

# CHAPTER -1

## Electrolytic solution

**Electrolyte solution:** conductive solution

### **Theory of electrolytes**

- Electrolytes are substances which allow the electricity to pass through them in their molten states or in the form of their aqueous solutions and undergo chemical decomposition. Or
- Any substance that produces ions when dissolved in a solvent (usually water) is an electrolyte.
- It is the electrically conductive solution that must be present for corrosion to occur.
- Substances whose solution in water conducts electric current.
- Conduction takes place by the movement of ions.

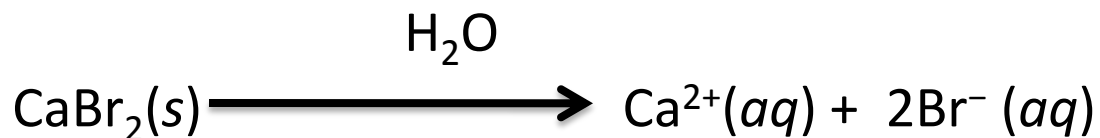
*Examples* are salts, acids and bases.

## Types of Electrolytes

**I. Strong electrolyte:** are highly ionized in the solution/ They completely dissociate to their ions when dissolved in solution.

- Ionic compounds are typically strong electrolytes.
- They are substances that only exist as ions in solution.
- They conduct electricity when molten or in aqueous solution.

Example: Strong acids(HCl), strong bases(NaOH) and salts (NaCl) are strong electrolytes.



**II. Weak electrolytes:** are only weakly ionized in the solution/ only partially dissociates in solution and produces relatively few ions (exist in water as a mixture of individual ions and in contact molecules).

- Polar covalent compounds are typically weak electrolytes.
- They conduct electricity weakly.
- Weak acids and weak bases are weak electrolytes.

**Examples:**  $\text{H}_2\text{CO}_3$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{NH}_4\text{OH}$ ,  $\text{NH}_3$  etc.



**III. Non-electrolyte:** Does not dissociate at all (present entirely as intact molecules) in solution and therefore does not produce any ions.

- Nonelectrolytes are typically polar covalent substances that do dissolve in water as molecules instead of ions.
- They do not conduct electricity at all.
- Examples are solutions of cane sugar, glucose, urea etc.

## **CONDUCTORS**

Conductors are the substances which allow the passage of electric current.

**N.B.** The best conductors are metals such as copper, silver, tin.

**Non conductors or insulators** are the substances which don't allow the passage of electrical current through them. Examples: rubber, wax, and wood.

## Types of conductors

**1. Metallic conductors.** There are metallic substances which allow the electricity to pass through them without undergoing any chemical change.

**2. Electrolytes.** There are substances which allow the electricity to pass through them in their molten states or in the form of their aqueous solutions and undergo chemical decomposition.

## Transport properties

**Mass transport** is the movement of material toward or away from the electrode surface.

There are three modes of **mass transport**:

- A) Diffusion** is the movement of material in response to a concentration gradient
- B) Convection** is the movement of material in response to a mechanical force, such as stirring a solution.
- C) Migration** is the movement of a cation or anion in response to an applied potential

# Faraday's law

Faraday's law relates the electric charge  $Q$ , which passes through a system during electrolysis, with the amount of substance of the ion  $n_i$  discharged at the electrode

$$n_i = \frac{Q}{z_i F},$$

where  $z_i$  is the ion charge.  $F$  is the **Faraday constant** which is, but for the sign, equal to the charge of 1 mole of electrons

$$F = NA |e^-| = 96485.3 \text{ C mol}^{-1}$$

Given that the charge is the product of the electric current  $I$  and the time of electrolysis  $\tau$ ,

$$Q = I \tau$$

$$m_i = M_i I \tau / z_i F$$

where  $M_i$  is the molecular mass of the ion

## Activity and Activity Coefficient

- The large number of oppositely charged ions in solutions of strong electrolytes influence one another through interionic attractive forces.
- For solution of nonelectrolytes, regardless of concentration, the number of ions is small and the interionic attractive forces are insignificant.
- As for strong electrolytes, ions can associate at high concentrations into groups known as ion pairs. Thus the values of the freezing point depression and the other colligative properties are less than expected for solutions of unhindered ions. Consequently, a strong electrolyte may be completely ionized, yet incompletely dissociated into free ions.
- You may think of the solution as having an “effective concentration” or, as it is called, an activity. This concept was first introduced by Lewis and Randall.



# Activity and Activity Coefficient

- The activity ( $a$ ), in general, is less than the actual or stoichiometric concentration of the solute ( $m$ ), not because the strong electrolytes are partly ionized, but rather because some of the ions are effectively “taken out of play” by the electrostatic forces of interaction.
- At infinite dilution in which the ions are so widely separated that they do not interact with one another, the activity  $a$  of an ion is equal to its concentration:  $a = m$ .
- As the concentration of the solution is increased, the ratio becomes less than unity because the effective concentration or activity of ions becomes less than the molal concentration. This ratio is known as the practical activity coefficient ( $\gamma$ ), thus:

$$a = \gamma m$$

# Activity and Activity Coefficient

- A cation and an anion in an aqueous solution may each have a different ionic activity.
- The activity of an electrolyte is defined by its mean ionic activity  $a_{\pm}$

$$a_{\pm} = (a_+^m a_-^n)^{1/(m+n)}$$

- where  $a_+$  is the activity of the cation, and  $a_-$  is the activity of the anion, the exponents  $m$  and  $n$  give the stoichiometric number of given ions that are in solution.
- Thus an NaCl solution has a mean ionic activity of  $a_{\pm} = (a_{\text{Na}^+} a_{\text{Cl}^-})^{1/2}$
- Whereas an  $\text{FeCl}_3$  solution has a mean ionic activity of  $a_{\pm} = (a_{\text{Fe}^{+3}} a_{\text{Cl}^-}^3)^{1/4}$

## Electric conductivity of electrolytes

Ohm's law applies in electrolytes just like in first-class conductors:

**Resistance** It measures the obstruction to the flow of current. The resistance of a conductor is proportional to the length ( $l$ ) and inversely proportional to the area of cross-section.

$$\rho = R \frac{A}{l}$$

where  $A$  is the cross-section and  $l$  is the length of the conductor and  $\rho$  ( $\rho$  (rho)) is the constant of proportionality and is called specific **resistance** or **resistivity**. The resistance depends upon the nature of the material. Its units are ohm ( $\Omega$ )

$R = \rho$ , if  $l = 1$  cm,  $a = 1$  cm<sup>2</sup>

In other words, specific resistance is the resistance between opposite faces of one centimeter cube of the conductor.

**Conductance.** It is a measure of the ease with which current flows through a conductor. The **conductivity**  $\kappa$  is the reciprocal value of resistivity.

$$\kappa = 1/\rho$$

### Example

The resistance  $R = 100 \Omega$  was measured in a potassium chloride solution. Each of the electrodes had a surface area of 4 cm<sup>2</sup>, and the distance between them was 2 cm. Calculate the conductivity

# Conductivity of Electrolyte Solution

- Ions in solution can be set in motion by applying a potential difference between two electrodes.
- The conductance ( $G$ ) of a solution is defined as the inverse of the resistance ( $R$ ):

$$G = \frac{1}{R}, \quad \text{in units of } \Omega^{-1}$$

- For parallel plate electrodes with area  $A$ , it follows:

$$G = \frac{\kappa A}{L}$$

Where,

$\kappa$  : the conductivity,

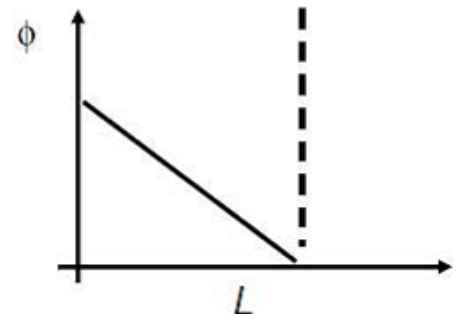
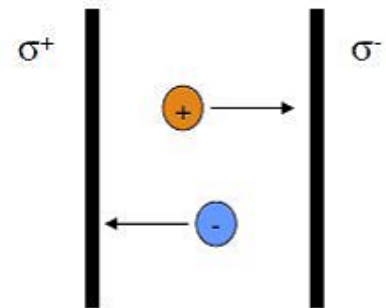
$L$  : the distance separating the plates

Units:

$$G \rightarrow S \text{ (siemens)}$$

$$R \rightarrow \Omega$$

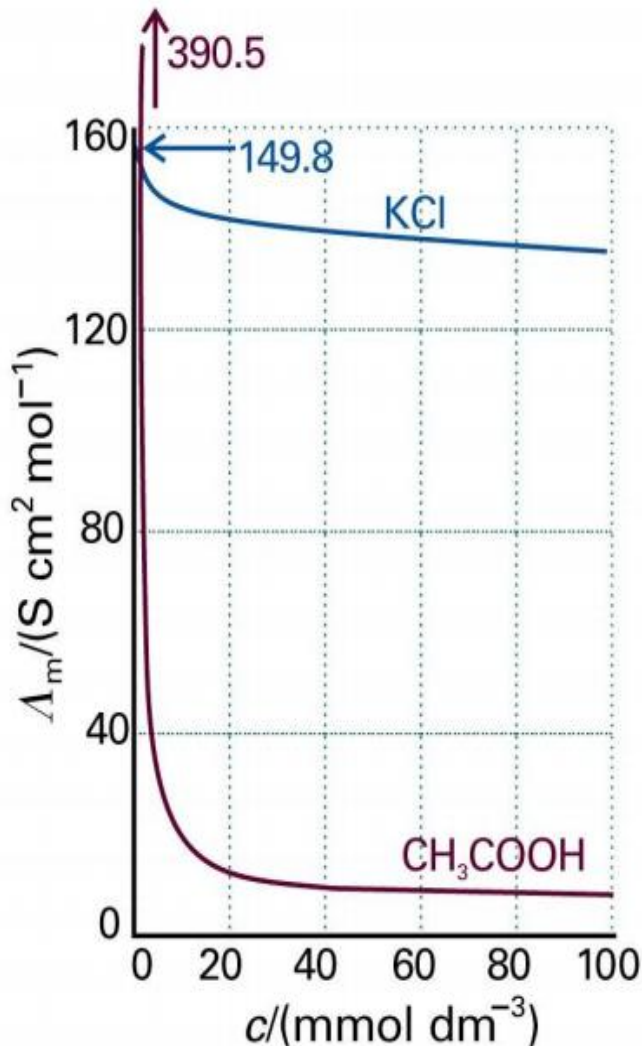
$$\kappa \rightarrow S \text{ m}^{-1}$$



- The conductivity of a solution depends on the number of ions present. Consequently, the molar conductivity  $\Lambda_m$  is used

$$\Lambda_m = \frac{\kappa}{C}$$

- ✓  $C$  is molar concentration of electrolyte and unit of  $\Lambda_m$  is  $S\ m^2\ mol^{-1}$



In real solutions,  $\Lambda_m$  depends on the concentration of the electrolyte. This could be due to:

- Ion-ion interactions  $\rightarrow \gamma_{\pm} \neq 1$
- The concentration dependence of conductance indicates that there are 2 classes of electrolyte
  - ✓ **Strong electrolyte**: molar conductivity depends slightly on the molar concentration
  - ✓ **Weak electrolyte**: molar concentration falls sharply as the concentration increases

In real solutions,  $\Lambda_m$  depends on the concentration of the electrolyte. This could be due to:

1. Ion-ion interactions  $\rightarrow \gamma_{\pm} \neq 1$

2. Incomplete dissociation of electrolyte

strong electrolyte,  
weak dependence of  $\Lambda_m$  on  $C$

weak electrolyte,  
strong dependence of  $\Lambda_m$  on  $C$

$$K = \frac{C}{R}$$

The quantity  $C$  is called the **conductivity cell constant**, and it is determined by calibration.

### Example

The resistance of a copper sulfate of the concentration  $c = 0.02 \text{ mol dm}^{-3}$  is  $R = 1440 \Omega$ , and the conductivity cell constant is  $C = 541 \text{ m}^{-1}$ . Calculate the molar conductivity of the solution.

# Strong Electrolyte

- Fully ionized in solution

- **Kohlrausch's law**  $\Lambda_m = \Lambda_m^0 - KC^{1/2}$

- ✓  $\Lambda_m^0$  is the limiting molar conductivity

- ✓  $K$  is a constant which typically depends on the stoichiometry of the electrolyte

- $C^{1/2}$  arises from ion-ion interactions as estimated by the Debye-Hückel theory.

- **Law of the independent migration of ions:** limiting molar conductivity can be expressed as a sum of ions contribution

$$\Lambda_m^0 = \nu_+ \lambda_+ + \nu_- \lambda_-$$

- ✓ ions migrate independently in the zero concentration limit

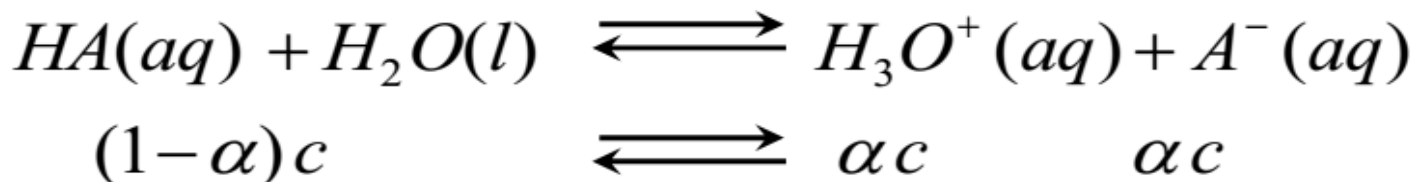
	$\lambda / (\text{mS m}^2 \text{ mol}^{-1})$		$\lambda / (\text{mS m}^2 \text{ mol}^{-1})$
$\text{H}^+$	34.96	$\text{OH}^-$	19.91
$\text{Na}^+$	5.01	$\text{Cl}^-$	7.63
$\text{K}^+$	7.35	$\text{Br}^-$	7.81
$\text{Zn}^{2+}$	10.56	$\text{SO}_4^{2-}$	16.00

For example, limiting molar conductivity of  $\text{BaCl}_2$  in water will be:  $12.73 + 2 \times 7.63 = 27.98 \text{ mS m}^2 \text{ mol}^{-1}$ .



# Weak Electrolyte

- Not fully ionized in solution



$$K_a = \frac{\alpha^2 c}{1-\alpha}, \quad \frac{1}{\alpha} = 1 + \frac{\alpha c}{K_a} \quad \alpha \text{ is degree of ionisation}$$

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$$\alpha^2 c = K_a - K_a \alpha$$

$$c\alpha^2 + K_a \alpha - K_a = 0$$

$$\alpha = \frac{-K_a \pm \sqrt{K_a^2 + 4K_a c}}{2c}$$

$$\alpha = \frac{-K_a}{2c} \pm \frac{\sqrt{K_a^2 + 4K_a c}}{2c}$$

$$\begin{aligned} \alpha &= \frac{-K_a}{2c} \pm \frac{K_a}{2c} \left( 1 + \frac{4c}{K_a} \right)^{1/2} \\ \alpha &= \frac{K_a}{2c} \left[ \left( 1 + \frac{4c}{K_a} \right)^{1/2} - 1 \right] \end{aligned}$$

- The molar Conductivity (at higher concentrations) can be expressed as:

$$\Lambda_m = \alpha \Lambda_m^0$$

- At infinite dilution, the weak acid is fully dissociated ( $\alpha = 100\%$ )
- It can be proven by the Ostwald dilution law which allows estimating limiting molar conductance:

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} + \frac{c\Lambda_m}{K_a(\Lambda_m^0)^2}$$

$$\Lambda_m = \alpha \Lambda_m^0$$

$$\frac{1}{\Lambda_m} = \frac{1}{\alpha \Lambda_m^0}$$

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} \times \frac{1}{\alpha}$$

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} \times \left( 1 + \frac{\alpha c}{K_a} \right)$$

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} + \frac{c}{K_a \Lambda_m^0} \times \frac{\Lambda_m}{\Lambda_m^0}$$

# Ionic equilibrium

## Acid & Bases

- **Arrhenius:** Acids are proton ( $\text{H}^+$ ) sources and bases are hydroxide ion ( $\text{OH}^-$ ) sources.

E.g.  $\text{HCl}$  is an acid and  $\text{NaOH}$  a base

- **Brønsted-Lowry:** Acids are proton sources and bases are proton acceptors. E.g.  $\text{HCl}$  is an acid and  $\text{NH}_3$  a base, these form the conjugate base  $\text{Cl}^-$  &  $\text{NH}_4^+$ .
- **Lewis:** Acids are electron pair acceptors and bases are electron pair donors. E.g.  $\text{AlCl}_3$  &  $:\text{NH}_3$ . to form  $\text{Cl}_3\text{Al}:\text{NH}_3$

## Strong acids and strong bases

Completely dissociate (split up) into ions in aqueous solution

e.g.  $\text{HCl} \longrightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$  MONOPROTIC 1 replaceable H

$\text{HNO}_3 \longrightarrow \text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$

$\text{H}_2\text{SO}_4 \longrightarrow 2\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$  DIPROTIC 2 replaceable H'

$\text{NaOH}(\text{s}) \longrightarrow \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq})$

# WEAK ACIDS

**Weak acids:-** partially dissociate into ions in aqueous solution

e.g. ethanoic acid



➤ When a weak acid dissolves in water an equilibrium is set up



➤ The water stabilises the ions

➤ To make calculations easier the dissociation can be written...



➤ The weaker the acid the less it dissociates the more the equilibrium lies to the left.

➤ The relative strengths of acids can be expressed as  $K_a$  or  $\text{p}K_a$  values

➤ The dissociation constant for the weak acid HA is

$$K_a = \frac{[\text{H}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]}$$

## WEAK BASES

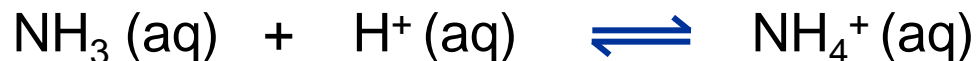
- Partially react with water to give ions in aqueous solution

e.g. ammonia

- When a weak base dissolves in water an equilibrium is set up



- As in the case of acids it is more simply written



- The weaker the base the less it dissociates the more the equilibrium lies to the left

- The relative strengths of bases can be expressed as  $K_b$  or  $\text{p}K_b$  values.

$$K_b = \frac{[\text{NH}_4^+(\text{aq})]}{[\text{NH}_3(\text{aq})][\text{H}^+(\text{aq})]}$$

## Hydrogen ion concentration $[H^+(aq)]$

- hydrogen ion concentration determines the acidity of a solution
- hydroxide ion concentration determines the alkalinity
- For strong acids and bases the concentration of ions is very much larger than their weaker counterparts which only partially dissociate.

**pH**:-hydrogen ion concentration can be converted to pH

$$pH = -\log_{10} [H^+(aq)]$$

to convert pH into hydrogen ion concentration

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

**POH**:-An equivalent calculation for bases converts the hydroxide ion concentration to POH.

$$pOH = -\log_{10} [OH^-(aq)]$$

in both the above,  $[ ]$  represents the concentration in  $\text{mol dm}^{-3}$

## Ionic product of water - $K_w$

Despite being covalent, water conducts electricity to a very small extent.

This is due to the slight ionisation ...



or, more simply



Applying the equilibrium law to the second equation gives

$$K_c = \frac{[\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{H}_2\text{O}(\text{l})]}$$

[ ] is the equilibrium concentration in  $\text{mol dm}^{-3}$

As the dissociation is small, the water concentration is very large compared with the dissociated ions and any changes to its value are insignificant; its concentration can be regarded as constant.



This “constant” is combined with ( $K_c$ ) to get a new constant ( $K_w$ ).

$$K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})] \text{ mol}^2 \text{ dm}^{-6} = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ (at } 25^\circ\text{C)}$$

Because the constant is based on an equilibrium,  $K_w$  varies with temperature.

The value of  $K_w$  varies with temperature because it is based on an equilibrium.

Temperature / °C	0	20	25	30	60
$K_w / 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$	0.11	0.68	1.0	1.47	5.6
$\text{H}^+ / \times 10^{-7} \text{ mol dm}^{-3}$	0.33	0.82	1.0	1.27	2.37
pH	7.48	7.08	7	6.92	6.63

What does this tell you about the equation  $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$  ?

- $K_w$  gets larger as the temperature increases
- This means the concentration of  $\text{H}^+$  and  $\text{OH}^-$  ions gets greater
- This means the equilibrium has moved to the right
- If the concentration of  $\text{H}^+$  increases then the pH decreases
- pH decreases as the temperature increases

*Because the equation moves to the right as the temperature goes up, it must be an ENDOTHERMIC process*

## Relationship between pH and pOH

Because  $\text{H}^+$  and  $\text{OH}^-$  ions are produced in equal amounts when water dissociates their concentrations will be the same.

- ❖  $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ mol dm}^{-3}$
- ❖  $K_w = [\text{H}^+] [\text{OH}^-] = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$  take logs of both sides
- ❖  $\log[\text{H}^+] + \log[\text{OH}^-] = -14$  multiply by minus
- ❖  $-\log[\text{H}^+] - \log[\text{OH}^-] = 14$  change to pH and pOH
- ❖  $\text{pH} + \text{pOH} = 14$  (at  $25^\circ\text{C}$ )

<b>[H<sup>+</sup>]</b>	<b>10<sup>0</sup></b>	<b>10<sup>-1</sup></b>	<b>10<sup>-2</sup></b>	<b>10<sup>-3</sup></b>	<b>10<sup>-4</sup></b>	<b>10<sup>-5</sup></b>	<b>10<sup>-6</sup></b>	<b>10<sup>-7</sup></b>	<b>10<sup>-8</sup></b>	<b>10<sup>-9</sup></b>	<b>10<sup>-10</sup></b>	<b>10<sup>-11</sup></b>	<b>10<sup>-12</sup></b>	<b>10<sup>-13</sup></b>	<b>10<sup>-14</sup></b>
<b>OH<sup>-</sup></b>	<b>10<sup>-14</sup></b>	<b>10<sup>-13</sup></b>	<b>10<sup>-12</sup></b>	<b>10<sup>-11</sup></b>	<b>10<sup>-10</sup></b>	<b>10<sup>-9</sup></b>	<b>10<sup>-8</sup></b>	<b>10<sup>-7</sup></b>	<b>10<sup>-6</sup></b>	<b>10<sup>-5</sup></b>	<b>10<sup>-4</sup></b>	<b>10<sup>-3</sup></b>	<b>10<sup>-2</sup></b>	<b>10<sup>-1</sup></b>	<b>10<sup>0</sup></b>
<b>pH</b>	<b>0</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>	<b>11</b>	<b>12</b>	<b>13</b>	<b>14</b>
<b>pOH</b>	<b>14</b>	<b>13</b>	<b>12</b>	<b>11</b>	<b>10</b>	<b>9</b>	<b>8</b>	<b>7</b>	<b>6</b>	<b>5</b>	<b>4</b>	<b>3</b>	<b>2</b>	<b>1</b>	<b>0</b>

**STRONGLY  
ACIDIC**

**WEAKLY  
ACIDIC**

**NEUTRAL**

**WEAKLY  
ALKALINE**

**STRONGLY  
ALKALINE**

## **N.B.**

- As they are based on the position of equilibrium and that varies with temperature, the above values are only true if the temperature is 25°C (298K)
- Neutral solutions may be regarded as those where  $[H^+] = [OH^-]$ .
- Therefore a neutral solution is pH 7 only at a temperature of 25°C (298K)
- $K_w$  is constant for any aqueous solution at the stated temperature

## Calculating pH - strong acids and alkalis

Strong acids and alkalis completely dissociate in aqueous solution

It is easy to calculate the pH; you **only need to know the concentration**.

➤ Calculate the pH of 0.02M HCl

HCl completely dissociates in aqueous solution  $\text{HCl} \longrightarrow \text{H}^+ + \text{Cl}^-$

One  $\text{H}^+$  is produced for each HCl dissociating so  $[\text{H}^+] = 0.02\text{M} = 2 \times 10^{-2} \text{ mol dm}^{-3}$

$$\text{pH} = -\log [\text{H}^+] = 1.7$$

➤ Calculate the pH of 0.1M NaOH

NaOH completely dissociates in aqueous solution  $\text{NaOH} \longrightarrow \text{Na}^+ + \text{OH}^-$

One  $\text{OH}^-$  is produced for each NaOH dissociating  $[\text{OH}^-] = 0.1\text{M} = 1 \times 10^{-1} \text{ mol dm}^{-3}$

The ionic product of water (at 25°C)  $K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

Therefore  $[\text{H}^+] = K_w / [\text{OH}^-] = 1 \times 10^{-13} \text{ mol dm}^{-3}$

$$\text{pH} = -\log [\text{H}^+] = 13$$

**Calculate the pH of a solution which is 1.0 M HF and 1.0M NaF.**

If the pH is 12.2 what was the initial concentration of the base?

## Calculating pH - weak acids

- Can't be calculated by just knowing the concentration
- Need to know... the original concentration and the extent of the ionization

The extent of the ionization is given by ...  $K_a$  . The dissociation constant for a weak acid

### The dissociation constant for a weak acid - $K_a$

A weak monobasic acid (HA) dissociates in water thus.



Applying the equilibrium law we get

$$K_c = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA(aq)}][\text{H}_2\text{O(l)}]}$$

[ ] is the equilibrium concentration in  $\text{mol dm}^{-3}$

In dilute solution, the concentration of water is large compared with the dissociated ions and any changes to its value are insignificant; its concentration can be regarded as 'constant'.

## The dissociation constant for a weak acid - $K_a$

A weak monobasic acid (HA) dissociates in water thus.



The dissociation constant  $K_a$  is then

$$K_a = \frac{[\text{H}^+(\text{aq})] [\text{A}^-(\text{aq})]}{[\text{HA(aq)}]} \quad \text{mol dm}^{-3}$$

The weaker the acid

- the less it dissociates
- the fewer ions you get
- the smaller  $K_a$

The stronger the acid

- the more the equilibrium lies to the right
- the larger  $K_a$
- very weak acids have very small  $K_a$  values
- it is easier to compare the strength as  $\text{p}K_a$  values

The conversion is carried out thus...

$$\text{p}K_a = -\log_{10} K_a$$

To convert  $\text{p}K_a$  into  $K_a$

$$K_a = \text{antilog} (-\text{p}K_a) \text{ or } 10^{-K_a}$$

## Calculating pH – weak acids

A weak acid is one which only partially dissociates in aqueous solution

A weak acid, HA, dissociates as follows  $\text{HA}_{(\text{aq})} \rightleftharpoons \text{H}^+_{(\text{aq})} + \text{A}^-_{(\text{aq})}$  (1)

Applying the Equilibrium Law

$$K_a = \frac{[\text{H}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]} \text{ mol dm}^{-3} \quad \text{K K K 2}$$

The ions are formed in equal amounts, so  $[\text{H}^+_{(\text{aq})}] = [\text{A}^-_{(\text{aq})}]$

therefore

$$K_a = \frac{[\text{H}^+(\text{aq})]^2}{[\text{HA}(\text{aq})]} \quad \text{K K K K 3}$$

Rearranging (3) gives  $[\text{H}^+(\text{aq})]^2 = [\text{HA}(\text{aq})] K_a$

therefore  $[\text{H}^+(\text{aq})] = \sqrt{[\text{HA}(\text{aq})] K_a} \quad \text{mol dm}^{-3}$

$$\text{pH} = -\log [\text{H}^+_{(\text{aq})}]$$

**ASSUMPTION** : HA is a weak acid so it will not have dissociated very much. You can assume that its equilibrium concentration is approximately that of the original concentration.

**Buffers:** Solutions that resist changes in pH when a small amount of acid or base is added.

**Calculating the effect of added  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  on buffer pH**

**PROBLEM:** Calculate the pH of the following solutions.

- (a) A buffer solution consisting of 0.50 M  $\text{CH}_3\text{COOH}$  and 0.50 M  $\text{CH}_3\text{COONa}$
  - (b) After adding 0.020 mol of solid  $\text{NaOH}$  to 1.0 L of the buffer solution in part (a)
  - (c) After adding 0.020 mol of  $\text{HCl}$  to 1.0 L of the buffer solution in part (a)
- $K_a$  of  $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$  (assume the additions cause negligible volume changes)

**PLAN:** We know  $K_a$  and can find initial concentrations of conjugate acid and base. Make assumptions about the amount of acid dissociating relative to its initial concentration. Proceed stepwise through changes in the system.

**SOLUTION:** (a)

concentration (M)	$\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{COO}^-(aq) + \text{H}_3\text{O}^+(aq)$			
initial	0.50	-	0.50	0
change	- x	-	+ x	+ x
equilibrium	0.50 - x	-	0.50 + x	x



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

$$[\text{CH}_3\text{COOH}]_{\text{eq}} \approx 0.50 \text{ M}$$

$$[\text{CH}_3\text{COO}^-]_{\text{eq}} \approx 0.50 \text{ M}$$

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

$$[\text{H}_3\text{O}^+] = x = K_a$$

$$\frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = 1.8 \times 10^{-5} \text{ M}$$

$$\text{pH} = 4.74$$

Check the assumption:  $1.8 \times 10^{-5} / 0.50 \times 100 = 3.6 \times 10^{-3} \%$

(b)  $[\text{OH}^-]_{\text{added}} = \frac{0.020 \text{ mol}}{1.0 \text{ L soln}} = 0.020 \text{ M NaOH}$

concentration (M)	$\text{CH}_3\text{COOH}(aq) + \text{OH}^-(aq) \rightleftharpoons \text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O}(l)$			
Before addition	0.50	-	0.50	-
Addition	-	0.020	-	-
after addition	0.48	0	0.52	-

(continued)

Set up a reaction table with the new values.

concentration (M)	<b><math>\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{COO}^-(aq) + \text{H}_3\text{O}^+(aq)</math></b>			
initial	0.48	-	0.52	0
change	- x	-	+ x	+ x
equilibrium	0.48 - x	-	0.52 + x	x

$$[\text{H}_3\text{O}^+] = 1.8 \times 10^{-5} \times \frac{0.48}{0.52} = 1.7 \times 10^{-5} \quad \text{pH} = 4.77$$

(c)  $[\text{H}_3\text{O}^+]_{\text{added}} = \frac{0.020 \text{ mol}}{1.0 \text{ L soln}} = 0.020 \text{ M } \text{H}_3\text{O}^+$

concentration (M)	<b><math>\text{CH}_3\text{COO}^-(aq) + \text{H}_3\text{O}^+(aq) \rightleftharpoons \text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l)</math></b>			
before addition	0.50	-	0.50	-
addition	-	0.020	-	-
after addition	0.48	0	0.52	-

(continued)

Set up a reaction table with the new values.

concentration (M)	$\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{COO}^-(aq) + \text{H}_3\text{O}^+(aq)$			
initial	0.52	-	0.48	0
change	- x	-	+ x	+ x
equilibrium	0.52 - x	-	0.48 + x	x

$$[\text{H}_3\text{O}^+] = 1.8 \times 10^{-5} \times \frac{0.52}{0.48} = 2.0 \times 10^{-5}$$

$$\text{pH} = 4.70$$

Note that this buffer resists changes in pH from additions of either strong acid or strong base!  
(What is the solution pH of 0.020 M HCl or 0.020 M NaOH?)

1. Calculate the pH of a buffer solution containing 0.25 M  $\text{NH}_3$  and 0.40 M  $\text{NH}_4\text{Cl}$ .  $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$

2. Then, if we add 20 mL of 1.0 M NaOH to 500 mL of the above buffer, what would the final pH be?

**Note:** the volume of the buffer changes in this problem, so we need to work in moles and calculate new concentrations.

We can predict whether a buffer will be acidic or basic by comparing values of  $K_a$  and  $K_b$ .

Acetic acid  $\text{CH}_3\text{CO}_2\text{H}$   $K_a = 1.8 \times 10^{-5}$

Acetate ion  $\text{CH}_3\text{CO}_2^-$   $K_b = 5.6 \times 10^{-10}$

$K_a > K_b$  so buffer will be acidic

Ammonia  $\text{NH}_3$   $K_b = 1.8 \times 10^{-5}$

Ammonium ion  $\text{NH}_4^+$   $K_a = 5.6 \times 10^{-10}$

$K_b > K_a$  so buffer will be basic

# The Henderson-Hasselbalch Equation

Calculating the pH of a buffer solution can be simplified by using an equation derived from the  $K_a$  expression called the **Henderson-Hasselbalch Equation**

The equation calculates the pH of a buffer from the  $K_a$  and initial concentrations of the weak acid and salt of the conjugate base

Note: the “x is small” approximation must be valid



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad [\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]}$$

$$-\log[\text{H}_3\text{O}^+] = -\log K_a - \log \left( \frac{[\text{HA}]}{[\text{A}^-]} \right)$$

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{base}]}{[\text{acid}]} \right)$$

**PROBLEM**

Calculate the pH of a 1-L solution to which has been added 6.0 mL of 1.5 M acetic acid and 5.0 mL of 0.4 M sodium acetate.

**SOLUTION**

First, calculate the final concentrations of acetic acid (HA) and acetate ( $A^-$ ). The final volume of the solution is  $1\text{ L} + 6\text{ mL} + 5\text{ mL} = 1.011\text{ L}$ .

$$[HA] = \frac{(0.006\text{ L})(1.5\text{ M})}{1.011\text{ L}} = 0.0089\text{ M}$$

$$[A^-] = \frac{(0.005\text{ L})(0.4\text{ M})}{1.011\text{ L}} = 0.0020\text{ M}$$

Next, substitute these values into the Henderson–Hasselbalch equation using the  $pK$  for acetic acid given in Table 2-4:

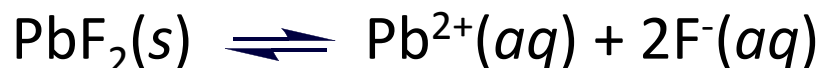
$$\begin{aligned} \text{pH} &= pK + \log \frac{[A^-]}{[HA]} \\ \text{pH} &= 4.76 + \log \frac{0.0020}{0.0089} \\ &= 4.76 - 0.65 \\ &= 4.11 \end{aligned}$$

## Equilibria of Slightly Soluble Ionic Compounds

Any “insoluble” ionic compound is actually *slightly* soluble in aqueous solution.

We assume that the very small amount of such a compound that dissolves will dissociate completely.

For a slightly soluble ionic compound in water, *equilibrium* exists between *solid solute* and *aqueous ions*.



$$Q_c = \frac{[\text{Pb}^{2+}][\text{F}^{-}]^2}{[\text{PbF}_2]}$$

$$Q_{\text{sp}} = Q_c[\text{PbF}_2] = [\text{Pb}^{2+}][\text{F}^{-}]^2$$

## $Q_{sp}$ and $K_{sp}$

$Q_{sp}$  is called the ***ion-product expression*** for a slightly soluble ionic compound.

For any slightly soluble compound  $M_pX_q$ , which consists of ions  $M^{n+}$  and  $X^{z-}$ ,

$$Q_{sp} = [M^{n+}]^p[X^{z-}]^q$$

When the solution is saturated, the system is at equilibrium, and  $Q_{sp} = K_{sp}$ , the ***solubility product constant***.

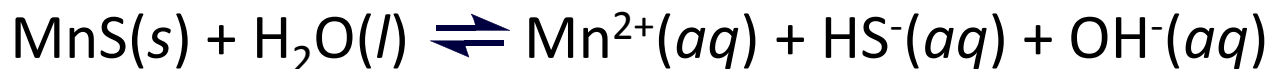
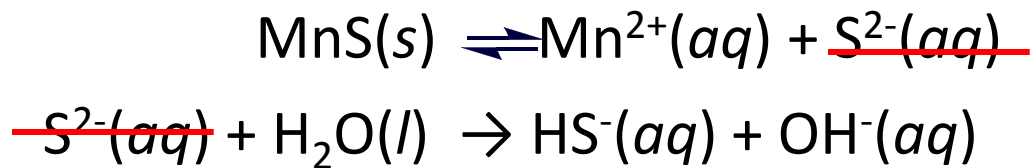
The  $K_{sp}$  value of a salt indicates how far the dissolution proceeds at equilibrium (saturation).



## Metal Sulfides

Metal sulfides behave differently from most other slightly soluble ionic compounds, since the  $S^{2-}$  ion is strongly basic.

We can think of the dissolution of a metal sulfide as a two-step process:



$$K_{\text{sp}} = [\text{Mn}^{2+}][\text{HS}^{-}][\text{OH}^{-}]$$

## Writing Ion-Product Expressions

**PROBLEM:** Write the ion-product expression at equilibrium for each compound:

(a) magnesium carbonate

(b) iron(II) hydroxide

(c) calcium phosphate

(d) silver sulfide

**PLAN:** We write an equation for a saturated solution of each compound, and then write the ion-product expression at equilibrium,  $K_{sp}$ . Note the sulfide in part (d).

**SOLUTION:**



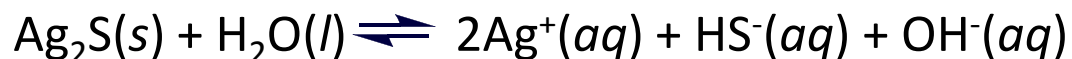
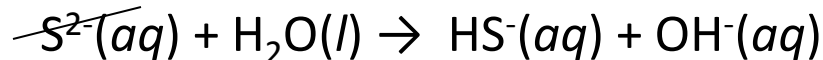
$$K_{sp} = [\text{Mg}^{2+}][\text{CO}_3^{2-}]$$



$$K_{sp} = [\text{Fe}^{2+}][\text{OH}^-]^2$$



$$K_{sp} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$$



$$K_{sp} = [\text{Ag}^+]^2[\text{HS}^-][\text{OH}^-]$$

<p><b>Solubility-Product Constants (<math>K_{sp}</math>) of Selected Ionic Compounds at 25°C</b></p>
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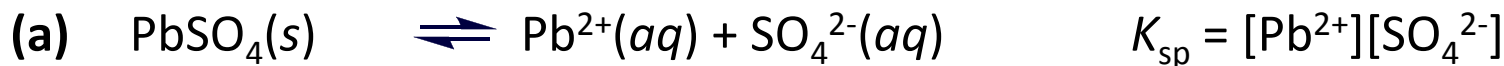
Name, Formula	$K_{sp}$
Aluminum hydroxide, $\text{Al}(\text{OH})_3$	$3 \times 10^{-34}$
Cobalt(II) carbonate, $\text{CoCO}_3$	$1.0 \times 10^{-10}$
Iron(II) hydroxide, $\text{Fe}(\text{OH})_2$	$4.1 \times 10^{-15}$
Lead(II) fluoride, $\text{PbF}_2$	$3.6 \times 10^{-8}$
Lead(II) sulfate, $\text{PbSO}_4$	$1.6 \times 10^{-8}$
Mercury(I) iodide, $\text{Hg}_2\text{I}_2$	$4.7 \times 10^{-29}$
Silver sulfide, $\text{Ag}_2\text{S}$	$8 \times 10^{-48}$
Zinc iodate, $\text{Zn}(\text{IO}_3)_2$	$3.9 \times 10^{-6}$

## Determining $K_{sp}$ from Solubility

- PROBLEM:**
- (a) Lead(II) sulfate ( $\text{PbSO}_4$ ) is a key component in lead-acid car batteries. Its solubility in water at  $25^\circ\text{C}$  is  $4.25 \times 10^{-3}$  g/100 mL solution. What is the  $K_{sp}$  of  $\text{PbSO}_4$ ?
  - (b) When lead(II) fluoride ( $\text{PbF}_2$ ) is shaken with pure water at  $25^\circ\text{C}$ , the solubility is found to be 0.64 g/L. Calculate the  $K_{sp}$  of  $\text{PbF}_2$ .

**PLAN:** We write the dissolution equation and the ion-product expression for each compound. This tells us the number of moles of each ion formed. We use the molar mass to convert the solubility of the compound to *molar solubility* (molarity), then use it to find the molarity of each ion, which we can substitute into the  $K_{sp}$  expression.

## SOLUTION:



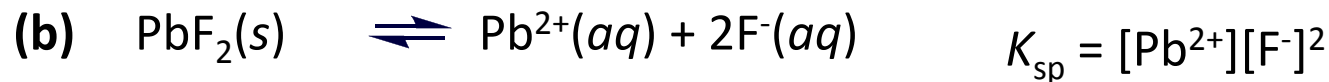
Converting from g/mL to mol/L:

$$\frac{4.25 \times 10^{-3} \text{ g PbSO}_4}{100 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol PbSO}_4}{303.3 \text{ g PbSO}_4} = 1.40 \times 10^{-4} \text{ mol/L PbSO}_4$$

Each mol of  $\text{PbSO}_4$  produces 1 mol of  $\text{Pb}^{2+}$  and 1 mol of  $\text{SO}_4^{2-}$ , so  $[\text{Pb}^{2+}] = [\text{SO}_4^{2-}] = 1.40 \times 10^{-4} \text{ mol/L}$

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = (1.40 \times 10^{-4})^2$$

$$\boxed{= 1.96 \times 10^{-8}}$$



Converting from g/L to mol/L:

$$\frac{0.64 \text{ g PbF}_2}{1 \text{ L soln}} \times \frac{1 \text{ mol PbF}_2}{245.2 \text{ g PbF}_2} = 2.6 \times 10^{-3} \text{ mol/L PbF}_2$$

Each mol of  $\text{PbF}_2$  produces 1 mol of  $\text{Pb}^{2+}$  and 2 mol of  $\text{F}^{-}$ , so  
 $[\text{Pb}^{2+}] = 2.6 \times 10^{-3} \text{ mol/L}$  and  $[\text{F}^{-}] = 2(2.6 \times 10^{-3}) = 5.2 \times 10^{-3} \text{ mol/L}$

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{F}^{-}]^2 = (2.6 \times 10^{-3})(5.2 \times 10^{-3})^2$$

$= 7.0 \times 10^{-8}$
------------------------

1.  $1.5 \times 10^{-4} \text{ g}$  of  $\text{CaF}_2$  dissolves in 10.00 mL solution at  $18^\circ\text{C}$ .

- I. Write the expression for  $K_{\text{sp}}$ .
- II. Find the molar solubility of  $\text{CaF}_2$ .
- III. Find the  $[\text{Ca}^{2+}]$  and  $[\text{F}^{-}]$ .
- IV. Calculate  $K_{\text{sp}}$ .

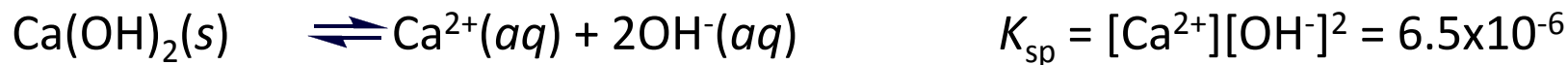
2. What is the molar solubility of  $\text{Mg}(\text{OH})_2$  if the value of  $K_{\text{sp}}$  is  $6.3 \times 10^{-10}$ ?

## Determining Solubility from $K_{sp}$

**PROBLEM:** Calcium hydroxide (slaked lime) is a major component of mortar, plaster, and cement, and solutions of  $\text{Ca}(\text{OH})_2$  are used in industry as a strong, inexpensive base. Calculate the molar solubility of  $\text{Ca}(\text{OH})_2$  in water if the  $K_{sp}$  is  $6.5 \times 10^{-6}$ .

**PLAN:** We write the dissolution equation and the expression for  $K_{sp}$ . We know the value of  $K_{sp}$ , so we set up a reaction table that expresses  $[\text{Ca}^{2+}]$  and  $[\text{OH}^-]$  in terms of  $S$ , the molar solubility. We then substitute these expressions into the  $K_{sp}$  expression and solve for  $S$ .

**SOLUTION:**



Concentration (mol/L)	$\text{Ca(OH)}_2(s)$	$\rightleftharpoons$	$\text{Ca}^{2+}(aq) + 2\text{OH}^-(aq)$
Initial	-		0
Change	-		+S
Equilibrium	-		S

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2 = (S)(2S)^2 = 4S^3 = 6.5 \times 10^{-6}$$

$$S = \sqrt[3]{\frac{K_{\text{sp}}}{4}} = \sqrt[3]{\frac{6.5 \times 10^{-6}}{4}} = 1.2 \times 10^{-2} \text{ mol/L}$$



## Calculating the Effect of a Common Ion on Solubility

**PROBLEM:** In previous Sample Problem , we calculated the solubility of  $\text{Ca(OH)}_2$  in water. What is its solubility in  $0.10 \text{ mol/L}$   $\text{Ca(NO}_3)_2$ ?  $K_{\text{sp}}$  of  $\text{Ca(OH)}_2$  is  $6.5 \times 10^{-6}$ .

**PLAN:** The addition of  $\text{Ca}^{2+}$ , an ion common to both solutions, should lower the solubility of  $\text{Ca(OH)}_2$ . We write the equation and  $K_{\text{sp}}$  expression for the dissolution and set up a reaction table in terms of  $S$ , the molar solubility of  $\text{Ca(OH)}_2$ . We make the assumption that  $S$  is small relative to  $[\text{Ca}^{2+}]_{\text{init}}$  because  $K_{\text{sp}}$  is low. We can then solve for  $S$  and check the assumption.

**SOLUTION:**



$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2$$

$[\text{Ca}^{2+}]_{\text{init}} = 0.10 \text{ mol/L}$  because  $\text{Ca}(\text{NO}_3)_2$  is a soluble salt, and dissociates completely in solution.

Concentration (mol/L)	$\text{Ca}(\text{OH})_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{OH}^-(aq)$		
Initial	-	0.10	0
Change	-	+S	+ 2S
Equilibrium	-	$0.10 + S$	2S

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2 = 6.5 \times 10^{-6} \approx (0.10)(2S)^2 = (0.10)(4S^2)$$

$$4S^2 \approx \frac{6.5 \times 10^{-6}}{0.10} \quad \text{so } S \approx \sqrt{\frac{6.5 \times 10^{-5}}{4}} \quad \boxed{= 4.0 \times 10^{-3} \text{ mol/L}}$$

Checking the assumption:  $\frac{4.0 \times 10^{-3} \text{ mol/L}}{0.10 \text{ mol/L}} \times 100 = 4.0\% < 5\%$