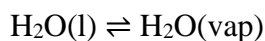


Equilibrium

Introduction

When a liquid evaporates in a closed container, molecules with relatively higher kinetic energy escape the liquid surface into the vapour phase and number of liquid molecules from the vapour phase strike the liquid surface and are retained in the liquid phase. It gives rise to a constant vapour pressure because of an equilibrium in which the number of molecules leaving the liquid equals the number returning to liquid from the vapour. Then the system has reached equilibrium state at this stage. Thus, at equilibrium, the rate of evaporation is equal to the rate of condensation. It may be represented by



The above double arrow indicates that the process simultaneously going in both directions. The equilibrium mixture means the mixture of reactants and products in the equilibrium state is called an **equilibrium mixture**.

Equilibrium in physical process:

We observe some physical process then the characteristics of system at equilibrium are better understand. The most important and familiar examples are **phase transformation process**.

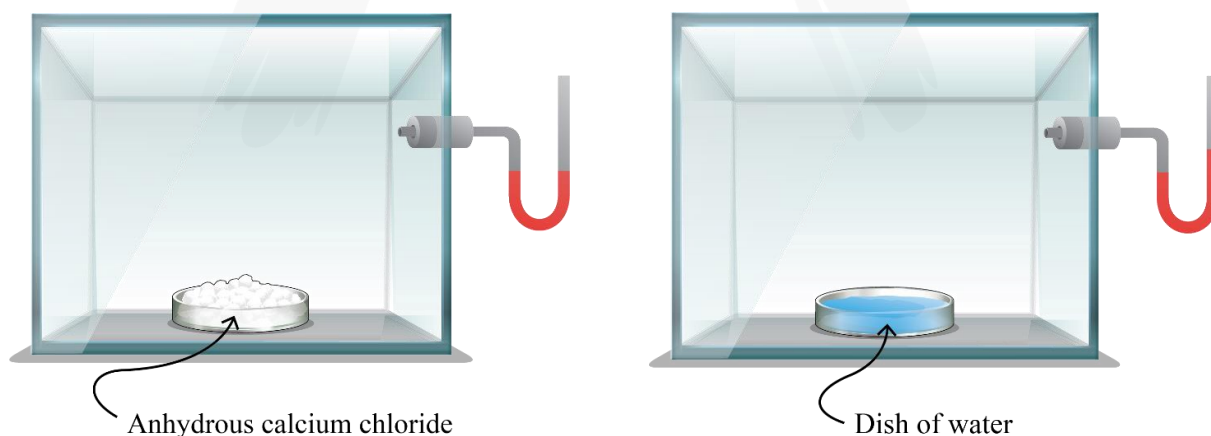
Eg. Solid \rightleftharpoons liquid
 Liquid \rightleftharpoons gas
 Solid \rightleftharpoons gas

(a) Solid-liquid equilibrium:

At particular temperature and pressure the ice and water are in equilibrium. The normal melting point or normal freezing point of the substance is the temperature at which the solid phase and liquid phases are equilibrium for any pure substance at atmospheric pressure. When the system at dynamic equilibrium will follow the conditions:

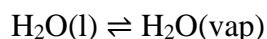
- Both the opposing processes occur simultaneously.
- Both the process occurs at the same rate then the amount of ice and water remains constant.

(b) Liquid-vapour equilibrium:



The number of water molecules from the gaseous state into liquid state increases until the equilibrium reached.

i.e rate of evaporation = rate of condensation



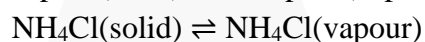
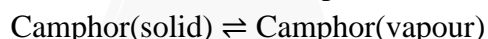
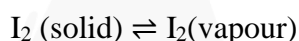
The equilibrium water pressure means at which pressure the water molecules remains constant at given temperature and vapour pressure of water increase with temperature. The evaporation of liquid depends on,

- The nature of the liquid
- The amount of liquid
- The applied temperature

For example in a closed vessel water and water vapour are in equilibrium position at atmospheric pressure (1.031 bar) and at 100° C. Which means that for any pure liquid at one atmospheric pressure (1.0301 bar), then the normal boiling point is said to be the temperature at which liquid and vapours are at equilibrium.

(c) Solid – vapour equilibrium:

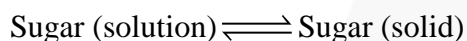
The examples of this type system considered when solids sublime to vapour phase.



Equilibrium Involving Dissolution of Solid or Gases in Liquids

Solids in liquids

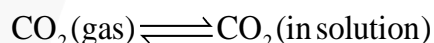
- We know from our experience that we can dissolve only a limited amount of salt or sugar in a given amount of water at room temperature.
- We call it a saturated solution when no more solute can be dissolved in it at a given temperature. The concentration of the solute in a saturated solution depends upon the temperature.



The rate of dissolution of sugar = rate of crystallisation of sugar.

Gases in liquids

- When a soda water bottle is opened, some of the carbon dioxide gas dissolved in it fizzes out rapidly. The phenomenon arises due to difference in solubility of carbon dioxide at different pressures.
- There is equilibrium between the molecules in the gaseous state and the molecules dissolved in the liquid under pressure i.e.,



- This equilibrium is governed by Henry's law, **which states that the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent.**

Some Features of Physical Equilibria

Process	Conclusion
Liquid \rightleftharpoons Vapour $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$	$P_{\text{H}_2\text{O}}$ constant at given temperature
Solid \rightleftharpoons Liquid $\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$	Melting point is fixed at constant pressure
Solute(s) \rightleftharpoons Solute (solution)	Concentration of solute in solution is constant at a given temperature.

$\text{Sugar(s)} \rightleftharpoons \text{Sugar (solution)}$	
$\text{Gas(s)} \rightleftharpoons \text{Gas(aq)}$ $\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{aq})$	$[\text{gas(aq)}]/[\text{gas(g)}]$ is constant at a given temperature $[\text{CO}_2(\text{aq})]/[\text{CO}_2(\text{g})]$ is constant at a given temperature

General characteristics of Equilibrium involving physical process:

Following characteristics are common to the system at equilibrium for which the physical process are discussed above:

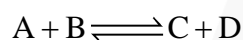
- At a given temperature, the equilibrium possible only in closed systems.
- If both the opposing processes occur at the same rate then the system is dynamic at stable condition.
- In a system, all measurable properties are remains constant.
- Equilibrium is characterized by constant value of one of its parameters given, and then it is attained for a physical process.

Equilibrium in chemical process:

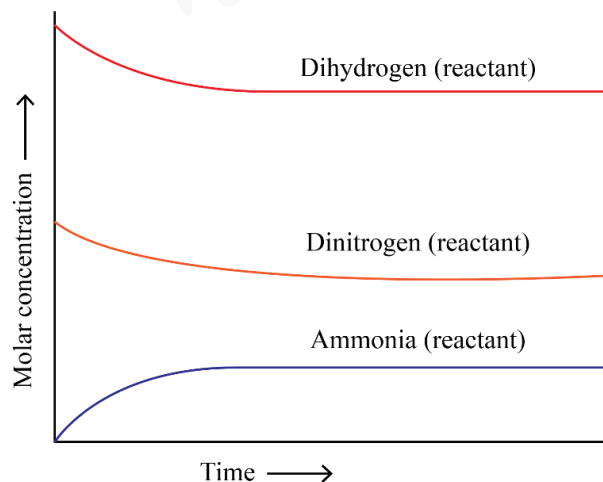
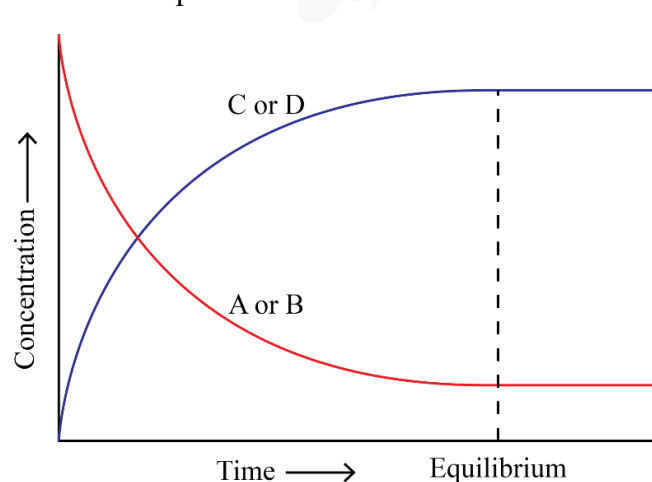
Compared to physical systems chemical reactions also attain a state of equilibrium. Those chemical reactions can occur both in forward and backward directions. The chemical equilibrium is dynamic in nature when the rates of forward and backward become equal with the concentrations and products are remains constant.

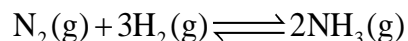
EQUILIBRIUM IN CHEMICAL PROCESSES – DYNAMIC EQUILIBRIUM

- For a better comprehension, let us consider a general case of a reversible reaction,



- With passage of time, there is accumulation of the products C and d and depletion of the reactions A and B. This leads to a decrease in the rate of forward reaction and an increase in the rate of the reverse reaction,
- Eventually, the two reactions occur at the same rate and the system reaches a state of equilibrium.
- Similarly, the reaction can reach the state of equilibrium even if we start with only C and D; that is, no A and B being present initially, as the equilibrium can be reached from either direction.
- The dynamic nature of chemical equilibrium can be demonstrated in the synthesis of ammonia by Haber's process.

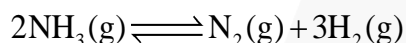
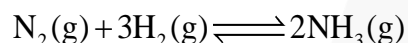




(H₂, N₂, NH₃ and D₂, N₂, ND₃) are mixed together and left for a while. Later, when this mixture is analysed, it is found that the concentration of ammonia is just the same as before. However, when this mixture is analysed by a mass spectrometer, it is found that ammonia and all deuterium containing forms of ammonia (NH₃, NH₂D, NHD₂ and ND₃) and dihydrogen and its deuterated forms (H₂, HD and D₂) are present. Thus one can conclude that scrambling of H and D atoms in the molecules must result from a continuation of the forward and reverse reactions in the mixture. If the reaction had simply stopped when they reached equilibrium, then there would have been no mixing of isotopes in this way.

Use of isotope (deuterium) in the formation of ammonia clearly indicates that **chemical reactions reach a state of dynamic equilibrium in which the rates of forward and reverse reactions are equal and there is no net change in composition.**

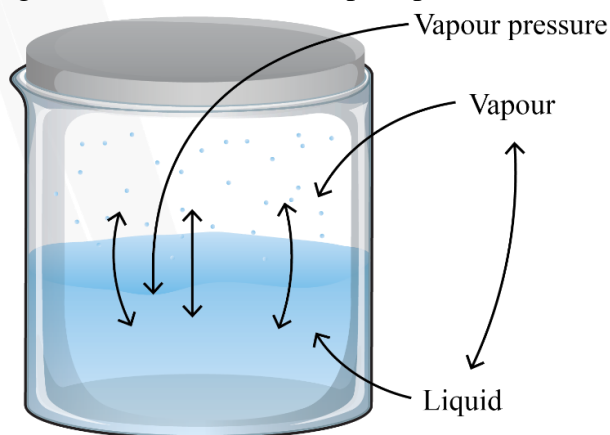
Equilibrium can be attained from both sides, whether we start reaction by taking, H₂(g) and N₂(g) and get NH₃(g) or by taking NH₃(g) and decomposing it into N₂(g) and H₂(g).



Equilibrium

When a liquid evaporates in a closed container, molecules with relatively higher kinetic energy escape the liquid surface into the vapour phase and number of liquid molecules from the vapour phase strike the liquid surface and are retained in the liquid phase. It gives rise to a constant vapour pressure because of an equilibrium in which the number of molecules leaving the liquid equals the number returning to liquid from the vapour. We say that the system has reached equilibrium state at this stage.

However, this is not static equilibrium and there is a lot of activity at the boundary between the liquid and the vapour. Thus, at equilibrium, the rate of evaporation is equal to the rate of condensation.

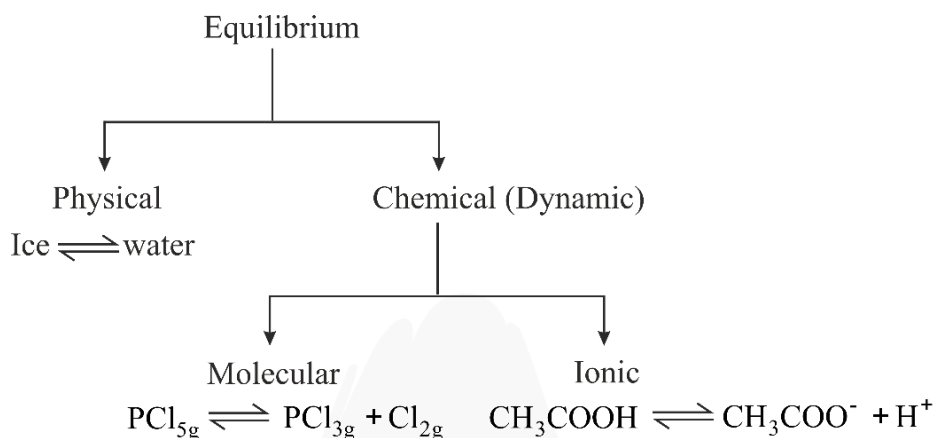


The mixture of reactants and products in the equilibrium state is called an equilibrium mixture. The reaction may be fast or slow depending on the experimental conditions and the nature of the reactants. When the reactants in a closed vessel at a particular temperature react to give products, the concentrations of the reactants keep on decreasing, while those of products keep on increasing for some time after which there is no change in the concentrations of either of the reactants or products. This stage of the system is the dynamic equilibrium and the rates of the forward and reverse reactions become equal. It is due to this dynamic equilibrium stage that there is no change in the concentrations of various species in the reaction mixture. Based on the extent to which the reactions proceed to reach the state of chemical equilibrium

Ionic Equilibrium

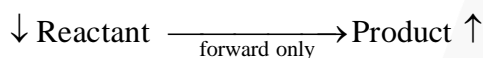
The extent of a reaction in equilibrium varies with the experimental conditions such as concentrations of reactants, temperature, etc. Optimisation of the operational conditions is very important in industry

and laboratory so that equilibrium is favourable in the direction of the desired product. Some important aspects of equilibrium involving physical and chemical processes are dealt in this unit along with the equilibrium involving ions in aqueous solutions which is called as ionic equilibrium.



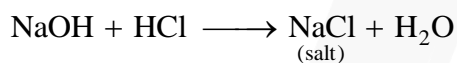
Chemical Equilibrium

Irreversible reactions



Ex:

(1) Neutralisation reaction



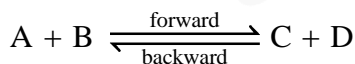
(2) Precipitation reaction.



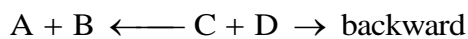
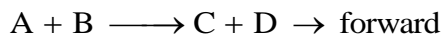
(3) Combustion reaction.



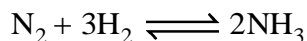
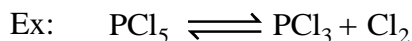
Reversible reaction



i.e:



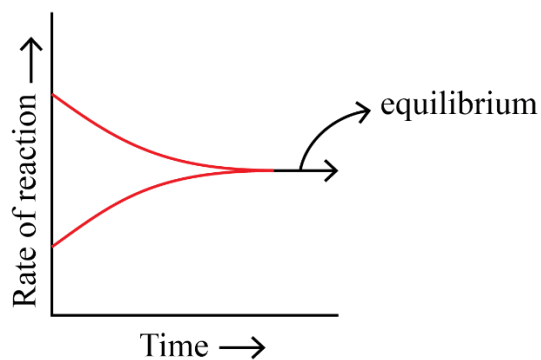
∴ finally comes to equilibrium.



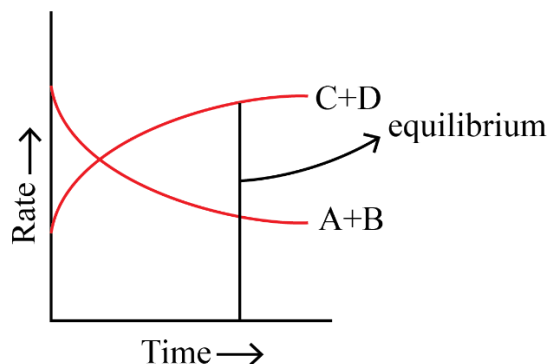
∴ Equilibrium is nothing but when,

Rate of forward Reaction = Rate of backward reaction.

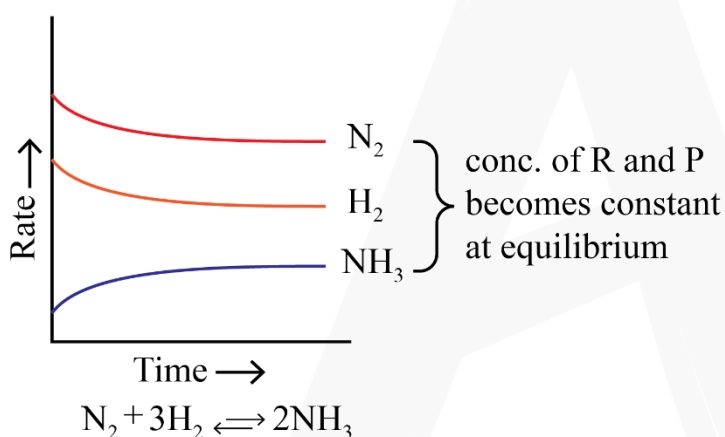
Graph 1



Graph 2



Graph 3



General Characteristics of Equilibria Involving Physical Processes

For the physical processes discussed above, following characteristics are common to the system at equilibrium:

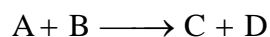
- (i) Equilibrium is possible only in a closed system at a given temperature.
- (ii) Both the opposing processes occur at the same rate and there is a dynamic but stable condition.
- (iii) All measurable properties of the system remain constant.
- (iv) When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameters at a given temperature.
- (v) The magnitude of such quantities at any stage indicates the extent to which the physical process has proceeded before reaching equilibrium.

Note:

Catalyst: Change the rate of reaction \rightarrow forward and backward } rate of achieving equilibrium.

Law of mass action: $A + B \rightleftharpoons C + D$

Forward reaction



$$R \text{ O } F \propto [A] [B]$$

$$R \text{ O } F = k_f [A] [B] \dots\dots (i)$$

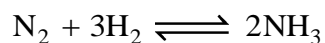
But equilibrium is when

$$R \text{ O } F = R \text{ O } B$$

$$k_f [A] [B] = k_b [C] [D]$$

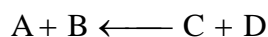
$$\frac{k_f}{k_b} = \frac{[C][D]}{[A][B]} = k_e$$

For example



$$\therefore k_e = \frac{[NH_3]^2}{[N_2]^1 [H_2]^3}$$

Backward reaction

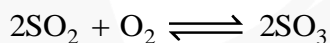


$$R \text{ O } B \propto [C] [D]$$

$$R \text{ O } B = k_b [C] [D] \dots\dots (ii)$$

Note: ROF (Rate of Forward Reaction)

ROB (Rate of Backward Reaction)



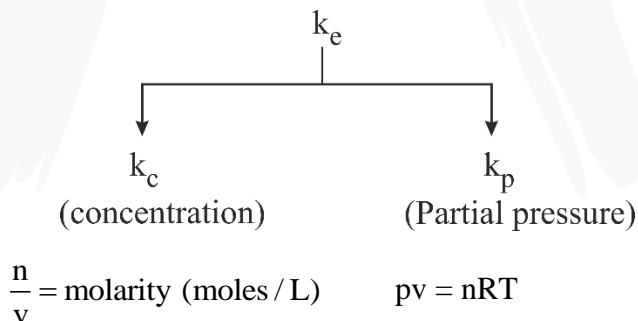
$$\therefore k_e = \frac{[SO_3]^2}{[SO_2]^2 [O_2]}$$

Conclusion

$$(1) k_e = \frac{k_f}{k_b}$$

(2) Rate of forward reaction = Rate of backward reaction

$$(3) k_e = \frac{[\text{Products}]}{[\text{Reactants}]} \quad [] \rightarrow \text{conc. at equilibrium}$$



For liquid and gas

$$p = \left(\frac{n}{v} \right) RT \quad p \propto \frac{n}{v} \text{ for gas}$$

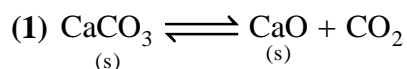
Note:

Case I: Solid is always taken as unity.

Case II: Liquid when taken with gas is taken as unity.

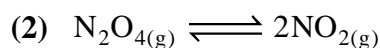
Case III: H_2O is taken as unity, if reaction is in aqueous medium.

Some more examples, fluid k_c ? k_p ?



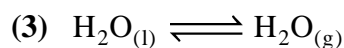
$$k_c = [\text{CO}_2]$$

$$k_p = (p_{\text{CO}_2})$$



$$k_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]^1}$$

$$k_p = \frac{(p_{\text{NO}_2})^2}{(p_{\text{N}_2\text{O}_4})^1}$$



$$k_c = [\text{H}_2\text{O}]^1$$

$$k_p = (p_{\text{H}_2\text{O}})$$

k_p = Not defined as no gas molecules

Relation between k_p & k_c

$$k_p = k_c \cdot (RT)^{\Delta n_g}$$

$$\text{where } \Delta n_g = n_p - n_R$$

Degree of Dissociation

No. of moles dissociated per mole of the reactant is termed as degree of dissociation. (α)

Range: $0 \leq \alpha \leq 1$

Note: When the value of α is 1, then the reaction is 100% completed and the reaction is irreversible reaction.



$$t = 0 \quad 1 \quad 0 \quad 0$$

$$t = \text{eq. } 1 - 0.6$$

if degree of dissociation = α

$$t = 0 \quad C \text{ moles} \quad 0 \quad 0$$

$$t = \text{eq. } C - C\alpha$$

$$\therefore \alpha = \frac{\text{No. of moles dissociated}}{\text{total moles of reaction}}$$

Similarly,

$$\% \alpha = \frac{\text{No. of moles dissociated}}{\text{total moles of reaction}} \times 100$$

Note: $\frac{\text{Total mass of mixture}}{\text{Total no. of moles}} = \text{Average molar mass observed}$

$$\frac{\text{Vapour density of mixture}}{\text{Total no. of moles}} = \text{Vapour density observed}$$

Assume, $(A \rightleftharpoons nB)$

$$t = 0 \quad \quad 1 \quad \quad 0 \quad \quad \} \text{ total moles} = 1 - \alpha + n\alpha$$

$$t = \text{eq.} \quad \quad 1 - \alpha \quad \quad n\alpha \quad \quad = 1 + \alpha(n - 1)$$

$$\therefore m = \frac{\text{Total mass of mixture}(M_R)}{\text{Total no. of moles}} = \frac{M}{1 + \alpha(n - 1)}$$

Similarly,

$$d = \frac{D}{1 + \alpha(n - 1)}$$

$$\left. \begin{array}{l} d_m \} \text{observed density / mass} \\ D_M \} \text{Actual density / mass} \end{array} \right\}$$

Applications of Equilibrium constant:

- To predict the extent of reaction on the basis of its magnitude.

The magnitude of (k_c) gives an idea of the relative amounts of the reactants and the products.

- If the value is larger than 10^3 it takes the reaction forward.

ie conc. of products > conc. of reactants.



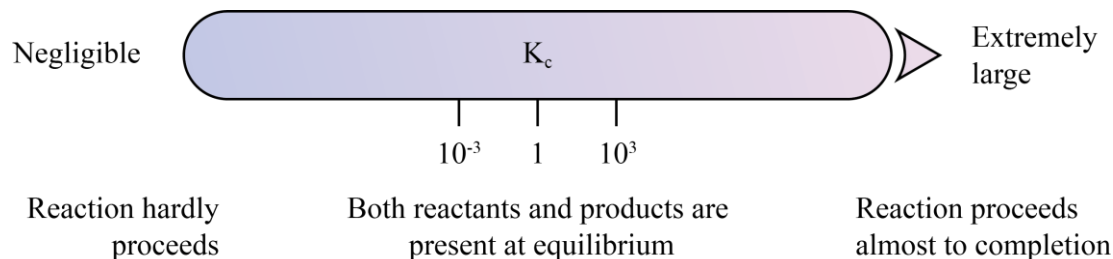
$$\therefore 5.4 \times 10^8 > 10^3$$

\therefore conc. of product is high ie the reaction is complete.

$k_c > 10^3 \rightarrow$ Reaction almost complete.

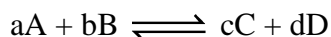
$k_c = 10^{-3} \leftrightarrow 10^3 \rightarrow$ Reactant/product are in equilibrium.

$k_c < 10^{-3} \rightarrow$ Reaction hardly proceeds.



Dependence of extent of reaction on K_c

- Predicting the direction of reaction



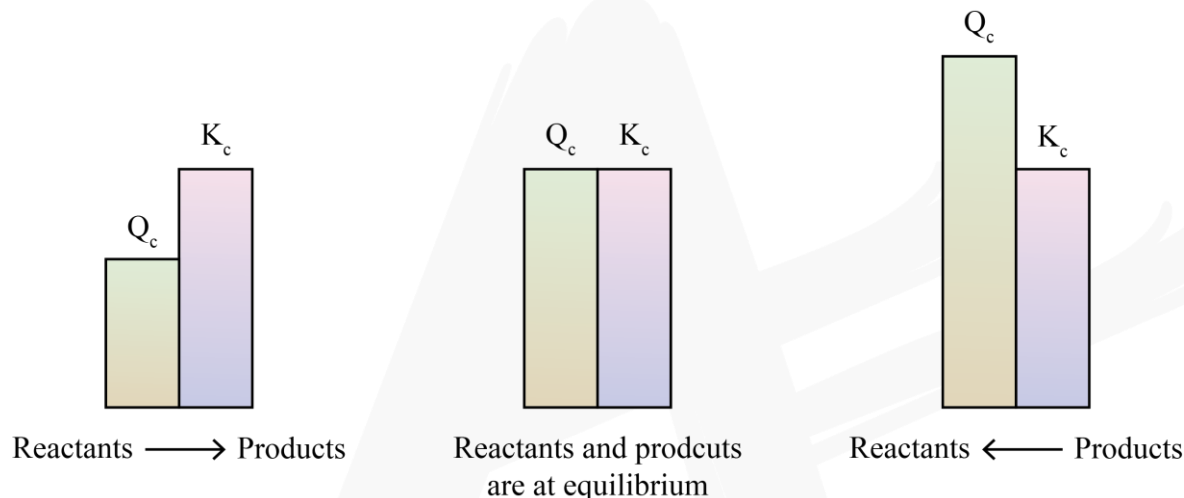
At any stage of a reaction other than the stage of chemical equilibrium, conc. ratio as given by the law of chemical equation is called as conc. Quotient (Q_c)

$$\text{conc. Quotient} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$Q = k \rightarrow$ reaction is in equilibrium.

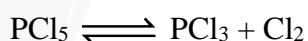
$Q > k \rightarrow$ reaction none backward.

$Q < k \rightarrow$ reaction will move forward.

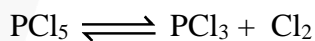


iii. Calculation of equation concentration.

Step 1: write the balanced equation for the reaction.



Step 2: write the balanced equation for the reaction.



t = 0	1	0	0
	1 - x	x	x

Step 3: Calculate equation conc. of each reactant and product.

$$C = \frac{x}{v}$$

Step 4: Write expression for k_p & k_c .

Step 5: Substitute and calculate x, k_c , k_p .

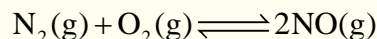
Q. The following concentrations were obtained for the formation of NH_3 from N_2 and H_2 at equilibrium at 500K. $[N_2] = 1.5 \times 10^{-2}M$. $[H_2] = 3.0 \times 10^{-2}M$ and $[NH_3] = 1.2 \times 10^{-2}M$. Calculate equilibrium constant. NCERT

Sol. The equilibrium constant for the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ can be written as,

$$K_c = \frac{[\text{NH}_3(\text{g})]^2}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]^3}$$

$$= \frac{(1.2 \times 10^{-2})^2}{(1.5 \times 10^{-2})(3.0 \times 10^{-2})^3} = 0.106 \times 10^4 = 1.06 \times 10^3$$

Q. At equilibrium, the concentrations of $\text{N}_2 = 3.0 \times 10^{-3}\text{M}$, $\text{O}_2 = 4.2 \times 10^{-3}\text{M}$ and $\text{NO} = 2.8 \times 10^{-3}\text{M}$ in a sealed vessel at 800K. What will be K_c for the reaction NCERT



Sol. For the reaction equilibrium constant, K_c can be written as,

$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(2.8 \times 10^{-3}\text{M})^2}{(3.0 \times 10^{-3}\text{M})(4.2 \times 10^{-3}\text{M})} = 0.622$$

Relationship between equilibrium constant (k), Reaction Quotient (Q) and Gibbs free energy(G).

The value of k_c do not depend on the rate of chemical reaction at equilibrium, it depends on value of ΔG .

Conditions:

$\Delta G = 0 \rightarrow$ Reaction at equilibrium

$\Delta G = -\text{ve} \rightarrow$ spontaneous reaction

$\Delta G = +\text{ve} \rightarrow$ non-spontaneous reaction

Reaction: $\Delta G^\circ + RT \ln Q$

ΔG = Gibbs free energy

ΔG° = Gibbs free energy at std conditions

Q = reaction Quotient.

If the reaction has attained equilibrium then $\Delta G = 0$.

$$\therefore 0 = \Delta G^\circ + RT \ln k.$$

$$\therefore \Delta G^\circ = -RT \ln k.$$

$$\therefore \Delta G^\circ = -2.303 RT \log k$$

The equation may also be expressed as

$$\left[k = e^{-\Delta G^\circ/RT} \right]$$

Now, if $\Delta G^\circ < 0$

ie $-\Delta G^\circ/RT \rightarrow +\text{ve value}$

$$-\Delta G^\circ/RT > 1$$

$$\therefore e^{-\Delta G^\circ/RT} > 1$$

$$\therefore k > 1$$

\therefore spontaneous process ie. reaction moves forward.

If $\Delta G^\circ > 0$,

$$\therefore -\Delta G^\circ/RT \rightarrow -\text{ve}$$

$$\therefore e^{-\Delta G^\circ/RT} > 1$$

∴ $k > 1$

∴ Non-spontaneous ie reaction hardly moves forward.

Q. The value of K_c for the reaction $2A \rightleftharpoons B + C$ is 2×10^{-3} . At a given time, the composition of reaction mixture is $[A] = [B] = [C] = 3 \times 10^{-4}$ M. In which direction the reaction will proceed?

Sol. For the reaction the reaction quotient Q_c is given by, $Q_c = [B][C]/[A]^2$ NCERT

as $[A] = [B] = [C] = 3 \times 10^{-4}$ M

$$Q_c = (3 \times 10^{-4})(3 \times 10^{-4}) / (3 \times 10^{-4})^2 = 1$$

as $Q_c > K_c$ So the reaction will proceed in the reverse direction.

Q. The value of ΔG° for the phosphorylation of glucose in glycolysis is 13.8 kJ/mol. Find the value of K_c at 298 K. NCERT

Sol. $\Delta G^\circ = 13.8 \text{ kJ/mol} = 13.8 \times 10^3 \text{ J/mol}$

$$\text{Also, } \Delta G^\circ = -RT \ln K_c$$

$$\text{Hence, } \ln K_c = -13.8 \times 10^3 \text{ J/mol}$$

$$(8.314 \text{ J mol}^{-1} \text{K}^{-1} \times 298 \text{ K})$$

$$\ln K_c = -5.569$$

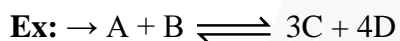
$$K_c = e^{-5.569}$$

$$K_c = 3.81 \times 10^{-3}$$

Le-Chatelier's Principle

When equilibrium is subjected to any change, reaction will move in such a direction so as to undo the effect.

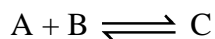
Change \rightarrow conc. pressure, temperature and no. of moles etc.



If conc. of D is decreased then the equilibrium will shift in forward direction so as to undo the change.

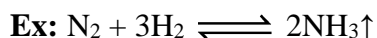
$$C = \frac{x}{v}$$

1. Change in concentration/no. of moles.



\uparrow in conc. of reactants favours the forward reaction.

\uparrow in conc. of products favours the backward reaction.



2. Change in pressure/volume

If $p \uparrow$ equilibrium shift to the direction where no. of moles are less and vice versa.

Note: Pressure hardly has any effect on the solid / liquid.

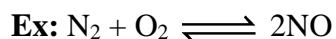


$$pv = nRT$$

Reason: $p \uparrow v \downarrow$ at constant temperature.

\therefore to decrease the conc. reaction shifts to the direction where no. of moles are less.

$$C = \frac{x}{v} \text{ if } n \downarrow c \downarrow$$



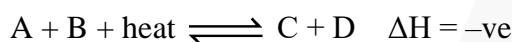
$P \uparrow \rightarrow$ Reaction would not shift as no of moles of gaseous substance are equal.

If $\Delta n_g = 0$, no effect on the reaction equilibrium.

$$\Delta n_g = n_P - n_R, 2 - 2 = 0$$

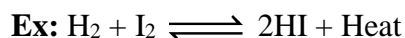
3. Change in temperature

$T \uparrow$ equilibrium shifts to that direction where heat is absorbed.



$T \uparrow$ reaction moves forward.

Thus, is for endothermic and vice versa for exothermic.

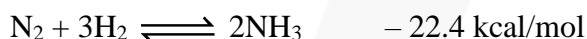


If $T \uparrow$ reaction moves backward.

The reaction which absorbs heat will move fast



We want $NH_3 \uparrow$, $T \uparrow$ or $T \downarrow$?



\therefore If $T \uparrow$ reaction goes forward

\therefore NH_3 production increases at high temperature.

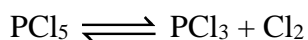
4. Addition of Inert gases.

(a) At constant volume.

The overall pressure is increased but the partial pressure and the molar concentration remains the same, so there will be no change in the state of equilibrium.

(b) At constant pressure

The volume increase thus decreases the no. of moles per unit volume, Thus the reaction proceeds to that side where the no. of moles per unit volume is more.



At const. volume \rightarrow No change

At const. pressure \rightarrow Shift's forward

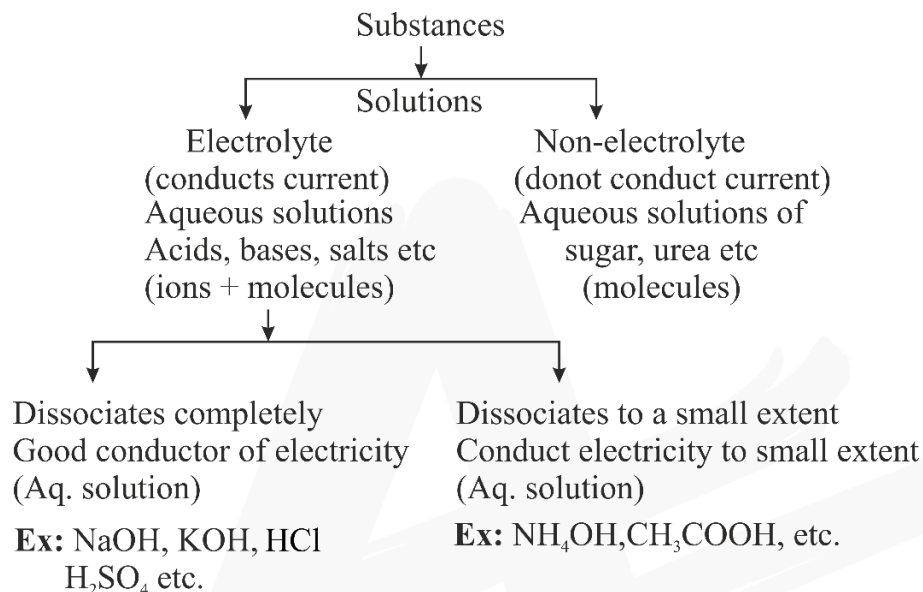
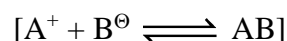
Effect of a Catalyst

- A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactions to products. It increases the rate of forward and reverse reactions that pass through the same transitions that pass through the same transition state and does not affect equilibrium.

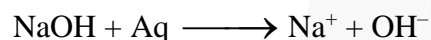
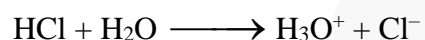
- Catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount. Catalyst does not affect the equilibrium composition of a reaction mixture.

Note : If a reaction has an exceedingly small K , a catalyst would be of little help.

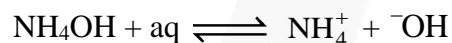
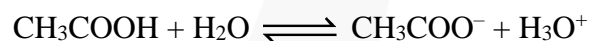
Ionic equilibrium



- As it dissociates completely



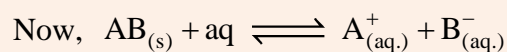
- As it dissociation to small extent



Note:

Degree of Dissociation: The fraction of total no. of molecules which dissociate into ions is called as degree of dissociation or degree of ionization (α)

$$\alpha = \frac{\text{No. of moles dissociated}}{\text{Total no. of moles taken}}$$

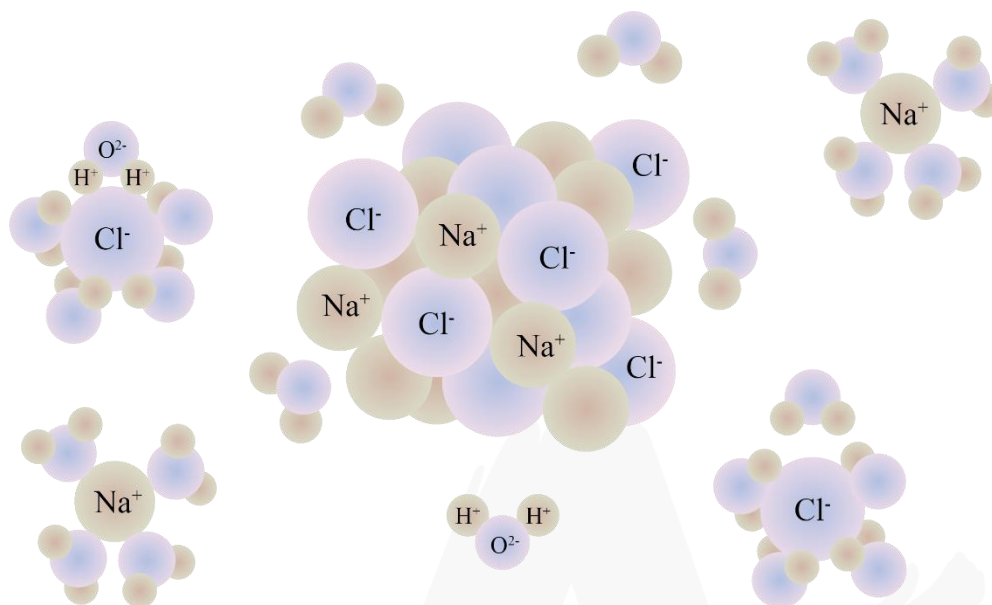


Ionic equilibrium

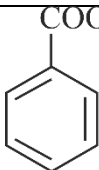
\therefore Applying law of chemical equilibrium.

$$K_i = \frac{[A^+][B^-]}{[AB]} \quad (\text{ionisation constant})$$

Acid/Base theories

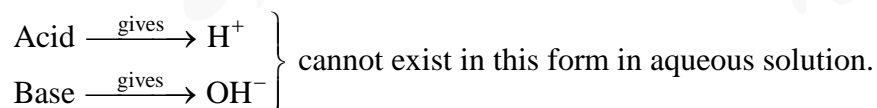


Arrhenius concept:

Acid → Substances which gives H^+ ions or H_3O^+ ions in aqueous solution	Base → Substances which gives OH^- ions in aqueous solution
Acid + aq \longrightarrow H_3O^+	Base + aq \longrightarrow OH^-
$\text{HCl} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$	$\text{NaOH} + \text{H}_2\text{O} \longrightarrow \text{Na}^+ + \text{OH}^-$
Ex: HCl , H_2O , CH_3COOH , H_2CO_3 , HCN , 	Ex: NaOH , $\text{Ca}(\text{OH})_2$, $\text{Cu}(\text{OH})_2$, NH_4OH

Limitation of Arrhenius concept

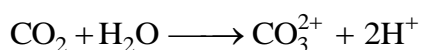
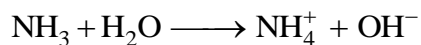
(1) According to Arrhenius



(2) Acids \longrightarrow CO_2 , SO_3 , SO_2 donot contain any H^+ still are acids.

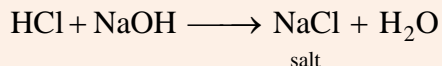
Bases \longrightarrow NH_3 , NaCO_3 , CaO donot contain any OH^- still are acids.

But only if taken in water



Note:

This reaction is termed as neutralization

**Bronsted – Lowry concept:**

Acid	Base (Electron rich sp.)
Substances which gives H^+ in aqueous solution	Substances which accepts H^+ in aqueous solution
ie. proton donor	ie. proton acceptor.
	Ex: $\text{H}_2\ddot{\text{O}}, \ddot{\text{N}}\text{H}_3, \text{R}-\ddot{\text{N}}\text{H}_2, \text{Cl}^-$



$\text{HCl}/\text{CH}_3\text{COOH}$ are acids as they donate H^+ to H_2O



$\text{NH}_3 / \text{CO}_3^{2-}$ are bases as they accept H^+ from water.

Note: $\text{H}_2\text{O} \rightarrow$ accepts $\text{H}^+ \rightarrow \text{H}_3\text{O}^+$

$\therefore \text{H}_2\text{O}$ is called as Amphoteric or Amphiprotic

$\text{H}_2\text{O} \rightarrow$ donates $\text{H}^+ \rightarrow \text{OH}^-$

Conjugate acid / base theory

Acid $\xrightarrow{-\text{H}^+}$ conjugate base

Base $\xrightarrow{+\text{H}^+}$ conjugate acid

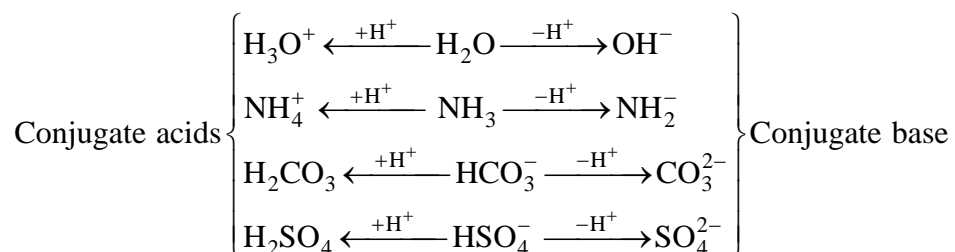
Weak acid $\xrightarrow{\text{gives}}$ strong conjugate base

Weak base \longrightarrow strong conjugate acid

Strong acid \longrightarrow weak conjugate base

Strong base \longrightarrow weak conjugate acid

Ex:



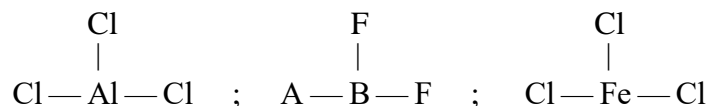
Lewis Theory:

Lewis acid: Substances which accept electron pair due to its e^- deficient nature.

Ex: BeCl_2 , BCl_3 , AlCl_3 .

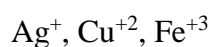
Type of lewis acid:

(1) Molecule with incomplete octet of central atom.



(2) Simple cations:

Most of the d-block cations are lewis acids.

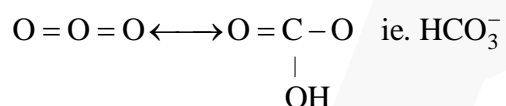


(3) Molecules with vacant d-orbitals.

Generally, p-block elements

Ex: SnCl_4 , SiF_4 etc.

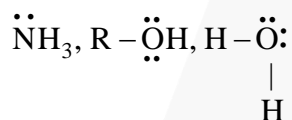
(4) Molecules in which atoms of different electronegativity are linked by multiple bonds.



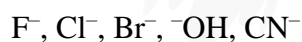
Lewis base: Substances which donate e^- pair due to e^- rich behaviour.

Type of lewis base:

(1) Neutral molecules with at least one lone pair.

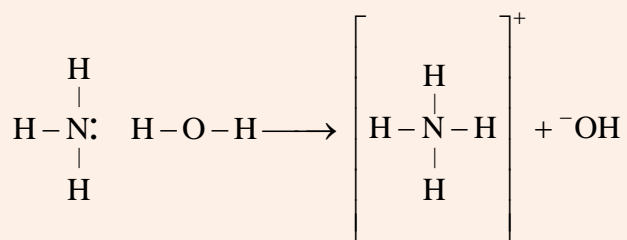


(2) Negatively charged ions



Note:

All lewis base are bronsted base but all bronsted acids may not be lewis acids.



Here $\text{NH}_3 \rightarrow$ Lewis base, Bronsted baes

$\text{H}_2\text{O} \rightarrow$ Bronsted acid, but no lewis acid (\because cannot accept e^- pair).

Q. What will be the conjugate bases for the following Bronsted acids: HF, H₂SO₄ and HCO₃⁻?

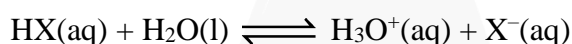
Sol. The conjugate bases should have one proton less in each case and therefore the corresponding conjugate bases are: F⁻, HSO₄⁻ and CO₃²⁻ respectively. **NCERT**

Q. Write the conjugate acids for the following Bronsted bases: NH₂⁻, NH₃ and HCOO⁻. **NCERT**

Sol. The conjugate acid should have one extra proton in each case and therefore the corresponding conjugate acids are: NH₃, NH₄⁺ and HCOOH respectively.

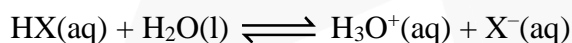
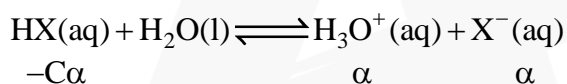
Ionization Constant of weak acids:

Consider a weak acid HX which is partially ionized in the aqueous solution. The equilibrium can be expressed by:



Initial concentration 0 0 0

Let α be the extent of ionization change (M)



Initial concentration C - C α C α C α

Here C is the initial concentration of the undissociated acid HX. Then the equilibrium constant for the above discussed acid dissociation equilibrium.

$$K_a = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

K_a is called **acid dissociation constant or ionization constant**. The pH scale for the hydrogen ion concentration has been so useful that besides pK_w

$$\text{pK}_a = -\log(K_a)$$

Q. The pH of 0.1M monobasic acid is 4.50. Calculate the concentration of species H⁺, A⁻ and HA at equilibrium. Also, determine the value of K_a and pK_a of the monobasic acid. **NCERT**

Sol. pH = -log[H⁺]

$$\text{Therefore, } [\text{H}^+] = 10^{-\text{pH}} = 10^{-4.50} = 3.16 \times 10^{-5}$$

$$[\text{H}^+] = [\text{A}^-] = 3.16 \times 10^{-5}$$

$$\text{Thus, } K_a = [\text{H}^+][\text{A}^-] / [\text{HA}]$$

$$[\text{HA}]_{\text{equilibrium}} = 0.1 - (3.16 \times 10^{-5}) \approx 0.1$$

$$K_a = (3.16 \times 10^{-5})^2 / 0.1 = 1.0 \times 10^{-8}$$

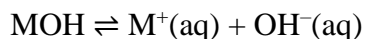
$$\text{pK}_a = -\log(10^{-8}) = 8$$

Alternatively, “Percent dissociation” is another useful method for measure of strength of a weak acid and is given as: Percent dissociation

$$= \frac{[\text{HA}]_{\text{dissociated}}}{[\text{HA}]_{\text{initial}}} \times 100\%$$

Ionization Constant of weak bases:

The ionization of base MOH can be represented by the following equation:



In a weak base there is partial ionization of MOH into M^+ and OH^- , the case is similar to that of acid-dissociation equilibrium. The equilibrium constant for base ionization is called base ionization constant and is represented by K_b . It can be expressed in terms of concentration in molarity of various species in equilibrium by the following equation:

$$K_b = \frac{[\text{M}^+][\text{OH}^-]}{[\text{MOH}]}$$

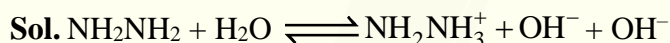
Alternatively, if c = initial concentration of base and α = degree of ionization of base i.e. the extent to which the base ionizes. When equilibrium is reached, the equilibrium constant can be written as:

$$K_b = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

The pH scale for the hydrogen ion concentration has been extended to get:

$$\text{p}K_b = -\log(K_b)$$

Q. The pH of 0.004M hydrazine solution is 9.7. Calculate its ionization constant K_b and $\text{p}K_b$.



NCERT

From the pH we can calculate the hydrogen ion concentration. Knowing hydrogen ion concentration and the ionic product of water we can calculate the concentration of hydroxyl ions. Thus we have:

$$[\text{H}^+] = \text{antilog}(-\text{pH})$$

$$= \text{antilog}(-9.7) = 1.67 \times 10^{-10}$$

$$[\text{OH}^-] = K_w/[\text{H}^+] = 1 \times 10^{-14} / 1.67 \times 10^{-10} = 5.98 \times 10^{-5}$$

The concentration of the corresponding hydrazinium ion is also the same as that of hydroxyl ion. The concentration of both these ions is very small so the concentration of the undissociated base can be taken equal to 0.004M.

Thus,

$$K_b = \frac{[\text{NH}_2\text{NH}_3^+][\text{OH}^-]}{[\text{NH}_2\text{NH}_2]}$$

$$= \frac{(5.98 \times 10^{-5})^2}{0.004} = 8.96 \times 10^{-7}$$

$$\text{p}K_b = -\log K_b = -\log(8.96 \times 10^{-7}) = 6.04.$$

Hydrolysis of salts:

The reactions between acids and base in definite proportions forms salts which undergo ionize in water. The cations or solutions formed on ionization of salts either exit as hydrated ions in aqueous solutions ions in aqueous solutions or interact with water to reform corresponding acids or bases depending upon the natural salts.

Consider three types of hydrolysis of the salts:

- Salts of weak acid and strong base.

$$\text{pH} = 7 + \frac{1}{2}\text{pK}_a - \frac{1}{2}\log C$$

- Salts of strong acid and weak base. Eg: NH_4Cl

$$\text{pH} = 7 - \frac{1}{2}\text{pK}_b - \frac{1}{2}\log C$$

- Salts of weak acid and weak base. Eg: $\text{CH}_3\text{COONH}_4$

$$\text{pH} = 7 + \frac{1}{2}\text{pK}_b - \frac{1}{2}\text{pK}_a$$

Q. The pK_a of acetic acid and pK_b of ammonium hydroxide are 4.76 and 4.75 respectively. Calculate the pH of ammonium acetate solution. **NCERT**

Sol. $\text{pH} = 7 + \frac{1}{2} [\text{pK}_a - \text{pK}_b]$

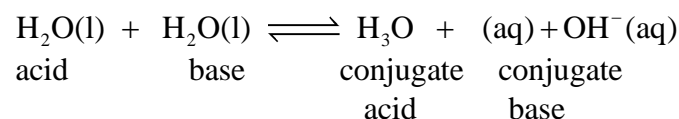
$$= 7 + \frac{1}{2} [4.76 - 4.75]$$

$$= 7 + \frac{1}{2} [0.01] = 7 + 0.005 = 7.005.$$

The Ionization Constant of Water and its Ionic Product

Some substances like water are unique in their ability of acting both as an acid and a base.

In presence of an acid, H_2O it accepts a proton and acts as the base while in the presence of a base, B^- it acts as an acid by donating a proton.



The dissociation constant is represented by,

$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

The concentration of water is omitted from the denominator as water is a pure liquid and its concentration remains constant. $[\text{H}_2\text{O}]$ is incorporated within the equilibrium constant to give a new constant, K_w , which is called the **ionic product of water**.

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (1 \times 10^{-7})^2 = 1 \times 10^{-14} \text{ M}^2$$

The value of K_w is temperature dependent as it is an equilibrium constant.

We can distinguish acidic, neutral and basic aqueous solutions by the relative values of the H_3O^+ and OH^- Concentrations:

Acidic: $[H_3O^+] > [OH^-]$

Neutral: $[H_3O^+] = [OH^-]$

Basic: $[H_3O^+] < [OH^-]$

Law of Chemical Equilibrium

- At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the Equilibrium Law or Law of Chemical Equilibrium. The equilibrium constant for a general reaction,

$aA + bB \rightleftharpoons cC + dD$ is expressed as,

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

Where $[A]$, $[B]$, $[C]$ and $[D]$ are the equilibrium concentrations of the reactants and products.

Equilibrium constant for the reaction,

$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$ is written as

$$K_c = \frac{[NO]^4 [H_2O]^6}{[NH_3]^4 [O_2]^5}$$

- Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction.**

Q. The following concentration were obtained for the formation of NH_3 from N_2 and H_2 at equilibrium at 500K. $[N_2] = 1.5 \times 10^{-2}M$. $[H_2] = 3.0 \times 10^{-2}M$ and $[NH_3] = 1.2 \times 10^{-2}M$. Calculate equilibrium constant. NCERT

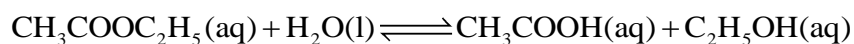
Sol. The equilibrium constant for the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ can be written as,

$$\begin{aligned} K_c &= \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3} \\ &= \frac{(1.2 \times 10^{-2})^2}{(1.5 \times 10^{-2})(3.0 \times 10^{-2})^3} = 0.106 \times 10^4 = 1.06 \times 10^3. \end{aligned}$$

Homogeneous Equilibria

- In a homogeneous system, all the reactants and products are in the same phase. For example, in the gaseous reaction,

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, reactants and products are in the homogeneous phase. Similarly, for the reactions,



and, $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$

all the reactants and products are in homogeneous solution phase. We shall now consider equilibrium constant for some homogeneous reactions.

Equilibrium Constant in Gaseous Systems

- So far we have expressed equilibrium constant of the reactions in terms of molar concentration of the reactants and products, and used symbol, K_c for it. For reactions involving gases, however, it is usually more convenient to express the equilibrium constant in terms of partial pressure.

The ideal gas equation is written as,

$$pV = nRT$$

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

Here, p is the pressure in Pa, n is the number of moles of the gas, V is the volume in m^3 and T is the temperature in Kelvin

Therefore,

n/V is concentration expressed in mol/m^3

If concentration c , is in mol/L or mol/dm^3 , and p is in bar then

$$P = cRT,$$

We can also write $p = [\text{gas}]RT$. Here, $R = 0.0831 \text{ bar litre/mol K}$

At constant temperature, the pressure of the gas is proportional to its concentration i.e.,

$$p \propto [\text{gas}]$$

For reaction in equilibrium $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

We can write either

$$K_c = \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]} \text{ or } K_c = \frac{(p_{\text{HI}})^2}{(p_{\text{H}_2})(p_{\text{I}_2})}$$

Further, since $p_{\text{HI}} = [\text{HI}(\text{g})]RT$

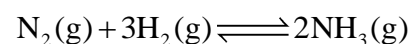
$$p_{\text{I}_2} = [\text{I}_2(\text{g})]RT$$

$$p_{\text{H}_2} = [\text{H}_2(\text{g})]RT$$

Therefore,

$$\begin{aligned} K_p &= \frac{(p_{\text{HI}})^2}{(p_{\text{H}_2})(p_{\text{I}_2})} = \frac{[\text{HI}(\text{g})]^2 [\text{RT}]^2}{[\text{H}_2(\text{g})] \text{RT} \cdot [\text{I}_2(\text{g})] \text{RT}} \\ &= \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]} = K_c \end{aligned}$$

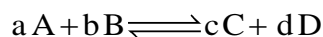
In this example, $K_p = K_c$ i.e., both equilibrium constants are equal. However, this is not always the case. For example, in reaction



$$\begin{aligned} K_p &= \frac{(p_{\text{NH}_3})^2}{(p_{\text{N}_2})(p_{\text{H}_2})^3} = \frac{[\text{NH}_3(\text{g})]^2 [\text{RT}]^2}{[\text{N}_2(\text{g})] \text{RT} \cdot [\text{H}_2(\text{g})]^3 (\text{RT})^3} \\ &= \frac{[\text{NH}_3(\text{g})]^2 [\text{RT}]^{-2}}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]^3} = K_c (\text{RT})^{-2} \end{aligned}$$

$$\text{Or } K_p = K_c (\text{RT})^{-2}$$

Similarly, for a general reaction

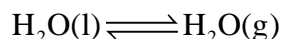


$$K_p = \frac{(p_C^c)(p_D^d)}{(p_A^a)(p_B^b)} = \frac{[C]^c[D]^d(RT)^{(c+d)}}{[A]^a[B]^b(RT)^{(a+b)}} = \frac{[C]^c[D]^d}{[A]^a[B]^b}(RT)^{(c+d)-(a+b)}$$

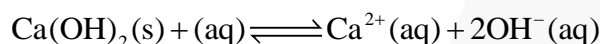
$$= \frac{[C]^c[D]^d}{[A]^a[B]^b}(RT)^{\Delta n} = K_c(RT)^{\Delta n}$$

Heterogeneous Equilibria

Equilibrium in a system having more than one phase is called heterogeneous equilibrium. The equilibrium between water vapour and liquid water in a closed container is an example of heterogeneous equilibrium.

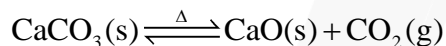


In this example, there is a gas phase and a liquid phase. In the same way, equilibrium between a solid and its saturated solution,



is a heterogeneous equilibrium.

Heterogeneous equilibria often involve pure solids or liquids. We can simplify equilibrium expressions for the heterogeneous equilibria involving a pure liquid or a pure solid, as the molar concentration of a pure solid or liquid is constant (i.e., independent of the amount present). In other words, if a substance 'X' is involved, then $[X(s)]$ and $[X(l)]$ are constant, whatever the amount of 'X' is taken. Contrary to this, $[X(g)]$ and $[X(aq)]$ will vary as the amount of X in a given volume varies. Let us take thermal dissociation of calcium carbonate which is an interesting and important example of heterogeneous chemical equilibrium.



On the basis of the stoichiometric equation, we can write,

$$K_c = \frac{[CaO(s)][CO_2(g)]}{[CaCO_3(s)]}$$

Since $[CaCO_3(s)]$ and $[CaO(s)]$ are both constant, therefore modified equilibrium constant for the thermal decomposition of calcium carbonate will be

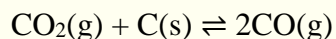
$$K'_c = [CO_2(g)] \text{ or } K_p = p_{CO_2}$$

- Q.** The value of K_p for the reaction, $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$ is 3.0 at 1000 K. If initially $p_{CO_2} = 0.48$ bar and $p_{CO} = 0$ bar and pure graphite is present, calculate the equilibrium partial pressure of CO and CO_2 .

NCERT

Sol. For the reaction,

Let 'x' be the decrease in pressure of CO_2 , then



Initial

Pressure: 0.48 bar 0

At equilibrium: $(0.48 - x)$ bar $2x$ bar

$$K_p = \frac{p_{CO}^2}{p_{CO_2}}$$

$$\begin{aligned}
 K_p &= (2x)^2/(0.48 - x) = 3 \\
 4x^2 &= 3(0.48 - x) \\
 4x^2 &= 1.44 - x \\
 4x^2 + 3x - 1.44 &= 0 \\
 a &= 4, b = 3, c = -1.44 \\
 x &= \frac{(-b \pm \sqrt{b^2 - 4ac})}{2a} \\
 &= [-3 \pm \sqrt{(3)^2 - 4(4)(-1.44)}] / 2 \times 4 \\
 &= (-3 \pm 5.66)/8 \\
 &= (-3 \pm 5.66)/8 \text{ (as value of } x \text{ cannot be negative hence we neglect that value)} \\
 x &= 2.66/8 = 0.33
 \end{aligned}$$

The equilibrium partial pressure are,

$$p_{\text{CO}} = 2x = 2 \times 0.33 = 0.66 \text{ bar}$$

$$p_{\text{CO}_2} = 0.48 - x = 0.48 - 0.33 = 0.15 \text{ bar}$$

Calculating Equilibrium Concentrations

In case of a problem in which we know the initial concentrations but do not know any of the equilibrium concentrations, the following three steps shall be followed:

Step 1. Write the balanced equation for the reaction.

Step 2. Under the balanced equation, make a table that lists for each substance involved in the reaction:

(a) the initial concentration,

(b) the change in concentration on going to equilibrium, and

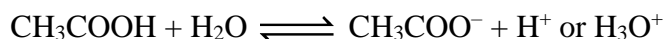
(c) the equilibrium concentration. In constructing the table, define x as the concentration (mol/L) of one of the substances that reacts on going to equilibrium, then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of x .

Step 3. Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for x . If you are to solve a quadratic equation, choose the mathematical solution that makes chemical sense.

Step 4. Calculate the equilibrium concentrations from the calculated value of x .

Step 5. Check your results by substituting them into the equilibrium equation.

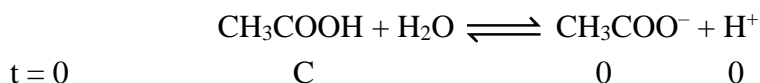
Ostwald's dilution law



$$\therefore k = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

If the solution is dilute $[\text{H}_2\text{O}] = \text{constant}$

$$\therefore k = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$



t = equation

$C - C\alpha$

$C\alpha$

$C\alpha$

$$C(1 - \alpha) \quad k_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{C\alpha \cdot C\alpha}{C(1 - \alpha)} = \frac{C^2\alpha^2}{C(1 - \alpha)} = \frac{C\alpha^2}{1 - \alpha}$$

For weak electrolytes, $\alpha \ll 1$

$$[\therefore k_a = C\alpha^2]$$

$$\therefore \frac{k_a}{C} = \alpha^2$$

$$\left[\therefore \alpha = \sqrt{\frac{k_a}{C}} \right]$$

If $n = 1$

$$\therefore C = \frac{n}{V} = \frac{1}{V}$$

$$\left[\therefore V = \frac{x}{C} \right]$$

$$C = \frac{x}{V} = \frac{1}{V}$$

$$\therefore \alpha = \sqrt{k_a \cdot V}$$

similarly for bases

$$\alpha = \sqrt{k_b \cdot V}$$

Definition: For a weak electrolyte, the degree of ionization is inversely proportional to the square root of concentration $\left[\alpha = \sqrt{\frac{k}{C}} \right]$ and directly proportional to volume $\left[\alpha = \sqrt{k \cdot V} \right]$ containing one mole of solute is called as Ostwald's dilution law.

Note: Degree of ionization of

$$\text{Acids } (\alpha) = \sqrt{\frac{k_a}{C}} \text{ or } \left(\frac{k_a}{C} \right)^{\frac{1}{2}} \text{ and } C\alpha = [\text{H}^+]$$

$$\text{Bases } (\alpha) = C\alpha = \sqrt{\frac{k_b}{C}} \text{ or } \left(\frac{k_b}{C} \right)^{\frac{1}{2}} \text{ and } C\alpha = [\text{OH}^-]$$

Ionic product of water (k_w)

\therefore water is a weak electrolyte



$$k = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

$$\therefore k \cdot [\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-]$$

$$k_w = [\text{H}^+][\text{OH}^-]$$

$$= 1.008 \times 10^{-14}$$

Ionic product of water.

It is the conc. of the product of H^+ and OH^- at a particular temperature.

At 298K or 25°C

$$k_w = 1.008 \times 10^{-14} [\text{mol}^2/\text{L}^2]$$

$$k_w = 1.008 \times 10^{-14}$$

$$= [\text{OH}^-][\text{H}^+]$$

For pure water $[\text{OH}^-] = [\text{H}^+] = 10^{-7} \text{ mol/L}$

\therefore any solution below $\text{pH} = 7$ will be acidic only at room temperature.

Neutral	Acidic	Basic
$[\text{OH}^-] = [\text{H}^+]$	$[\text{H}^+] > [\text{OH}^-]$	$[\text{H}^+] < [\text{OH}^-]$

Note: $k_w = [\text{OH}^-][\text{H}^+]$

$$k_w = x \cdot x$$

$$k_w = x^2$$

$$10^{-14} = x^2$$

$$\therefore x = 10^{-7}$$

Q. What will be the conjugate bases for the following Brönsted acids : HF , H_2SO_4 and HCO_3^- ?

Sol. The conjugate bases should have one proton less in each case and therefore the corresponding

conjugate bases are : F^- , HSO_4^- and CO_3^{2-} respectively.

NCERT

Q. Write the conjugate acids for the following Brönsted bases : NH_2^- , NH_3 and HCOO^- .

NCERT

Sol. The conjugate acid should have one extra proton in each case and therefore the corresponding

conjugate acids are : NH_3 , NH_4^+ and HCOOH respectively.

Q. Classify the following species into Lewis acids and Lewis bases and show how these act as such:

(a) HO^-

(b) F^-

(c) H^+

(d) BCl_3

NCERT

Sol. (a) Hydroxyl ion is a Lewis base as it can donate an electron lone pair ($:\text{OH}^-$).

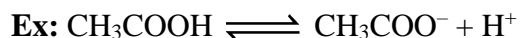
(b) Fluoride ion acts as a Lewis base as it can donate any one of its four electron lone pairs.

(c) A proton is a Lewis acid as it can accept a lone pair of electrons from bases like hydroxyl ion and fluoride ion.

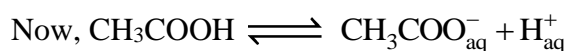
(d) BCl_3 acts as a Lewis acid as it can accept a lone pair of electrons from species like ammonia or amine molecules.

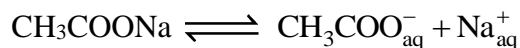
Common ION Effect

Defination: In an ionic equilibrium when a salt containing a common ion is added, the equilibrium shifts to the backward direction, this is called as common ion effect.



The oppression in the dissociation of a weak electrolyte by the addition of a strong electrolyte having a common ion is called as common ion effect.





∴ According to Le Chatelier's principle equilibrium shifts to the left side.

Q. Calculate the pH of a 0.10M ammonia solution. Calculate the pH after 50.0 mL of this solution is treated with 25.0 mL of 0.10M HCl. The dissociation constant of ammonia, $K_b = 1.77 \times 10^{-5}$

Sol. $\text{NH}_3 + \text{H}_2\text{O} \longrightarrow \text{NH}_4^+ + \text{OH}^-$

NCERT

$$K_b = [\text{NH}_4^+][\text{OH}^-] / [\text{NH}_3] = 1.77 \times 10^{-5}$$

Before neutralization,

$$[\text{NH}_4^+] = [\text{OH}^-] = x$$

$$[\text{NH}_3] = 0.10 - x \approx 0.10$$

$$x^2 / 0.10 = 1.77 \times 10^{-5}$$

$$\text{Thus, } x = 1.33 \times 10^{-3} = [\text{OH}^-]$$

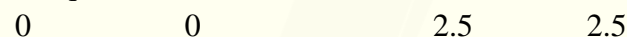
$$\text{Therefore, } [\text{H}^+] = K_w / [\text{OH}^-] = 10^{-14} / (1.33 \times 10^{-3}) = 7.51 \times 10^{-12}$$

$$\text{pH} = -\log(7.5 \times 10^{-12}) = 11.12$$

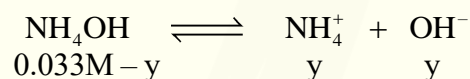
On addition of 25 mL of 0.1M HCl solution (i.e., 2.5 mmol of HCl) to 50 mL of 0.1M ammonia solution (i.e., 5 mmol of NH_3), 2.5 mmol of ammonia molecules are neutralized. The resulting 75 mL solution contains the remaining unneutralized 2.5 mmol of NH_3 molecules and 2.5 mmol of NH_4^+ .



At equilibrium



The resulting 75 mL of solution contains 2.5 mmol of NH_4^+ ions (i.e., 0.033 M) and 2.5 mmol (i.e., 0.033 M) of unneutralised NH_3 molecules. This NH_3 exists in the following equilibrium:



Where, $y = [\text{OH}^-] = [\text{NH}_4^+]$

The final 75 mL solution after neutralisation already contains 2.5 mmol NH_4^+ ion (i.e. 0.033M), thus total concentration of NH_4^+ ions is given as:

$$[\text{NH}_4^+] = 0.033 + y$$

As y is small, $[\text{NH}_4\text{OH}] \approx 0.033\text{M}$ and $[\text{NH}_4^+] \approx 0.033\text{M}$ and $[\text{NH}_4^+] = 0.033\text{M}$.

We know,

$$K_b = [\text{NH}_4^+][\text{OH}^-] / [\text{NH}_4\text{OH}] = y(0.033) / (0.033) = 1.77 \times 10^{-5}\text{M}$$

$$\text{Thus, } y = 1.77 \times 10^{-5} = [\text{OH}^-]$$

$$[\text{H}^+] = 10^{-14} / 1.77 \times 10^{-5} = 0.56 \times 10^{-9}$$

Hence, $\text{pH} = 9.24$

Note: "Due to common ion effect, conc. of ion which is not in common decreases".

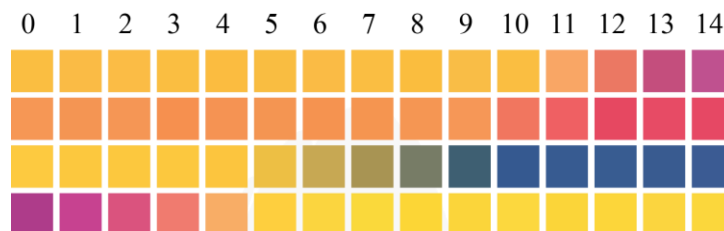
pH

pH may be defined as negative logarithm of hydronium ion concentration.

$$\text{ie } \text{pH} = -\log [\text{H}_3\text{O}^+] \text{ or } \text{pH} = \log \frac{1}{[\text{H}_3\text{O}^+]}$$

pH may also be defined as log of reciprocal of H_3O^+ ion concentration.

pH scale:



pH - paper with four strips that may have different colours at the same pH

Relationship between pH / pOH

We know, $\text{pH} = -\log[\text{H}^+]$ also $\text{pOH} = -\log[\text{OH}^-]$

$$\therefore [\text{H}^+][\text{OH}^-] = k_w = 10^{-14} (25^\circ\text{C})$$

$$\begin{aligned}\therefore \log [\text{H}^+] + \log [\text{OH}^-] &= \log k_w \\ &= \log 10^{-14}\end{aligned}$$

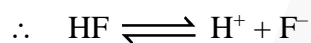
$$\text{or } \log [\text{H}^+] + \log [\text{OH}^-] = -14$$

$$-\log [\text{H}^+] - \log [\text{OH}^-] = -\log k_w = 14$$

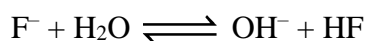
$$\text{or } \text{pH} + \text{pOH} = \text{p}k_w = 14$$

Relation between $\text{p}k_a$ / $\text{p}k_b$

Consider HF as weak acid & F^- as its conjugate base



$$\therefore k_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} \dots\dots\dots (1)$$



$$k_b = \frac{[\text{OH}^-][\text{HF}]}{[\text{F}^-]} \dots\dots\dots (2)$$

Multiplying equation (1) and (2)

$$\frac{[\text{OH}^-][\text{HF}]}{[\text{F}^-]} \times \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$$

$$\therefore k_a \times k_b = [\text{H}^+][\text{OH}^-] = k_w$$

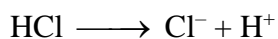
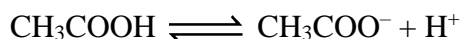
$$\therefore k_a \times k_b = k_w$$

Taking log;

$$\log k_a + \log k_b = \log k_w$$

$$\therefore -\log k_a - \log k_b = -\log k_w = -\log 10^{-14} = 14$$

$$\therefore pK_a + pK_b = pK_w = 14$$



pH scale

$$\text{pH} + \text{pOH} = 14$$

$$K_w = [\text{H}^+][\text{OH}^-]$$

Q. The concentration of hydrogen ion in a sample of soft drink is $3.8 \times 10^{-3}\text{M}$. What is its pH?

Sol. $\text{pH} = -\log [3.8 \times 10^{-3}]$

NCERT

$$= -\{\log [3.8] + \log [10^{-3}]\}$$

$$= -\{(0.58) + (-3.0)\} = -\{-2.42\} = 2.42$$

Therefore, the pH of the soft drink is 2.42 and it can be inferred that it is acidic.

Q. Calculate pH of a $1.0 \times 10^{-8}\text{M}$ solution of HCl.

NCERT

Sol. $2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$

$$K_w = [\text{OH}^-][\text{H}_3\text{O}^+] = 10^{-14}$$

Let, $x = [\text{OH}^-] = [\text{H}_3\text{O}^+]$ from H_2O . The H_3O^+ concentration is generated (i) from the ionization of HCl dissolved i.e.,

$\text{HCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})$, and (ii) from ionization of H_2O . In these very dilute solutions, both sources of H_3O^+ must be considered:

$$[\text{H}_3\text{O}^+] = 10^{-8} + x$$

$$K_w = (10^{-8} + x)(x) = 10^{-14}$$

$$\text{or } x^2 + 10^{-8}x - 10^{-14} = 0$$

$$[\text{OH}^-] = x = 9.5 \times 10^{-8}$$

$$\text{So, pOH} = 7.02 \text{ and pH} = 6.98$$

Definition: The solution which resist any change in the pH on addition of a small amount of acid or base is called as buffer solution.

2 Types of buffer solution

(1) Solution of single substance salt of weak acid CH_3COOH weak base NH_4OH .

(2) Solution of mixture

(i) Acidic buffer (pH 4–7)

(weak acid) + (salt of weak acid + strong base)



(II) Basic buffer (7–10 pH)

(weak base) + (salt of weak base + strong acid)

(NH₄OH)

(NH₄Cl), NH₄OH → WB, HCl → SA

Note: WB → Weak Base

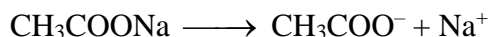
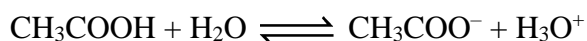
Ex: NH₄OH

NH₄NO₃, NH₄OH → WB, HNO₃ → SA

SA → Strong Acid

Ex: Human blood

Buffer action: The property of a buffer solution to resist the change in its pH value even when small amount of acid or base are added to it buffer action.

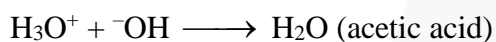


(1) Add few drops acid (strong)



Thus H₃O⁺ or H⁺ ion gets consumed and hence pH remains constant.

(2) Add few drops of base (strong)



As H⁺ or H₃O⁺ are consumed and the equilibrium shifts towards right side.

Thus, more CH₃COOH dissociate to make up the base of H₃O⁺ ion, hence the pH of the solution doesn't change.

Note: Buffer capacity / Buffer index = $\frac{\text{No. of moles of acid / litre}}{\text{change in pH}}$.

Notes End

Important NCERT Questions

Q1. A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased. [NCERT Exercise]

(a) What is the initial effect of the change on vapour pressure?

(b) How do rates of evaporation and condensation change initially?

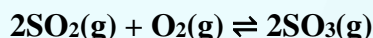
(c) What happens when equilibrium is restored finally and what will be the final vapour pressure?

Sol. (a) On increasing the volume of the container, the vapour pressure will initially decrease because the same amount of vapours are now distributed over a large space.

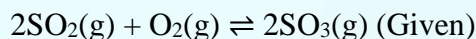
(b) On increasing the volume of the container, the rates of evaporation will increase initially because now more space is available. Since the amount of the vapours per unit volume decrease on increasing the volume, therefore, the rate of condensation will decrease initially.

(c) Finally, equilibrium will be restored when the rates of the forward and backward processes become equal. However, the vapour pressure will remain unchanged because it depends upon the temperature and not upon the volume of the container.

Q2. What is K_c for the following equilibrium when the equilibrium concentration of each substance is: $[SO_2] = 0.60M$, $[O_2] = 0.82M$ and $[SO_3] = 1.90M$? [NCERT Exercise]



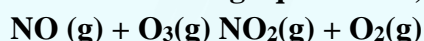
Sol. As per the question,



$$\begin{aligned} K_c &= \frac{[SO_3]^2}{[SO_2]^2[O_2]} \\ &= \frac{(1.9)^2 M^2}{(0.6)^2 (0.82) M^3} \\ &= 12.229 M^{-1} \text{ (approximately)} \end{aligned}$$

Hence, K for the equilibrium is $12.229 M^{-1}$.

Q3. For the following equilibrium, $K_c = 6.3 \times 10^{14}$ at $1000K$ [NCERT Exercise]



Both the forward reverse reactions in the equilibrium are elementary bimolecular reactions. What is k_c for the reverse reaction?

Sol. For the reverse reaction $K_c = \frac{1}{K_c}$

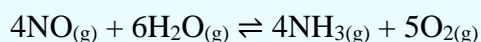
$$\begin{aligned} &= \frac{1}{6.3 \times 10^{14}} \\ &= 1.59 \times 10^{-15} \end{aligned}$$

Q4. The equilibrium constant expression for a gas reaction is,

$$K_c = \frac{[NH_3]^4 [O_2]^5}{[NO]^4 [H_2O]^6} \quad \text{[NCERT Exercise]}$$

Write the balanced chemical equation corresponding to this expression.

Sol. The balanced chemical equation corresponding to the given expression can be written as:



Q5. A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, the concentration of PCl_5 was found to be $0.5 \times 10^{-1} \text{ mol L}^{-1}$. If value of $K_c = 8.3 \times 10^{-3}$, what are the concentration of PCl_3 and Cl_2 at equilibrium?



[NCERT Exercise]

Sol. Consider the conc. of both PCl_3 and Cl_2 at equilibrium be $x \text{ mol L}^{-1}$. The given reaction is:



At equilibrium $0.5 \times 10^{-10} \text{ mol L}^{-1}$ $x \text{ mol L}^{-1}$ $x \text{ mol L}^{-1}$

It is given that the value of equilibrium constant, K_c is $8.3 \times 10^{-10} \text{ mol L}^{-3}$

Now we can write the expression for equilibrium as:

$$\frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = K_c$$

$$\Rightarrow \frac{x \times x}{0.5 \times 10^{-10}} = 8.3 \times 10^{-3}$$

$$\Rightarrow x^2 = 4.15 \times 10^{-4}$$

$$\Rightarrow x = 2.04 \times 10^{-2}$$

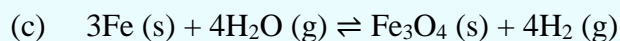
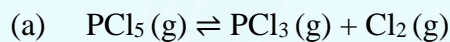
$$= 0.0204$$

$$= 0.02 \text{ (approximately)}$$

Therefore, at equilibrium,

$$[\text{PCl}_3] = [\text{Cl}_2] = 0.02 \text{ mol L}^{-1}$$

Q6. Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibrium is subjected to a decrease in pressure by increasing the volume?



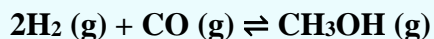
Sol. (a) The number of moles of reaction products will increase. According to Le Chatelier's principle, if pressure is decreased, then the equilibrium shifts in the direction in which the number of moles of gases is more. In the given reaction, the number of moles of gaseous products is more than that of gaseous reactants. Thus, the reaction will proceed in the forward direction. As a result, the number of moles of reaction products will increase.

(b) The number of moles of reaction products will decrease.

(c) The number of moles of reaction products remains the same.

Q7. Explain, giving reasons, which of the following sets of quantum numbers are not possible.

- (a) Addition of H_2
- (b) Addition of CH_3OH
- (c) Removal of CO
- (d) Removal of CO



- Sol.** (a) According to Le Chatelier's principle, on the addition of H_2 , the following of the given reaction will shift in the forward direction.
- (b) On addition of CH_3OH , the equilibrium will shift in the backward direction.
- (c) On removing CO , the equilibrium will shift in the backward direction.
- (d) On removing CH_3OH , the equilibrium will shift in the forward direction.

Q8. Predict which of the following reaction will have appreciable concentration of reactants and products:

[NCERT Exercise]

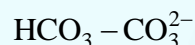
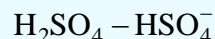
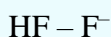
- (a) $Cl_2(g) \leftrightarrow 2Cl(g)$; $K_c = 5 \times 10^{-39}$
- (b) $Cl_2(g) + 2NO(g) \leftrightarrow 2NOCl(g)$; $K_c = 3.7 \times 10^8$
- (c) $Cl_2(g) + 2NO_2(g) \leftrightarrow 2NO_2Cl(g)$; $K_c = 1.8$

Sol. If the value of K_c lies between 10^{-3} and 10^3 , a reaction has an appreciable concentration of reactants and products. Thus, the reaction given in (C) will have an appreciable concentration of reactants and products.

Q9. What will be the conjugate bases for the Bronsted acids: HF , H_2SO_4 and HCO_3 .

[NCERT Exercise]

Sol. The following shows the conjugate bases for the Bronsted acids:



Q10. The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3} M. What is its pH?

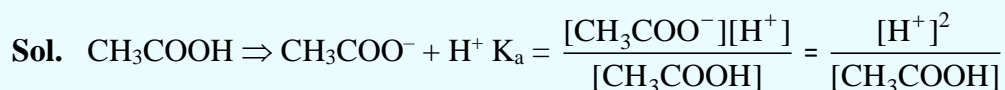
[NCERT Exercise]

Sol. $pH = -\log[H_+]$

$$\begin{aligned}
 &= -\log(3.8 \times 10^{-3}) \\
 &= -\log 3.8 - \log 10^{-3} \\
 &= -\log 3.8 + 3 \\
 &= -0.5798 + 3 \\
 &= 2.423
 \end{aligned}$$

Q11. The ionization constant of acetic acid is 1.74×10^{-5} . Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH.

[NCERT Exercise]



$$\Rightarrow [\text{H}^+] = \sqrt{K_a[\text{CH}_3\text{COOH}]} = \sqrt{(1.74 \times 10^{-5})(5 \times 10^{-2})} = 9.33 \times 10^{-4} \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = [\text{H}^+] = 9.33 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log(9.33 \times 10^{-4}) = 4 - 0.9699 = 4 - 0.97 = 3.03$$

Q12. The degree of ionization of a 0.1 M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the p_{K_a} of bromoacetic acid. [NCERT Exercise]



Initial conc.	C	0	0
Conc. at eqm.	$C - C\alpha$	$C\alpha$	$C\alpha$

$$K_a = \frac{C\alpha - C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \approx C\alpha^2 = 0.1 \times (0.132)^2 = 1.74 \times 10^{-3}$$

$$p_{K_a} = -\log(1.74 \times 10^{-3}) = 3 - 0.2405 = 2.76$$

$$[\text{H}^+] = C\alpha = 0.1 \times 0.132 = 1.32 \times 10^{-2} \text{ M}$$

$$\text{pH} = -\log(1.32 \times 10^{-2}) = 2 - 1.1206 = 1.88$$

Q13. Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below: [NCERT Exercise]

(I) Human saliva, 6.4

(II) Human stomach fluid, 1.2

(III) Human muscle-fluid, 6.83

(IV) Human blood, 7.38.

Sol. (I) Human saliva, 6.4

$$\text{pH} = 6.4$$

$$6.4 = -\log [\text{H}^+] \quad [\text{H}^+] = 3.98 \times 10^{-7}$$

(II) Human stomach fluid, 1.2

$$\text{pH} = 1.2$$

$$1.2 = -\log [\text{H}^+]$$

$$\therefore [\text{H}^+] = 0.063$$

(III) Human muscle fluid 6.83

$$\text{pH} = 6.83$$

$$\text{pH} = -\log [\text{H}^+]$$

$$\therefore 6.83 = -\log [\text{H}^+] \quad [\text{H}^+] = 1.48 \times 10^{-7} \text{ M}$$

(IV) Human blood, 7.38

$$\text{pH} = 7.38 = -\log [\text{H}^+]$$

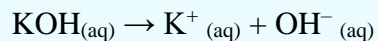
$$\therefore [\text{H}^+] = 4.17 \times 10^{-8} \text{ M}$$

Q14. If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298K. Calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH?

Sol. $[\text{KOH}_{(\text{aq})}] = 0.561 / (1/5) \text{ g/L}$

$$= 2.805 \text{ g/L}$$

$$= 2.805 \times (1/56.11) = 0.05 \text{ M}$$



$$[\text{OH}^-] = 0.05 \text{ M} = [\text{K}^+] [\text{H}^+] [\text{OH}^-] = K_w$$

$$[\text{H}^+] = K_w / [\text{OH}^-] [\text{H}^+] = 10^{-14} / 0.05$$

$$[\text{H}^+] = 2 \times 10^{-13} \text{ M}$$

$$\text{pH} = -\log[\text{H}^+]$$

$$\text{pH} = -\log[2 \times 10^{-13}]$$

$$\text{pH} = 12.70$$

Q15. The pH of 0.1 M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.

Sol. $C = 0.1 \text{ M}$

$$\text{pH} = 2.34$$

$$-\log [\text{H}^+] = \text{pH}$$

$$-\log [\text{H}^+] = 2.34$$

$$[\text{H}^+] = 4.5 \times 10^{-3}$$

Also,

$$[\text{H}^+] = c\alpha$$

$$4.5 \times 10^{-3} = 0.1 \times \alpha$$

$$\alpha = 0.1 / (4.5 \times 10^{-3})$$

$$\alpha = 0.045$$

$$K_a = c\alpha^2$$

$$K_a = 0.1 \times (0.045)^2$$

$$K_a = 0.0002025$$

$$K_a = 2.025 \times 10^{-4}$$

Ab Phod Do!

