UNIT-I
JOUL-THOMSON EFFECT

Terms used in Thermodynamics:

System: A system is defined as a small quantity of a matter which is under considerable and which was separated from the surroundings by a real (or) imaginary boundary.

Surroundings:
Rest of the universe excluding the system is called surrounding.

Eg:- A reaction is carried out in a beaker. The contents of the beaker (like water or any solution etc.,) constitute the system, walls of the beaker serves as boundary and the beaker, air are acts as surroundings.

TYPES OF SYSTEMS: There are three types of systems.

1) Isolated System: A system which can exchange neither energy nor matter with its surroundings is known as an ***isolated system***.
Eg: Consider a system consisting of water in contact with its vapour in a closed and insulated vessel.

2) Open system: A system which can exchange both matter as well as energy with its surroundings is known as an Open System.
Eg: Consider evaporation of water in an Open Beaker.

3) Closed System: A system which can exchange energy but not matter with its surroundings is known as Closed System.
Eg: Consider a system consisting of water in contact with its vapour in a closed vessel.

EXTENSIVE PROPERTIES: The property which is dependent of amount of substance present in the system. Eg:- Mass, Volume, Internal Energy, Free Energy, Enthalpy, Entropy etc.,

INTENSIVE PROPERTIES: The property which is independent of amount and dependent only on nature of the substance present in the system. Eg:- Density, Surface Tension, Viscosity, Refractive Index, Temperature, Pressure, Concentration, Specific gravity, Specific heat etc.,

STATE FUNCTIONS / STATE VARIABLES:
The Fundamental properties which determine the state of a system are referred to as State Variables / State Functions / Thermodynamic parameters.

They are:
1) Pressure (P) 2) Temperature (T) 3) Volume (V)
4) Internal Energy (E) 5) Enthalpy (H) 6) Entropy (S)
7) Free Energy (G) 8) No. of moles (n)

THERMODYNAMIC PROCESS: The operation by which a thermodynamic system changes from one state to another state is called ***Thermodynamic Process.***

The various types of processes are:

Isothermal Process A process in which although heat enters (or) leaves the system yet the temperature of system remains constant throughout the process is called ***Isothermal Process:***

"IN THE ISOTHERMAL PROCESS $dT = 0$"

Eg: A Chemical reaction taking place in a closed but not insulated vessel.

Adiabatic Process: A process during which no heat enters (or) leaves the system during any step of the process is known as ***Adiabatic Process.***

Eg: A Chemical reaction taking place in a closed and insulated vessel.

"IN THE ADIABATIC PROCESS $dQ = 0$"

Isobaric Process: A process during which pressure of the system remains constant throughout the system is known as Isobaric Process.
Eg: Heating of water to its boiling point, and its vaporization takes place at the same atmospheric pressure.
"IN THE ISOBARIC PROCESS *dP = 0*"

Isochoric Process: A process during which volume of the system remains constant throughout the system is known as Isochoric Process.
Eg: Heating of substance in a non expanding chamber.
"IN THE ISOCHORIC PROCESS *dV = 0*"

Cyclic Process: A process during which the system comes to its initial state through a number of different processes is called Cyclic Process.
"IN THE CYCLIC PROCESS *dE = 0; dH =0*"

INTERNAL ENERGY:
A fixed quantity of any substance under a given set of conditions possesses a definite amount of energy associated with it. This amount of energy differs from different substances. Thus ***"Energy stored in the substance at constant temperature and pressure is called INTERNAL ENERGY"***. It is denoted by "E".

A system or a substance can be brought from one state A to another state B through different paths. Since E is a state function, its magnitude depends only on the state variables of the system. The change in E i.e., $\Delta E = E_B - E_A$:is independent of the path taken by the system in going from state A to state B. However, the heat (Q) and work (W) are path functions. Therefore, the values adjust themselves depending on the path taken. In any path taken (Q-W) is equal to ΔE. This is the first law of thermodynamics.

$Q = \Delta E + W$ ----> (This is first law of thermo dynamics)

ENTHALPY (H):
Heat changes in a system can take place at constant volume or at constant pressure.
- If the process is carried out at constant volume, no mechanical work is done since V is constant and therefore $\Delta V = 0$. Hence $P\Delta V$ i.e., W = 0.
  From 1st law of thermodynamics, $Q = \Delta E + W$ => $Q = \Delta E + P\Delta V$
  But at Constant Volume $\Delta V = 0$;
  $$\therefore Q_V = \Delta E$$
- If the process is carried out at constant pressure, the volume of the system changes and the work "W" is denoted by $P\Delta V$. Thefore
  From 1st law of thermodynamics, $Q = \Delta E + W$ => $Q = \Delta E + P\Delta V$
  $\Rightarrow Q_P = E_2 - E_1 + P(V_2 - V_1)$
  $\Rightarrow Q_P = (E_2 + PV_2) - (E_1 + PV_1)$
  Q_P is heat absorbed at constant pressure. (E +PV) is called enthalpy and is denoted by H.
  $$\therefore H = E + PV$$
  $\Rightarrow$ Then, $Q_P = (E_2 + PV_2) - (E_1 + PV_1)$
  $$Q_P = (H_2 - H_1) = \Delta H$$
  Thus increase in enthalpy (ΔH) is equal to the heat absorbed at constant pressure. Since E, P, V are state function, H is also state function.

"Enthalpy (H) is the amount of heat exchange by a system with it's surroundings at constant pressure and Temperature".

"H = E + PV" AND **"ΔH = ΔE + PΔV"**

The absolute value of "H" cannot be determined directly by experiment. But the change in enthalpy (ΔH) during the chemical change can be experimentally and directly determined.

$$\Delta H = [H_{products} - H_{reactants}]$$

ENTROPY (S):

Def:-   Entropy of a system is a measure of randomness (or) disorder of the system and is denoted by symbol S.

It is a most important thermodynamic function in order to make clear and thorough understanding of second law of thermodynamics. It is a state function.

"It can also the regarded as the measure of unavailable energy."

- The change in entropy of a system is given by
  - ⇨ $\Delta S = S_{final} - S_{initial}$:
  - ⇨ $= S_2 - S_1$:

Entropy is expressed in Joule/degree. $\Delta S = q / T$

Significance: When a system goes from a more orderly to less state, there is an increase in its randomness and hence entropy of the system increases. Conversely, if there is an increase in orderliness, there is a decrease in entropy.

- When a solid changes to a liquid, an increase in entropy takes place because the randomness of molecules increases.
- Conversely, the solidification brings about more orderly state and consequently there is a decrease in entropy.
- Vapourisation produces randomness in the distribution of molecules, hence an increase in entropy.

So, **"All substances in their normal crystalline state at the absolute zero temperature would be in the condition of maximum orderly arrangement, and hence, entropy of a substance at   0 K is zero".**

- ❖ Note: (Entropy signifies unavailable form of energy of the system).

FREE ENERGY: (G):

Def: *"Free energy change (ΔG) of a system is a measure of energy available for doing useful work."*

Thus, {Energy available as useful work = Total energy available – Nonavailable form of energy}

➔   G = H – TS (or)

The change in free energy between two state of system…

$$\Delta G = G_2 - G_1$$
$$= (H_2 - T_2S_2) - (H_1 - T_1S_1)$$
$$= (H_2 - H_1) - (T_2S_2 - T_1S_1)$$
$$= \Delta H - (T_2S_2 - T_1S_1)$$

Hence, at constant temperature (i.e., $T_1 = T_2$)

ΔG   =   ΔH - TΔS

Theoretical explanation (Physical significance) of Free Energy:

From the 1st law of thermodynamics,   q   = ΔE + Wexpansion + Wnon-expansion
                                         q   = ΔE + PΔV + Wnon-expansion
                                         q   = ΔH + Wnon-expansion ➔ (1)

From the entropy equation,   ΔS = q/T
                                      => q   = TΔS ➔ (2)

from (1) and (2)   TΔS = ΔH + Wnon-expansion   (or)
                       ΔH - TΔS = - Wnon-expansion   (or)
                        ΔG   = -Wnon-expansion

i.e., ΔG is a measure of useful work obtainable in a reversible reaction at constant temperature and pressure.
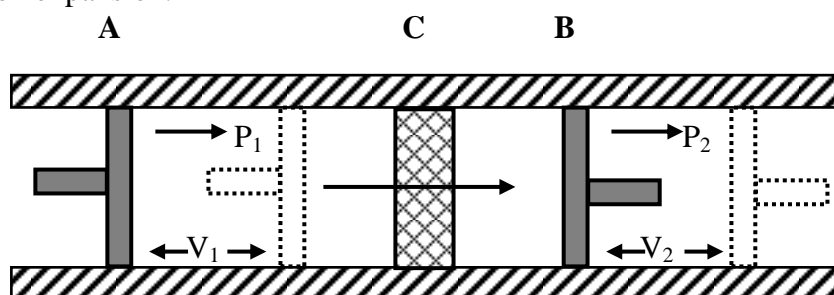
JOULE-THOMSON EFFECT:

"The phenomenon of change of temperature produced when a gas is made to expand adiabatically from a region of high pressure to a region of extremely low pressure is known as the Joule-Thomson effect."

But, Hydrogen and Helium are exceptions as they get warmed up under similar conditions. However, at very low temperature (below -80^0C for H_2 and -240^0C for He), these gases also show the above behaviour.

Inversion Temperature: The temperature below which a gas becomes cooler on expansion is known as the Inversion Temperature. (Inversion Temperature of Hydrogen is -80^0C and Helium is -240^0C).

Joule-Thomson Experiment:

A tube thoroughly insulated (to ensure adiabatic conditions) is fitted with a porous plug C in the middle and two pistons A and B on the sides. The pressures on the left and right sides of the plug are kept at P_1 and P_2 respectively where $P_1 > P_2$.

A volume V_1 of the gas enclosed between piston A and porous plug C at a higher pressure P_1 is forced very slowly (so as not to change the pressure P_1) through the porous plug by moving the piston A inwards; and is allowed to expand to volume V_2 at a lower pressure P_2 by moving the piston B outward. The change in temperature is found by taking readings on the two thermometers and it was observed that when the experiment is done at room temperature, all gases (except H_2 and He) show a fall in temperature on expansion.

Joule-Thomson effect and change in enthalpy:

Since the process is carried out adiabatically,

$$Q = 0$$

According to first law of thermodynamics,

$$\Delta E = Q - W \qquad \therefore \Delta E = -W \dots\dots\dots(i) \qquad (or) \; W = -\Delta E$$

Thus when the work of expansion is done adiabatically, the internal energy and hence temperature of the gas decreases.

Further on the left side of the plug, the work is done on the system whereas on the right side of the plug, work is done by the system.

Work done on the system on the left side $= -P_1 V_1$

Work done by the system on the right side $= P_2 V_2$

$\therefore$ Net work done by the system, $W = P_2 V_2 - P_1 V_1$ ……………….. (ii)

Substituting the value of W in equation (i), we get

$$\Delta E = -(P_2 V_2 - P_1 V_1)$$
$$= P_1 V_1 - P_2 V_2$$

Further we know that $\Delta E = E_2 - E_1 \qquad \therefore \; E_2 - E_1 = P_1 V_1 - P_2 V_2$

(or) $E_2 + P_2 V_2 = E_1 + P_1 V_1$ (or) $H_2 = H_1 \; (\because H = E + PV) \implies \qquad \therefore \qquad \Delta H = 0$

Thus, when a gas expands adiabatically through porous plug, the enthalpy of the system remains constant while internal energy changes.

Joule-Thomson coefficient:

Joule and Thomson further introduced the term Joule-Thomson coefficient, represented by μ, for expressing the change in temperature produced by change in pressure during adiabatic expansion of a real gas. They defined μ by the expression

$$\mu = \left(\frac{\delta T}{\delta P}\right)_H$$

From the above expression, it is obvious that

(i)   if μ is positive (i.e., when dT and dP both are negative), the gas cools on adiabatic expansion. Most gases have positive μ and hence they cool on expansion at room temperature.

(ii)   If μ is negative (i.e., when dT is positive and dP is negative), the gas warms up on adiabatic expansion at room temperature. Hydrogen and Helium have negative μ and hence, they warm up on expansion at room temperature.

(iii)   If μ = zero (i.e., when dT = 0) the gas neither cooled nor warms up on adiabatic expansion.
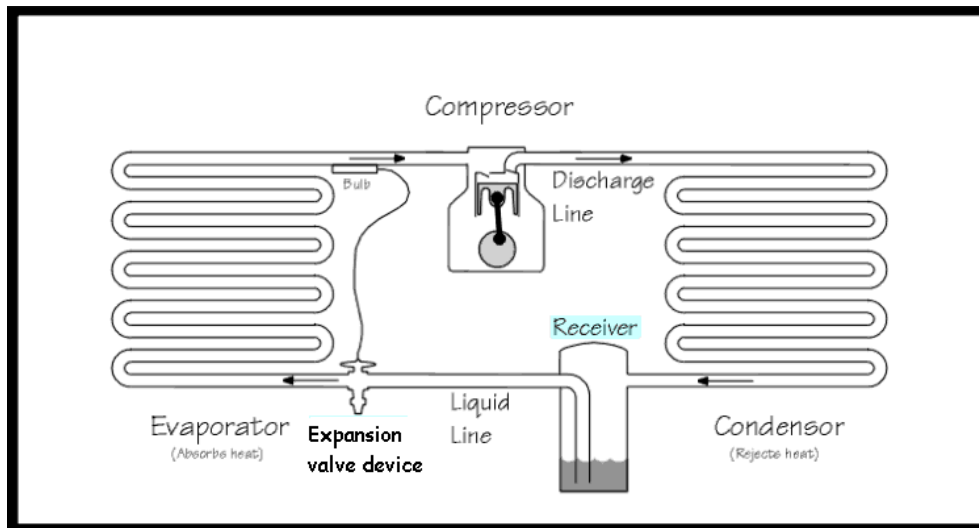
Application of Joule Thomson effect in Air Conditioning and Refrigeration:
REFRIGERATION:

"A machine which is used for producing low temperature below surrounding and maintaining an enclosure at that temperature is called Refrigerator".

There are four main components in a refrigeration:

   1) Compressor   2) Condensor   3) Metering Device   4) Evaporator

Compressor:

The compressor compresses the low pressure refrigerant vapour from the evaporator into high pressure vapour. The inlet to the compressor is called the Suction Line. It brings the low pressure vapour into the compressor. After the compressor compresses the refrigerant into a high pressure vapour, it removes through the outlet called the discharge line.

Condensor:

The discharge line leaves the compressor and runs to the inlet of the condenser. Because the refrigerant was compressed, it becomes a hot high pressure vapour. The hot vapour enters the condenser and starts to flow through the tubes. Cool air is blown across the outside of the tubes of condenser. Since the air is cooler than the refrigerant, heat transfers from the tubes of condenser to the cooler air. As the heat is removed from the refrigerant, it reaches it's saturated temperature and starts to change its state, into a

high pressure liquid. The high pressure liquid leaves the condenser through the liquid line and travels to the metering device.

Metering Device:
Metering devices regulate how much liquid refrigerant enters the evaporator. Commonly used metering device is TXV (Thermal Expansion Valve). As the metering device regulates the amount of refrigerant going into the evaporator, the device lets small amounts of refrigerant out into the line and looses the high pressure. Thus, a low pressure, cooler liquid refrigerant enters the evaporative coil.
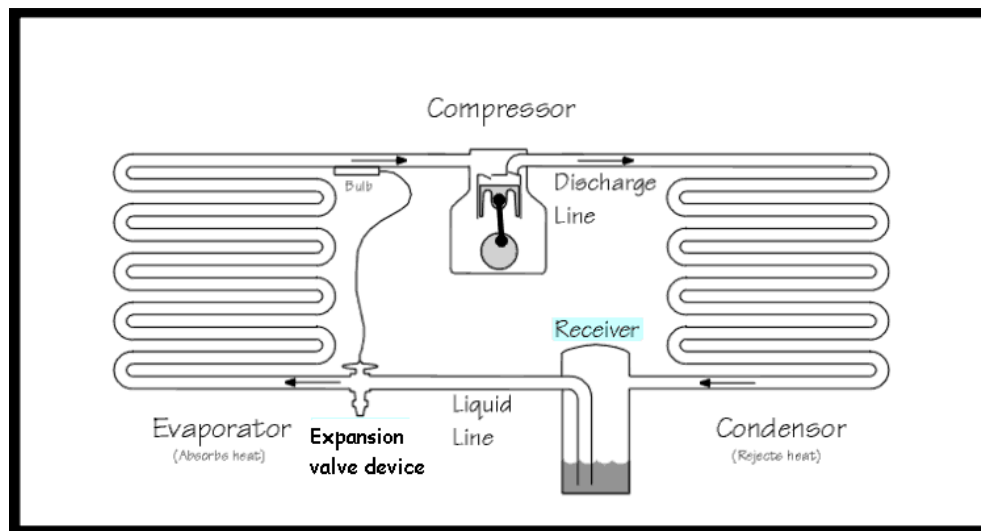
Evaporator:
Low pressure liquid leaves the metering device and enters the evaporator. The cooler refrigerant in the evaporator tubes, absorb the warm room air. The change of temperature cause the refrigerant to boil and changes from a low pressure liquid to a low pressure cold vapor. The low pressure vapour is pulled into the compressor and the cycle starts over.

AIR CONDITIONING:
Principle: "The warm air from the room is being removed and cycled back in as cooler air. This cycle contains until the thermostat reaches the desired temperature."

An air conditioner is basically a refrigerator without the insulated box. It uses the evaporation of a refrigerant, like Freon, to provide cooling. The mechanism of the Freon evaporation cycle are the same in a refrigerator as in an air conditioner.

Mechanism:
There are four main components in a refrigeration:
1)   Compressor   2) Condensor   3) Metering Device   4) Evaporator

The compressor compresses cool Freon gas, causing it to become hot, high-pressure Freon gas. This hot gas runs through a set of coils so it can dissipate its heat, and it condenses into a liquid. The Freon liquid runs through an expansion valve, and in the process it evaporates to become cold, low-pressure Freon gas. This cold gas runs through a set of coils that allow the gas to absorb heat and cool down the air inside the room. Freon is mixed with a small amount of lightweight oil. This oil lubricates the compressor.

SOLUBILITY PRODUCT & COMMON ION EFFECT

Definition of Solubility Product:
It is defined as the Product of the concentrations of the Cation and Anion in a Saturated solution of a Salt is known as "Solubility Product". It is denoted by K_{SP}.

From the definition, saturated solution of any salt contains the following two equilibria.

$$AB \underset{(Solid)}{<=>} AB \underset{(soluble)}{<=>} A^+ + B^-$$
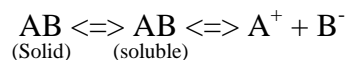
By applying law of mass action on both equilibria.

For equilibrium (1), $\quad k_I = \dfrac{[A^+][B^-]}{[AB]_{soluble}}$ $\qquad$ For equilibrium (2), $\quad k_{II} = \dfrac{[AB]_{soluble}}{[AB]_{solid}}$

$\therefore k_I \times k_{II} = \dfrac{[A^+][B^-]}{[AB]_{soluble}} \times \dfrac{[AB]_{soluble}}{[AB]_{solid}}$

$k_I \times k_{II} \times [AB]_{solid} = K_{SP} = [A+][B-]$ Where K_{SP} = solubility product.

In general, the formula of K_{SP} for a salt $A_xB_y = x^x.y^y.S^{x+y}$

Problem:1
The solubility product k_{sp} of the sparingly soluble salt Ag_2CrO_4 is 4×10^{-12} at a particular temperature. Calculate the solubility of silver chromate in grams per litre at that temperature. The molecular weight of silver chromate is 264.

Problem:2
What is the solubility of Ag_2CrO_4 in water if the value of solubility product, $K_{sp} = 1.7 \times 10^{-11} (mol / L)^3$.

Problem:3
The Ksp of AgCl is $1.8 \times 10^{-10} M^2$. What is molar solubility of AgCl in pure water.

Problem:4
The Ksp of Ag_2CrO_4 is $9 \times 10^{-12} M^3$. What is molar solubility of Ag_2CrO_4 in pure water.

Problem:5
The Ksp of $Cr(OH)_3$ is $1.2 \times 10^{-15} M^4$. What is molar solubility of $Cr(OH)_3$ in pure water.

Ionic Product of Water:
It is the product of H^+ and OH^- ion concentration in water (or) in aqueous solution at a given temperature.

Ionic product of Water $\qquad H_2O <=> H^+ + OH^-$

$\therefore K [H_2O] = [H^+][OH^-]$ (or) $Kw = [H^+][OH^-]$

Where Kw is known as Ioninc Product of water.

Kw at $25^0C = [H^+][OH^-] = 1.0 \times 10^{-14} mole^2 / litre^2$.

Common Ion Effect:
The phenomenon of suppression of solubility of an electrolyte in water by the addition of another electrolyte which has one ion common with the electrolyte.

Consider AB is a salt; Then $AB <=> A^+ + B^-$

If A^+ (or) B^- is added through another electrolyte AX (or) YB equilibrium shift towards left and then degree of dissociation of AB will decreases and consequently the solubility also.

Eg:- $CH_3COOH <=> CH_3COO^- + H^+$

$\qquad CH_3COONa \rightarrow CH_3COO^- + Na^+$ (addition of CH_3COONa)
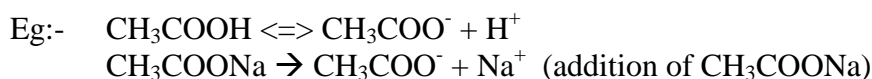
The addition of CH_3COO^- ion (common ion) through CH_3COONa reduces the ionization of CH_3COOH because of increase in Concentration of CH_3COO^- shifts the equilibrium to left and the degree of dissociation is decreased.

Eg:- The dissociation of NH_4OH is decreased by addition of NH_4Cl due to common ion NH_4^+ ion.

$$NH_4OH <=> NH_4^+ + OH^-$$
$$NH_4Cl \rightarrow NH_4^+ + Cl^- \text{ (addition of } NH_4Cl)$$
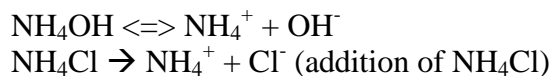
Applications of Common ion effect:

1) The concentration of S^{2-} in II group (or) OH^- ion in group III of chemical analysis is controlled by HCl and NH_4Cl on the basis of common ion effect.
2) The common ion effect principle is used in controlling the H^+ ion concentration in buffer solutions.

Applications of Solubility Product:

1) Determination of solubilities of sparingly soluble salts by using the Solubility Product Formula:
$K_{SP} = x^x.y^y.S^{x+y}$

2) If ionic product $< K_{SP}$ => The solution is unsaturated.
If ionic product $= K_{SP}$ => The solution is saturated.
If ionic product $> K_{SP}$ => The solution is super saturated.

3) **In the Qualitative Analysis:**
Cations are classified into different groups in the salt analysis on the basis of solubility product.
- The cations of group I (Pb^{2+}, Ag^+) are precipitated as their chlorides when we add HCl because their solubility products are low. Chlorides of metal ions of other groups are comparatively more soluble and therefore they are not precipitated.
- The cations of group II (Hg^{2+}, Cu^{2+}) are precipitated as their sulphides when H2S gas is passed through their acidified solution.
  - Function of dilute HCl in group II analysis:
    - $H_2S <=> 2H^+ + S^{2-}$
 $HCl \rightarrow H^+ + Cl^-$

Due to the common ion of H^+ ions, the degree of dissociation of H_2S is suppressed, so the concentration of S^{2-} decreases.

At this low value of S^{2-} only the ionic product of group II exceeds the solubility product. Hence, the Sulphides of group II get precipitated.
- The cations of group III (Al^{3+}, Fe^{2+}, Fe^{3+}) are precipitated as their hydroxides by adding NH_4OH to their salt solutions containing NH_4Cl.
  - Function of NH_4Cl in group III analysis:
    - $NH_4OH <=> NH_4^+ + OH^-$
      $NH_4Cl \rightarrow NH4^+ + Cl^-$

Due to the common ion of $NH4^+$ ions, the degree of dissociation of NH_4OH is suppressed, so the concentration of OH^- decreases.

At this low value of $[OH^-]$ only the ionic product of group III exceeds the solubility product. Hence, the Hydroxides of group III get precipitated.

- The cations of group IV (Mn^{2+}, Zn^{2+}) are precipitated as their sulphides by passing H2S gas through their solution containing NH_4OH.

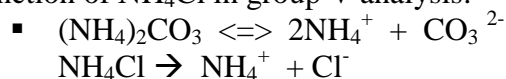o Function of NH$_4$OH in group IV analysis:
- H$_2$S $\Longleftrightarrow$ 2H$^+$ + S^{2-} ……………..(1)
  2NH$_4$OH $\Longleftrightarrow$ 2OH$^-$ + 2NH^{4+}
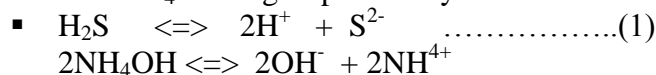
H+ ions react with OH$^-$ ions to give H$_2$O. Due to the decrease in the [H$^+$], the equilibrium (1) shifts towards right and [S^{2-}] increases. As a result ionic product increases and becomes sufficient to exceed the solubility product of group IV cations. Hence cations of group IV get precipitated.

In the absence of NH$_4$OH, sulphide of group IV cations are not precipitated because the [S^{2-}] is not sufficient and K$_{SP}$ value of group IV are higher.

- The cations of group V (Ca^{2+}, Ba^{2+}) are precipitated as their carbonates on adding (NH$_4$)$_2$CO$_3$ to their solution containing NH$_4$Cl and NH$_4$OH.
  o Function of NH$_4$Cl in group V analysis:
  - (NH$_4$)$_2$CO$_3$ $\Longleftrightarrow$ 2NH$_4$$^+$ + CO$_3$$^{2-}$
    NH$_4$Cl $\rightarrow$ NH$_4$$^+$ + Cl$^-$

Due to the common ion of NH$_4$$^+$ ions, the degree of dissociation of (NH$_4$)$_2$CO$_3$ is suppressed, so the concentration of CO$_3$$^{2-}$ decreases.

At this low value of CO$_3$$^{2-}$ only the ionic product of group V exceeds the solubility product. Hence, the carbonates of group V get precipitated.

  o Function of NH$_4$OH:
  Ammonium carbonate solution usually contains large amount of ammonium bicarbonate. The bicarbonates of V group cations are soluble so they do not get precipitated. Therefore, NH$_4$OH is added to convert NH$_4$HCO$_3$ into (NH$_4$)$_2$CO$_3$.

- The remaining cations are group VI cations (NH$_4$$^+$, Mg^{2+}).

4) **Salting out of soaps:** Soaps are sodium salts of higher fatty acids.
Addition of NaCl increases the concentration of sodium ions and hence the ionic product exceeds the solubility product of the soap which is separated out.

CHEMICAL EQUILIBRIUM
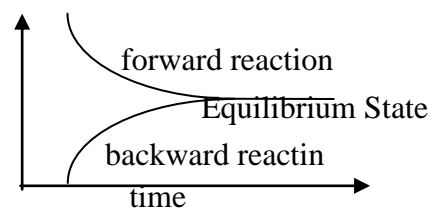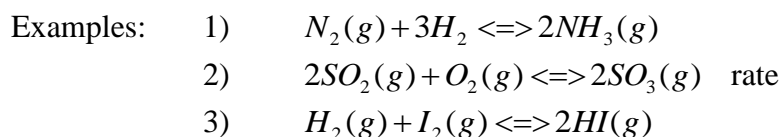
Equilibrium State (or) Equilibrium Process:

"The state at which the velocity of forward reaction becomes equal to the velocity of backward reaction in a reversible reaction is called equilibrium state (or) Chemical equilibrium."

Consider a reversible reaction. **A+B <=> C+D taking place in a closed vessel.**

At the beginning we have only the reactants A and B. Their concentrations are maximum. As the reaction proceeds the reactants A and B change into the products C and D. The concentrations of the products increase gradually.

The rate of forward reaction diminishes while the reverse reaction sets in and proceeds with increasing speed. A state is soon reached where the speeds of forward and backward reactions become equal. i.e., Rate of forward reaction V_f = The rate of backward reaction (V_b)

The system is said to have attained a state of equilibrium. Once equilibrium is reached there is no further change in the composition of the system. The system appears to be stand still although it is dynamic. The products are formed by forward reaction just as fast as they change back into reactants by the reverse reaction.

Examples:
1) $N_2(g) + 3H_2 <=> 2NH_3(g)$
2) $2SO_2(g) + O_2(g) <=> 2SO_3(g)$
3) $H_2(g) + I_2(g) <=> 2HI(g)$

rate — forward reaction / Equilibrium State / backward reactin — time

Dynamic Equilibrium:

The forward and reverse reactions of a reversible reaction continue to take place with equal rates simultaneously at the equilibrium stage also. Hence the equilibrium is called *Dynamic Equilibrium*.
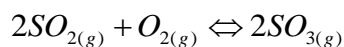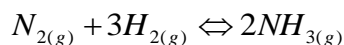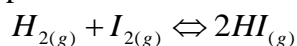
CHARACTERISTICS OF CHEMICAL EQUILIBRIUM:

1) The rate of the forward reaction is equal to the rate of the backward reaction. ($V_f = V_b$)
2) The concentrations of the reactants and the products remain unchanged with time.
3) The observable properties such as pressure, concentration, density, colour also remain unchanged with time.
4) The equilibrium is dynamic in nature. Both the forward reaction and the reverse reaction continue to take place simultaneously with equal rates.
5) A catalyst does not alter the state of equilibrium or the composition of the chemical substances of the reaction at the equilibrium. It only speeds up the attainment of the equilibrium.
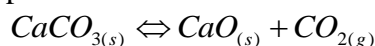6) Chemical equilibrium can be established from either side of the reversible reaction.

Types of Chemical Equilibrium:

There are mainly two types of equilibria:

a) Homogeneous: Equilibrium is said to be homogeneous if reactants and products are in same phase.

$$H_{2(g)} + I_{2(g)} \Leftrightarrow 2HI_{(g)}$$

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

$$2SO_{2(g)} + O_{2(g)} \Leftrightarrow 2SO_{3(g)}$$

b) Heterogeneous: Equilibrium is said to be heterogeneous if reactants and products are in different phase.

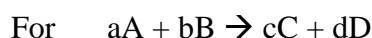$$CaCO_{3(s)} \Leftrightarrow CaO_{(s)} + CO_{2(g)}$$

LAW OF MASS ACTION:

According to this law "the rate of a chemical reaction is directly proportional to product of active masses of reactants each raised to a power equal to corresponding stoichiometric coefficient appearing in the balanced chemical equation".

<center>(or)</center>

"the rate of a chemical reaction is directly proportional to the product of active masses of the reactants".

For $\quad$ aA + bB $\rightarrow$ cC + dD

Rate of reaction $\infty \quad [A]^a.[B]^b$
Rate of reaction $= \quad k[A]^a.[B]^b$
Where k is rate constant or velocity constant of the reaction at that temperature.

Equilibrium constant in terms of Concentration: (Kc):

Consider a chemical reaction like: $\quad$ aA+bB $\Leftrightarrow$ cC + dD
From Law of mass action
$\qquad$ Rate of forward reaction $\quad r_f \propto [A]^a.[B]^b$ (or) $\quad r_f = k_f [A]^a.[B]^b$
$\qquad$ Rate of backward reaction $\quad r_b \propto [C]^c.[D]^d$ (or) $\quad r_b = k_b [C]^c.[D]^d$
At equilibrium $\qquad r_f = r_b$
$\qquad \therefore k_f [A]^a.[B]^b = k_b [C]^c.[D]^d$

$$\therefore \frac{k_f}{k_b} = \frac{[C]^c.[D]^d}{[A]^a.[B]^b} = K_c$$

$\qquad k_f / k_b = Kc$, an equilibrium constant in terms of Concentration.

Equilibrium constant in terms of Partial Pressure: (Kp):

Consider a chemical reaction like: $\quad$ aA+bB $\Leftrightarrow$ cC + dD

Then, $\dfrac{[P_C]^c.[P_D]^d}{[P_A]^a.[P_B]^b} = K_P$

Relation between Kp and Kc:

For a general equation, $\qquad$ aA+bB $\Leftrightarrow$ cC + dD

Where a, b, c and d are coefficients of the reacting substances.

$$\frac{[P_C]^c.[P_D]^d}{[P_A]^a.[P_B]^b} = K_P$$

From gas equation: $\quad$ PV = nRT $\qquad$ => $\qquad P = \left(\dfrac{n}{V}\right)RT$; (n/v is the concentration term)

So, $\quad P_A = [A]RT; \quad P_B = [B]RT; \quad P_C = [C]RT; \quad P_D = [D]RT;$

Hence, $\qquad$ Kp = $([C]RT)^c. ([D]RT)^d / ([A]RT)^a ([B]RT)^b$
$\qquad\qquad$ Kp = $[C]^c[D]^d / [A]^a[B]^b$ x $(RT)^{(c+d)-(a+b)}$
$\qquad$ => $\qquad$ Kp = Kc x $(RT)^{\Delta n}$ $\qquad$ Where $\Delta n = (c+d)-(a+b)$ = change in the No.of moles.
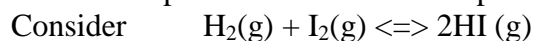If $\Delta n = 0$ $\qquad$ Kp = Kc
If $\Delta n > 0$ $\qquad$ Kp > Kc
If $\Delta n < 0$ $\qquad$ Kp < Kc

The factors which influence the position of equilibrium:
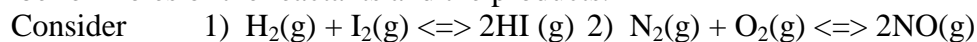**The factors which influencing the equilibrium position are:**
1) Concentration, 2) Pressure, 3) Temperature and 4) Catalyst.
1) Concentration: Increase of reactant concentrations pushes the equilibrium state to the products side and increase of the products concentrations pushes to the equilibrium to the reactants side.
Consider $H_2(g) + I_2(g) <=> 2HI (g)$
Increase of H_2 (or) I_2 concentrations pushes the equilibrium in favours of HI and similarly the increase of HI concentrations pushes the equilibrium in favour of H_2 and I_2.

2) Pressure: Pressure will have no effect on the equilibrium reactions in which there is no change in the number of moles of the reactants and the products.
Consider   1) $H_2(g) + I_2(g) <=> 2HI (g)$ 2) $N_2(g) + O_2(g) <=> 2NO(g)$
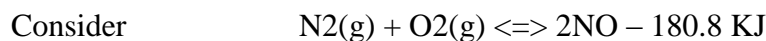But in the case of reactions in which there is a change in the number of moles of the reactants and the products, increase of pressure pushes the reaction equilibrium in the direction in which there is a decrease in the number of moles.
Consider   1) $PCl_5(g) <=> PCl_3(g) + Cl_2(g)$
In the above reaction, increase of pressure favours the backward reaction and decrease of pressure favour the forward reaction.

3) Temperature: Increase of temperature favour the endothermic reaction and decrease of temperature favours exothermic reactions.
Consider $N2(g) + O2(g) <=> 2NO - 180.8 KJ$
IN the above reaction, increase of temperature favours the forward reaction because it is endothermic and decrease of temperature favours backward reaction because it is exothermic.

4) Catalyst: A catalyst increases the rate of both the forward and the backward reactions. Hence, a catalyst will have no effect on the position of equilibrium. It will only hasten the attainment of the equilibrium.
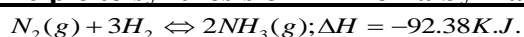
Le-Chatelier's Principle:
"If a system at equilibrium is subjected to the change of pressure, temperature (or) concentration, the system is shifted in such a way as to nullify (or) reduce the effect of change".
From Le-Chatelier's principle, it has been concluded that:
1)   Increase of pressure favours the reaction where there is decreasein volume.
2)   Decrease of pressure favours the reaction where there is increase in volume.
3)   Increase of temperature favours the reaction where there is endothermic reaction.
4)   Decrease of temperature favours the reaction where there is exothermic reaction.
5)   Increase of concentration of reactants and decrease in concentration of the products will favours the forward reaction.
6)   Decrease of concentration of reactants and increase in concentration of the products will favours the backward reaction.

Applications of Le-Chatelier's Principle to synthesis of Ammonia by Haber's Process:
$$N_2(g) + 3H_2 \Leftrightarrow 2NH_3(g); \Delta H = -92.38 K.J.$$
4volumes (1+3)   2volumes
Nitrogen and Hydrogen combine to form ammonia. The formation of ammonia is reversible and exothermic reaction. It is accompanied by decrease in volume.
Effect of concentration:
By adding one or both of the reactants to the equilibrium mixture, the reaction will proceed in the direction in which the concentration of added components are used up. Similarly, by removing ammonia from the mixture, equilibrium shifts in the same direction. Therefore, by increasing the

concentration of H_2 and N_2 and simultaneously by removing the ammonia maximum yield of ammonia can be produced.

Effect of Pressure:

1 volume of N2 combines with 3 volumes of H2 to form 2 volumes of NH3. There is decrease in volume in the forward reaction (4 volumes to 2 volumes). According to Le Chateliers principle increase of pressure favours the reaction where there is decrease in volume. So higher the pressure, greater the yield of ammonia. In practice 200 atmospheres are used in the manufacture of ammonia by Haber's Process.

Effect of Temperature:

The formation of ammonia is exothermic reaction. According to Le-Chateliers principle low temperatures favour the forward reaction. But at low temperatures the reaction is too slow. Therefore an optimum temperature (725K to 775K) is chosen in Haber's process.

To speed up the reaction, a catalyst, finely divided iron is used. To increase the activity of the catalyst "Mo" (or) a mixture of K_2O and Al_2O_3 is used as promoter.

The Optimum conditions are:

```
Pressure       : 200atm
Temperature    : 725 – 775 K
Catalyst       : Fe (Powdered)
Promoter       : Mo (or) K₂O + Al₂O₃
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Applications of Le-Chatelier's Principle to synthesis of SO_3 by Contacts Method:

$$2SO_2(g) + O_2 \Leftrightarrow 2SO_3(g); \Delta H = -189 K.J.$$

3 volumes (2+1)   2volumes

The formation of SO3 is reversible and exothermic reaction. It is accompanied by decrease in volume.

Effect of concentration:

By adding one or both of the reactants to the equilibrium mixture, the reaction will proceed in the direction in which the concentration of added components are used up. Similarly, by removing SO_3 from the mixture, equilibrium shifts in the same direction. Therefore, by increasing the concentration of SO_2 and O_2 and simultaneously by removing the SO_3 maximum yield of SO_3 can be produced.

Effect of Pressure:

2 volumes of SO_2 and 1 volume of O_2 combine to give 2 volumes of SO_3. The formation of SO_3 is accompanied by decrease in volume (3volumes to 2 volumes). According to Le Chateliers principle increase of pressure favours the reaction where there is decrease in volume. But, in contact process high pressures are not used because towers used in the manufacture are corroded by the acid at these high pressure. But, low pressures favour the decomposition of SO3. Hence, optimum pressures (1.5 to 1.7 atmospheres) are used.

Effect of Temperature:

The formation of SO_3 is exothermic reaction. According to Le-Chateliers principle low temperatures favour the forward reaction. But at low temperatures the reaction is too slow. Therefore an optimum temperature (673K) is chosen in Contacts process.

To speed up the reaction, a catalyst, V_2O_5 (or) Platinised Asbestos.

The Optimum conditions are:

```
Pressure       : (1-2) atm
Temperature    : 673K
Catalyst       : V₂O₅ (or)
                 Platinised Asbestos
```

OSMOSIS AND REVERSE OSMOSIS

Osmosis:
When two solutions of different concentrations are separated by a semi permeable membrane, the solvent flows from the dilute solution into the concentrated solution through the semipermeable membrane until the concentrations of both the solutions becomes equal. This is known as *Osmosis.*
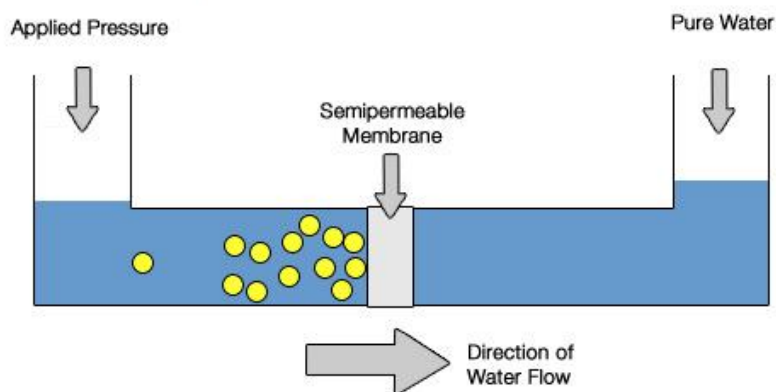
Osmotic Pressure (π) :
The excess pressure which must be applied to a solution to prevent the flow of the solvent into it through a semipermeable membrane is known as *Osmotic Pressure of the solution.*

Reverse Osmosis:
If a pressure higher than the osmotic pressure is applied on the high concentrated solution, the solvent will flow from the higher concentration solution to lower concentration solution through the semi-permeable membrane. Since here the flow of solvent is in the reverse direction to the osmosis, the process is called as *reverse osmosis.*
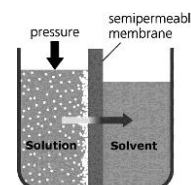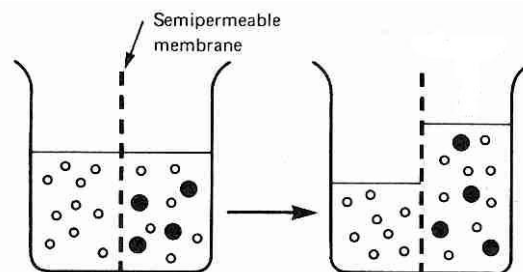
Desalination of Brackish Water (or) Sea water by the use of Reverse Osmosis:

Brackish water is pumped continuously at high pressure (>25 atmospheres) (or)a pressure of 15-40 Kg/cm^2 is applied then water flows from brackish water into fresh water. The flow of water is proportional to applied pressure. Concentrated brine and fresh water are withdrawn through their respective outlets. This method, however, has not yet been used on large scale production of fresh water. The technique is only successful in the recovery of fresh water from brackish water.

Advantages:
- Colloidal SiO_2 can be removed by reverse osmosis, which even cannot be removed by demineralization.
- It is simple and reliable process.
- Capital and operating expenses are low.
- The life of the semi-permeable membrane is about 2 years.
- The Semi-permeable membrane can be easily replaced within a few minutes, thereby nearly uninterrupted water supply can be provided.
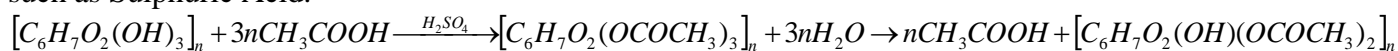
LIMITATIONS OF DESALINATION PROCESS:

1) *Waste disposal:* The process of desalination requires pretreatment and cleaning: chemicals which are added to wwater before desalination to make the treatment more efficient and successful. These chemicals can be used for only a limited amount of time. These chemicals often find their way back into the ocean, where they poison plant and animal life.

2) *Brine:* Brine is the side product of desalination. Most desalination plants pump this brine back into the ocean, which present environmental drawback. Ocean species are not adjust to the immediate change in salinity caused by the release of brine into the area.

3) *Health Concerns:* Desalination is not a perfected technology and desalinated water can be harmful to human health. By-products of the chemicals used in desalination can get through into the pure water and endanger the people who drink it. Desalination water can also be acidic to both pipes and digestive system.

4) *Energy Use:* Desalination plants have the disadvantage of requiring large amounts of power. Other water treatment technologies are more energy efficient.

TYPES OF MEMBRANES:

1) Cellulose Acetate: It is made by reacting natural cellulose with acetic acid in presence of a catalyst such as Sulphuric Acid.

$$[C_6H_7O_2(OH)_3]_n + 3nCH_3COOH \xrightarrow{H_2SO_4} [C_6H_7O_2(OCOCH_3)_3]_n + 3nH_2O \rightarrow nCH_3COOH + [C_6H_7O_2(OH)(OCOCH_3)_2]_n$$

Because of good clarity, stability, toughness, impact strength and high tensile strength this can be used as a semi-permeable membrane.

2) Polymethyl Methacrylate: (PMMA):-

It is also known as Lucits (or) Plexiglass and is obtained by polymerization of methyl methacrylate in presence of hydrogen peroxide.

methyl methacrylate   poly(methyl methacrylate)
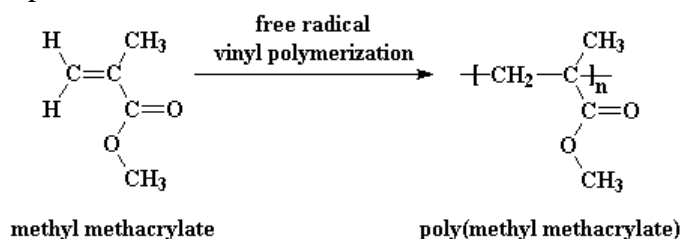
Because of its rigidness to viscous consistency, optical transparency, it can be employed as semipermeable membrane.