(ii) At room temperature (≈ 300 K) will K_p be greater than, less than or equal to K_p at 900 K.
(iii) How will the equilibrium be affected if the volume of the vessel containing the three gases is reduced, keeping the temperature constant. What happens?
(iv) What is the effect of adding 1 mole of $He_{(g)}$ to a flask containing SO_2, O_2 and SO_3 at equilibrium at constant volume?

Soln.: (i) The equilibrium constant for this reaction is written in terms of the partial pressure of the reactants and products. So,

$$K_p = \frac{p^2_{SO_3(g)}}{p^2_{SO_2(g)} \times p_{O_2(g)}}$$

(ii) This reaction is exothermic. So, its equilibrium constant should increase with the lowering of temperature

($d \ln K/dT = \Delta_r H^\circ/RT^2$). Therefore, the value of K_p at 300 K will be greater than the value at 900 K.

(iii) When the volume of the vessel is reduced, the volume of the reaction mixture will decrease. As a result, pressure of the gaseous mixture will increase. According to the Le Chatelier's principle, the system will move in a direction to undo the effect of the pressure increase. The system therefore will move in a direction so as to decrease the number of moles of the gaseous substances in the system. The number of moles decrease in going from reactants to the product side. Therefore, a decrease in the volume of the reacting system will shift the equilibrium to the right. That is, more $SO_{3\,(g)}$ will be formed from the reactants.

(iv) Addition of helium to the reaction mixture at equilibrium under constant volume has no effect on the equilibrium.

IONIC EQUILIBRIUM

Acids and Bases

Concept	Acid	Base
• Arrhenius concept (1884)	A substance which gives H^+ ion when dissolved in water. *e.g.*, HCl, H_2SO_4, HNO_3	A substance which gives OH^- ions when dissolved in water. *e.g.*, KOH, NaOH, $Ca(OH)_2$
• Bronsted-Lowry concept (1923)	Proton donors *e.g.*, CH_3COOH, HCl, HNO_3	Proton acceptors *e.g.*, NH_3, Cl^-, CO_3^{2-}
• Lewis concept (1939)	Electron acceptor *e.g.*, H^+, SO_3, SO_2, $AlCl_3$, Ag^+	Electron donor *e.g.*, O_2^-, $\ddot{N}H_3$, $H_2\ddot{\underset{\cdot\cdot}{O}}$

Illustration 4

Classify the following as acid or base and also mention the concept on the basis of which these are so.

(i) $HCl_{(aq)}$ (ii) $Na_2CO_{3(aq)}$ (iii) $CO_{2(g)}$
(iv) H_2O (v) NH_4^+

Soln.: (i) $HCl_{(aq)}$: Acid according to Arrhenius concept and Bronsted–Lowry concept

$$HCl \rightarrow H^+ + Cl^- \qquad \text{(proton donor)}$$

(ii) $Na_2CO_{3(aq)}$: Base according to Bronsted–Lowry concept

$$Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{2-}$$

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \qquad \text{(proton acceptor)}$$

(iii) $CO_{2(g)}$: Acid according to Lewis concept.
In case of CO_2 (O = C = O), double bond exists between carbon and oxygen. Since oxygen is more electronegative than carbon, a slight positive charge is induced on carbon and hence it can accept an electron pair.

(iv) H_2O : Both acid and base *i.e.*, amphoteric according to Arrhenius concept and Bronsted–Lowry concept

$$H_3O^+ \underset{\text{proton acceptor}}{\rightleftharpoons} H_2O \overset{\text{proton donor}}{\rightleftharpoons} H^+ + OH^-$$

(v) NH_4^+ : Acid according to Arrhenius, Bronsted–Lowry and Lewis concept.

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \text{(proton donor and electron deficient)}$$

Electrolytes

- When an ionic compound is dissolved in water or melted, it gets split into its ions. The process is known as **ionization** or **dissociation**. Since the ions have either positive or negative charge, the aqueous solution of such compounds can conduct electricity.
- A compound whose aqueous solution or melt conducts electricity is known as **electrolyte**, whereas **non-electrolyte** is the compound whose neither aqueous solution nor melt conducts electricity.
- **Strong and weak electrolytes :** Electrolytes which dissociate almost completely into ions in aqueous solution are known as strong electrolytes, *e.g.*, NaCl, HCl, NaOH, H_2SO_4, etc. They are very good conductors of electricity. They have degree of dissociation nearly one *i.e.*, $\alpha \approx 1$.
  Whereas those electrolytes which dissociate only partially into ions in aqueous solution are known as weak electrolytes, *e.g.*, CH_3COOH, NH_4OH, etc.
  They have conductivity smaller than that of strong electrolytes. Their value of degree of dissociation is much smaller than one *i.e.*, $\alpha << 1$. An equilibrium is set up in case of partially ionized weak electrolytes between ions and unionized electrolyte.

  e.g. $NH_4OH_{(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$

- **Degree of ionisation (α) :** The fraction of total number of molecules dissociated into ions at a particular temperature is known as degree of ionisation or degree of dissociation. It is denoted by α.

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{Total number of moles}}$$

Degree of ionisation depends on temperature and increases with increase in temperature.

- **Ostwald's dilution law :** It is applicable only to weak electrolytes, not to strong electrolytes. Consider a weak electrolyte AB with initial concentration 'C' (moles L^{-1}) and degree of dissociation 'α'. Then,

$$AB_{(aq)} \rightleftharpoons A^+_{(aq)} + B^-_{(aq)}$$

Initial concentration	C	0	0
At equilibrium	$C(1-\alpha)$	$C\alpha$	$C\alpha$

Applying law of equilibrium to the above equilibrium

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

Where, K is known as dissociation constant.

As α is very small for weak electrolytes ($\alpha << 1$) then $(1-\alpha) \approx 1$, $\therefore$ $C\alpha^2 = K$

$$\alpha = \sqrt{\frac{K}{C}} \quad \text{or} \quad \alpha \propto \frac{1}{\sqrt{C}}$$

Thus, degree of dissociation of weak electrolyte is inversely proportional to the square root of molar concentration of its solution. If V is the volume of solution in litres containing 1 mole of the electrolyte, then

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

$$\therefore \quad \alpha = \sqrt{KV} \quad \text{or} \quad \alpha \propto \sqrt{V}$$

i.e., we can say that degree of dissociation of weak electrolyte is directly proportional to the square root of volume of solution containing one mole of the solute.

Thus it can be said that degree of dissociation of weak electrolytes increases with dilution.

Illustration 5

A solution of organic acid ($K_a = 10^{-8}$) dissociates 0.1 %. What is the concentration of the acid solution?

Soln.: $\alpha = 0.1\% = \frac{0.1}{100} = 10^{-3}$, $K = C\alpha^2$

$$\therefore \quad C = \frac{K}{\alpha^2} = \frac{10^{-8}}{(10^{-3})^2} = 10^{-2} \text{ i.e., } 0.01 \text{ M}$$

- **Ionisation of an acid HA**

HA	+ H_2O	$\rightleftharpoons$	H_3O^+	+ A^-
n	excess		0	0
$n - n\alpha$			$n\alpha$	$n\alpha$

(α = degree of ionisation)

- **Ionisation constant of acid (K_a) :**

$$K_a = \frac{[H_3O^+][A]}{[HA]} = \frac{\frac{n\alpha}{V} \times \frac{n\alpha}{V}}{\frac{n(1-\alpha)}{V}}$$

$$= \frac{(C\alpha)(C\alpha)}{(1-\alpha)C} \qquad (\because \frac{n}{V} = \text{concentration} = C)$$

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

If α is very small then $1 - \alpha \approx 1$

So, $K_a = \alpha^2 C \Rightarrow \alpha = \sqrt{\frac{K_a}{C}}$

$$[H_3O^+] = C\alpha = C\sqrt{\frac{K_a}{C}} = \sqrt{K_a C}$$

- **Ionisation of a base BOH**

	BOH + H_2O	$\rightleftharpoons$	B^+	+ OH^-
Initial	C	excess	0	0
At equilibrium	$C(1-\alpha)$		$C\alpha$	$C\alpha$

- **Ionisation constant of a base (K_b) :**

$$K_b = \frac{[B^+][OH^-]}{[BOH]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)}$$

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

If α is small, $K_b = \alpha^2 C$

$$\alpha = \sqrt{\frac{K_b}{C}} = \sqrt{K_b V}$$

V = volume of solution containing 1 mole.

$$[OH^-] = C\alpha = \sqrt{K_b C}$$

- **Ionisation of polybasic acids and polyacidic bases :** Acids which have more than one ionisable proton per molecule of the acid are known as polybasic or polyprotic acids. For example oxalic acid ($(COOH)_2$), sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4), carbonic acid (H_2CO_3), etc.

Consider any dibasic acid,

$$H_2A_{(aq)} \xrightleftharpoons{K_{a_1}} H^+ + HA^-$$

$$HA^- \xrightleftharpoons{K_{a_2}} H^+ + A^{2-}$$

The ionization constants K_{a_1} and K_{a_2} are given as

$$K_{a_1} = \frac{[H^+][HA^-]}{[H_2A]}, \quad K_{a_2} = \frac{[H^+][A^{2-}]}{[HA^-]}$$

It has been found that $K_{a_1} > K_{a_2}$

For example,

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- ; K_{a_1} = 7.52 \times 10^{-3}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} ; K_{a_2} = 6.23 \times 10^{-8}$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} ; K_{a_3} = 4.80 \times 10^{-13}$$

It is observed that $K_{a_1} > K_{a_2} > K_{a_3}$.

The reason for decrease in the dissociation constant of successive stages is that in the first dissociation, a neutral molecule gives a proton (H^+), while in the second stage of dissociation, the proton is coming from a negatively charged molecule and in the third step of dissociation, a doubly negatively charged molecule is giving a proton which in turn is more difficult than first two dissociations.

Similarly, polyacidic bases also ionise in steps with respective ionisation constants like K_{b_1}, K_{b_2}, etc.

For any polyacidic base, $K_{b_1} > K_{b_2} > K_{b_3}$ and so on.

STRENGTH OF ACIDS AND BASES

- Strength of acid is measured in terms of H^+ produced *i.e.*, greater the number of H^+ produced in aqueous solution, stronger is the acid. Whereas strength of base is measured in terms of OH^- produced *i.e.*, greater the number of OH^- produced in aqueous solution, stronger is the base.

$$\underset{\text{Acid}}{HA} + \text{water} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{or} \quad K_a \propto [H^+]$$

where, K_a is the dissociation constant of acid HA.

Similarly for a base, $K_b \propto [OH^-]$ where K_b is the dissociation constant of a base BOH.

- **Relative strength of acids and bases :** According to Ostwald's dilution law, for weak acids,

$$K_a = C\alpha^2, \ \alpha = \sqrt{\frac{K_a}{C}} \quad \text{or} \quad \alpha \propto \sqrt{K_a}$$

For two weak acids of equimolar concentration,

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

Degree of dissociation is considered as measure of strength of an acid

$$\therefore \quad \frac{\text{Strength of acid 1 } (HA_1)}{\text{Strength of acid 2 } (HA_2)} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

Similarly, for equimolar weak bases,

$$\frac{\text{Strength of base 1 } (B_1OH)}{\text{Strength of base 2 } (B_2OH)} = \frac{\sqrt{K_{b_1}}}{\sqrt{K_{b_2}}}$$

Relative strength of some of the acids are as follows:

$HClO_4 > HBr > HCl > HNO_3 > H_2SO_4 > H_3O^+ > H_2SO_3 > H_2CO_3 > CH_3COOH$

$HClO_4 > HClO_3 > HClO_2 > HClO$

Relative strength of some of the bases are as follows:

$KOH > NaOH > Ca(OH)_2 > NH_4OH$

$NH_3 > NH_2{\cdot}NH_2 > NH_2OH$

Illustration 6

Compare the strength of HCN ($K_a = 4.9 \times 10^{-10}$) with 0.01 M aqueous solution of formic acid in which it is 14.5 % dissociated.

Soln.: Applying,

$$\frac{\text{Strength of formic acid}}{\text{Strength of HCN}} = \sqrt{\frac{K_a\text{ (formic acid)}}{K_a\text{ (HCN)}}}$$

Degree of dissociation of HCOOH (α) = 14.5 %

$$= \frac{14.5}{100} = 0.145$$

K_a (HCOOH) $= C\alpha^2 = 0.01 \times (0.145)^2 = 2.1 \times 10^{-4}$

$$\text{Thus,} \quad \frac{\text{Strength of formic acid}}{\text{Strength of HCN}} = \sqrt{\frac{2.1\times10^{-4}}{4.9\times10^{-10}}} = 6.5\times10^2$$

i.e., Formic acid is 6.5×10^2 times stronger than HCN or we can say that HCN is 6.5×10^2 times weaker than formic acid.

HYDROGEN ION CONCENTRATION AND pH SCALE

- Sorensen (1909) defined pH of a solution as negative logarithm of the hydrogen ion concentration of the solution.

$$\text{Thus,} \quad pH = -\log[H^+] = \log\frac{1}{[H^+]} \quad \text{or} \quad [H^+] = 10^{-pH}$$

Likewise, pOH of a solution

$$pOH = -\log[OH^-] = \log\frac{1}{[OH^-]}$$

$K_w = [H^+][OH^-]$

$\quad$ = ionic product of water = 10^{-14} (mol/L)^2

$pK_w = -\log K_w$

$pK_w = pH + pOH = 14$

- Relationship between $[H^+]$, $[OH^-]$ and pH value of the solution is

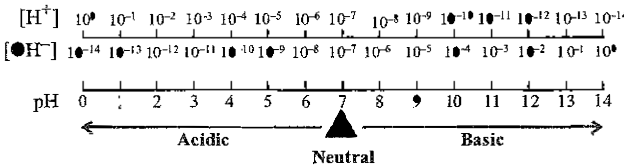

Illustration 7

How much KOH should be dissolved in one litre of solution to prepare a solution having a pH of 12 at 25°C?

Soln.: KOH is a strong alkali and is completely dissociated into the constituent ions,

$KOH + H_2O \text{ (excess)} \longrightarrow K^+_{(aq)} + OH^-_{(aq)}$

In a solution having pH = 12, the hydrogen ion concentration is given by the equation

$pH = -\log[H^+]$

$12 = -\log[H^+]$

or $[H^+] = 10^{-12}$ mol L^{-1}

Since, the ionic product in water should have a fixed value, hence at 25°C

$K_w = 1.0 \times 10^{-14}$

So, $1.0 \times 10^{-14} = [H^+][OH^-]$

$$\text{This gives,} \quad [OH^-] = \frac{1.0\times10^{-14}}{10^{-12}} = 1.0\times10^{-2}\ \text{mol L}^{-1}$$

Since KOH is completely dissociated, hence

$[KOH] = [OH^-] = 1.0 \times 10^{-2}$ mol L^{-1}

Molar mass of KOH = (39 + 16 + 1) g mol^{-1}

$\quad$ = 56 g mol^{-1}

Then, conc. of KOH = 1.0×10^{-2} mol L^{-1} × 56 g mol^{-1}

$\quad$ = 0.56 g L^{-1}

Thus, 0.56 g of KOH should be dissolved per litre of the solution to obtain a solution of pH 12.

- **pK_a and pK_b**

$pK_a = -\log K_a$

$pK_b = -\log K_b$

$K_a \times K_b = [H^+][OH^-]$

So, $K_a \times K_b = K_w$ or $pK_w = pK_a + pK_b$

HYDROLYSIS OF SALTS

- Salt hydrolysis is a process in which a salt reacts with water to give acid and the base.

$$\underset{\text{Salt}}{BA} + \underset{\text{Water}}{H_2O} \rightarrow \underset{\text{Acid}}{HA} + \underset{\text{Base}}{BOH}$$

Hydrolysis is the reverse of neutralization.

- **Salts of strong acid and strong base**
  Example : KCl, NaCl, K_2SO_4, Na_2SO_4, KNO_3, $NaNO_3$, etc.
  Consider the hydrolysis of NaCl,
  $NaCl + H_2O \rightarrow NaOH + HCl$
  or, $Na^+ + Cl^- + H_2O \rightarrow Na^+ + OH^- + H^+ + Cl^-$
  or, $H_2O \rightarrow H^+ + OH^-$
  Thus such salts only ionize and do not hydrolyse. It is obvious from the above reactions that $[H^+] = [OH^-]$ *i.e.*, solution is neutral.
- **Salts of weak acid and strong base**
  Example : CH_3COONa, Na_3PO_4, K_2CO_3, Na_2CO_3, etc.
  Consider the hydrolysis of CH_3COONa,
  $CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$
  or, $CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$
  i.e., $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$
  Such salts undergo **anionic hydrolysis** since anion reacts with water to give **basic solution**.
  Hydrolysis constant, $K_h = \frac{K_w}{K_a}$
  where, K_w is ionic product of water and K_a is dissociation constant of weak acid.
  Degree of hydrolysis, $h = \sqrt{\frac{K_h}{C}}$ or $h = \sqrt{\frac{K_w}{K_a \times C}}$
  and $pH = \frac{1}{2}[pK_w + pK_a + \log C]$.
- **Salt of strong acid and weak base**
  Example : NH_4Cl, $CuSO_4$, $CaCl_2$, $AlCl_3$, etc.
  $\underset{\text{Salt}}{BA} + H_2O \rightleftharpoons \underset{\text{Weak base}}{BOH} + \underset{\text{Strong acid}}{HA}$
  or $B^+ + A^- + H_2O \rightleftharpoons BOH + H^+ + A^-$
  i.e., $B^+ + H_2O \rightleftharpoons BOH + H^+$
  These salts undergo **cationic hydrolysis** since cation reacts with water to give **acidic solution**.
  Hydrolysis constant, $K_h = \frac{K_w}{K_b}$
  where K_w is ionic product of water and K_b is dissociation constant of weak base.
  Degree of hydrolysis $h = \sqrt{\frac{K_h}{C}}$ or $h = \sqrt{\frac{K_w}{K_b \times C}}$
  and $pH = \frac{1}{2}[pK_w - pK_b - \log C]$.
- **Salts of weak acid and weak base**
  Example : CH_3COONH_4, $AlPO_4$, $(NH_4)_2CO_3$, etc.
  $\underset{\text{Salt}}{BA} + H_2O \rightleftharpoons \underset{\text{Weak base}}{BOH} + \underset{\text{Weak acid}}{HA}$
  or, $B^+ + A^- + H_2O \rightleftharpoons BOH + HA$
  These salts involve both ***cationic and anionic hydrolysis*** to give ***almost neutral solution*** since both acid and base produced are weak.
  Hydrolysis constant, $K_h = \frac{K_w}{K_a \times K_b}$
  where, K_w = ionic product of water
  K_a = dissociation constant of weak acid
  K_b = dissociation constant of weak base
  Degree of hydrolysis, $h = \sqrt{K_h}$ or $h = \sqrt{\frac{K_w}{K_a \times K_b}}$
  and $pH = \frac{1}{2}[pK_w + pK_a - pK_b]$.

Illustration 8

Calculate the hydrolysis constant of the salt containing NO_2^- ions (Given K_a for $HNO_2 = 4.5 \times 10^{-10}$).

Soln.: NO_2^- comes from weak acid.

Thus, for salts of weak acid, $K_h = \frac{K_w}{K_a}$

$K_w = 10^{-14}$

$\therefore \quad K_h = \frac{10^{-14}}{4.5 \times 10^{-10}} = 2.2 \times 10^{-5}$

BUFFER SOLUTIONS

- Buffer solution is defined as a solution which resists the change in its pH value when small amount of acid or base is added to it or when the solution is diluted. Buffer solution has a definite pH value at specific temperature and it does not change on keeping for a long time.
- **Types of buffer solutions**

Types	pH
Acidic buffers (pH < 7) (mixture of weak acid + its salt with a strong base) *e.g.*, $CH_3COOH + CH_3COONa$ (pH = 4.7) $H_2NCH_2COOH + Cl^-H_3\overset{+}{N}CH_2COOH$ (pH = 2.4)	$pH = pK_a + \log\frac{[Salt]}{[Acid]}$
Basic buffers (pH > 7) (mixture of weak base and its salt with strong acid) *e.g.*, $H_3BO_3 + Na_2B_4O_7$ (pH = 8.0) $Na_2HPO_4 + Na_3PO_4$ (pH = 11.5)	$pH = pK_w - \left(pK_b + \log\frac{[Salt]}{[Base]}\right)$

- **Buffer capacity :** The number of equivalents of a strong acid (or a strong base) required to change the pH of one litre of a buffer solution by one unit keeping the total amount of the acid and the salt in the buffer constant, is called buffer capacity.