Welcome to


Equilibrium

$\mathrm{K}(\mathrm{RT})^{\Delta}$
$\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]$

## Equilibrium

## State in which there are no observable

 changes with timeState in which observable properties (pressure, temperature, volume \& concentration) remain constant.



In this type of equilibrium, the system is at rest and no actual change is happening either at the macroscopic level or the microscopic level.

The dynamic equilibrium can be defined as the state of a system at which the rate of movement in the forward and backward directions (chemical reaction) is equal and no net change takes place.

## Types of Chemical Reactions

Irreversible
Reversible

## Irreversible Reaction

Reaction which proceeds in one direction only

Reactants are almost completely converted into products

Products do not react to form the reactants again

Represented by a single arrow ( $\longrightarrow$ )


Do not attain equilibrium state

## Examples of Irreversible Reaction

## Precipitation reaction

$$
\mathrm{NaCl}(\mathrm{aq})+\mathrm{AgNO}_{3}(\mathrm{aq}) \longrightarrow \mathrm{AgCl}(\mathrm{~s})+\mathrm{NaNO}_{3}(\mathrm{aq})
$$

Neutralization reaction

$$
\mathrm{HCl}(\mathrm{aq})+\mathrm{NaOH}(\mathrm{aq}) \longrightarrow \mathrm{NaCl}(\mathrm{~s})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

## Reversible Reaction

## Reaction which proceeds

 in both the directionsReaction never goes to completion

Products react to form the reactants again

Represented by a double arrow ( $\rightleftharpoons$ )


Attains equilibrium state

## Examples of Reversible Reaction

$$
\mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}(\mathrm{~g})
$$

$$
\mathrm{PCl}_{5}(\mathrm{~g}) \rightleftharpoons \mathrm{PCl}_{3}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g})
$$

Homogeneous

## Equilibrium

Heterogeneous
Equilibrium

## Homogeneous Equilibrium

All reactants and products are in the same phase
$\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(l)+\mathrm{CH}_{3} \mathrm{COOH}(l) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}(l)+\mathrm{H}_{2} \mathrm{O}(l)$

$$
\mathrm{H}_{2}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{HCl}(\mathrm{~g})
$$

## Heterogeneous Equilibrium

Reactants and products are in more than one phase

$$
3 \mathrm{Fe}(\mathrm{~s})+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \rightleftharpoons \mathrm{Fe}_{3} \mathrm{O}_{4}(\mathrm{~s})+4 \mathrm{H}_{2}(\mathrm{~g})
$$

$$
\mathrm{CaCO}_{3}(\mathrm{~s}) \rightleftharpoons \mathrm{CaO}(\mathrm{~s})+\mathrm{CO}_{2}(\mathrm{~g})
$$

$$
\mathrm{C}(\text { diamond, s) } \rightleftharpoons \mathrm{C} \text { (graphite, s) }
$$

## Equilibrium Processes

Physical
Equilibrium
Equilibrium
Chemical Equilibrium

## Phase Transformation Processes



## Physical Equilibrium



## Chemical Equilibrium

Equilibrium in chemical processes

State in which the driving forces, i.e., the factors taking the reaction in the forward $\&$ the backward direction are balancing each other


## Chemical Equilibrium

As reaction proceeds,

$\square$
Rate of the forward reaction

$$
R \rightleftharpoons P
$$

At equilibrium


Rate of the backward reaction


## Graphical Representation




## Graphical Representation




## Chemical Equilibrium



Example:

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})
$$

## Equilibrium Mixture

Mixture of reactants
\& products in the equilibrium state

## Example

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})
$$

## Conditions for Chemical Equilibrium Involving Gaseous Phase



## Remember!!

## At equilibrium, all macroscopic properties such as


of the system appear to be constant

## $\mathrm{CaCO}_{3}(\mathrm{~s}) \rightleftharpoons \mathrm{CaO}(\mathrm{s})+\mathrm{CO}_{2}(\mathrm{~g})$



## Extent of the Reaction



## Characteristics of Chemical Equilibrium



## Characteristics of Chemical Equilibrium



## Characteristics of Chemical Equilibrium

In general, the state of equilibrium in a chemical
reaction can be achieved
from either direction

## Case - I

Let after 75 \% conversion equilibrium is achieved

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})
$$


0.2
0.6

0

0.05
0.15
0.3

## Case - I

## Same equilibrium state can be achieved starting from product

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})
$$


0.4

0.05
0.15
0.3
$25 \%$ conversion

## Case - II

Let after $50 \%$ conversion of $\mathbf{N}_{\mathbf{2}}$ equilibrium is achieved

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})
$$

 starting only from $\mathrm{NH}_{3}$ (backward direction)

## Law of Mass Action



At a particular temperature,

Rate of a chemical reaction is proportional to the product of active masses of reactants raised to the powers of their stoichiometric coefficients

> Proposed by
> Guldberg and Waage

## Active Mass

## Effective amount of reacting <br> species taking part in the reaction

Active masses are dimensionless quantities but for our purposes we generally take them with dimensions of molarity, partial pressure etc.

## Active Mass

## B

> Active masses of pure liquids \& solids


| [Solid] or |
| :---: |
| [Liquid] |$=\frac{\text { Moles }}{\text { Volume }}=\frac{\text { Mass }}{\text { Molar mass x Volume }}$

$=\frac{\text { Density }}{\text { Molar mass }}=$ Constant

$$
\overline{0}
$$

## Mathematical Expression for Law of Mass Action

$$
\mathrm{a} \mathrm{~A}+\mathrm{bB} \longrightarrow \text { Products }
$$



According to law of mass action,


## Mathematical Expression for Law of Mass Action

$$
a \mathrm{~A}+\mathrm{bB} \rightleftharpoons \mathrm{cC}+\mathrm{dD}
$$

According to law of mass action,


## Application of Law of Mass Action


$\mathrm{K}_{\mathrm{C}}$ Equilibrium Constant

## Equilibrium Constant


$\mathrm{K}_{\mathrm{C}}$ and $\mathrm{K}_{\mathrm{p}}$ are temperature dependent only

## Equilibrium Constant ( $\mathrm{K}_{\mathrm{c}}$ )

$\mathrm{K}_{\mathrm{C}}$ is the equilibrium constant when the active masses are expressed in concentrations

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})
$$

$k_{f}$ and $k_{b}$ depends only on temperature.


## Example

$\mathrm{CaCO}_{3}(\mathrm{~s}) \rightleftharpoons \mathrm{CaO}(\mathrm{s})+\mathrm{CO}_{2}(\mathrm{~g})$


Activity of pure solids is taken as 1
$\mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(\mathrm{aq})$


## Example

$$
\mathrm{CH}_{3} \mathrm{COOH}(l)+\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(l) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}(l)+\mathrm{H}_{2} \mathrm{O}(l)
$$

Here, water is not acting as the solvent


## Equilibrium Constant ( $K_{p}$ )

Equilibrium reaction which contains at least one gaseous component

$$
\mathrm{aA}(\mathrm{~g})+\mathrm{bB}(\mathrm{~g}) \rightleftharpoons \mathrm{cC}(\mathrm{~g})+\mathrm{dD}(\mathrm{~g})
$$

$K_{P}=\frac{\left(P_{C}\right)^{c}{ }_{e q}\left(P_{D}\right)^{d}{ }_{e q}}{\left(P_{A}\right)^{a}{ }_{e q}\left(P_{B}\right)^{b}{ }_{e q}}$

Equilibrium constant in terms of partial pressure

## $K_{p}$ and $K_{c}$

$$
\mathrm{aA}(\mathrm{~g})+\mathrm{bB}(\mathrm{~g}) \rightleftharpoons \mathrm{cC}(\mathrm{~g})+\mathrm{dD}(\mathrm{~g})
$$



## Relation between $\mathrm{K}_{\mathrm{p}}$ and $\mathrm{K}_{\mathrm{c}}$

## For an ideal gas

$\mathrm{PV}=\mathrm{nRT}$

Where,


Partial pressure of Gas

## C Concentration of Gas

## R

## Universal Gas Constant

Temperature

## Relation between $\mathrm{K}_{\mathrm{p}}$ and $\mathrm{K}_{\mathrm{c}}$

$$
\mathrm{aA}(\mathrm{~g})+\mathrm{bB}(\mathrm{~g}) \rightleftharpoons \mathrm{cC}(\mathrm{~g})+\mathrm{dD}(\mathrm{~g})
$$



$$
C=\frac{P}{R T}
$$

Relation between $\mathrm{K}_{\mathrm{p}}$ and $\mathrm{K}_{\mathrm{c}}$

$$
K_{c}=\frac{\left(P_{C}\right)^{c}{ }_{e q}\left(P_{D}\right)^{d} e_{e q}}{\left(P_{A}\right)^{a_{e q}}\left(P_{B}\right)^{b} e_{e q}} R T(a+b)-(c+d)
$$

$$
\mathrm{K}_{\mathrm{c}}=\quad=\quad \mathrm{K}_{\mathrm{p}}(\mathrm{RT})^{-\Delta \mathrm{n}_{\mathrm{g}}}
$$

$$
\mathrm{K}_{\mathrm{p}}=\mathrm{K}_{\mathrm{c}}(\mathrm{RT})^{\Delta \mathrm{n}_{\mathrm{g}}}
$$

## $\Delta \mathrm{n}_{\mathrm{g}}$



$$
\text { Example: } \quad \mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})
$$

$$
\Delta n_{g}=2-(3+1)=-2
$$

## Unit of $K_{p}$

## Unit of $K_{p} \quad(a t m)^{\Delta n_{g}}$

Example: $\quad \mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})$

$$
\text { Unit of } K_{p}=(\mathrm{atm})^{\Delta \mathrm{n}_{\mathrm{g}}}=\text { atm }^{-2}
$$



## $K_{p} \& K_{x}$

## $\mathrm{aA}(\mathrm{g})+\mathrm{bB}(\mathrm{g}) \rightleftharpoons \mathrm{cC}(\mathrm{g})+\mathrm{dD}(\mathrm{g})$

$$
K_{P}-\rightarrow \frac{\left(P_{C}\right)_{e q}^{c}\left(P_{D}\right)^{d}{ }_{e q}}{\left(P_{A}\right)^{a_{e q}}\left(P_{B}\right)^{b}{ }_{e q}}
$$

$$
K_{\chi}-\rightarrow \frac{\left(\chi_{\mathrm{C}}\right)^{\mathrm{c}}{ }_{\mathrm{eq}}\left(\chi_{\mathrm{D}}\right)^{\mathrm{d}}{ }_{\mathrm{eq}}}{\left(\chi_{\mathrm{A}}\right)^{\mathrm{a}}{ }_{\mathrm{eq}}\left(\chi_{\mathrm{B}}\right)^{\mathrm{b}}{ }_{\mathrm{eq}}}
$$

## Relation between $\mathrm{K}_{\mathrm{p}}$ \& $\mathrm{K}_{\chi}$



## Characteristics of Equilibrium Constant

If reaction is reversed, the equilibrium constant is reciprocated
${ }^{--} \mathrm{A}(\mathrm{aq})+\mathrm{B}(\mathrm{aq}) \rightleftharpoons \mathrm{C}(\mathrm{aq})$
$\ldots K_{c}=\frac{[C]}{[A][B]}=K$
$C(a q) \rightleftharpoons A(a q)+B(a q)$

$$
\mathrm{K}_{\mathrm{C}^{\prime}}=\frac{[\mathrm{A}][\mathrm{B}]}{[\mathrm{C}]}=\frac{1}{\mathrm{~K}}
$$

## Characteristics of Equilibrium Constant

If a reaction is multiplied by a factor ' $n$ ', the value of the equilibrium constant becomes $K^{1}=(K)^{n}$

$$
\begin{array}{ll}
A(a q)+B(a q) \rightleftharpoons C(a q) & \frac{1}{2} A(a q)+\frac{1}{2} B(a q) \rightleftharpoons \frac{1}{2} C(a q) \\
& K_{C}=\frac{[C]}{[A][B]}=K
\end{array}
$$

## Characteristics of Equilibrium Constant

If we add two or more equilibrium 3 reactions, final equilibrium constant is the product of individual constants.
$A+B \rightleftharpoons C$
$K_{1}=\frac{[C]}{[A][B]}$


$$
\begin{gathered}
A+B \rightleftharpoons D \\
K=K_{1} \times K_{2}=\frac{[D]}{[A][B]}
\end{gathered}
$$

## Characteristics of Equilibrium Constant

Equilibrium constant does not depend upon concentration of reactants, presence of catalyst, direction from which equilibrium is reached

It depends only on the temperature and the stoichiometric coefficients

## Temperature Dependence of Equilibrium Constant

If $\mathrm{K}_{1}$ \& $\mathrm{K}_{2}$ are the equilibrium constants at temperature $\mathrm{T}_{1} \& \mathrm{~T}_{2}$


## $\Delta H^{\circ} \quad$ Standard Enthalpy change

For the reaction:

$$
\mathrm{A}_{2}(\mathrm{~g})+\mathrm{B}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{AB}(\mathrm{~g})
$$

$$
\begin{gathered}
\text { To calculate } \\
\hline\left[\mathrm{A}_{2}\right]_{\mathrm{eq}} \&\left[\mathrm{~B}_{2}\right]_{\mathrm{eq}}
\end{gathered} \begin{aligned}
& \text { Given } \\
& \begin{array}{l}
\mathrm{K} \\
\mathrm{C}
\end{array}=16 \\
& {\left[\mathrm{~A}_{2}\right]_{0}=1 \mathrm{M}} \\
& {\left[\mathrm{~B}_{2}\right]_{0}=1 \mathrm{M}} \\
& \mathrm{~V}=1 \mathrm{~L}
\end{aligned}
$$

$\left[A_{2}\right]_{0}$ Initial Concentration of $A_{2}$
$\left[B_{2}\right]_{0}$ Initial Concentration of $B_{2}$

$$
\mathrm{A}_{2}(\mathrm{~g})+\mathrm{B}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{AB}(\mathrm{~g})
$$

Concentration at $\mathbf{t}=0$ ( $\mathrm{mol} \mathrm{L}^{-1}$ )

Concentration at $t=t_{\text {eq }}$ ( $\mathrm{mol} \mathrm{L}^{-1}$ ) $1-x \quad 1-x$ $2 x$


## Calculating Equilibrium Concentrations



Taking square root on both sides


## Calculating Equilibrium Concentrations



Calculating Equilibrium Concentrations

$$
\begin{aligned}
& {\left[A_{2}\right]_{\mathrm{eq}}=\left(\left[A_{2}\right]_{o}-\frac{x}{V}\right)=1-\frac{2}{3}=\frac{1}{3} M} \\
& {\left[B_{2}\right]_{\mathrm{eq}}=\left[\left[B_{2}\right]_{o}-\frac{x}{V}\right]=1-\frac{2}{3}=\frac{1}{3} M}
\end{aligned}
$$

## Applications of Equilibrium Constant



Predicting the direction of equilibrium

Case 1


For the reaction,

$$
R \rightleftharpoons P
$$

$$
\mathrm{K}_{\mathrm{eq}}=\frac{[\mathrm{P}]_{\mathrm{eq}}}{[\mathrm{R}]_{\mathrm{eq}}}
$$



## Case - II



## Case - III



## Predicting the Extent of Reaction



## Applications of Equilibrium Constant

Predicting the extent of reaction


## Reaction Quotient (Q)

At any point in a reaction, ratio of concentration terms
having the same form
as the equilibrium
constant expression


## Reaction Quotient (Q)

For a reaction, $\quad \mathrm{aA}(\mathrm{aq})+\mathrm{bB}(\mathrm{aq}) \rightleftharpoons \mathrm{cC}(\mathrm{aq})+\mathrm{dD}(\mathrm{aq})$



## Reaction Quotient (Q)



To achieve equilibrium


## Reaction Quotient (Q)



To achieve equilibrium


## Reaction Quotient (Q)



## Degree of Dissociation ( $\alpha$ )



## Degree of Dissociation ( $\alpha$ )

$$
\mathrm{PCl}_{5}(\mathrm{~g}) \rightleftharpoons \mathrm{PCl}_{3}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g})
$$



## Degree of Dissociation ( $\alpha$ )

At t = 0, only $\mathrm{PCl}_{5}$ is present

## At $\mathrm{t}=\mathrm{t}_{\text {eq }}, \mathrm{PCl}_{5}, \mathrm{PCl}_{3}$ \& $\mathrm{Cl}_{2}$ are present



## Degree of Dissociation ( $\alpha$ )



## Calculating Moles in Terms of $\alpha$

$$
A_{n} \rightleftharpoons n A
$$

Before Dissociation (mole)

$a$

After Dissociation (mole)

After Dissociation (mole)

$a-a \alpha$
n a $\alpha$

## Calculating Moles in Terms of $\alpha$



Total moles at equilibrium


## Calculating Moles in Terms of $\alpha$

$$
2 \mathrm{AB}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{AB}(\mathrm{~g})+\mathrm{B}_{2}(\mathrm{~g})
$$

Before Dissociation
(mole)
$0 \quad 0 \quad 0$

After Dissociation (mole)
$a-a \alpha \quad a \alpha \quad \frac{a \alpha}{2}$

Total moles at equilibrium

$$
=\mathrm{a}-\mathrm{a} \alpha+\mathrm{a} \alpha+\frac{\mathrm{a} \alpha}{2}
$$

$$
=a\left(1+\frac{\alpha}{2}\right)
$$



## Molar Mass of Equilibrium Mixture

Total moles at equilibrium


## Molar Mass of Equilibrium Mixture

Initial mass


From the Law of
Conservation of mass


Let the initial molar mass be $\mathbf{M}$ and $\mathbf{M}_{\text {mix }}$ be the molar mass of the mixture

## Molar Mass of Equilibrium Mixture

$$
M \text { a }=[a(1+(n-1) \alpha)] M_{\text {mix }}
$$

$$
\begin{aligned}
& \mathbf{M}_{\text {mix }}=\frac{\mathbf{M}}{1+(n-1) \alpha}=1+\frac{M}{M_{\text {mix }}}=1+(n-1) \alpha \quad \text { Where, } n \neq 1
\end{aligned}
$$

## Relation between $\alpha$ and Vapour Density



Let, $\square$ Vapour density of gas
d Vapour density of mixture


Not applicable for $\mathrm{n}=1$
E.g.: Dissociation of $\mathrm{HI}(\mathrm{g}) \& \mathrm{NO}(\mathrm{g})$

## Plot of Vapour Density vs $\alpha$



## Thermodynamics of Equilibrium

Consider a reversible reaction,

$$
\mathrm{aA}(\mathrm{aq})+\mathrm{bB}(\mathrm{aq}) \rightleftharpoons \mathrm{cC}(\mathrm{aq})+\mathrm{dD}(\mathrm{aq})
$$



$$
\Delta G \quad=\quad \Delta G^{\circ}+\quad+\quad 2.303 R T \log Q
$$

## Thermodynamics of Equilibrium

At Equilibrium,


$$
\Delta G^{\circ}=\quad=-2.303 R T \log K_{e q}
$$

## Thermodynamics of Equilibrium

$\Delta \mathbf{G}^{\circ}=\Delta \mathbf{H}^{\circ}-\mathbf{T} \Delta \mathbf{S}^{\circ}$
$-2.303 R T \log \mathrm{~K}_{\text {eq }}=\Delta \mathrm{H}^{\circ}-\mathrm{T} \Delta \mathrm{S}^{\circ}$


## Thermodynamics of Equilibrium


Slope $=\frac{-\Delta H^{\circ}}{2.303 R} y$-Intercept $=\frac{\Delta S^{\circ}}{2.303 R}$

## Thermodynamics of Equilibrium



## Equilibrium Constant \& Temperature



## $\mathrm{K}_{1}$ <br> Equilibrium constant at $\mathrm{T}_{1}$

Equilibrium constant at $\mathrm{T}_{2}$

## Equilibrium Constant \& Temperature

Assuming $\Delta \mathrm{H}^{\circ}$ and $\Delta \mathrm{S}^{\circ}$ remains constant in this temperature range
$\Rightarrow$ Eq. (1) - (2)

van't Hoff equation

## Remember!!



Reaction at constant $T \& P$ is feasible in the direction which leads to a lowering of Gibbs free energy.

## For a reaction <br> $\mathrm{R} \rightleftharpoons \mathrm{P}$



Equilibrium occurs at a minimum value of Gibbs energy

Extent of reaction $\qquad$


Industrially, the aim is to have maximum product yield with minimum energy expenditure

After equilibrium is established, more product formation stops.

And reaction can be carried out in the desired direction

## Le Chatelier's Principle

If a change is applied to the system at equilibrium, then the equilibrium will be shifted in that direction


In which it can minimise the effect of the change applied and the equilibrium is established again under new conditions.

## Factors Affecting Equilibrium

Change in the concentration of reactant or product

Change in temperature

Change in volume

Effect of addition of inert gas

Effect of addition of catalyst

## Effect of Change in Concentration

If the concentration of a component is increased, reaction shifts in a direction which tends to decrease its concentration

## Effect of Change in Concentration

$$
\mathrm{A}(\mathrm{aq})+\mathrm{B}(\mathrm{aq}) \rightleftharpoons \mathrm{C}(\mathrm{aq})+\mathrm{D}(\mathrm{aq})
$$

$$
Q_{C}=\frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}
$$



## Effect of Change in Concentration



Concentration of the added species ([A] or [B]) will be more at new equilibrium than that at the old equilibrium under the same set of conditions.

## Effect of Change in Concentration

$$
\mathrm{A}(\mathrm{aq})+\mathrm{B}(\mathrm{aq}) \rightleftharpoons \mathrm{C}(\mathrm{aq})+\mathrm{D}(\mathrm{aq})
$$

$$
Q_{C}=\frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}
$$



## Effect of Change in Concentration



Concentration of the added species ([C] or [D]) will be more at new equilibrium than that at the old equilibrium under the same set of conditions.

## Conclusions

Addition of any solid component does not affect the equilibrium

[Reactant]

Equilibrium shifts in the forward direction

Equilibrium shifts in the backward direction

## Effect of Temperature



## Exothermic Reaction

For the reaction,

$$
\mathrm{A}(\mathrm{aq})+\mathrm{B}(\mathrm{aq}) \rightleftharpoons \mathrm{C}(\mathrm{aq})+\mathrm{D}(\mathrm{aq})
$$



## Exothermic Reaction

If
Forward reaction
Exothermic

Then
Backward reaction Endothermic

Reaction shifts
backward direction

## Endothermic Reaction

For the reaction,

$$
\mathrm{A}(\mathrm{aq})+\mathrm{B}(\mathrm{aq}) \rightleftharpoons \mathrm{C}(\mathrm{aq})+\mathrm{D}(\mathrm{aq})
$$



## Endothermic Reaction

If
Forward reaction
Endothermic

Then
Backward reaction
Exothermic

Reaction shifts forward direction

## Temperature Dependence of Equilibrium Constant

If $K_{1} \& K_{2}$ are the equilibrium constants at temperature $\mathrm{T}_{1} \& \mathrm{~T}_{\mathbf{2}}$


## $\Delta H^{\circ} \quad$ Standard Enthalpy change

R Universal gas constant

## Effect of Change in Pressure

On increasing pressure, equilibrium will shift in the direction in which pressure decreases i.e., number of moles in the reaction decreases and vice versa


## Effect of Change in Pressure

For the reaction,


## Effect of Change in Pressure

For the reaction,

## $\mathrm{A}(\mathrm{g}) \rightleftharpoons 2 \mathrm{~B}(\mathrm{~g})$

$$
\Delta n_{g}=+v e
$$

$$
Q_{P}=\frac{P_{B}^{2}}{P_{A}}=\frac{\left(\chi_{B} P_{\text {Total }}\right)^{2}}{\chi_{A} P_{\text {Total }}}
$$

## Effect of Change in Pressure

For the reaction,

$$
\mathbf{Q}_{P}=\frac{P_{B}}{P_{A}{ }^{2}}=\frac{\chi_{B} P_{\text {Total }}}{\left(\chi_{A} P_{\text {Total }}\right)^{2}}
$$

$2 \mathrm{~A}(\mathrm{~g}) \rightleftharpoons \mathrm{B}(\mathrm{g})$

$$
\Delta n_{g}=-v e
$$



## Example

$$
\mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}(\mathrm{~g})
$$

If $\quad P \uparrow \Rightarrow$ No Shift as $\Delta n_{g}=0$


## Effect of Change of Pressure

Solids \& liquids are incompressible or negligibly compressible.

Change in pressure has no effect on equilibria involving solid \& liquid

## Effect of Change in Volume

Volume
Pressure

Hence, the reaction will shift in the direction in which pressure increases i.e., in the direction in which the number of moles of gases increases and vice versa.

## Effect of Change in Volume



## Effect of Change in Volume

For the reaction,

$$
\mathrm{A}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{~B}(\mathrm{~g})
$$

$$
\Delta \mathrm{n}_{\mathrm{g}}=+\mathrm{ve}
$$



If Volume

Reaction shifts where the moles of gas

## Reaction goes forward

$$
\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}_{2}(\mathrm{~g})
$$

## Effect of Change in Volume

## For the

 reaction,$$
2 \mathrm{~A}(\mathrm{~g}) \rightleftharpoons \mathrm{B}(\mathrm{~g})
$$

$$
\Delta n_{g}=-\mathrm{ve}
$$

## If Volume

Reaction shifts where the moles of gas

Reaction goes backward

$$
3 \mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{O}_{3}(\mathrm{~g})
$$

## Example

## For the

 reaction,$$
3 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{N}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})
$$



## Example

$$
\mathrm{NH}_{4} \mathrm{COONH}_{2}(\mathrm{~s})_{\underset{(\mathrm{g}}{ })} 2 \mathrm{NH}_{3}(\mathrm{~g})+\mathrm{CO}_{2}
$$

## v $\uparrow \Rightarrow$ Forward shift


$\left[\mathrm{NH}_{3}\right]$ and $\left[\mathrm{CO}_{2}\right]$ remains same

## Catalyst and Effect of Catalyst

Substance which can alter the speed of a chemical reaction without itself getting consumed at the end of the reaction

Due to the catalyst, the state of equilibrium is not affected

Catalyst lowers the activation energy of both the forward and the reverse reactions by the same amount,

It alters the forward and the reverse rate equally and hence, the equilibrium will be attained faster

## Effect of Addition of an Inert Gas



Addition of an inert gas increases the number of moles of the gas in the system

Inert gas molecules do not interact with the reactant or the product molecules

No change in the moles of the reactants \& the products

## Effect of Addition of an Inert Gas

## At constant <br> V

When $\Delta \mathbf{V}=0 \quad$| Partial pressures of the |
| :---: |
|  |
| products do not change |
| i.e., $Q_{p}$ do not change |

No disturbance in equilibrium

$$
\mathrm{A}(\mathrm{~g}) \rightleftharpoons \mathrm{B}(\mathrm{~g})
$$

$\mathrm{A}(\mathrm{g}) \rightleftharpoons 2 \mathrm{~B}(\mathrm{~g})$
$2 \mathrm{~A}(\mathrm{~g}) \rightleftharpoons \mathrm{B}(\mathrm{g})$

## Effect of Addition of an Inert Gas

## At constant P



Equilibrium shifts in that direction where the moles of gas is more

## Phase Transition

> In phase transition processes, the increase in pressure shifts the equilibrium towards the denser phase.

## Phase Transition

$$
C\left(\text { Graphite, s) } \rightleftharpoons C \left(\text { Diamond, s) } \quad \Delta_{r} H \quad=\quad+1.9 \mathrm{~kJ} \mathrm{~mol}^{-1}\right.\right.
$$



## Phase Transition

Increase in pressure favours the formation of the denser state, i.e. diamond


## Phase Transition

As $\Delta H$ is $+v e$, the increase in temperature favours the formation of diamond


## Phase Transition

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{~s}) \rightleftharpoons \mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

$$
\Delta_{r} H^{\circ}=\quad=\quad+6 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

Increase in pressure favours the formation of the denser state, i.e. water

As $\Delta H$ is +ve , the increase in temperature favours the formation of water

## Phase Transition



$$
\begin{gathered}
\text { Pressure } \uparrow \quad \begin{array}{c}
\text { Equilibrium shifts where the volume } \\
\text { is decreasing i.e., backward }
\end{array}
\end{gathered}
$$

## Formation of Ammonia

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g}) \ldots \Delta \mathrm{H}=-22.4 \mathrm{kcal} / \mathrm{mol}
$$

The reaction will shift in the forward direction at low temperature

At high pressure, the reaction will shift in the forward direction

2

$$
\begin{aligned}
& b=\$ \\
& z+s, s
\end{aligned}
$$

## Simultaneous Equilibria

Container with two or more equilibria existing simultaneously involving one or more common species

Then in all equilibrium, the concentration of the common species is the total concentration of that species due to all the equilibria

## Simultaneous Equilibria

Let's look at these two equilibria established simultaneously in a vessel

$$
\mathrm{A}(\mathrm{~s}) \rightleftharpoons \mathrm{X}(\mathrm{~g})+\mathrm{Y}(\mathrm{~g})
$$

$$
\mathrm{B}(\mathrm{~s}) \rightleftharpoons \mathrm{Z}(\mathrm{~g})+\mathrm{Y}(\mathrm{~g})
$$

## Simultaneous Equilibria

$$
\mathrm{A}(\mathrm{~s}) \rightleftharpoons \mathrm{M}(\mathrm{~g})+\mathrm{N}(\mathrm{~g}) \quad \mathrm{B}(\mathrm{~s}) \rightleftharpoons \mathrm{W}(\mathrm{~g})+\mathrm{N}(\mathrm{~g})
$$

At $\mathrm{t}=0$

At $\mathrm{t}=\mathrm{t}_{\text {eq }}$
-w

$$
p_{1}+p_{2}
$$

$$
-q
$$

$p_{2}$

$$
p_{2}+p_{1}
$$

$$
K p_{1}=\left(p_{1}\right)\left(p_{1}+p_{2}\right)
$$

## Ionic Equilibrium

Equilibrium between the ionized and the non-ionized form of a species

$$
\mathrm{AB}(\mathrm{aq}) \rightleftharpoons \mathrm{A}^{+}(\mathrm{aq})+\mathrm{B}^{-}(\mathrm{aq})
$$

## Quick Contrast

| Non - electrolytic <br> substances | Electrolytic substances |
| :---: | :---: |
| Do not produce ions <br> in $\mathrm{H}_{2} \mathrm{O}$ | Have tendency to produce <br> ions in $\mathrm{H}_{2} \mathrm{O}$ |
| Their solutions do not <br> conduct electricity | Their solutions conduct <br> electricity |
| E.g: Urea, Glucose | E.g: Acids, Bases, Salts |

## Electrolytes



## Electrolytes

## Weak Electrolytes

## Strong Electrolytes

Examples: $\mathrm{HCl}, \mathrm{NaOH}$

## Ionic Equilibrium

## Equilibrium is observed in Weak electrolytes

Weak electrolytes undergo partial ionization in aqueous solutions

$$
y^{b} \$
$$

## Acid-Base Concepts



## Arrhenius Concept

## Arrhenius Acid

Substances that dissociates in water to give hydrogen ion or $\mathrm{H}^{+}(\mathrm{aq})$

$$
\mathrm{HA}(\mathrm{aq}) \longrightarrow \mathrm{H}^{+}(\mathrm{aq})+\mathrm{A}^{-}(\mathrm{aq})
$$

## Types of Acids



## Examples

$$
\mathrm{HCl}(\mathrm{aq}) \longrightarrow \mathrm{H}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq})
$$

$$
\mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq}) \longrightarrow 2 \mathrm{H}^{+}(\mathrm{aq})+\mathrm{SO}_{4}{ }^{2-}(\mathrm{aq})
$$

$$
\mathrm{H}_{3} \mathrm{PO}_{4}(\mathrm{aq}) \rightleftharpoons 3 \mathrm{H}^{+}(\mathrm{aq})+\mathrm{PO}_{4}{ }^{3-}(\mathrm{aq})
$$

## Arrhenius Acid

$$
\mathrm{HA}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{A}^{-}
$$

$\mathrm{H}^{+}$ions in water are extremely hydrated (in form of $\mathrm{H}_{3} \mathrm{O}^{+}, \mathrm{H}_{5} \mathrm{O}_{2}^{+}$, $\mathrm{H}_{7} \mathrm{O}_{3}{ }^{+}$) due to its high charge density
$\mathrm{H}^{+}$ions form bonds with the oxygen atoms of the solvent water molecules to form trigonal pyramidal hydronium ions.

$$
\mathrm{H}_{3} \mathrm{O}^{+} \text {or }\left[\mathrm{H}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{+}
$$

## Existence of $\mathrm{H}^{+}$in Water

Generalised formula
of hydronium ion:
$\left[\mathrm{H}\left(\mathrm{H}_{2} \mathrm{O}\right)_{x}\right]^{+}$where ' x ' is the number of water molecules attached

$$
\mathrm{H}_{5} \mathrm{O}_{2}^{+}, \mathrm{H}_{7} \mathrm{O}_{3}^{+}, \mathrm{H}_{9} \mathrm{O}_{4}^{+}
$$ etc.

## Existence of $\mathrm{H}^{+}$Ion in Water



## Arrhenius Concept

## Arrhenius Base

Substances that dissociates in water to produce hydroxyl ions or OH- (aq)

$$
\mathrm{BOH}(\mathrm{aq}) \longrightarrow \mathrm{B}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

## Types of Bases

| Arrhenius Bases |  |  |
| :---: | :---: | :---: |
| Monoacidic | Diacidic | Triacidic |
| Gives single $\mathrm{OH}^{-}$ <br> per molecule | Gives a maximum <br> of two $\mathrm{OH}^{-}$per <br> molecule | Gives a maximum of three $\mathrm{OH}^{-}$ <br> per molecule |
| KOH | $\mathrm{Ca}(\mathrm{OH})_{2}$ | $\mathrm{Al}(\mathrm{OH})_{3}$ |

$\mathrm{NaOH}(\mathrm{aq}) \longrightarrow \mathrm{Na}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
Examples:
$\mathrm{NH}_{4} \mathrm{OH}(\mathrm{aq}) \rightleftharpoons \mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$

## Limitations of Arrhenius Theory

Limited to aqueous solutions only

Does not account for the basic nature of substances that do not contain hydroxide ion (E.g. $\mathrm{NH}_{3}$ )

## Bronsted - Lowry Concept

## Species which can donate $\mathbf{H}^{+}$

$$
\mathrm{HX}+\mathrm{B} \longrightarrow \mathrm{HB}^{+}+\mathrm{X}^{-}
$$



Species which can accept $\mathrm{H}^{+}$

## Bronsted Base

$$
\mathrm{HX}+\mathrm{B} \longrightarrow \mathrm{HB}^{+}+\mathrm{X}^{-}
$$

## Bronsted - Lowry Concept



## Conjugate Acid-Base Pair

Acid-base pair, related through the loss or gain of a proton

Conjugate pair

## Example <br> $\mathrm{H}_{2} \mathrm{O}$ \& $\mathrm{H}_{3} \mathrm{O}^{+} ; \mathrm{CH}_{3} \mathrm{COOH} \& \mathrm{CH}_{3} \mathrm{COO}^{-}$

## Conjugate Acid-Base Pair

Conjugate Acid-Base pair


## Conjugate Acid

Species formed by the gain of a proton by a base is called the conjugate acid of that base.


Conjugate Acid


## Conjugate Base



## Conjugate Acid-Base Pairs

Conjugate base of very weak acid is

Strong

Conjugate base of strong acid is

Very weak


## Relative Strength of Acid - Base Pair



Reaction will always favour in a direction from a stronger acid to a weaker acid or from a stronger base to a weaker base

## Amphiprotic Species



## Acid-Base Concepts



## Lewis Acids

Species which can accept
a pair of electrons from another species

## Lewis Acids



## Lewis Bases



## Properties of Water

Water acts as an acid as well as base according to Arrhenius \& Bronsted-Lowry theory, but according to Lewis concept it is a base, not an acid

Self ionization of water or Autoprotolysis

$$
\mathrm{H}_{2} \mathrm{O}(l)+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \quad \mathrm{Or} \quad \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

## Properties of Water

In self-ionization of water

## Equal number of

 ions are formed

So, pure water is neither acidic nor basic

## Molar Concentration

## Molarity of water

Number of moles

Volume of the solution

## For water

- Density $=1 \mathrm{~g} / \mathrm{cc}$
- Molar mass = $18 \mathrm{~g} / \mathrm{mol}$
- Volume = 1 L


## Molar Concentration



## Ionization Constant of Water $\left(\mathrm{K}_{\mathrm{w}}\right)$

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$



$$
\mathrm{K}_{\mathrm{eq}}\left[\mathrm{H}_{2} \mathrm{O}\right]=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]
$$

## Ionization Constant of Water ( $\mathrm{K}_{\mathrm{w}}$ )

## At $25^{\circ} \mathrm{C}$

## Experimental data



The product of the molar concentrations of $\mathrm{H}^{+}$and $\mathrm{OH}^{-}$ions

$$
\left[\mathrm{H}^{+}\right]=\left[\mathrm{OH}^{-}\right]=10^{-7} \mathrm{M}
$$

## Degree of Ionization of Water

$$
\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$


55.55

## Degree of Ionization of Water



## Absolute Dissociation Constant of Water

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

$$
\mathrm{K}_{\mathrm{eq}}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{H}_{2} \mathrm{O}\right]}
$$



## pH Scale

Concentration of $\mathrm{H}^{+}$ ions is written in a simplified form
introduced by Sorenson known as pH scale


Sorenson
pH is defined as negative logarithm of activity of $\mathrm{H}^{+}$ions


Activity of $\mathrm{H}^{+}$ions

## pH Scale

In a dilute solution,

## Activity of $\mathrm{H}^{+}$ions Concentration of free $\mathrm{H}^{+}$ions or $\mathrm{H}_{3} \mathrm{O}^{+}$ions

pH scale was marked from
0 to 14 with the central point at 7 at $25^{\circ} \mathrm{C}$ taking water as the solvent

## pH Scale

In general, for any quantity ' $X$ ', we can define a term pX as


## pH Scale



Taking logarithm and multiplying by ( -1 ) on both sides,


## pH Scale

At any temperature,


At $25^{\circ} \mathrm{C}$,
$\mathrm{pK}_{\mathrm{w}}=\mathrm{pH}+\mathrm{pOH} \quad=\quad 14$

## pH Scale

At $25^{\circ} \mathrm{C}$


## pH Scale

## Acidic strength

Tendency of an acid to give $\mathrm{H}_{3} \mathrm{O}^{+}$or $\mathrm{H}^{+}$ions in water
Tendency
to give $\mathrm{H}^{+}$

## Basic strength

Tendency of a base to give $\mathrm{OH}^{-}$ions in water

## pH Scale

## $\mathrm{H}_{2} \mathrm{O}() \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$

Dissociation of water is endothermic


## pH Scale



## pH Scale


$\mathrm{K}_{\mathrm{w}}$ decreases from $10^{-14}$ at $25^{\circ} \mathrm{C}$ to $\left(0.293 \times 10^{-14}\right)$ at $10^{\circ} \mathrm{C}$
$\left[\mathrm{H}^{+}\right]=\sqrt{\mathrm{K}_{\mathrm{w}}}=\sqrt{0.293 \times 10^{-14}}=0.541 \times 10^{-7}$
$\mathrm{pH}=\left(-\log \left[\mathrm{H}^{+}\right]\right)=\int .27$
$\Rightarrow \quad$ Now 7.27 is the midpoint of the new pH scale

## pH Scale


$\mathrm{K}_{\mathrm{w}}$ increases from $10^{-14}$ at $25^{\circ} \mathrm{C}$ to $38.02 \times 10^{-14}$ at $90^{\circ} \mathrm{C}$
$\left.\left.\left[\mathrm{H}^{+}\right]=\sqrt{\mathrm{K}_{\mathrm{w}}}\right)=\sqrt{38.02 \times 10^{-14}}\right)=\int 10^{-6.21}$

$$
\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=6.21
$$

$\Rightarrow \quad$ Now 6.21 is the midpoint of the new pH scale

## Strong Acid Solution

$\mathrm{H}^{+}$ions coming from water can be neglected

$\left[\mathrm{H}^{+}\right]=$| Molarity of the |
| :---: |
| strong acid |
| solution |$\quad \mathbf{x}$| Number of $\mathrm{H}^{+}$ |
| :---: |
| ions per acid |
| molecule |

## Strong Acid Solution

$\left[\mathrm{H}^{+}\right]_{\text {Strong acid }} \quad<\quad 10^{-6} \mathrm{M}$
$\mathrm{H}^{+}$ions coming from water cannot be neglected

$\left[\mathrm{H}^{+}\right]=$| $\left[\mathrm{H}^{+}\right]$from |
| :---: |
| strong acid |$+$| $\left[\mathrm{H}^{+}\right]$coming from |
| :---: |
| water in the |
| presence of the |
| strong acid |

## Mixture of Two Strong Acids



## Mixture of Two Strong Acids



Moles of $\mathrm{H}^{+}$ions from I - solution

$$
=\quad\left[\mathrm{H}^{+}\right]_{1} \mathrm{~V}_{1}
$$

Moles of $\mathrm{H}^{+}$ions
$=$
from II - solution
$\left[\mathrm{H}^{+}\right]_{2} \mathrm{~V}_{2}$

## Mixture of Two Strong Acids

$$
\begin{array}{ll}
V_{f} & =\quad V_{1}+V_{2}
\end{array}
$$

$\left[\mathrm{H}^{+}\right]_{\mathrm{f}} \mathrm{V}_{\mathrm{f}} \quad=\quad\left[\mathrm{H}^{+}\right]_{1} \mathrm{~V}_{1} \quad+\quad\left[\mathrm{H}^{+}\right]_{2} \mathrm{~V}_{2}$


## Mixture of Two Strong Bases



## Mixture of a Strong Acid and a Strong Base

Acid - base neutralization reaction will take place

Solution will be acidic or basic depending upon which is taken in excess

## Mixture of a Strong Acid and a Strong Base



Moles of $\mathrm{H}^{+}$ions from I - solution

$$
=\quad\left[\mathrm{H}^{+}\right] \mathrm{V}_{1}
$$

Moles of $\mathrm{OH}^{-}$ions
from II - solution

$$
=\left[\mathrm{OH}^{-}\right] \mathrm{V}_{2}
$$

## Mixture of a Strong Acid and a Strong Base



Final solution will be acidic in nature
Final solution will be basic in nature

## Weak Acid



## Factors Affecting Degree of Ionization



## Ionization of Weak Acids

Consider a weak acid 'HA'

$$
\mathrm{HA}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{A}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})
$$



Equilibrium constant for the dissociation of HA

## Ionization Constant of Weak Acids $\left(\mathrm{K}_{\mathrm{a}}\right)$

For a weak acid


Ionization constant for weak acids and it is a measure of its strength.

Acidic strength

## pH of Weak Acids

$$
\mathrm{HA}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{A}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})
$$

| Initial |
| :---: |
| Concentration |
| $(\mathrm{t}=0)$ |


| Equilibrium |
| :---: |
| Concentration <br> $\left(\mathrm{t}=\mathrm{t}_{\text {eq }}\right)$ |$(\mathrm{c}-\mathrm{c} \alpha)$

## pH of a Weak Acid



## Ostwald's Dilution Law




At infinite dilution, $\alpha$ reaches its maximum value, i.e. unity. Weak electrolyte starts behaving like a strong electrolyte!


## pH of a Weak Acid

$$
\left[\mathrm{H}^{+}\right]=\left(\mathrm{K}_{\mathrm{a}} \times \mathrm{c}\right)^{\frac{1}{2}}
$$

Taking logarithm and multiplying by -1 on both sides

$$
-\log \left[H^{+}\right]=-\log \left(\mathrm{K}_{\mathrm{a}} \times \mathrm{c}\right)^{\frac{1}{2}}
$$

pH of a weak acid

$$
\mathrm{pH}=\left(\frac{1}{2}\left(\mathrm{pK}_{\mathrm{a}}-\log \mathrm{c}\right)\right.
$$

## pH of a Weak Acid

If $\alpha$ obtained from $\sqrt{\frac{K_{a}}{c}}$ is greater than 0.1,
solve quadratic equation and get accurate $\boldsymbol{\alpha}$


Now pH calculation can be done

## Ionization Constant of Weak Bases $\left(\mathrm{K}_{\mathrm{b}}\right)$

## Consider a weak base

 'MOH'$\mathrm{MOH}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{M}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$

$$
\mathrm{K}_{\mathrm{b}}=\frac{\left[\mathrm{M}^{+}\right]\left[\mathrm{OH}^{-}\right]}{[\mathrm{MOH}]}
$$




## Weak Base

For weak bases, pH can't be calculated directly


## Ionization Constant of Weak Bases $\left(\mathrm{K}_{\mathrm{b}}\right)$

$$
\mathrm{MOH}(\mathrm{aq})+\underset{(\mathrm{aq})}{\mathrm{H}_{2} \mathrm{O}(1)} \underset{\mathrm{a}}{ } \quad \mathrm{M}^{+}(\mathrm{aq})+\mathrm{OH}^{-}
$$

| Initial |
| :---: |
| Concentration |
| $(t=0)$ |


| Equilibrium |
| :---: |
| Concentration <br> $\left(t=t_{\text {eq }}\right)$ |$(c-c \alpha)$

## Ionization Constant of Weak Bases $\left(\mathrm{K}_{\mathrm{b}}\right)$



## pH of Weak Bases

pOH of a weak base

$$
\mathrm{pOH}=\frac{1}{2}\left(\mathrm{pK}_{\mathrm{b}}-\log \mathrm{c}\right)
$$

$$
\mathrm{pOH}=\frac{1}{2}\left(\mathrm{pK}_{\mathrm{b}}-\log \mathrm{c}\right)
$$

At $25^{\circ} \mathrm{C}$,
$\mathrm{pH}+\mathrm{pOH}$
14

Valid if

$$
\alpha<\quad<\quad 0.1 \text { or } 10 \%
$$

## Remember!!

If $\alpha$ obtained from $\sqrt{\frac{\mathrm{K}_{\mathrm{b}}}{\mathrm{c}}}$ is greater than 0.1,
solve quadratic equation and get accurate $\alpha$


Now pOH calculation can be done

## Relation between $\mathrm{pK}_{\mathrm{a}}$ and $\mathrm{pK}_{\mathrm{b}}$

Consider a weak acid HA,
Conjugate base of HA is $\mathbf{A}^{-}$

$$
\mathrm{HA}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{A}^{-}(\mathrm{aq})
$$

$$
\mathrm{A}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{OH}^{-}(\mathrm{aq})+\mathrm{HA}(\mathrm{aq})
$$



## Relation between $\mathrm{pK}_{\mathrm{a}}$ and $\mathrm{pK}_{\mathrm{b}}$

Multiply equation (i) and (ii)


For an acid-base conjugate pair
$\mathrm{K}_{\mathrm{a}} \times \mathrm{K}_{\mathrm{b}}$


## Relation between $\mathrm{pK}_{\mathrm{a}} \mathrm{and}_{\mathrm{pK}}^{\mathrm{b}}$

Taking logarithm and multiplying by $\mathbf{- 1}$ on both sides


$$
-\log \left(\mathrm{K}_{\mathrm{a}}\right)-\log \left(\mathrm{K}_{\mathrm{b}}\right) \quad=\quad-\log \left(\mathrm{K}_{\mathrm{w}}\right)
$$

At $25^{\circ} \mathrm{C}$



## Dissociation of Electrolytes in Water

| Strong <br> electrolyte |
| :---: |
| Weak $(\mathrm{aq})$ <br> Welectrolyte |
| $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{Cl}_{3}^{-}(\mathrm{aq})$ |
| $\mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq})$ |

## Dissociation of $\mathrm{CH}_{3} \mathrm{COOH} \& \mathrm{HCl}$

Weak electrolyte<br>Strong electrolyte

$$
\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq})
$$

$\mathrm{HCl}(\mathrm{aq}) \longrightarrow \mathrm{Cl}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq})$ $!$
$\vdots$
$\vdots$

Common Ion

## Common Ion Effect

$$
\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq})
$$

On adding HCl,
$\mathrm{HCl}(\mathrm{aq}) \longrightarrow \mathrm{Cl}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq})$

Concentration of the common ion ( $\mathrm{H}^{+}$)

## Common Ion Effect

## Based on Le Chatelier's Principle

## $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq})$

Equilibrium will be shifted backwards

When a substance is present in a solution, it may affect the dissociation of another substance.

## Common Ion Effect

If $\mathrm{H}^{+}$is the common ion,

Suppression in the dissociation of a weak electrolyte by the addition of a strong electrolyte having a common ion


## Mixture of Weak Acid \& Strong Acid


Initial
Concentration
(M)

$$
\mathrm{HA}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{A}^{-}(\mathrm{aq})
$$

$C_{2}$
(Comes from
strong acid)

$$
c_{2}(1-\alpha)
$$

$c_{1}+c_{2} \alpha$
$c_{2} \alpha$

Mixture of Weak Acid \& Strong Acid

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}
$$

$$
\mathrm{K}_{\mathrm{a}}=\quad \frac{\left(\mathrm{c}_{1}+\mathrm{c}_{2} \alpha\right)\left(\mathrm{c}_{2} \alpha\right)}{\left(\mathrm{c}_{2}(1-\alpha)\right)} \cdots \cdots \cdots(\mathrm{i})
$$

## Mixture of Weak Acid \& Strong Acid

Weak acid's dissociation will be further suppressed because of presence of strong acid therefore $\alpha \ll 1$


## Mixture of Weak Acid \& Strong Acid

If $\alpha$ from (ii) comes < 0.1

Assumption is correct


$$
\left[\mathrm{H}^{+}\right]_{\text {Total }}=\mathrm{c}_{1}
$$

If $\alpha$ from (ii) comes $\geq 0.1$

Solve quadratic equation in $\alpha$ (equation (i) ) to get exact $\alpha$

$$
\left[\mathrm{H}^{+}\right]_{\text {Total }}=\mathrm{c}_{1}+\mathrm{c}_{2} \alpha
$$



## Mixture of Two Weak Monoprotic Acids



$$
\mathrm{HA}(\mathrm{aq}) \quad \rightleftharpoons \quad \mathrm{H}^{+}(\mathrm{aq}) \quad+\quad \mathrm{A}^{-}(\mathrm{aq})
$$

$$
\begin{array}{llll}
t=0 & c_{1} & 0 & 0
\end{array}
$$

$$
t=t_{e q}
$$

$$
c_{1}\left(1-\alpha_{1}\right)
$$

$$
c_{1} \alpha_{1}+c_{2} \alpha_{2}
$$

$$
\mathrm{c}_{1} \alpha_{1}
$$

## Mixture of Two Weak Monoprotic Acids

$$
\mathrm{HB}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq}) \quad+\quad \mathrm{B}^{-}(\mathrm{aq})
$$

$$
t=0
$$

$$
\mathrm{t}=\mathrm{t}_{\mathrm{eq}}
$$

$$
c_{2}\left(1-\alpha_{2}\right)
$$

$$
c_{2} \alpha_{2}+c_{1} \alpha_{1}
$$

$$
\mathrm{c}_{2} \alpha_{2}
$$

## Mixture of Two Weak Monoprotic Acids

$$
\begin{aligned}
K_{a_{1}} & =\frac{\left(c_{1} \alpha_{1}+c_{2} \alpha_{2}\right)\left(c_{1} \alpha_{1}\right)}{\left(c_{1}\right)\left(1-\alpha_{1}\right)} \ldots \ldots \ldots \text { (i) } \\
K_{a_{2}} & =\frac{\left(c_{1} \alpha_{1}+c_{2} \alpha_{2}\right)\left(c_{2} \alpha_{2}\right)}{\left(c_{2}\right)\left(1-\alpha_{2}\right)} \ldots \ldots \ldots{ }^{\text {(ii }}
\end{aligned}
$$

Both acids will dissociate less than in their individual aqueous solutions of the same concentration because of

Common ion effect exerted by $\mathrm{H}^{+}$ions of one on other

Mixture of Two Weak Monoprotic Acids

For the weak acid 'HA'
$\alpha_{1}$
$\ll$
1
$1-\alpha_{1}$
$=$
1

For the weak acid 'HB'
$\alpha_{2}$
$\ll$
1
$1-\alpha_{2}$
$=$
1

Mixture of Two Weak Monoprotic Acids
$\therefore$ From (i) and (ii) we get

$$
\begin{equation*}
\mathrm{K}_{\mathrm{a}_{1}} \mathrm{c}_{1}=\left(\mathrm{c}_{1} \alpha_{1}+\mathrm{c}_{2} \alpha_{2}\right)\left(\mathrm{c}_{1} \alpha_{1}\right) \tag{iii}
\end{equation*}
$$

$$
\begin{equation*}
\mathrm{K}_{\mathrm{a}_{2}} \mathrm{c}_{2}=\left(\mathrm{c}_{1} \alpha_{1}+\mathrm{c}_{2} \alpha_{2}\right)\left(\mathrm{c}_{2} \alpha_{2}\right) \tag{iv}
\end{equation*}
$$

Mixture of Two Weak Monoprotic Acids
Adding (iii) and (iv)

$$
\mathrm{K}_{\mathrm{a}_{1}} \mathrm{c}_{1}+\mathrm{K}_{\mathrm{a}_{2}} \mathrm{c}_{2}=\left(\mathrm{c}_{1} \alpha_{1}+\mathrm{c}_{2} \alpha_{2}\right)^{2}
$$

$\left[\mathrm{H}^{+}\right]=\mathrm{c}_{1} \alpha_{1}+\mathrm{c}_{2} \alpha_{2}=\sqrt{\mathrm{K}_{\mathrm{a}_{1}} \mathrm{c}_{1}+\mathrm{K}_{\mathrm{a}_{2}} \mathrm{c}_{2}}$
$\mathrm{pH} \quad=\quad-\log \left[\mathrm{H}^{+}\right]$

$$
\mathrm{pH}=-\frac{1}{2} \log \left(\mathrm{~K}_{\mathrm{a}_{1}} \mathrm{c}_{1}+\mathrm{K}_{\mathrm{a}_{2}} \mathrm{c}_{2}\right)
$$

## Mixture of Two Weak Monoprotic Acids



Contribution of HB in $\left[\mathrm{H}^{+}\right]$can be neglected


## Acidity of a Base

The total number of ionizable hydroxyl ( $\mathrm{OH}^{-}$) ions present in one molecule of a base

Acidity
$\mathrm{NaOH}(\mathrm{aq}) \longrightarrow \mathrm{Na}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
$\mathrm{Mg}(\mathrm{OH})_{2}(\mathrm{aq})$
$\mathrm{Mg}^{2+}(\mathrm{aq})+2 \mathrm{OH}^{-}$ (aq)

## Polyacidic Base

$$
\mathrm{Ca}(\mathrm{OH})_{2}(\mathrm{aq}) \longrightarrow \mathrm{Ca}^{2+}(\mathrm{aq})+2 \mathrm{OH}^{-}(\mathrm{aq})
$$

Bases which contain more than one ionizable hydroxyl ions

$$
\mathrm{Al}(\mathrm{OH})_{3}(\mathrm{aq}) \rightleftharpoons \mathrm{Al}^{3+}(\mathrm{aq})+3 \mathrm{OH}^{-}(\mathrm{aq})
$$

## Basicity of an Acid

The total number of ionizable hydrogen $\left(\mathrm{H}^{+}\right)$ ions present in one molecule of an acid

## Basicity

$\mathrm{HCl}(\mathrm{aq}) \longrightarrow \mathrm{H}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq})$
$\mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq}) \longrightarrow 2 \mathrm{H}^{+}(\mathrm{aq})+\mathrm{SO}_{4}^{2-}(\mathrm{aq})$

## Polybasic or Polyprotic Acid

Acids which contain more than one ionizable protons

$$
\mathrm{H}_{3} \mathrm{PO}_{4}(\mathrm{aq}) \rightleftharpoons 3 \mathrm{H}^{+}(\mathrm{aq})+\mathrm{PO}_{4}^{3-}(\mathrm{aq})
$$

Number of ionizable protons in $\mathrm{H}_{3} \mathrm{PO}_{4}=3$

## $\mathrm{K}_{\mathrm{a}}$ for the Dissociation of a Dibasic Acid



$$
\mathrm{H}_{2} \mathrm{X}(\mathrm{aq}) \stackrel{\mathrm{K}_{\mathrm{a}_{1}}}{\rightleftharpoons} \mathrm{H}^{+}(\mathrm{aq})+\mathrm{HX}^{-}(\mathrm{aq})
$$

$$
\mathrm{HX}^{-}(\mathrm{aq}) \stackrel{\mathrm{K}_{\mathrm{a}_{2}}}{\rightleftharpoons} \mathrm{H}^{+}(\mathrm{aq})+\mathrm{X}^{2-}(\mathrm{aq})
$$



## Overall K a for the Reaction

$$
\mathrm{H}_{2} \mathrm{X}(\mathrm{aq}) \rightleftharpoons 2 \mathrm{H}^{+}(\mathrm{aq})+\mathrm{X}^{2-}(\mathrm{aq})
$$

$$
\mathrm{K}_{\mathrm{a}}--\cdots \rightarrow \frac{\left[\mathrm{H}^{+}\right]^{2}\left[\mathrm{X}^{2-}\right]}{\left[\mathrm{H}_{2} \mathrm{X}\right]}
$$

$$
K_{a} \quad=\quad K_{a_{1}} \times K_{a_{2}}
$$

Where $\mathrm{K}_{\mathrm{a}}$ is the ionization constant of $\mathrm{H}_{2} \mathrm{X}$

Ka for the Dissociation a Tribasic Acid

| $\mathrm{H}_{3} \mathrm{PO}_{4}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{PO}_{4}^{-}(\mathrm{aq})$ | $\mathrm{K}_{\mathrm{a}_{1}}$ | In general, for polybasic acids, |
| :---: | :---: | :---: |
| $\vdots$ |  |  |
| $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{HPO}_{4}^{2-}(\mathrm{aq})$ | $\mathrm{K}_{\mathrm{a}_{2}}$ | If we assume an acid having ' $n$ ' ionizable protons, for E.g. $\mathrm{H}_{\mathrm{n}} \mathbf{A}$ |
| $\mathrm{HPO}_{4}^{2-}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{PO}_{4}^{3-}(\mathrm{aq})$ | $\mathrm{K}_{\mathrm{a}_{3}}$ | $\mathrm{K}_{\mathrm{a}}=\mathrm{K}_{\mathrm{a}_{1}} \times \mathrm{K}_{\mathrm{a}_{2}} \times \mathrm{K}_{\mathrm{a}_{3}} \times \ldots . \mathrm{K}_{\mathrm{a}_{n}}$ |

Comparison of $K^{\text {a }}$ for Polyprotic Acids

$$
\mathrm{K}_{\mathrm{a}_{1}} \gg \mathrm{~K}_{\mathrm{a}_{2}} \gg \mathrm{~K}_{\mathrm{a}_{3}} \gg \mathrm{~K}_{\mathrm{a}_{4}} \ldots . .
$$

$\mathrm{H}^{+}$is lost much more easily from a neutral $\mathrm{H}_{\mathrm{n}} \mathbf{A}$ molecule than from a $\mathrm{H}_{\mathrm{n}-1} \mathbf{A}^{-}$ ion

$$
\left[\mathrm{H}^{+}\right]_{1} \gg\left[\mathrm{H}^{+}\right]_{2} \gg\left[\mathrm{H}^{+}\right]_{3} \gg\left[\mathrm{H}^{+}\right]_{4} \ldots
$$

$$
K_{a_{1}}>K_{a_{2}}>K_{a_{3}} .
$$

Because $\mathrm{K}_{\mathrm{a}_{1}}$ is much larger than $\mathrm{K}_{\mathrm{a}_{2}}$, virtually all the $\left[\mathrm{H}^{+}\right]$in a solution comes from the $1^{\text {st }}$ step of ionization

Let's consider a weak polyprotic acid $\mathrm{H}_{2} \mathrm{CO}_{3}$ of concentration $\mathrm{c}_{1}$

$$
\mathrm{H}_{2} \mathrm{CO}_{3}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{HCO}_{3}^{-}(\mathrm{aq})
$$

At $t=t_{\text {eq }} \quad c_{1}\left(1-\alpha_{1}\right) \quad c_{1} \alpha_{1}\left(1+\alpha_{2}\right) \quad c_{1} \alpha_{1}\left(1-\alpha_{2}\right)$

$$
\mathrm{HCO}_{3}^{-}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{CO}_{3}^{2-}(\mathrm{aq})
$$

$\mathrm{Att}=\mathrm{t}_{\text {eq }} \quad \mathrm{c}_{1} \alpha_{1}\left(1-\alpha_{2}\right) \quad \mathrm{c}_{1} \alpha_{1}\left(1+\alpha_{2}\right) \quad \mathrm{c}_{1} \alpha_{1} \alpha_{2}$

## Polyprotic Acids

$$
\mathrm{K}_{\mathrm{a}_{1}}-\cdots=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{HCO}_{3}^{-}\right]}{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]}=\frac{\mathrm{c}_{1} \alpha_{1}\left(1+\alpha_{2}\right) \mathrm{c}_{1} \alpha_{1}\left(1-\alpha_{2}\right)}{\mathrm{c}_{1}\left(1-\alpha_{1}\right)}
$$

$$
\mathrm{K}_{\mathrm{a}_{2}}-\cdots \frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{CO}_{3}^{2-}\right]}{\left[\mathrm{HCO}_{3}^{-}\right]}=\frac{c_{1} \alpha_{1}\left(1+\alpha_{2}\right) c_{1} \alpha_{1} \alpha_{2}}{c_{1} \alpha_{1}\left(1-\alpha_{2}\right)}
$$

Polyprotic Acids


## Polyprotic Acids

## Total $\left[\mathrm{H}^{+}\right]$released after ionization,



## Mixture of a Polyprotic Weak Acid \& a Strong Acid

## pH

Generally, pH can be calculated by taking the concentration of strong acid only

Other calculations can be done by considering the dissociation equilibria of the weak polyprotic acid

## pH of a Mixture of a Weak Monoprotic $\mathcal{A}$ a Weak Polyprotic Acid

$\left[\mathrm{H}^{+}\right]$calculation can be done similar to the case of a mixture of two weak monoprotic acids


## Salts and Salt Hydrolysis

Salts formed by the reaction between an acid $\&$ a base in definite proportions undergo ionization in water

Process of interaction of water with cations/anions or both of the salts is called hydrolysis
lons formed either exist as hydrated ions or interact with water

## Salt Hydrolysis

Salts of strong acids \& bases only get hydrated and not hydrolysed, whereas salts of other types do get hydrolysed.

Cation of weak base on reaction with water will produce $\mathrm{H}^{+}$ions and the anion of weak acid on reaction with water produce $\mathrm{OH}^{-}$ions
pH of the solution is affected by this interaction.

## Salt Hydrolysis

Cationic Hydrolysis

$$
\mathrm{B}^{+}(\mathrm{aq})+2 \mathrm{H}_{2} \mathrm{O} \underset{(\mathrm{aq})}{()_{\mathrm{\sim}}} \mathrm{BOH}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}
$$

Anionic Hydrolysis

$$
\mathrm{A}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{HA}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$



## SA Strong Acid

SB
Strong Base

## WA

Weak Acid
Weak Base


## Salt of Strong Acid - Strong Base



Neither of the ions will undergo hydrolysis

Solution involves only the equilibrium of ionization of water

At $25^{\circ} \mathrm{C}$,


## Salt of WA + SB



## Hydrolysis of Salt of Weak Acid \& Strong Base

Completely ionised in an aqueous solution


## Hydrolysis of Salt of Weak Acid \& Strong Base

## $\mathrm{CH}_{3} \mathrm{COONa}(\mathrm{aq}) \longrightarrow \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{Na}^{+}$ (aq)

Acetate ion formed undergoes hydrolysis in water

$$
\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

$\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$

$K_{h}$
Hydrolysis constant of the salt

## Hydrolysis of Salt of Weak Acid \& Strong Base

```
CH
```

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}
$$

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

$$
\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]
$$

## Hydrolysis of Salt of Weak Acid \& Strong Base



## Hydrolysis of Salt of Weak Acid \& Strong Base

$$
\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

| $t=0$ | $c$ | 0 | 0 |
| :---: | :---: | :---: | :---: |
| $t=t_{e q}$ | $c(1-h)$ | $c h$ | ch |



Hydrolysis of Salt of Weak Acid \& Strong Base

$$
K_{h}=\frac{c h \times c h}{c(1-h)}=\frac{c h^{2}}{(1-h)}
$$

If $\mathrm{h} \ll 1$

$$
\mathrm{K}_{\mathrm{h}}=\mathrm{ch}^{2}=\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{~K}_{\mathrm{a}}}
$$

## Hydrolysis of Salt of Weak Acid \& Strong Base

$$
h=\sqrt{\frac{\mathrm{K}_{\mathrm{h}}}{\mathrm{c}}}=\sqrt{\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{~K}_{\mathrm{a}} \mathrm{c}}}
$$

$$
\left[\mathrm{OH}^{-}\right]=\mathrm{ch}
$$

$$
\left.\left[\mathrm{OH}^{-}\right]=c \times \sqrt{\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{~K}_{\mathrm{a}} \mathrm{c}}}\right) \rightarrow \quad\left[\mathrm{OH}^{-}\right]=\sqrt{\frac{\mathrm{K}_{\mathrm{w}} \mathrm{c}}{\mathrm{~K}_{\mathrm{a}}}}
$$

## Hydrolysis of Salt of Weak Acid \& Strong Base

$$
\left[\mathrm{H}^{+}\right]=\frac{\mathrm{K}_{\mathrm{w}}}{\left[\mathrm{OH}^{-}\right]}=\sqrt{\frac{\mathrm{K}_{\mathrm{w}} \mathrm{~K}_{\mathrm{a}}}{\mathrm{c}}}
$$

Taking logarithm on both sides and multiplying by (-1)

$$
-\log \left[\mathrm{H}^{+}\right]=-\frac{1}{2} \log \mathrm{~K}_{\mathrm{w}}-\frac{1}{2} \log \mathrm{~K}_{\mathrm{a}}+\frac{1}{2} \log \mathrm{c}
$$

## Hydrolysis of Salt of Weak Acid \& Strong Base

$\mathrm{pH}=\frac{1}{2}\left[\mathrm{pK}_{\mathrm{w}}+\mathrm{pK}_{\mathrm{a}}+\log \mathrm{c}\right]<$| Valid if, |
| :---: |
| $\mathrm{h}<0.1$ or $10 \%$ |

$\mathrm{pH}=7+\frac{1}{2}\left[p K_{\mathrm{a}}+\log \mathrm{c}\right]$

If $h$ obtained from $\sqrt{\frac{\mathrm{K}_{\mathrm{h}}}{\mathrm{c}}}>0.1$, then solve the quadratic equation and get h

## Salt of SA + WB



## Hydrolysis of Salt of Strong Acid \& Weak Base



Completely ionised in an aqueous solution


## Hydrolysis of Salt of Strong Acid \& Weak Base

$$
\mathrm{NH}_{4} \mathrm{Cl}(\mathrm{aq}) \longrightarrow \mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq})
$$

Ammonium ion formed undergoes hydrolysis in water

$$
\mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{NH}_{4} \mathrm{OH}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq})
$$

## Hydrolysis of Salt of Strong Acid \& Weak Base

$$
\mathrm{NH}_{4}^{+}(\mathrm{aq})+\underset{(\mathrm{aq})}{\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons} \mathrm{NH}_{4} \mathrm{OH}(\mathrm{aq})+\mathrm{H}^{+} \mathrm{K}_{\mathrm{h}}=\frac{\left[\mathrm{NH}_{4} \mathrm{OH}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{NH}_{4}^{+}\right]}
$$

$\mathrm{NH}_{4} \mathrm{OH}(\mathrm{aq}) \rightleftharpoons \mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$


$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

$$
\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]
$$

## Hydrolysis of Salt of Strong Acid \& Weak Base



```
NH
```


$c(1-h)$

$\square$


Hydrolysis of Salt of Strong Acid \& Weak Base

$$
K_{h}=\frac{c h \times c h}{c(1-h)}=\frac{c h^{2}}{(1-h)} \quad h=\sqrt{\frac{K_{h}}{c}}=\sqrt{\frac{K_{w}}{K_{b} c}}
$$

If $h \ll 1$

$$
\mathrm{ch}^{2}=\mathrm{K}_{\mathrm{h}}=\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{~K}_{\mathrm{b}}}
$$

$$
\left[\mathrm{H}^{+}\right]=\mathrm{c} \times \sqrt{\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{~K}_{\mathrm{b}} \mathrm{c}}}
$$

Hydrolysis of Salt of Strong Acid \& Weak Base

$$
\left[\mathrm{H}^{+}\right]=\sqrt{\frac{\mathrm{K}_{\mathrm{w}} \mathrm{c}}{\mathrm{~K}_{\mathrm{b}}}}
$$

Taking logarithm on both sides and multiplying by -1 $-\log \left[\mathrm{H}^{+}\right]=\frac{-1}{2} \quad \log _{\mathrm{K}_{\mathrm{w}}}-\frac{1}{2} \quad \log \mathrm{c}+\frac{1}{2} \quad \log$

$$
\mathrm{pH}=\frac{1}{2}\left[\mathrm{pK}_{\mathrm{w}}-\mathrm{pK}_{\mathrm{b}}-\log \mathrm{c}\right]
$$

Valid if h < 0.1 or 10\%
$\mathrm{pH}=$
$7-\frac{1}{2}\left[\mathrm{pK}_{\mathrm{b}}+\log \mathrm{c}\right]$
At $25^{\circ} \mathrm{C}$

## Hydrolysis of Salt of Weak Acid \& Weak Base

Salt of WA + WB
$\mathrm{CH}_{3} \mathrm{COONH}_{4}$

Completely ionized in an aqueous solution


## Hydrolysis of Salt of Weak Acid \& Weak Base

## lons formed undergo hydrolysis as

## $\mathrm{CH}_{3} \mathrm{COONH}_{4}$

$\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{NH}_{4} \mathrm{OH}(\mathrm{aq})$
$\mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{NH}_{4} \mathrm{OH}(\mathrm{aq})$

$$
\left.\mathrm{K}_{\mathrm{h}}\right)=\left(\frac{\left[\mathrm{NH}_{4} \mathrm{OH}\right]\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{COO}\right]}\right.
$$

## Hydrolysis of Salt of Weak Acid \& Weak Base

$$
\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq})
$$

$$
\begin{gathered}
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]} \\
\mathrm{NH}_{4} \mathrm{OH}(\mathrm{aq}) \rightleftharpoons \mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
\end{gathered}
$$

$$
\mathrm{K}_{\mathrm{b}}=\frac{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{NH}_{4} \mathrm{OH}\right]}
$$

## Hydrolysis of Salt of Weak Acid \& Weak Base

$\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
$\frac{K_{w}}{K_{a} K_{b}}$
$\left[\mathrm{CH}_{3} \mathrm{COOH}\right]\left[\mathrm{NH}_{4} \mathrm{OH}\right]$ $\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]\left[\mathrm{NH}_{4}{ }^{+}\right]$

## Hydrolysis of Salt of Weak Acid \& Weak Base

$$
\mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\underset{(\mathrm{aq})}{\mathrm{H}_{2} \mathrm{O}(\mathrm{l})} \underset{\mathrm{CH}}{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{NH}_{4} \mathrm{OH}
$$


$\mathrm{c}(1-\mathrm{h})$


$$
\mathrm{K}_{\mathrm{h}}=\frac{\left[\mathrm{NH}_{4} \mathrm{OH}\right]\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]}
$$

## Remember!!

For numerical analysis, even if $\mathrm{K}_{\mathrm{a}}$ of weak acid \& $\mathrm{K}_{\mathrm{b}}$ of weak base are different.

Degree of hydrolysis of cations \& anions are taken equal as they are very close to each other.

## Hydrolysis of Salt of Weak Acid \& Weak Base

$$
K_{h}=\frac{c h \times c h}{c^{2}(1-h)^{2}}=\frac{h^{2}}{(1-h)^{2}} \quad \frac{h}{(1-h)}=\sqrt{K_{h}}
$$

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}-\mathrm{K}=\frac{\mathrm{c}(1-\mathrm{h})\left[\mathrm{H}^{+}\right]}{\mathrm{ch}}
$$

$$
\left[\mathrm{H}^{+}\right]=\left[\mathrm{K}_{\mathrm{a}} \frac{\mathrm{~h}}{1-\mathrm{h}} \Rightarrow \quad\left[\mathrm{H}^{+}\right]=\mathrm{K}_{\mathrm{a}} \sqrt{\mathrm{~K}_{\mathrm{h}}}\right.
$$

## Hydrolysis of Salt of Weak Acid \& Weak Base



| If $\mathrm{K}_{\mathrm{a}}=\mathrm{K}_{\mathrm{b}}$ | $\mathrm{pH}=7$ | Neutral solution |
| :---: | :---: | :---: |
| If $\mathrm{K}_{\mathrm{a}}>\mathrm{K}_{\mathrm{b}}$ | $\mathrm{pH}<7$ | Acidic solution |
| If $\mathrm{K}_{\mathrm{a}}<\mathrm{K}_{\mathrm{b}}$ | $\mathrm{pH}>7$ | Basic solution |


| Type of Salt | Expressio n for $\mathrm{K}_{\mathrm{h}}$ | Expression for h | Expression for pH |
| :---: | :---: | :---: | :---: |
| Salt of WA \& SB | $\mathrm{K}_{\mathrm{h}}=\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{K}_{\mathrm{a}}}$ | $h=\sqrt{\frac{K}{h}}$ | $\begin{gathered} \mathrm{pH}=\frac{1}{2}\left[\mathrm{pK}_{\mathrm{w}}+\mathrm{pK}_{\mathrm{a}}+\log \mathrm{c}\right] \\ \text { (if } \mathrm{h}<0.1 \text { ) } \end{gathered}$ |
| Salt of SA \& WB | $\mathrm{K}_{\mathrm{h}}=\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{K}_{\mathrm{b}}}$ | $h=\sqrt{\frac{K}{h}}$ | $\begin{gathered} \mathrm{pH}=\frac{1}{2}\left[\mathrm{pK}_{\mathrm{w}}-\mathrm{pK}_{\mathrm{b}}-\log \mathrm{c}\right] \\ \text { (if } \mathrm{h}<0.1 \text { ) } \end{gathered}$ |
| Salt of WA \& WB | $\mathrm{K}_{\mathrm{h}}=\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{~K}_{\mathrm{a}} \mathrm{~K}_{\mathrm{b}}}$ | $\frac{h}{1-}=\sqrt{K_{h}}$ | $\mathrm{pH}=\frac{1}{2}\left[\mathrm{pK}_{\mathrm{w}}+\mathrm{pK}_{\mathrm{a}}-\mathrm{pK}_{\mathrm{b}}\right]$ |

## Remember!!

If $h$ is not less than 0.1 , then solve quadratic equation in order to obtain $h$ and then determine $\left[\mathrm{H}^{+}\right]$or $\left[\mathrm{OH}^{-}\right]$.

## Salt of Weak Polyprotic Acids

## Consider $\mathrm{H}_{3} \mathrm{PO}_{4}$

Hydrolysis of polyvalent ions

Ions like $\mathrm{PO}_{4}{ }^{3-}, \mathrm{CO}_{3}{ }^{2-}, \mathrm{Zn}^{2+}$, $\mathrm{Fe}^{3+}$ etc. form salts like $\mathrm{K}_{3} \mathrm{PO}_{4}, \mathrm{Na}_{2} \mathrm{CO}_{3}, \mathrm{ZnSO}_{4}$,

## $\mathrm{FeCl}_{3}$

$$
\mathrm{H}_{3} \mathrm{PO}_{4}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{PO}_{4}^{-}(\mathrm{aq})
$$

$$
\mathrm{H}_{2} \mathrm{PO}_{4}^{-}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{HPO}_{4}^{2-}(\mathrm{aq})
$$

$$
\mathrm{K}_{\mathrm{a}_{2}}
$$

$$
\mathrm{HPO}_{4}^{2-}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{PO}_{4}^{3-}(\mathrm{aq})
$$

## Salt of Weak Polyprotic Acids

$$
\begin{array}{r}
\mathrm{PO}_{4}^{3-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{HPO}_{4}^{2-}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \\
\mathrm{K}_{\mathrm{h}_{1}}=\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{~K}_{\mathrm{a}_{3}}} \\
\mathrm{HPO}_{4}^{2-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{2} \mathrm{PO}_{4}^{-}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \quad \mathrm{K}_{\mathrm{h}_{2}}=\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{~K}_{\mathrm{a}_{2}}} \\
\mathrm{H}_{2} \mathrm{PO}_{4}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \stackrel{\stackrel{\mathrm{aq}}{\stackrel{a}{2}}}{ } \mathrm{H}_{3} \mathrm{PO}_{4}(\mathrm{aq})+\mathrm{OH}^{-} \quad \mathrm{K}_{\mathrm{h}_{3}}=\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{Ka}_{1}}
\end{array}
$$

## Salt of Weak Polyprotic Acids



Thus, pH is calculated only using the first step of hydrolysis

Consider a salt $\mathrm{Na}_{3} \mathrm{PO}_{4}$ of concentration $=\mathrm{c}$

$$
\mathrm{PO}_{4}^{3-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(1) \rightleftharpoons \mathrm{HPO}_{4}^{2-}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

| $c$ | 0 | 0 |
| :---: | :---: | :---: |
| $c(1-h)$ | ch |  |

Salt of Weak Polyprotic Acids

If $h \ll 1$

$$
\mathrm{K}_{\mathrm{h}_{1}}=\frac{\mathrm{ch} . \mathrm{ch}}{\mathrm{c}(1-\mathrm{h})}=\quad \mathrm{ch}^{2}
$$

$\mathrm{h}=\sqrt{\frac{\mathrm{K}_{\mathrm{h}_{1}}}{\mathrm{c}}}=\sqrt{\frac{\mathrm{K}_{\mathrm{w}_{3}}}{\mathrm{~K}_{\mathrm{a}} \mathrm{c}}}$

## Salt of Weak Polyprotic Acids

$$
\begin{aligned}
& {\left[\mathrm{OH}^{-}\right]=c \times \sqrt{\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{~K}_{\mathrm{a}_{3}} \mathrm{c}}}} \\
& {\left[\mathrm{OH}^{-}\right]=\sqrt{\frac{\mathrm{K}_{\mathrm{w}} \mathrm{c}}{\mathrm{~K}_{\mathrm{a}_{3}}}}}
\end{aligned}
$$



## Salt of Weak Polyprotic Acids

Taking logarithm on both sides and multiplying by (-1)

$$
-\log \left[\mathrm{H}^{+}\right]=-\frac{1}{2} \log \mathrm{~K}_{\mathrm{w}}-\frac{1}{2} \log \mathrm{~K}_{\mathrm{a}_{3}}+\frac{1}{2} \log \mathrm{c}
$$

$$
\mathrm{pH}=\frac{1}{2}\left[\mathrm{pK}_{\mathrm{w}}+\mathrm{pK}_{\mathrm{a}_{3}}+\log \mathrm{c}\right]
$$

$$
\text { If } h>0.1
$$

Then its exact value should be Then
$\left[\mathrm{OH}^{-}\right]=\quad \mathrm{ch}$ obtained by solving quadratic equation.

## Amphiprotic Ions

To calculate the pH when $\mathrm{Na}_{3} \mathrm{PO}_{4}$ is hydrolyzed, we can say that only $\mathrm{PO}_{4}^{3-}$ is hydrolyzed.

But in $\mathrm{Na}_{2} \mathrm{HPO}_{4}$ and
$\mathrm{NaH}_{2} \mathrm{PO}_{4}$, the ions 2hydrolyzed are $\mathrm{HPO}_{4}$ and $\mathrm{H}_{2} \mathrm{PO}_{4}$.
Both are amphiprotic ions.

## Amphiprotic Ions



## Amphiprotic Ions

Assuming


Amphiprotic lons


## Buffer Solution



## Types of Buffer Solutions



## Acidic Buffer Solutions

> Solution of a weak acid and its salt with a strong base

## $\mathrm{CH}_{3} \mathrm{COOH}+$ $\mathrm{CH}_{3} \mathrm{COONa}$

## $\mathrm{H}_{3} \mathrm{PO}_{4}+\mathrm{NaH}_{2} \mathrm{PO}_{4}$

## pH Calculation

## Buffer solution consisting of a

weak acid $\left(\left[\mathrm{CH}_{3} \mathrm{COOH}\right]=\mathrm{c}_{1}\right)$ \& its salt $\left(\left[\mathrm{CH}_{3} \mathrm{COONa}\right]=\mathrm{c}_{2}\right)$

$$
\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq})
$$

Initial
Concentration ( $\mathrm{t}=0$ )
$C_{1}$
$\mathrm{C}_{2}$
0

Equilibrium Concentration ( $\mathrm{t}=\mathrm{t}_{\mathrm{eq}}$ )

## pH Calculation

$$
\begin{equation*}
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}=\frac{\left(\mathrm{c}_{2}+\mathrm{c}_{1} \alpha\right) \mathrm{c}_{1} \alpha}{\mathrm{c}_{1}(1-\alpha)} \tag{i}
\end{equation*}
$$

Assuming

$$
\begin{equation*}
\alpha=\frac{\mathrm{K}_{\mathrm{a}}}{\mathrm{c}_{2}} \tag{ii}
\end{equation*}
$$

## pH Calculation



Taking logarithm on both the sides and multiplying by (-1),


## pH Calculation



Mixing a weak acid solution and a solution of its salt with a strong base

For e.g.: Mixture of $1 \mathrm{~mol} \mathrm{CH}_{3} \mathrm{COOH}$ and 1 mol $\mathrm{CH}_{3} \mathrm{COONa}$

## Dissociation of a Weak Electrolyte in Water

## $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}^{+}$ (aq)

## Adding $\mathrm{CH}_{3} \mathrm{COONa}$ to $\mathrm{CH}_{3} \mathrm{COOH}$ solution

$\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{COONa}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}($ ()

## Preparation of Acidic Buffer

Mixing a weak acid solution and lesser amount of a strong base solution than that required for neutralization

## For e.g. Mixture of $1 \mathrm{~mol} \mathrm{CH}_{3} \mathrm{COOH}$ and 0.5 mol NaOH

Mixing a salt solution of a weak acid and a strong base with lesser amount of a strong acid solution than that required for complete reaction

For e.g.: Mixture of $1 \mathrm{~mol} \mathrm{CH}_{3} \mathrm{COONa}$ and 0.5 mol HCl

## Basic Buffer Solutions

Solution of a weak base and its salt with a strong acid

## pOH Calculation

## Buffer solution consisting of a

 weak base $\left(\left[\mathrm{NH}_{4} \mathrm{OH}\right]=\mathrm{c}_{1}\right)$ \& its salt $\left(\left[\mathrm{NH}_{4} \mathrm{Cl}\right]=\mathrm{c}_{2}\right)$$$
\mathrm{NH}_{4} \mathrm{OH}(\mathrm{aq}) \rightleftharpoons \mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

Initial
Concentration ( $\mathrm{t}=0$ )
$C_{1}$
$C_{2}$
0

Equilibrium Concentration ( $\mathrm{t}=\mathrm{t}_{\mathrm{eq}}$ )
pOH Calculation

$$
\left.\mathrm{K}_{\mathrm{b}}=\frac{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{NH}_{4} \mathrm{OH}\right]}\right)=\left(\frac{\left(c_{2}+\mathrm{c}_{1} \alpha\right) \mathrm{c}_{1} \alpha}{\mathrm{c}_{1}(1-\alpha)} \ldots \ldots\right. \text { (i) }
$$

Assuming
$\alpha \quad \ll$ 1
$\alpha=\frac{\mathrm{K}_{\mathrm{b}}}{\mathrm{c}_{2}}$
(ii)

## pOH Calculation



Taking logarithm on both the sides and multiplying by (-1),

$-\log \left[\mathrm{OH}^{-}\right]=$| $-\log$ |
| :---: |
| $\mathrm{K}_{\mathrm{b}}$ |$+$| [Base] |
| :---: |
| [Cation of <br> salt] |

## pOH Calculation



## Preparation of Basic Buffer

Mixing a weak base solution and a solution of its salt with a strong acid

For e.g.: Mixture of $1 \mathrm{~mol} \mathrm{NH}_{4} \mathrm{OH}$ and $1 \mathrm{~mol} \mathrm{NH}_{4} \mathrm{Cl}$

## Dissociation of a Weak Electrolyte in Water

$$
\mathrm{NH}_{4} \mathrm{OH}(\mathrm{aq}) \rightleftharpoons \mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

## Adding $\mathrm{NH}_{4} \mathrm{Cl}$ to $\mathrm{NH}_{4} \mathrm{OH}$ Solution

$$
\mathrm{NH}_{4} \mathrm{OH}(\mathrm{aq})+\mathrm{NH}_{4} \mathrm{Cl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

## Preparation of Basic Buffer

Mixing a weak base solution and lesser amount of a strong acid solution than that required for neutralization

For e.g.: Mixture of 1 mole $\mathrm{NH}_{4} \mathrm{OH}$ and 0.5 mole HCl

Mixing a salt solution of a weak base and a strong acid with lesser amount of a strong base solution than that required for complete reaction

For e.g.: Mixture of 1 mole $\mathrm{NH}_{4} \mathrm{Cl}$ and 0.5 mole NaOH

## Salt Buffer Solutions

> Solution of the salt
> of a weak acid and a weak base

## Buffer Action

Solution of a weak acid (HA) and its highly ionized salt

$$
\text { Addition of acid }>\mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{A}^{-} \rightleftharpoons \mathrm{H}_{2} \mathrm{O}+\mathrm{HA}
$$

Thus, the solution does not contain excess of $\mathrm{H}_{3} \mathrm{O}^{+}$
pH value remains almost the same

## Buffer Action

Solution of a weak acid (HA) and its highly ionized salt

$$
\text { Addition of base }>\mathrm{OH}^{-}+\mathrm{HA} \longrightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{A}^{-}
$$

Thus, the solution does not contain excess of $\mathrm{OH}^{-}$
pH value remains almost the same
pH Range of Buffer


Particular weak acid (or base) that can be employed for making useful buffer solution of pH (or pOH ) lies within the range of $\left(\mathrm{pK}_{\mathrm{a}} \pm 1\right)$ or $\left(\mathrm{pK}_{\mathrm{b}} \pm 1\right)$.

## Buffer Capacity

It is defined as the moles of a strong acid or a strong base required to change the pH of 1 L of a buffer by one unit.

## Buffer Capacity

The ratio of the small amount of acid or base added to the change in pH caused in the buffer.

Let there be a buffer solution of volume 1 L with 'b' mol of anion (coming from salt) and 'a' mol of weak acid. If ' $x$ ' mol of a strong acid (monobasic) is added to it,


## Maximum Buffer Capacity

Buffer shows maximum buffer capacity when the amounts of acid (or base) and the anion (or cation) from the salt are the same.

$$
\text { [Acid] }=\text { [Anion of salt] }
$$

Maximum Buffer Capacity
For an Acidic
Buffer
solution
$\mathrm{pH}=$
$\mathrm{pK}_{\mathrm{a}}$
$+$
[Anion of
$\log$
salt]
[Acid]

If

$$
\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}
$$

## Remember!!



For preparing a buffer solution of the required pH

Acid whose $\mathrm{pK}_{\mathrm{a}}$ value is close to the required pH is taken

## Applications of Buffer

In industrial processes e.g. Electroplating, leather industry

In biological processes, e.g., pH of our blood remains constant at about 7.4. Buffer action in blood is due to $\mathrm{H}_{2} \mathrm{CO}_{3}+\mathrm{HCO}_{3}^{-}$ions

## Acid - Base Titration

Out of an acid \& a base solution, taking a known volume of one of them in a flask \& taking the other in a burette \& finding the volume required for complete neutralization.

Equivalence point is achieved when
stoichiometrically equivalent amount of acid \& base have combined

## Acid - Base Titration

pH calculation at equivalence point can be done according to the nature of the species formed at the equivalence point


If the salt of a strong acid \&
a weak base is formed

## Acid - Base Titration



## Indicators

Indicators are either weak organic acids or weak organic bases having characteristically different
 colours in their ionised \& unionised forms.

$$
\mathrm{HIn}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{In}^{-}(\mathrm{aq})
$$

## Indicators

$$
\mathrm{HIn}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{In}^{-}(\mathrm{aq})
$$

$$
\left[\mathrm{H}^{+}\right]=\frac{\mathrm{K}_{\mathrm{In}}[\mathrm{HIn}]}{[\mathrm{In}]}
$$



## Indicators



## Example:

Phenolphthalein (HPh) is a weak acid;

$$
\mathrm{HPh}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \stackrel{\rightharpoonup}{(\mathrm{aq})}
$$

Colourless


## Example

Methyl orange (MOH) is a weak base;


## Did You Know?

Human eye can't identify color change of indicators accurately!!

Solution acquires a distinct colour characteristic of In$^{-}$ if
[In] $\quad \geq \quad 10$ [HIn]

## Indicators

$$
\mathrm{pH} \quad=\quad \mathrm{pK}_{\mathrm{In}} \quad+\quad \log \frac{\left[\mathrm{In}^{-}\right]}{[\mathrm{HIn}]}
$$

If


Indicators


If
[HIn]

$$
\geq
$$

10 [ $\mathrm{In}^{-}$]
pH
$\leq$
$\mathrm{pK}_{\text {In }}-1$

Indicators
$\mathrm{HIn}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\operatorname{In}^{-}(\mathrm{aq})$

Colour A
$\mathrm{pH} \leq \mathrm{pK}_{\mathrm{In}}-1$

Colour B

$$
\mathrm{pH} \geq \mathrm{pK}_{\mathrm{In}}+
$$

1
pH range of Indicator
$\mathrm{pK}_{\text {In }}-1$
$\leq$
pH
$\leq$
$\mathrm{pK}_{\mathrm{In}}+1$

## pH Range of Indicator

pH range between which the indicator changes its colour.



Methyl Orange


Phenolphthalein


Phenol Red


Bromothymol Blue

## pH Range of Indicator

| Indicator | pH Range <br> of Indicator | Colour changed |
| :---: | :---: | :---: |
| Phenolphthalein | $(8.3-10)$ | Colourless to pink |
| Methyl Orange | $(3.1-4.4)$ | Red to yellow |
| Phenol Red | $(6.4-8.2)$ | Yellow to red |
| Bromothymol blue | $(6-7.6)$ | Yellow to blue |

## Titration of Strong Acid vs Strong Base

$$
\text { Consider } 40 \mathrm{~mL}, 0.1 \mathrm{M} \mathrm{HCl} \text { vs } 0.1 \mathrm{M} \mathrm{NaOH}
$$

Titration of Strong Acid vs Strong Base

Eg. HCl vs NaOH

| Volume of NaOH added | pH of solution |
| :---: | :---: |
| 0 mL | 1 |
| 10 mL | 1.22 |
| 20 mL | 1.48 |
| 30 mL | 1.84 |
| 39 mL | 2.90 |

## Titration of Strong Acid vs Strong Base

| Volume of NaOH added | pH of solution |
| :---: | :---: |
| 39.9 mL | 3.9 |
| 40 mL | 7 |
| 40.1 mL | 10.1 |
| 41 mL | 11.1 |
| 50 mL | 12.05 |

## Titration of Strong Acid vs Strong Base

Strong Acid \& Strong Base


## Selection of Indicator

Selected indicator should be such that

It offers a colour change near the vicinity of the pH of the solution at the equivalence point.

The steep section of the titration curve at the equivalence point must encompass an interval of pH values at least as large as the pH transition range of an indicator.
pH transition range of the indicator must coincide with the steep portion of the titration curve.

## In a Nutshell...

An indicator can be considered suitable for detecting the end-point of a particular titration if

Some part of pH range of the indicator lies within the pH range of the titration

## Titration of Strong Acid vs Strong Base

pH range of titration: 4 - 10

Almost all common indicators (E.g.: Phenolphthalein, Methyl orange, Phenol red) can be used for endpoint detection.

Bromothymol blue indicator has its pH range containing the equivalence point pH .

So it will serve as the best indicator for the given titration.

## Titration of Weak Acid vs Strong Base

$20 \mathrm{~mL}, 0.5 \mathrm{M} \mathrm{CH}_{3} \mathrm{COOH}\left(\mathrm{pK}_{\mathrm{a}}=4.7\right)$ vs 0.5 M NaOH


## Titration of Weak Acid vs Strong Base

| Volume of NaOH added | pH of solution |
| :---: | :---: |
| 19 mL | 6 |
| 20 mL | 9.05 |
| 21 mL | 12.09 |
| 30 mL | 13 |
| Equivalence point: Complete |  |
| Neutralization |  |
| Salt of WA \& SB (CH $\left.{ }_{3} \mathrm{COONa}=0.25 \mathrm{M}\right)$ |  |

## Titration of Weak Acid vs Strong Base

Weak Acid \& Strong Base

pH range of titration: 7 - 10
Common indicators that can be used are Phenolphthalein \& Phenol red.

## Titration of Strong Acid vs Weak Base

$100 \mathrm{~mL}, 0.05 \mathrm{M} \mathrm{NH}_{4} \mathrm{OH}\left(\mathrm{pK}_{\mathrm{b}}=4.74\right)$ vs 0.1 M HCL

Eg: HCl vs $\mathrm{NH}_{4} \mathrm{OH}$

| Volume of HCL added | pH |
| :---: | :---: |
| 0 mL | 10.98 |
| 10 mL | 9.86 |
| 20 mL | 9.43 |
| 25 mL | 9.26 |

Half Equivalence Point
(Maximum buffer capacity)

## Titration of Strong Acid vs Weak Base

$100 \mathrm{~mL}, 0.05 \mathrm{M} \mathrm{NH}_{4} \mathrm{OH}\left(\mathrm{pK}_{\mathrm{b}}=4.74\right)$ vs 0.1 M HCL

| Volume of HCL added | pH |
| :---: | :---: |
| 40 mL | 8.65 |
| 50 mL | 5.37 |
| 60 mL | 2.2 |
| 70 mL | 1.93 |
| Equivalence point |  |

## Titration of Strong Acid vs Weak Base

Strong Acid \& Weak Base

pH range of titration: 4-7
Common indicators that can be used are Methyl orange, Methyl red \& Phenol red.

## Titration of Weak Acid vs Weak Base

Titration of Weak Acid vs
Weak Base

## Eg: $\mathrm{CH}_{3} \mathrm{COOH}$ vs $\mathrm{NH}_{4} \mathrm{OH}$

## Titration of Weak Acid vs Weak Base

In this particular case, neither the steep rise of pH near the equivalence point occurs

Nor the rise of pH encompasses an interval equal to the pH transition range of any of the indicators.

No common indicators can perform appropriately in this small pH range.

However, if this titration is carried out, then Phenol Red would be the best indicator.

## Solubility

Maximum amount of solute that can be dissolved in a specified amount of solvent at a specified temperature to form a saturated solution.

## Unit:

mol/L

## Classification of Salts

| Category I | Soluble | Solubility $>0.1 \mathrm{M}$ |
| :---: | :---: | :---: |
| Category II | Slightly soluble | $0.01 \mathrm{M}<$ Solubility $<0.1 \mathrm{M}$ |
| Category III | Sparingly <br> soluble | Solubility $<0.01 \mathrm{M}$ |

Solubility > 0.1 M
0.01 M < Solubility < 0.1 M

Solubility < 0.01 M

Soluble
Slightly soluble
Sparingly soluble

## Solubility



An equilibrium is established between the undissolved salt and its ions in the solution.

Considering $\mathrm{BaSO}_{4}$, a sparingly soluble salt, being added in water:

$$
\mathrm{BaSO}_{4}(\mathrm{~s})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{Ba}^{2+}(\mathrm{aq})+\mathrm{SO}_{4}^{2-}(\mathrm{aq})
$$

Dissolution

Precipitation

## Solubility Product

$$
\mathrm{BaSO}_{4}(\mathrm{~s})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{Ba}^{2+}(\mathrm{aq})+\mathrm{SO}_{4}^{2-}(\mathrm{aq})
$$

$$
\mathrm{K}_{\mathrm{eq}}=\frac{\left[\mathrm{Ba}^{2+}\right]\left[\mathrm{SO}_{4}^{2-}\right]}{\left[\mathrm{BaSO}_{4}\right]----\cdots, \text { Constant }}
$$

## Solubility Product

$$
\mathrm{K}_{\mathrm{eq}}\left[\mathrm{BaSO}_{4}\right] \quad=\left[\mathrm{Ba}^{2+}\right]\left[\mathrm{SO}_{4}^{2-}\right]
$$



Experimental value of

$$
\mathrm{K}_{\text {sp }} \text { is } 1.5 \times 10^{-9}
$$

## Solubility Product

Product of molar concentrations of ions in the saturated solution raised to a power equal to the coefficient of the ion

Depends only on temperature for a particular salt.

## Relation between $\mathrm{K}_{\text {sp }}$ \& Solubility

For a solid salt of the general formula $\mathrm{M}_{\mathrm{x}} \mathrm{X}_{\mathrm{y}}$ with molar solubility S ,

$$
\mathrm{M}_{\mathrm{x}} \mathrm{X}_{\mathrm{y}}(\mathrm{~s}) \rightleftharpoons \mathrm{x} \mathrm{M}^{\mathrm{p}^{+}}(\mathrm{aq})+\mathrm{y} \mathrm{X}^{\mathrm{q}}(\mathrm{aq})
$$

Equilibrium concentration

$$
\text { Where, } x \times p=y \times q
$$

Relation between $\mathrm{K}_{\text {sp }}$ \& Solubility

$$
\mathrm{K}_{\mathrm{sp}}=
$$

$\left[\mathrm{M}^{\mathrm{p}+]^{\mathrm{x}}}\left[\mathrm{X}^{\mathrm{C}}\right]^{\mathrm{y}}\right.$

$$
=
$$

$$
s^{(x+y)} \int=\int \frac{\mathrm{K}_{\text {sp }}}{x^{x} y^{y}}
$$

$$
s \quad=\left(\frac{k_{\text {sp }}}{x^{x} \cdot y^{y}}\right)^{\frac{1}{x+y}}
$$

## Ionic Product

For a solution of a salt at a specific concentration, the product of the concentrations of the ions, each raised to the power equal to the coefficient of the ions

## Solubility Product vs lonic Product

Solubility product $\left(\mathrm{K}_{\text {sp }}\right)$
Ionic product ( $\mathrm{K}_{\mathrm{ip}}$ )

Applicable to only saturated solutions

Measures the maximum amount of ions that the solution can dissolve

Applicable to saturated as well as unsaturated solutions

Measures the actual amount of ions in the solution

## Solubility Product vs Ionic Product

$$
\mathrm{M}_{\mathrm{x}} \mathrm{X}_{\mathrm{y}}(\mathrm{~s}) \rightleftharpoons \mathrm{x} \mathrm{M}^{\mathrm{p}+}(\mathrm{aq})+\mathrm{y} \mathrm{X}^{\mathrm{q}}(\mathrm{aq})
$$



Solution is unsaturated

More salt can dissolve

No precipitate formation

## Solubility Product vs Ionic Product

$$
M_{x} X_{y}(s) \rightleftharpoons x M^{p+}(a q)+y X^{q-}(a q)
$$



Solution will become saturated

No precipitate formation

## Solubility Product vs Ionic Product

$$
M_{x} X_{y}(s) \rightleftharpoons x M^{p+}(a q)+y X^{q-}(a q)
$$



Solution is holding more salt that it can dissolve

Precipitate formation takes place

Conditions for Precipitation

$$
\mathrm{K}_{\mathrm{ip}}<\mathrm{K}_{\mathrm{sp}}
$$

$\mathrm{K}_{\mathrm{ip}}=\mathrm{K}_{\mathrm{sp}}$

$$
\mathrm{K}_{\mathrm{ip}}>\mathrm{K}_{\mathrm{sp}}
$$ solution solution occurs



## Effect of Common Ion on the Solubility of Sparingly Soluble Salts

Presence of a common ion in the solution decreases the solubility of a given sparingly soluble salt.

## Solubility in the Presence of a Common Ion

Sparingly

soluble salt
$A B \quad A B(s) \rightleftharpoons A^{+}(a q) \quad+B^{-}(a q)$
$s+c_{1} \quad s$

Soluble salt
$A X(s) \longrightarrow A^{+}(a q) \quad+X^{-}(a q)$


Solubility in the Presence of a Common Ion

$$
\mathrm{K}_{\mathrm{sp}}
$$

$$
\mathrm{K}_{\mathrm{sp}}
$$

$$
=
$$

$\left(s+c_{1}\right)(s)$

If $s \ll c_{1}$
$\mathrm{s}+\mathrm{c}_{1}$

$$
\approx
$$

$\mathrm{C}_{1}$
s
$\frac{\mathrm{K}_{\mathrm{sp}}}{\mathrm{c}_{1}}$

## Effect of pH on Solubility



At low pH, [Anion] $\downarrow$
Due to its protonation

Solubility of salt

## Simultaneous Solubility



Simultaneous solubility of each salt will be less than its individual solubility because of

Common ion effect exerted by ion coming from other salt

## Simultaneous Solubility

$$
\mathrm{AgCl}(\mathrm{~s})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{Ag}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq}) \quad \mathrm{K}_{\mathrm{sp}_{1}}
$$


$\mathrm{AgBr}(\mathrm{s})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{Ag}^{+}(\mathrm{aq})+\mathrm{Br}^{-}(\mathrm{aq}) \quad \mathrm{K}_{\mathrm{sp}_{2}}$

$$
s_{1}+s_{2} \quad s_{2}
$$

Simultaneous Solubility

Therefore,

$$
\mathrm{K}_{\mathrm{sp}_{1}}=\quad=\quad\left(\mathrm{s}_{1}+\mathrm{s}_{2}\right)\left(\mathrm{s}_{1}\right)
$$

------- (i)

$$
\begin{equation*}
\mathrm{K}_{\mathrm{sp}_{2}}=\quad=\quad\left(\mathrm{s}_{1}+\mathrm{s}_{2}\right)\left(\mathrm{s}_{2}\right) \tag{ii}
\end{equation*}
$$

Adding equation (i) \& (ii)

$$
\mathrm{K}_{\mathrm{sp}_{1}}+\mathrm{K}_{\mathrm{sp}_{2}}=\quad=\quad\left(\mathrm{s}_{1}+\mathrm{s}_{2}\right)^{2}
$$

Simultaneous Solubility
Therefore, $\mathrm{s}_{1}+\mathrm{s}_{2}=\sqrt{\mathrm{K}_{\mathrm{sp}_{1}}+\mathrm{K}_{\mathrm{sp}_{2}}}$

$\square$ $=\sqrt{\frac{\mathrm{K}_{\mathrm{sp}_{2}}}{\sqrt{\mathrm{~K}_{\mathrm{sp}_{1}}+\mathrm{K}_{\mathrm{sp}_{2}}}}}$

## Solubility Exchange

One precipitate is mixed with a solution of an ion to get another precipitate and another ion in solution.

$$
\mathrm{AgCl}(\mathrm{~s})+\mathrm{NaBr}(\mathrm{aq}) \rightleftharpoons \mathrm{AgBr}(\mathrm{~s})+\mathrm{NaCl}(\mathrm{aq})
$$

$$
\mathrm{K}_{\mathrm{sp}}(\mathrm{AgCl}) \quad=\quad\left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right]
$$

$$
\mathrm{K}_{\mathrm{sp}}(\mathrm{AgBr}) \quad=\quad\left[\mathrm{Ag}^{+}\right]\left[\mathrm{Br}^{-}\right]
$$

## Selective Precipitation

If a single solution has two or more ions both having the tendency to precipitate with an ion of a reagent

The ion which requires less concentration of ions of the reagent for precipitation will precipitate out first.

Solubility of Salts Involving Anion from Weak Acid

Consider a sparingly soluble salt 'MA' where A'is the anion of weak acid 'HA'

$$
\mathrm{MA}(\mathrm{~s}) \rightleftharpoons \underset{\mathrm{s}}{\mathrm{M}^{+}}(\mathrm{aq})+\mathrm{A}^{-}(\mathrm{aq})
$$

$$
\mathrm{K}_{\mathrm{sp}}=\mathrm{s}\left[\mathrm{~A}^{-}\right]
$$

$$
\mathrm{A}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{HA}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

$$
\mathrm{K}_{\mathrm{h}}=\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{~K}_{\mathrm{a}}}
$$

## Solubility of Salts Involving Anion from Weak Acid

$$
K_{h}=\frac{K_{w}}{K_{a}}=\frac{[H A]\left[\mathrm{OH}^{-}\right]}{\left[A^{-}\right]}
$$



## Solubility of Salts Involving Anion from Weak Acid

Putting equation (ii) in equation (i)



Solubility of Salts Involving Anion from Weak Acid in a Buffer Solution


## Solubility of Salts Involving Anion from Weak Acid

Let $\mathrm{AgCN}(\mathrm{s})$ be added to a buffer solution having $\mathrm{H}^{+}\left(\left[\mathrm{H}^{+}\right]=\mathrm{c}\right)$

$$
\mathrm{AgCN}(\mathrm{~s}) \rightleftharpoons \mathrm{Ag}^{+}(\mathrm{aq})+\mathrm{CN}^{-}(\mathrm{aq}) \quad \mathrm{K}_{\mathrm{eq}}=\mathrm{K}_{\mathrm{sp}}
$$

$$
s \quad s-x
$$

$$
\mathrm{CN}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq}) \rightleftharpoons \mathrm{HCN}(\mathrm{aq})
$$

$$
K_{e q}=\frac{1}{\left(K_{a}\right)_{H C N}}
$$

## Solubility of Salts Involving Anion from Weak Acid

Adding both equations, we get

$$
\mathrm{AgCN}(\mathrm{~s})+\mathrm{H}^{+}(\mathrm{aq}) \rightleftharpoons \mathrm{Ag}^{+}(\mathrm{aq})+\mathrm{HCN}(\mathrm{aq})
$$

$$
\frac{\mathrm{K}_{\mathrm{sp}}}{\mathrm{~K}_{\mathrm{a}}}
$$



## Solubility of Salts Involving Anion from Weak Acid

HCN is a weak acid. So, $\mathrm{K}_{\mathrm{a}}$ will be very small
$\frac{1}{\left(\mathrm{~K}_{\mathrm{a}}\right)_{\mathrm{HCN}}}$ is very high


## Solubility of Salts Involving Anion from Weak Acid



## Effect of Complex Formation on Solubility

Consider the solubility of AgCl in a solution of $\mathrm{NH}_{3}$ (where $\left[\mathrm{NH}_{3}\right]=$ a)


$$
\begin{array}{ccc}
\mathrm{Ag}^{+}(\mathrm{aq})+2 \mathrm{NH}_{3}(\mathrm{aq}) & \rightleftharpoons\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}\right]^{+}(\mathrm{aq})  \tag{ii}\\
\mathrm{x}-\mathrm{y} & \mathrm{a}-2 \mathrm{y} & \mathrm{y}
\end{array}
$$

## Effect of Complex Formation on Solubility

$$
\mathrm{K}_{\mathrm{sp}}(\mathrm{AgCl})=(\mathrm{x}-\mathrm{y}) \mathrm{x}
$$

$$
K_{f}=\frac{y}{(x-y)(a-2 y)^{2}}
$$

Formation constant of $\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}\right]^{+}$

## Effect of Complex Formation on Solubility

Adding equations (i) \& (ii), we get

$$
\mathrm{AgCl}(\mathrm{~s})+2 \mathrm{NH}_{3}(\mathrm{aq}) \rightleftharpoons\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}\right]^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq})
$$

$$
\mathrm{K}=\mathrm{K}_{\mathrm{sp}} \times \mathrm{K}_{\mathrm{f}}
$$

$$
K_{s p} \times K_{f}=\frac{x y}{(a-2 y)^{2}}
$$

## Effect of Complex Formation on Solubility

If the complex is stable, then $\mathrm{K}_{\mathrm{f}}$ will be high


$$
\mathrm{K}_{\mathrm{sp}} \times \mathrm{K}_{\mathrm{f}} \int=\frac{\mathrm{x}^{2}}{(\mathrm{a}-2 \mathrm{x})^{2}}
$$

Due to the formation of complex, solubility increases.

