plated cathode, cadmium-plated anode, and a potassium hydroxide electrode. The positive and negative plates, which are prevented from shorting by the separator, are rolled together and put into the case. This is a "jelly-roll" design and allows the NiCd cell to deliver much more current than a similar-sized alkaline battery. The reactions are

$$\begin{array}{ll}
\text{anode:} & \mathrm{Cd}(s) + 2\mathrm{OH}^-(aq) \longrightarrow \mathrm{Cd(OH)_2}(s) + 2\mathrm{e}^- \\
\text{cathode:} & \mathrm{NiO_2}(s) + 2\mathrm{H_2O}(l) + 2\mathrm{e}^- \longrightarrow \mathrm{Ni(OH)_2}(s) + 2\mathrm{OH}^-(aq) \\
\hline
\text{overall:} & \mathrm{Cd}(s) + \mathrm{NiO_2}(s) + 2\mathrm{H_2O}(l) \longrightarrow \mathrm{Cd(OH)_2}(s) + \mathrm{Ni(OH)_2}(s)
\end{array}$$



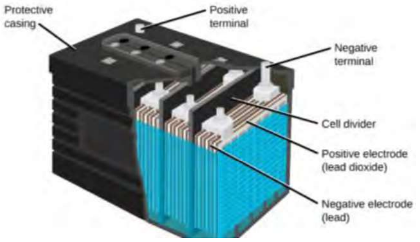
Lithium ion batteries (Figure) are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are

$$\begin{array}{ll}
\text{anode:} & \mathrm{LiCoO_2} \rightleftharpoons \mathrm{Li}_{x-1}\mathrm{CoO_2} + x\,\mathrm{Li}^+ + x\,\mathrm{e}^- \\
\text{cathode:} & x\,\mathrm{Li}^+ + x\,\mathrm{e}^- + x\,\mathrm{C_6} \rightleftharpoons x\,\mathrm{LiC_6} \\
\hline
\text{overall:} & \mathrm{LiCoO_2} + x\,\mathrm{C_6} \rightleftharpoons \mathrm{Li}_{x-1}\mathrm{CoO_2} + x\,\mathrm{LiC_6}
\end{array}$$



The lead acid battery (Figure) is the type of secondary battery used in your automobile. It is inexpensive and capable of producing the high current required by automobile starter motors. The reactions for a lead acid battery are;

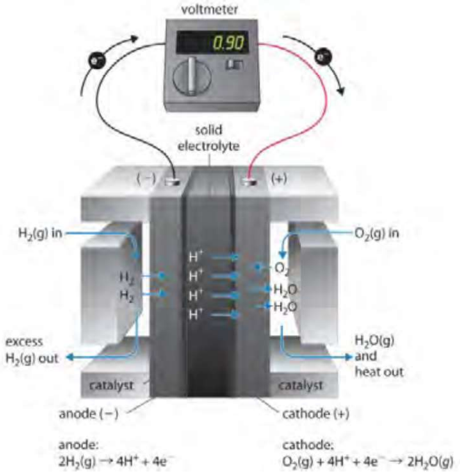
$$\begin{array}{ll} \text{anode:} & Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2e^- \\ \text{cathode:} & PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l) \\ \hline \text{overall:} & Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l) \end{array}$$

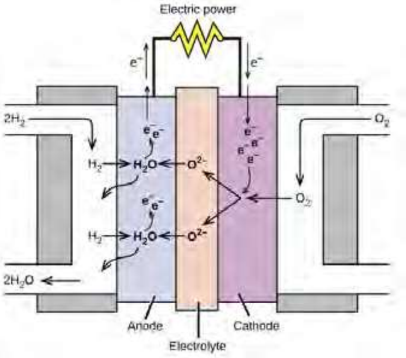


Fuel Cells

A fuel cell is a galvanic cell that requires a constant external supply of reactants because the products of the reaction are continuously removed. Unlike a battery, it does not store chemical or electrical energy; a fuel cell allows electrical energy to be extracted directly from a chemical reaction. In principle, this should be a more efficient process than, for example, burning the fuel to drive an internal combustion engine that turns a generator, which is typically less than 40% efficient, and in fact, the efficiency of a fuel cell is generally between 40% and 60%. Unfortunately, significant cost and reliability problems have hindered the wide-scale adoption of fuel cells. In practice, their use has been restricted to applications in which mass may be a significant cost factor, such as US manned space vehicles. These space vehicles use a hydrogen/oxygen fuel cell that requires a continuous input of H_2(g) and O_2(g), as illustrated in Figure. The electrode reactions are as follows:

The overall reaction represents an essentially pollution-free conversion of hydrogen and oxygen to water, which in space vehicles is then collected and used. Although this type of fuel cell should produce 1.23 V under standard conditions, in practice the device achieves only about 0.9 V. One of the major barriers to achieving greater efficiency is the fact that the four-electron reduction of O2(g)O2(g) at the cathode is intrinsically rather slow, which limits current that can be achieved. All major automobile manufacturers have major research programs involving fuel cells: one of the most important goals is the development of a better catalyst for the reduction of O2(g)O2(g).





$$\begin{array}{ll} \text{anode:} & 2H_2 + 2O^{2-} \longrightarrow 2H_2O + 4e^- \\ \text{cathode:} & O_2 + 4e^- \longrightarrow 2O^{2-} \\ \hline \text{overall:} & 2H_2 + O_2 \longrightarrow 2H_2O \end{array}$$

A fuel cell requires an external supply of reactants as the products of the reaction are continuously removed. In a fuel cell, energy is not stored; electrical energy is provided by a chemical reaction.

Question Bank

Department of Chemistry, BIT, Mesra

CH101: Chemistry

Module V: Phase and Chemical equilibrium

1. Discuss the following terms: Phase, Component, Degree of Freedom.

2.a. Calculate the number of components in the following systems:

i)KCl-NaCl-H_2O

ii)$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

b.Calculate the number of degrees of freedom in the following systems

i) $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$

ii) An aqueous solution of sodium chloride

c. What is the maximum degree of freedom for a:

i) Single component system.

ii) Pure substance under equilibrium.

5. Draw a neat phase diagram of water system, Discuss the behaviour of various equilibrium involved in the system with varying pressure and temperature. How does the melting point of ice change with the pressure and why?

6. What is condensed system? Why in such a case the phase rule equation is $F=C-P+1$?

7.Construct the phase diagram of lead-silver system and describe its use in understanding:

i) Eutectic point ii) Desilverization of argentiferrous lead

8. Define and compare the terms triple point and Eutectic point.

9. What is " reduced phase rule"? Explain the terms involved in it.

10.Give the cooling curves (not to scale- temp vs time) for the following:

i) 100% pure Ag

ii) 50% Pb & 50% Ag

iii) 97.4% Pb & 2.6% Ag

11. What is chemical equilibrium? Explain with example.

12. What are the characteristics of equilibrium state?

13. State and explain the law of chemical equilibrium.

14. What is equilibrium constant? What is Kp and Kc? What are their significances?

15. What is the relation between Kp and Kc?

16. What is the relation between equilibrium constant & Gibbs free energy? Hence explain about endothermic and exothermic reactions.

17. What are two types of chemical equilibrium? Explain about Homogeneous equilibria and Heterogeneous equilibria.

18. What is EMF? Describe the measurement of EMF of a cell.

19. Write short note on batteries.

20. Describe about primary and secondary batteries with example.

21. Write short note on;

(a) Zinc-carbon battery

(b) Alkaline battery

(c) Nickel-cadmium battery

(d) Lithium ion battery

(e) Lead acid battery

22. Describe the principle of fuel cell.