## BEHAVIOUR OF GASES

1. Gas law
(i) Boyle's law : $\mathrm{V} \propto \frac{1}{\mathrm{P}}\left(\mathrm{n}, \mathrm{T}=\right.$ const.) $\mathrm{P}_{1} \mathrm{~V}_{1}=\mathrm{P}_{2} \mathrm{~V}_{2}$
(ii) Charle's law $\quad V \propto T\left(n, P=\right.$ const.) $\frac{V_{2}}{V_{1}}=\frac{T_{2}}{T_{1}}$
(iii) Gay lussac's law : $\quad \mathrm{P} \propto \mathrm{T}\left(\mathrm{n}, \mathrm{V}=\right.$ const.) $\frac{\mathrm{P}_{2}}{\mathrm{P}_{1}}=\frac{\mathrm{T}_{2}}{\mathrm{~T}_{1}}$
(iv) Avogadro's law :
$\mathrm{V} \propto$ moles $\propto$ number of molecules ( $\mathrm{P}, \mathrm{T}=$ const.)
Ideal gas equations $\mathrm{PV}=\mathrm{nRT}$
$R=0.082$ lit atm $\mathrm{mol}^{-1} \mathrm{~K}^{-1}$
$\mathrm{R}=8.314 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}$ or $8.314 \mathrm{~N} \times \mathrm{m} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$
$\mathrm{R}=2 \mathrm{cal} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$
$R=8.314 \times 10^{7} \mathrm{erg} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$
2. Graham's Diffusion law :

It is applicable for non reacting gases

$$
\begin{aligned}
& r \propto \frac{1}{\sqrt{d}} \\
& \mathrm{r} \propto \frac{1}{\sqrt{\mathrm{VD}}} \\
& \mathrm{r} \propto \frac{1}{\sqrt{\mathrm{Mw}}} \quad(\mathrm{P}, \mathrm{~T}=\text { const. }) \\
& V D=\frac{d_{\text {gas }}}{d H_{2}}=\frac{M w}{2} \\
& \text { rate of diffusion } r=\frac{\ell_{\text {diffusedgas }}}{t_{\text {timetake }}} \\
& \text { (Where, } \ell=\text { distance travelled by diffused gas) } \\
& r=\frac{V_{\text {diffusedgas }}}{\mathbf{t}_{\text {timetaken }}} \\
& r=\frac{\mathbf{n}_{\text {diffused gas }}}{\mathbf{t}_{\text {timetaken }}}
\end{aligned}
$$

## 3. Dalton's law of Partial Pressure

$P_{\text {mixture }}=\underbrace{P_{1}+P_{2}+P_{3}}_{\text {Partial pressure }}$ (T \& Vconst)
$P_{1}=P_{\text {moist gas }}=P_{\text {dry gas }}+P_{\text {water vapours }}$

## BEHAVIOUR OF GASES

Methods of determination of partial pressure ( $P_{A} \& P_{B}$ are partial pressure)
(i) From ideal gas equation

$$
\mathrm{P}_{\mathrm{A}} \mathrm{~V}=\mathrm{n}_{\mathrm{A}} \mathrm{RT} \text { and } \mathrm{P}_{\mathrm{B}} \mathrm{~V}=\mathrm{n}_{\mathrm{B}} \mathrm{RT}
$$

(ii) In the form of mole fraction.

$$
\begin{array}{l|r}
P_{A}=X_{A} P_{T}=\frac{n_{A}}{n_{t}} P_{T} & X_{A}+X_{B}=1 \\
P_{B}=X_{B} P_{T}=\frac{n_{B}}{n_{t}} P_{T} \\
P_{T}=\text { sum of partial pressure of all gases }
\end{array}
$$

(iii) In the form of volume fraction

$$
P_{A}=\frac{V_{A}}{V} P_{T} \text { and } P_{B}=\frac{V_{B}}{V} P_{T}
$$

(iv) If individual pressure and individual volume are given

$$
P_{A}=\frac{V_{A}}{V} P_{1} \text { and } P_{B}=\frac{V_{B}}{V} P_{2}
$$

$P_{1}, P_{2}=$ pressure of gases before mixing
$P_{A^{\prime}} P_{B}=$ pressure of gases after mixing

## 4. Kinetic gas Equation

$P V=\frac{1}{3} m N V_{r m s}^{2}$

## 5. Average KE (KEav)

$$
\begin{aligned}
& \text { KEav }=\frac{3}{2} \mathrm{nRT} \quad \text { (n moles) } \\
& \text { KEav }=\frac{3}{2} \mathrm{RT} \quad \text { (1 mol or NA molecular) } \\
& \text { KEav }=\frac{3}{2} \mathrm{kT} \quad \text { (1 molecule) } \\
& \mathrm{K}=1.38 \times 10^{-23} \mathrm{JK}^{-1}
\end{aligned}
$$

6. 

$$
\begin{array}{l|l|l}
V_{r m s}=\sqrt{\frac{v_{1}^{2}+v_{2}^{2}+\ldots . . v_{n}^{2}}{N}} & V_{a v s}=\frac{v_{1}+v_{2}+v_{3} \ldots . . v_{n}}{N} & \\
V_{\text {rms }}=\sqrt{\frac{3 R T}{M w}} & V_{\text {avs }}=\sqrt{\frac{8 R T}{\pi M w}} & V_{\text {mps }}=\sqrt{\frac{2 R T}{M w}} \\
V_{\text {rms }}=\sqrt{\frac{3 P V}{M W}} & V_{\text {avs }}=\sqrt{\frac{8 P V}{\pi M w}} & V_{\text {mps }}=\sqrt{\frac{2 P V}{M w}} \\
V_{\text {rms }}=\sqrt{\frac{3 P}{d}} & V_{\text {avs }}=\sqrt{\frac{8 P}{\pi d}} & V_{\text {mps }}=\sqrt{\frac{2 P}{d}}
\end{array}
$$

Vrms
$\sqrt{3} \quad: \quad \sqrt{\frac{8}{\pi}} \quad: \quad \sqrt{2}$
1.732 : 1.596 : 1.414
1.224 : 1.128 : 1
7. Maxwell's distributions of molecular speeds :

8. Variation of compressibility factor ( $Z$ ) :

## Variation of $Z$ with pressure at constant temperature :



## Variation of $\mathbf{Z}$ with pressure at different temperature (for same gas ) :



## Conclusions :

$Z=1$ for ideal gas ; $\quad Z>1$ at all pressures for $\mathrm{He} / \mathrm{H}_{2}$
$Z<1$ at low pressure (for all other gases) ; $Z>1$ at high pressure (for all other gases)
Compressibility factor $(z)=\frac{P\left(V_{m}\right) \text { obs }}{R T}$
If $z=1$. the gas show ideal gas behaviour
If $z>1$, the gas show positive deviation
If $z<1$, the gas show negative deviation

## 9. Vanderwaal's Equation

$\left(P+\frac{a^{2}}{V^{2}}\right)(V-n b)=n R T$
$P_{1}=P_{R}+\frac{a n^{2}}{V^{2}} \quad \Rightarrow P_{1}>P_{R}$
$a \uparrow$ force of attraction $\uparrow$ liquification $\uparrow$
$b \uparrow$ effective size of molecule $\uparrow$
incompressible vol $\uparrow$, compressible vol $\downarrow$
(i) At high pressure, Vanderwaal's equation is $\mathrm{PV} \mathrm{V}_{\mathrm{m}}-\mathrm{Pb}=\mathrm{RT}$
(ii) At low pressure, Vander waal's equation is

$$
\mathrm{PV}_{\mathrm{m}}+\frac{\mathrm{a}}{\mathrm{~V}_{\mathrm{m}}}=\mathrm{RT}
$$

## Virial Equation of state :

$Z$ is expressed in power series expansion of $P$ or $\left(\frac{1}{V_{m}}\right)$
$Z=1+\frac{B}{V_{m}}+\frac{C}{V_{m}^{2}}+\frac{D}{V_{m}^{3}}+$ $\qquad$
Van der waal's equation in virial form :
$\mathrm{Z}=1+\frac{1}{\mathrm{~V}_{\mathrm{m}}}\left(\mathrm{b}-\frac{\mathrm{a}}{\mathrm{RT}}\right)$
If $\left(b-\frac{a}{R T}\right)=0 \Rightarrow$ at $T=\frac{a}{R b} ; Z=1$
so at $T=\frac{a}{R b}$, gas will behave as an ideal gas (or follows Boyles law)
But at constant temperature, ideal gas equation is obeying Boyles law as $T=\frac{a}{R b}$, so the temperature is called Boyles' temperature.
$T_{B}=\frac{a}{R b}$
$Z=1-\frac{a}{V_{m} R T}$


For a single gas, if we have two graphs as above, we must conclude $T_{2}<T_{1}$.
At Boyles' temperature 'a/RT' factor is compensated by 'b' factor, so $Z=1$.

## 10. Critical constant of a gas (Andrews isotherm)

When pressure increases at constant temperature volume of gas decreases

P


$$
T_{4}>T_{c}>T_{3}>T_{2}>T_{1}
$$



Isotherms of $\mathrm{CO}_{2}$ at various temperatures

## 11. Critical point

Critical point : At this point, all the physical properties of liquid phase will be equal to physical properties in vapour such that density of liquid = density of vapour
Inversion temperature : The inversion temperature is the critical temperature below which a known ideal gas (all gases in reality) that is expanding at constant enthalpy will experience a termperature decreases, and above which will experience a temperature increases.
$\mathrm{T}_{\mathrm{c}}$ or critical temp : Temperature above which a gas can not be liquified
Higher is the critical temperature, higher will be ease of liquification.
$\mathbf{P}_{\mathrm{c}}$ or critical pressure : Minimum pressure which must be applied at critical temperature to convert the gas into liquid.
$\mathrm{V}_{\mathrm{c}}$ or critical volume : Volume occupied by one mole of gas at $\mathrm{T}_{\mathrm{c}} \& \mathrm{P}_{\mathrm{c}}$.
$T_{i}=\frac{2 a}{R b}$
$T_{C}=\frac{8 \mathrm{a}}{27 \mathrm{Rb}}$
$V_{c}=3 b$
$P_{C}=\frac{a}{27 b^{2}}$

## THERMODYNAMICS

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## Work

Mechanical work $=$ force $\times$ displacement $=F \times d$
Electrical work $=$ pot. diff. $\times$ quantity of current $=E \times Q$
Gravitational work $=$ gravitational force $\times$ height $=m g \times h$
Mechanical Work $=$ pressure $\times$ change in volume $=-\mathrm{P} \times \Delta \mathrm{V}$
For expansion $\mathrm{W}=-\mathrm{ve}\left(\because \mathrm{V}_{2}>\mathrm{V}_{1}\right)$
For compression $\mathrm{W}=+\mathrm{ve}\left(\because \mathrm{V}_{2}<\mathrm{V}_{1}\right)$
Units of work $1 \mathrm{cal}=4.184 \times 10^{7} \mathrm{erg}=4.184 \mathrm{~J}$

## Enthalpy :

Enthalpy $(\mathrm{H})$ is defined as the total heat contant of the system at constant pressure,
$H=E+P V$
$\Delta H=\Delta E+\Delta(P V)$
or
$\Delta \mathrm{H}=\Delta \mathrm{E}+\left(\mathrm{P}_{2} \mathrm{~V}_{2}-\mathrm{P}_{1} \mathrm{~V}_{1}\right)$
$\Delta \mathrm{H}=\Delta \mathrm{E}+\mathrm{P} \Delta \mathrm{V}+\mathrm{V} \Delta \mathrm{P}$
at constant pressure $\Delta H=\Delta E+P \Delta V$
so
$\Delta \mathrm{H}=\Delta \mathrm{E}+\Delta \mathrm{n}_{\mathrm{g}} \mathrm{RT}$ (For chemical reaction at constant temperature)

## First Law of Thermodynamics

Mathematically
$q=\Delta E-w$
or $\Delta \mathrm{E}=\mathrm{q}+\mathrm{w}$
$q=$ heat absorbed or evolved (+ve if absorbed and -ve if evolved)

## For Isothermal Process

$\mathrm{dT}=0 \because \Delta \mathrm{E}=0 \mathrm{q}=-\mathrm{W}$ (This is true for ideal gas only)
i.e., heat absorbed is used in work done by the system.

## For Adiabatic Process

$\because q=0 \quad \therefore \Delta E=W$
i.e., Internal energy is used up in work done by the system. If work is done on the system. Its internal energy will increase and if work is done by the system its internal energy decreases. In adiabatic process work behave as state function.

## THERMODYNAMICS

## For isobaric Process

$\because d P=0 \quad q_{p}=\Delta H$

## Work done

(1) For irreversible process $W=-\operatorname{Pext} \times \Delta V$
(2) For reversible process - $W=-\int_{v_{1}}^{v_{2}} P d V$
(3) For reversible isothermal process -

$$
W=-2.303 n R T \log _{10} \frac{V_{2}}{V_{1}}=-2.303 n R T \log _{10} \frac{P_{1}}{P_{2}}
$$

(4) In adiabatic process $W=\Delta E$

For an ideal gas $W=n C_{v}\left(T_{2}-T_{1}\right)$
or $\quad W=\frac{n R}{(\gamma-1)}\left(T_{2}-T_{1}\right)$
(5) When an ideal gas is freely expand in vacuum then the obtained work done is zero because $P_{\text {ext. }}=0$
(6) Reversible expansion process are more efficient than the irrvesible expansion process.

## Entropy

Entropy of a system is a measure of the degree of randomness or disorderness of the system and is denoted by S .
(1) $\Delta S$ for reversible isothermal process -
$\Delta S=\frac{q_{\text {rev. }}}{T}=\frac{-W_{\text {rev. }}}{T}=\frac{2.303 n R T \log \frac{V_{2}}{V_{1}}}{T}$
$\Delta S=2.303 \mathrm{nRlog} \frac{\mathrm{V}_{2}}{\mathrm{~V}_{1}}=2.303 \mathrm{nRlog} \frac{\mathrm{P}_{1}}{\mathrm{P}_{2}}$
( $\mathrm{q}_{\text {rev }}=$ heat supplied to a system at temp. TK in a reversible manner)
(2) $\Delta S=S_{\text {products }}-S_{\text {reactants }}$
(3) $\Delta \mathrm{S}_{\text {total }}=\Delta \mathrm{S}_{\text {system }}+\Delta \mathrm{S}_{\text {surroundings }}$
$\Delta S_{\text {total }}=\frac{+q}{T_{\text {system }}}+\frac{-q}{T_{\text {surroudings }}}$
If $\mathrm{T}_{\text {system }}<\mathrm{T}_{\text {surroundings }}$ heat flows from hot region to cold one $\Delta \mathrm{S}_{\text {total }}$ is +ve and heat flow is spontaneous.
If $\Delta \mathrm{S}_{\text {total }}$ is -ve the process is non spontaneous.
(4) $\Delta S$ for reversible adiabatic process $\Delta S=\frac{\mathrm{q}_{\text {rev. }}}{\mathrm{T}}=0$

## THERMODYNAMICS

(5) $\Delta S$ for reversible isobaric process $=2.303 n C_{p} \log \frac{T_{2}}{T_{1}}$
(6) $\Delta S$ for reversible isochoric process $=2.303 n C_{V} \log \frac{T_{2}}{T_{1}}$
(7) $\Delta \mathrm{S}$ for phase transition $\mathrm{q}_{\mathrm{rev}}=\Delta \mathrm{H}_{\mathrm{rev}} \Rightarrow \Delta \mathrm{S}=\frac{\Delta \mathrm{H}_{\mathrm{rev}}}{\mathrm{T}}$

- Entropy change of fusion, $\Delta \mathrm{S}_{\mathrm{f}}=\frac{\Delta \mathrm{H}_{f}}{\mathrm{~T}}$
( $\mathrm{T}=$ freezing point or melting point)
- Entropy change of vapourization, $\Delta S_{v}=\frac{\Delta H_{v}}{T}(T=$ boiling point $)$
(8) Standard entropy $\left(S^{\circ}\right)=$ entropy of one mole of substance at 1 atm and $25^{\circ} \mathrm{C}$


## Free Energy

Free energy $(G)$ is a measure of maximum useful work done.
G = H - TS,
At constant T \& P

$$
\Delta \mathrm{G}=\Delta \mathrm{H}-\mathrm{T} \Delta \mathrm{~S} \text { (Gibbs - Helmholtz equation) }
$$

$$
\Delta \mathrm{G}=\mathrm{G}_{\text {products }}-\mathrm{G}_{\text {reactants }}
$$

(i) $\Delta \mathrm{G}^{\circ}=\Delta \mathrm{G}^{\circ}{ }_{\text {f products }}-\Delta \mathrm{G}_{\text {freactants }}^{\circ}$
(ii) $\Delta G^{\circ}$ for the element $=0$
(iii) $\Delta G^{\circ}=-2.303 R T \log K(K=$ equilibrium constant $)$

If $\Delta G^{\circ}$ is -ve, $K>1$

$$
\begin{aligned}
& \Delta G^{\circ}=0, K=0 \\
& \Delta G^{\circ} \text { is }+\mathrm{ve}, \mathrm{~K}<1
\end{aligned}
$$

Condition for spontaneity of a chemical reaction is $\Delta G=-v e$

| $\Delta \mathrm{H}$ | $\Delta \mathrm{S}$ | $\Delta \mathrm{H}-\mathrm{T} \Delta \mathrm{S}$ | Behaviour |
| :---: | :---: | :---: | :---: |
| -ve | +ve | $\therefore \Delta \mathrm{G}=-\mathrm{ve}$ | Spontaneous atall temperatures |
| +ve | -ve | $\therefore \Delta \mathrm{G}=+\mathrm{ve}$ | Non-spontaneousat alltemperatures |
| +ve | +ve | $\begin{aligned} & \Delta G=- \text { ve(if } \Delta H<T \Delta S) \\ & \Delta G=+ \text { ve(if } \Delta H>T \Delta S) \end{aligned}$ | Spontaneous <br> Non-spontaneous |
| -ve | -ve | $\begin{aligned} & \Delta G=-\mathrm{ve}(\text { if } \Delta H>T \Delta S) \\ & \Delta G=+\mathrm{ve} \text { (if } \Delta H<T \Delta S) \end{aligned}$ | Spontaneous <br> Non-spontaneous |

## CHEMICAL EQUILIBRIUM

1. Equilibrium is a Dynamic Process :

Equilibrium is established in a system when reactants combine to form products at the same rate at which products combine to form reactants.

$$
\left(\frac{d x}{d t}\right)_{f}=\left(\frac{d x}{d t}\right)_{b} \operatorname{orR}_{f}=R_{b}
$$

Chemical equilibrium can be approached from either side. A catalyst can fasten the approach of equilibrium but does not alter the state of equilibrium. System can xbe homogeneous or heterogeneous.
For a reaction in equilibrium

$$
\begin{aligned}
& a A+b B \rightleftharpoons c C+d D \\
& K_{c}=\frac{[C]^{c}[D]^{d}}{[A]^{d}[B]^{b}} \quad \text { in terms of active mass } \\
& K_{P}=\frac{\left[P_{C}\right]^{c}\left[P_{D}\right]^{d}}{\left[P_{A}\right]^{d}\left[P_{B}\right]^{b}} \text { in terms of partial pressure } \\
& K_{x}=\frac{\left[X_{C}\right]^{c}\left[X_{D}\right]^{d}}{\left[X_{A}\right]^{d}\left[X_{B}\right]^{b}} \quad \text { in terms of mole fraction }
\end{aligned}
$$

Partial pressure of solid is taken as unity and in calculation of partial pressure of solids their number of moles are not considered.
$K_{p}=K_{c}(R T)^{\Delta n g}$
(i) When $\Delta \mathrm{n}_{\mathrm{g}}=0$ then $\mathrm{K}_{\mathrm{p}}=\mathrm{K}_{\mathrm{c}}$
(ii) When $\Delta \mathrm{n}_{\mathrm{g}}>0$ then $\mathrm{K}_{\mathrm{p}}>\mathrm{K}_{\mathrm{c}}$
(iii) When $\Delta \mathrm{n}_{\mathrm{g}}<0$ then $\mathrm{K}_{\mathrm{p}}<\mathrm{K}_{\mathrm{c}}$
$\Delta \mathrm{n}_{\mathrm{g}}=(\mathrm{c}+\mathrm{d})-(\mathrm{a}+\mathrm{b})$
Note : While determining $\Delta \mathrm{n}_{\mathrm{g}}$, take only gaseous species.
Properties of equilibrium constant :
For $\quad A+B \rightleftharpoons C+D ; K_{c}=K$
then (i) $C+D \rightleftharpoons A+B ; K_{C}=\frac{1}{K}$
(ii) $\quad 2 \mathrm{~A}+2 \mathrm{~B} \rightleftharpoons 2 \mathrm{C}+2 \mathrm{D} ; \mathrm{K}_{\mathrm{c}}=\mathrm{K}^{2}$
(iii) $\frac{A}{2}+\frac{B}{2} \rightleftharpoons \frac{C}{2}+\frac{D}{2} ; K_{C}=\sqrt{K}$
(iv) $\quad \mathrm{A} \rightleftharpoons \mathrm{B} ; \mathrm{K}_{\mathrm{C}}=\mathrm{K}_{1}$
$\mathrm{B} \rightleftharpoons \mathrm{C} ; \mathrm{K}_{\mathrm{c}}=\mathrm{K}_{2}$
$\mathrm{C} \rightleftharpoons \mathrm{D} ; \mathrm{K}_{\mathrm{C}}=\mathrm{K}_{3}$
then $\qquad$ $\mathrm{K}_{\mathrm{c}}=\mathrm{K}_{1} \cdot \mathrm{~K}_{2} \cdot \mathrm{~K}_{3}$
(v)

$\mathrm{K}_{\mathrm{c}}=\mathrm{K}_{1}$
$\mathrm{K}_{\mathrm{c}}=\mathrm{K}_{2}$
then
$K_{c}=\frac{K_{1}}{K_{2}}$

Reaction quotient Q for the reversible reaction

$$
\begin{aligned}
& \mathrm{A}+\mathrm{B} \rightleftharpoons \mathrm{C}+\mathrm{D} \\
& \mathrm{Q}=\frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}
\end{aligned}
$$

$Q$ is taken at any condition of system.
$\Rightarrow$ If $Q=K_{\text {eq. }}$ then system is in equilibrium
$\Rightarrow$ If $Q>K_{\text {eq. }}$. system proceeds in backward side to attain equilibrium
$\Rightarrow$ If $\mathrm{Q}<\mathrm{K}_{\text {eq. }}$ system proceeds in forward side to attain equilibrium
For the equilibrium $A \rightleftharpoons n B$
Degree of dissociation $\alpha=\frac{D-d}{D(n-1)}$
where n is the number of moles of products from one mole of reactant, D is the theoretical vapour density (if no dissociation takes place) and dis the observed vapour density (due to dissociation or association) vapour density $\times 2=$ molecular weight.
Vapour density $\times 2=$ molecular weight.
Degree of dissocaition ( $\alpha$ ) $=\frac{\text { Number of dissociated moles ( } \mathrm{x} \text { ) }}{\text { Initial number of moles (a) }}$
Equilibrium constant (K) depends upon temperature and way of writting the reaction.
Le-Chatelier's principle : If the system at equilibrium is subjected to change of any one of the factors such as concentration, temperature or pressure, the system adjusts itself in such a way as to nullify the effect of that change.
The following conclusion have been derived from this principle.
(i) Increases in concentration of any substance favours the reaction in which it is used up.
(ii) High pressure is favourable for the reaction in which there is decreases in volume or number of moles.
(iii) A rise in temperature favours the endothermic reaction.
(iv) At constant volume : There is no effect of adding inert gas on the state of equilibrium at constant volume.
(v) At constant pressure : On adding of inert gas at constant pressure, the reaction proceeds in that direction where the sum of stoichiometric coefficient of gaseous components is greater.

## CHEMICAL EQUILIBRIUM

## Application of Le-Chatelier's principle :

(i) Ice water system (melting of ice) :

Ice + Heat $\rightleftharpoons$ Water
It is an endothermic process and there is decrease in volume. Thus, the favourable conditions for melting of ice are ; (a) High temperature and (b) High pressure.
(ii) Solubility of gases in liquids :

When a gas dissolves in a liquid, there is decreases in volume. Thus, increase in pressure will favour the dissolution of gas in liquid.

IONIC EQUILIBRIUM

## IONIC EQUILIBRIUM

## Acid and Base

- Arrhenius Concept : Acid ionises in water to give $\mathrm{H}_{3} \mathrm{O}^{+}$ion while base ionises to give $\mathrm{OH}^{-}$ ion. Ex HCl, NaOH
- Bronsted-Lowry's Protonic Concept : Acid is $\mathrm{H}^{+}$ion donor and base is $\mathrm{H}^{+}$ion acceptor. HCl and $\mathrm{Cl}^{-}$is a conjugate acid -9 base pair. If acid is weak, its conjugate base is strong and vice-versa. A substance that can accept $\mathrm{H}^{+}$ion as well as can donate $\mathrm{H}^{+}$ion is called amphiprotic or amphoteric.


A Bronsted Lowery acid - base reaction is always favoured in the direction from the stronger to the weaker acid/base combinations.

## Lewis Concept :

Lewis acid is an electron - pair acceptor.
Lewis base in an electron pair donor.
All lewis bases are bronsted Lowry bases but all the lewis acid are not bronsted acids.
$\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1 \times 10^{-14}$ at 298 K
$\mathrm{K}_{\mathrm{w}}$ is called ionic product of water or autoionisation or autoprotolysis constant.
In a mixture of strong acid or bases.
$\left[\mathrm{H}^{+}\right]=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{\sum \mathrm{NV}}{\sum \mathrm{V}},\left[\mathrm{OH}^{-}\right]=\frac{\sum \mathrm{NV}}{\sum \mathrm{V}}$
In a mixture of acid and base, resultant is
(a) acidic mixture if $N_{1} V_{1}$ (acid) $>N_{2} V_{2}$ (base)

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{\mathrm{N}_{1} \mathrm{~V}_{1}-\mathrm{N}_{2} \mathrm{~V}_{2}}{\mathrm{~V}_{1}+\mathrm{V}_{2}}
$$

(b) basic mixture if $\mathrm{N}_{2} \mathrm{~V}_{2}$ (base) $>\mathrm{N}_{1} \mathrm{~V}_{1}$ (acid)

$$
\left[\mathrm{OH}^{-}\right]=\frac{\mathrm{N}_{2} \mathrm{~V}_{2}-\mathrm{N}_{1} \mathrm{~V}_{1}}{\mathrm{~V}_{1}+\mathrm{V}_{2}}
$$

(c) neutral mixture if $\mathrm{N}_{1} \mathrm{~V}_{1}$ (acid) $=\mathrm{N}_{2} \mathrm{~V}_{2}$ (base)

For conjugation acid-base pairs

$$
\begin{aligned}
& \mathrm{K}_{\mathrm{a}} \mathrm{~K}_{\mathrm{b}}=\mathrm{K}_{\mathrm{w}}=1 \times 10^{-14} \text { at } 25^{\circ} \mathrm{C} \\
& \mathrm{~K}_{\mathrm{a}} \mathrm{~K}_{\mathrm{b}}=\mathrm{K}_{\mathrm{w}}=10^{-12} \text { at } 90^{\circ} \mathrm{C}
\end{aligned}
$$

Where $\mathrm{K}_{\mathrm{a}}$ is the ionisation constant of acid and $\mathrm{K}_{\mathrm{b}}$ is the ionisation constant of its conjugate base.


According to ostwald dilution low $\alpha \propto \sqrt{\text { dilution }}$
At infinite dilution , $\propto=100 \%$
For a weak acid by Ostwald dilution law

$$
\begin{aligned}
& \mathrm{K}_{\mathrm{a}}=\frac{\mathrm{C} \alpha^{2}}{(1-\alpha)}=\mathrm{C} \alpha^{2} \quad\left[\mathrm{H}^{+}\right]=\mathrm{C} \alpha \\
& {\left[\mathrm{H}^{+}\right]=\sqrt{\mathrm{K}_{\mathrm{a}} \mathrm{C}, \mathrm{pH}}=\frac{1}{2}\left[\mathrm{pK}_{\mathrm{a}}-\log \mathrm{C}\right]}
\end{aligned}
$$

and for weak base

$$
\begin{aligned}
& \mathrm{K}_{\mathrm{b}}=\frac{\mathrm{C} \alpha^{2}}{(1-\alpha)}=\mathrm{C}^{2} \quad\left[\mathrm{OH}^{-}\right]=\mathrm{C} \alpha \\
& {\left[\mathrm{OH}^{-}\right]=\sqrt{\mathrm{K}_{\mathrm{b}} \mathrm{C}} \quad \mathrm{pOH}=\frac{1}{2}\left[\mathrm{pK}_{\mathrm{b}}-\log \mathrm{C}\right]}
\end{aligned}
$$

Ostwald dilution law is only applicable for weak electrolytes
Buffer solutions are which have resistive nature for pH change
(i) On dilution pH of buffer solution remains unchanged.
(ii) When small amount of SA or SB is mixed in buffer solution then pH of buffer solution remains almost unchanged.

## Types of buffer Solution :

(i) Simple buffer solution (Aq. solution of WAWB salts)
(ii) Mixed buffer solution :
(a) Acidic buffer solution (WA + WASB salts)
(b) Basic buffer solution (WB + WBSA salt)

Henderson - Hasselbalch equation for buffer
Acidic : $\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log \frac{\text { [conjugatebase] or [salt] }}{\text { [weak acid] }}$
$\frac{\text { [conjugateacid]or[salt] }}{\text { [weakbase] }}$
Ionisation of weak electrolyte is decreased in the presence of common ion is called common ion effect. Solubility product of the sparingly soluble salt $\mathrm{A}_{x} \mathrm{~B}_{\mathrm{y}}$ with solution (s) mol/litre in saturated solution.

$$
A_{x} B_{y} \rightleftharpoons x A+y B \quad K_{s p}=x^{x} y^{y}(s)^{x+y}
$$

Salt analysis of inorganic mixture depends on common ion effect and values of solubility products. In the presence of common ion solubility of electrolyte always decreases.
Solute $A B$ is precipitate if $\left[\mathrm{A}^{+}\right]\left[\mathrm{B}^{-}\right]>\mathrm{K}_{\mathrm{sp}}$

## Salt and Salt Hydrolysis :

Salt + Water $\xlongequal[\text { Neutralisation }(\Delta \mathrm{H}=-\mathrm{ve})]{\text { Hydrolysis }(\Delta \mathrm{H}+\mathrm{ve})}$ Acid + base

## Types of Salt :

(i) General (ii) acidic (iii) basic (iv) Mixed (v) Double (vi) Complex.

## Types of General Salts :

(a) SASB
(b) SAWB
(c) WASB
(d) WAWB

| Types of salt | Nameof <br> hydrolysis | Nature of aqueous solution andpH |
| :---: | :---: | :---: |
| SASB | - | Neutral, $\mathrm{pH}=7$ |
| SAWB | Cationic | Acidic, $\mathrm{pH}<7$ |
| WASB | Anionic | Basic, $\mathrm{pH}>7$ |


|  | $\mathrm{K}_{\mathrm{a}}>\mathrm{K}_{\mathrm{b}}$ | $\mathrm{K}_{\mathrm{b}}>\mathrm{K}_{\mathrm{a}}$ | $\mathrm{K}_{\mathrm{a}}=\mathrm{K}_{\mathrm{b}}$ |
| :---: | :---: | :---: | :---: |
| Hydrolysis | Cationic -anionic | Anionic - Cationic | Neutralhydrolysis |
| Nature | Acidic | Basic | Neutral |
| pH | $\mathrm{pH}<7$ | $\mathrm{pH}>7$ | $\mathrm{pH}=7$ |

Summary :

| Typeofsalt | $\begin{aligned} \mathrm{K}_{\mathrm{b}}= & \frac{\mathrm{K}_{\mathrm{w}}}{\text { lonisation }} \\ & \begin{array}{l} \text { constant } \\ \text { of weak acid } \end{array} \end{aligned}$ | $\mathrm{h}=\sqrt{\frac{\mathrm{K}_{\mathrm{b}}}{\mathrm{C}}}$ | $\left[\mathrm{H}^{+}\right]$ | pH |
| :---: | :---: | :---: | :---: | :---: |
| SASB | - | - | - | 7 |
| WASB | $\mathrm{K}_{\mathrm{h}}=\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{K}_{\mathrm{a}}}$ | $h=\sqrt{\frac{K_{w}}{K_{a} \times C}}$ | $\sqrt{\frac{K_{w} \times K_{a}}{C}}$ | $7+\frac{1}{2} \mathrm{pK}_{\mathrm{a}}+\frac{1}{2} \log \mathrm{C}$ |
| SAWB | $\mathrm{K}_{\mathrm{h}}=\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{K}_{\mathrm{b}}}$ | $h=\sqrt{\frac{K_{w}}{K_{b} \times C}}$ | $\sqrt{\frac{K_{w} \times C}{K_{b}}}$ | $7-\frac{1}{2} \mathrm{pK}_{\mathrm{a}}-\frac{1}{2} \log \mathrm{C}$ |
| WAWB | $\mathrm{K}_{\mathrm{h}}=\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{~K}_{\mathrm{a}} \times \mathrm{K}_{\mathrm{b}}}$ | $h=\sqrt{\frac{K_{w}}{K_{a} \times K_{b}}}$ | $\sqrt{\frac{K_{w} \times K_{a}}{K_{b}}}$ | $7+\frac{1}{2} \mathrm{pK}_{\mathrm{a}}-\frac{1}{2} \mathrm{pK}_{\mathrm{b}}$ |

## Group Precipitation

(i) $\mathrm{K}_{\mathrm{sp}}>$ [][] > lonic product $\Rightarrow$ unsaturated
(ii) $\mathrm{K}_{\mathrm{sp}}=[][]=$ lonic product $\Rightarrow$ saturated
(iii) $\quad \mathrm{K}_{\mathrm{sp}}<[][]$ l lonic product $\Rightarrow$ super saturated

$$
\Rightarrow \text { precipitation occurs }
$$

= For precipitation of common salt ( NaCl ),
HCl gas is passed $\&$ for soap ( $\mathrm{C}_{17} \mathrm{H}_{35} \mathrm{COONa}$ ), NaCl is mixed. For amphiprotic anion (as $\mathrm{HCO}_{3}{ }^{-}$)

$$
\mathrm{pH}=\frac{\mathrm{pK}_{1}+\mathrm{pK}_{2}}{2}
$$

For acidic indicator ( HIn ),
$\mathrm{HIn} \rightleftharpoons \mathrm{H}^{+}+\mathrm{In}^{-}$,
For basic indicator ( InOH )
$\mathrm{pH}=\mathrm{pK}_{\mathrm{ln}}+\log \frac{\left[\mathrm{ln}^{-}\right]}{[\mathrm{HIn}]}$,
$\mathrm{InOH} \rightleftharpoons \mathrm{In}^{+}+\mathrm{OH}^{-}$

Colour change of the indicator is explained by:
(i) Ostwald's Theory

| Name of indicator | Colour <br> in acidic <br> medium | Colour <br> in basic <br> medium | Working <br> $\mathbf{p H}$ range <br> of indicators |
| :--- | :---: | :---: | :---: |
| Methyl orange $(\mathrm{MeOH})$ | Orange red | Yellow | 3.1 to 4.5 |
| Methyl red | Red | Yellow | 4.2 to 6.2 |
| Phenol red | Yellow red | Red | 6.2 to 8.2 |
| Phenolphthalein $(\mathrm{HPh})$ | Colourless | Pink | 8.2 to 10.2 |

## Acid-Base Titration

| Type of Titration | pH range of Titration | Suitable indicators |
| :--- | :---: | :---: |
| SA/SB. | $3-11$ | All indicators <br> (MeOH, HPh etc.) |
| SA/WB | $3-7$ | Methy orange <br> (MeOH) and methyl red |
| WA/SB | $7-11$ | Phenolphthalein <br> (Hph) |
| WA/WB | $6.5-7.5$ | Phenol red |

