Lecture-9

Solubility Product & pH

Text

Essentials of Physical Chemistry

By Bahl & Tuli

What is solubility product law?

The product of concentrations of ions arising out of a sparingly (weakly soluble) salt in a saturated solution at any constant temperature is a constant.

For example, lead sulphate is a sparingly soluble electrolyte.

$$\underset{\text{(solid)}}{PbSO_4} \rightarrow \underbrace{Pb^{+2} + SO_4^{-2}}_{\text{(in solution)}}$$

Solubility Product (contd.)

According to the solubility product law,

$$[Pb^{+2}]\ [SO_4^{-2}] = \text{a constant}$$

where $[Pb^{+2}]$ = concentration of Pb^{+2} ions as gram ions per liter and $[SO_4^{-2}]$ = concentration of SO_4^{-2} ions as gram ions per liter.

Example-1: The solubility of $PbSO_4$ in H_2O at 25^0C is found to be 0.0037 gm/100gm H_2O. Find its solubility product (K_{sp}) at that temperature.

Solution:

The molecular weight of $PbSO_4$ = 303.37

The solubility of $PbSO_4$ = 0.0037g/100g of H_2O

= 0.0037g/100ml of H_2O

= 0.037g/1000ml of H_2O

= 0.037 g/liter

∴ = 0.037÷303.37 mole/liter

= 1.2×10^{-4} mole/liter.

Since $PbSO_4$ dissociates completely in H_2O, each molecule of it on dissociation produces,

1.2×10^{-4} moles Pb^{+2} ions/liter

1.2×10^{-4} moles SO_4^{-2} ions/liter

$\therefore\ K_{sp} = [Pb^{+2}]\ [SO_4^{-2}] = (1.2 \times 10^{-4})(1.2 \times 10^{-4})$

$= (1.44 \times 10^{-8})$ **Ans.**

Problem 2. The solubility product of $CuCl_2$ is 3.2×10^{-7} at 25^0C. Calculate the solubility of $CuCl_2$ in mole $litre^{-1}$.

- $CuCl_2$ is a sparingly soluble salt.
- Let x is the solubility of $CuCl_2$ in mole $litre^{-1}$
- The following equilibrium exists in its saturated solution:
- $$CuCl_2 \leftrightarrow Cu^{+2} + 2Cl^-$$
- *Equilibrium concentration*, x x 2x
- Therefore, solubility product, $K_{sp} = [Cu^{+2}]\,[Cl^-]^2$
- or, $3.2 \times 10^{-7} = [x]\,[2x]^2$
- or, $4x^3 = 3.2 \times 10^{-7}$
- $\therefore$ $x = 4.3 \times 10^{-3}$ mole $litre^{-1}$
-

Ans

29 59

$CuCl_2 \rightleftharpoons Cu^{2+} + 2Cl^-$

x 2x

$K_{sp} = x(2x)^2$

$\Rightarrow 4x^3 = 3.2\times10^{-7}$

$\Rightarrow x^3 = \frac{3.2\times10^{-7}}{4}$

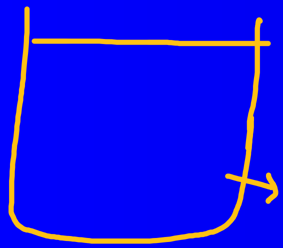
$x = \sqrt[3]{\frac{3.2\times10^{-7}}{4}}$

$= 4.3\times10^{-3}\,M$

Problem 3. K_{sp} of CaF_2 is 1.7×10^{-10} and its mol. wt. is 78 g $mole^{-1}$. What volume of the saturated solution will contain 0.078 g of CaF_2?

- CaF_2 is a sparingly soluble salt.
- Let x is the solubility of CaF_2 in mole $litre^{-1}$
- The following equilibrium exists in its saturated solution:
- $CaF_2 \leftrightarrow Ca^{+2} + 2F^-$
- *Equilibrium concentration*, x x 2x
- Therefore, solubility product, $K_{sp} = [Ca^{+2}]\,[F^-]^2$
- or, $1.7 \times 10^{-10} = [x]\,[2x]^2$
- or, $4x^3 = 1.7 \times 10^{-10}$
- $\therefore$ $x = 3.5 \times 10^{-4}$ mole $litre^{-1}$
- $\therefore$ 1 litre saturated solution contains 3.5×10^{-4} mole of CaF_2

1L



3g 2g

1004

$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$

x x $2x$

$K_{sp} = [Ca^{2+}][F^-]^2$

$x = 3.5 \times 10^{-4}$ Mol/litre $\times 78$ CaF_2

$= 273 \times 10^{-4}$ g

3.1

3g 100 g

H_2O

$3.5 \times 10^{-4} \times 78$ g

1L —— =

0.078 g

273×10^{-4}

→ 0.078 g

1L 500

$\frac{0.078}{273 \times 10^{-4}}$

0.07 — 3.5×10^{-4} — $1 L$

……Problem-3 (contd.)

1×10^{-3} — $\frac{1 \times 10^{-3}}{3.5 \times 10^{-4}}$

- No. moles of CaF_2 = 0.078g / (78g/mole)
- = 1.0×10^{-3} moles $= 2.857 L$
- $\therefore$ Volume of the solution = $$\frac{1\,litre \times 1.0 \times 10^{-3}\ mole}{3.5 \times 10^{-4}\ mole}$$
- = 2.857 litre $\simeq$ 2.9 L
- Thus, 0.078 g of CaF2 is contained in 2.9 litres of the saturated solution. Ans

$$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$$

$x \qquad x \qquad 2x$

0.078

$$K_{sp} = 4x^3 = x(2x)^2$$

$$x = 3.5 \times 10^{-4}\ mol/L$$

$$0.078\ CaF_2 \approx \frac{0.078}{78} = 1 \times 10^{-3}\ mol$$

3.5×10^{-4} mol —— 1 L

1×10^{-3}

$$\frac{1 \times 10^{-3}}{3.5 \times 10^{-4}} = 2.857$$

$\approx$ 2.9 L

Solubility Product vs Ionic Product

The *solubility product* of an insoluble substance is the product of the concentrations of its ions at equilibrium.

The *ionic product* is the product of actual concentrations of ions that may or may not be in equilibrium with the solid.

Solubility Product Principle

- When the ionic product is equal to the solubility product, the solution is saturated.
- When the ionic product exceeds the solubility product, the solution is supersaturated and precipitation will occur.
- When the ionic product is less than the solubility product, the solution will be unsaturated.

$AgCl \rightleftharpoons Ag^+ + Cl^-$

Common-ion effect

AgCl

The reduction of the degree of dissociation of a salt by the addition of a common-ion is called the ***common-ion effect***. For example- NaCl in AgCl solution.

AgCl

$$AgCl_{(s)} \leftrightarrows Ag^+_{(aq)} + Cl^-_{(aq)}$$

Cl

Addition of NaCl shift equilibrium to left due to excess Cl^- ions and decrease solubility of AgCl.

Application of Solubility Product Principle

(1) Purification of common salt.

A saturated solution of common salt freed from suspended impurities is taken and HCl gas passed through it. The equilibrium

Cl⁻

$$\underset{\text{(solid)}}{NaCl} \rightleftharpoons \underset{\text{(dissolved)}}{NaCl} \rightleftharpoons Na^+ + Cl^-$$

NaCl

On passing HCl gas, the concentration of Cl^- ions is increased because HCl is highly ionized. The ionic product $[Na^+][Cl^-]$ thus considerably increases so much so that it exceeds the solubility product of sodium chloride at the given temperature. The result is a supersaturated solution of NaCl from which solid NaCl precipitates out in order to restore the equilibrium.

Application…(contd)

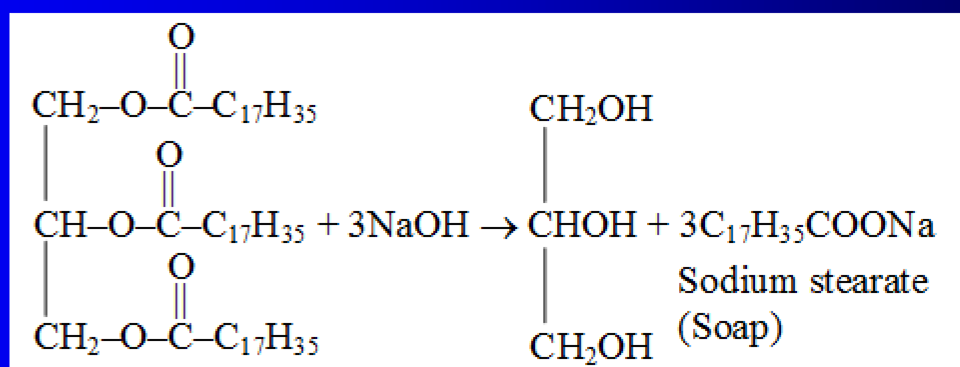
NaCl

(2) Salting out of soap

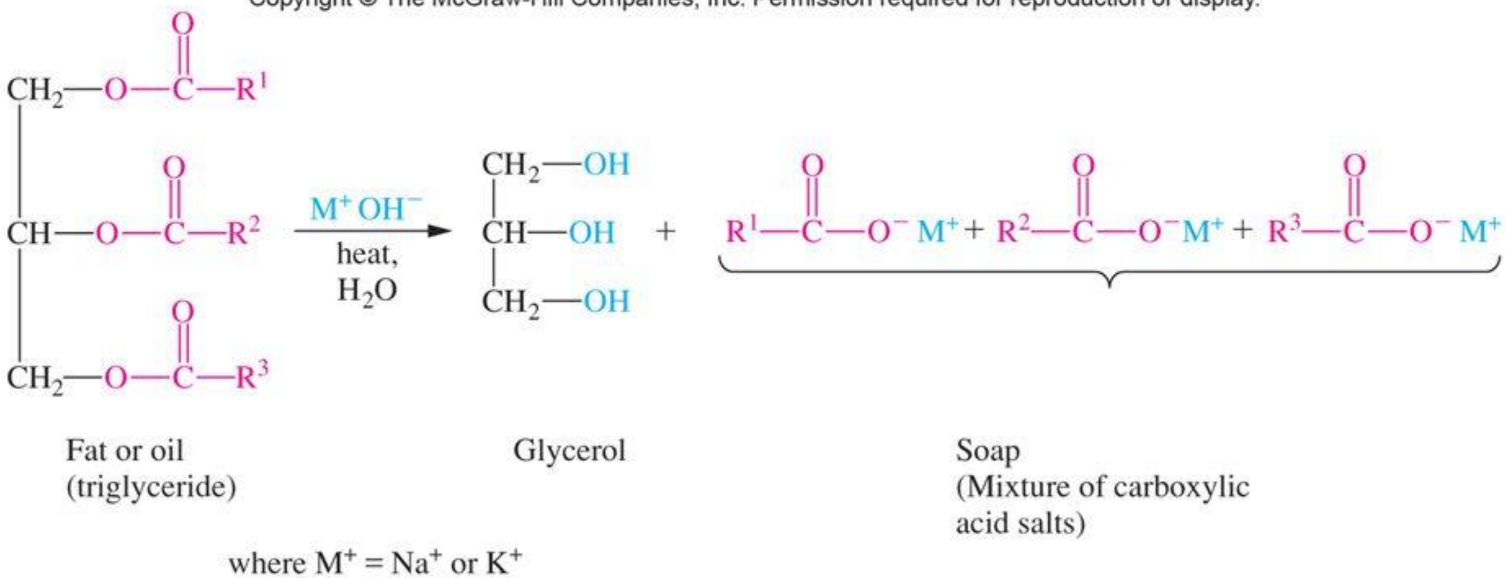
Ordinary soap is a mixture of the sodium salts of higher fatty acids and is abtained in the form of a concentrated solution as a result of saponification. From the solution, soap precipitates out on the addition of a saturated common salt solution because the concentration of $[Na^+]$ ions increases and the ionic product $[Na^+][C_nH_{2n+1}COO^-]$ exceeds the solubility product of soap at that temperature.

Saponification

- Saponification is a process that involves conversion of fat or oil into soap and alcohol by the action of heat in the presence of aqueous alkali. Soaps are salts of fatty acids whereas fatty acids are saturated monocarboxylic acids that have long carbon chains e.g. $CH_3(CH_2)_{14}COOH$.



Hydrolysis of fat (saponification)



Problem 4. Calculate the solubility of AgCl ($K_{sp} = 1.7 \times 10^{-10}$) in 0.01 M NaCl solution.

- $AgCl \leftrightarrow Ag^+ + Cl^-$ $\quad\quad$ $NaCl \leftrightarrow Na^+ + Cl^-$

  equilib. conc. $\quad$ x $\quad$ x $\quad$ x $\quad\quad$ 0.01 $\quad$ 0.01 $\quad$ 0.01M
- Complete ionization of the salt in aqueous solution is assumed. Therefore, total concentration of Cl^- in the solution =
- 0.01 M (from NaCl) + x M (from AgCl)
- As AgCl is sparingly soluble, x is negligibly small.
- $\therefore [Cl^-] \simeq 0.01$ M
- $\therefore \; K_{sp} = [Ag^+] [Cl^-]$
- *or,* $1.7 \times 10^{-10} = (x)(0.01)$ M
- or, $x = 1.7 \times 10^{-8}$ M
- $\therefore$ The solubility of AgCl in 0.01M NaCl solution is 1.7×10^{-8} M Ans

x

$AgCl \quad K_{sp} = 1.7 \times 10^{-10}$ $\quad$ $0.01\,M\ NaCl$

$NaCl \rightarrow Na^+ + Cl^-$

$\rightarrow \quad 0.01 \quad 0.01$

$AgCl \rightleftharpoons Ag^+ + Cl^-$

$x \quad\quad x \quad\quad x$

$K_{sp} = [Ag^+][Cl^-]$

$x \rightarrow 0.01$

$x + 0.01 = 0.01$

$= x \times (x + 0.01)$

$1.7 \times 10^{-10} = 0.01x$

$\approx x = 1.7 \times 10^{-5}$

$1.7 \times 10^{-10} = x^2 + 0.01x$

$x^2 + 0.01x - 1.7 \times 10^{-10} = 0$

$ax^2 + bx + c = 0$

$x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Problem 5. K_{sp} of $Mg(OH)_2$ is 1.8×10^{-11} at 25^0C. Calculate the solubility of $Mg(OH)_2$ in 0.1 M aqueous NaOH solution.

- $Mg(OH)_2 \leftrightarrow Mg^{+2} + 2OH^-$ $\quad$ $NaOH \leftrightarrow Na^+ + OH^-$

  equilib. conc. $\quad x \quad x \quad 2x + 0.1 \quad 0.1 \quad 0.1 \quad 0.1M$
- Complete ionization of the salt in aqueous solution is assumed. Therefore, total concentration of OH^- in the solution =
- 0.1 M (from NaOH) + 2x M (from $Mg(OH)_2$)
- As $Mg(OH)_2$ is sparingly soluble, x is negligibly small.
- $\therefore [OH^-] = (0.1 + 2x)M \cong 0.1$ M
- $\therefore K_{sp} = [Mg^{+2}][OH^-]^2$ $\qquad$ $\cancel{2x^2 = K_{sp}}$
- *or,* $1.8 \times 10^{-11} = (x)(0.1)^2$ M
- or, $x = 1.8 \times 10^{-9}$ M
- $\therefore$ The solubility of $Mg(OH)_2$ in 0.1M NaOH solution is 1.8×10^{-9}M

Ans

x M

$NaOH \rightarrow Na^+ + OH^-$

0.1

$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

$x \qquad 2x$

$[OH^-] = 2x + 0.1$

$[Mg^{2+}] = x$

$1.5 \times 10^{-11} = 2x^2$

$= 2x + 0.1 \approx 2 \times 0.1$

$K_s = [Mg^{2+}] \times [OH^-]^2$

$1.8 \times 10^{-11} = x(2x + 0.1)^2$

$= (0.1)x^2$

$= 0.01x$

$2x^2 + 0.1x - 1.8 \times 10^{-11} = 0$

0.1 M NaOH

$ax^2 + bx + c = 0$

$x = 1$

$x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$x = 1.8 \times 10^{-9}$ M

solubility of $Mg(OH)_2 = 1.8 \times 10^{-9}$ M

H_3O^+

7

$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$

$K = \frac{[H^+][OH^-]}{[H_2O]}$

$[H^+] = [OH^-] = 10^{-7}$

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

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

$pH < 7$ $pOH > 7$

$\rightarrow pK_w = pH + pOH$

$pH > 7$ $pOH < 7$

$14 = pH + pOH$

0.3M $\quad$ 0.1M CaF_2 $\quad$ 1L

or

$$CaF_2 \rightleftharpoons Ca^{2+} + 2F^{2-}$$

0.1 + 2×0.1 $\quad$ 0.1 $\quad$ 0.1

$$K_{sp} = Ca^{2+} \times [F^{2-}] \times [F^{2-}]$$

$$= 0.1 \times 0.2 \times 0.2$$

$$= 0.004$$

Next Class: Quiz-4

SOLUTION, SOLUBILITY, SOLUBILITY-PRODUCT

$H_2O \rightleftharpoons H_3O$

$H^+ + OH^-$

$K = \frac{[H^+][OH^-]}{[H_2O]}$

Ionic Product of Water: Ionization of Water

Water is known to be slightly ionized,

$$H_2O \rightleftharpoons H^+ + OH^-$$

$K_{sp} = [H^+][OH^-]$

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

But H^+ ions get hydrated to H_3O^+ ions by water, acting as a base. Water act as an acid by losing H^+ ion. Thus

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

Ionization of Water (contd.)

Applying law of chemical equilibrium,

$$K = \frac{[H^+][OH^-]}{[H_2O]} \qquad K = \frac{[H_3O^+][OH^-]}{[H_2O][H_2O]}$$

In case of dilute solution,

$K\,[H_2O] = [H^+]\,[OH^-]$, or $K\,[H_2O]^2 = [H_3O^+]\,[OH^-]$

Since the ionic concentrations are very small, the concentration of unionized water may be taken as constant, thus

$$K\,[H_2O] = K_w, \qquad \text{or} \qquad K\,[H_2O]^2 = K_w$$

$H_2O \rightleftharpoons H^+ + OH^-$

$K_w = [H^+][OH^-]$
$pK_w = pH + pOH$

Ionization of Water (contd.)

$$\therefore \; K_w = [H^+]\,[OH^-] = [H_3O^+]\,[OH^-]$$

K_w is known as ionic product of water and may be defined as the product of concentration of H^+ ions and OH^- ions in pure water. It is constant at constant temperature.

$K_w = 10^{-14}$

At 25^0C, the value of K_w is 1×10^{-14}.

$-\log(10^{-14} = [H^+][OH^-])$

$[H^+] = [OH^-] = 10^{-7}$ M

$pK_w = pH + pOH$

$pK_w = pH + pOH$

Ionization of Water (contd.)

In case of pure water and also in the case of neutral solutions, the molar concentration of H^+ ions and OH^- ions are equal.

$[H^+] = [OH^-] = \sqrt{(1 \times 10^{-14})} = 1 \times 10^{-7}$ moles/litre

For neutral solution $[H^+] = [OH^-] = \sqrt{(1 \times 10^{-14})} = 1 \times 10^{-7}$ moles/litre.

For acidic solution $[H^+] > 1 \times 10^{-7} > [OH^-]$ moles/litre.

For basic solution $[OH^-] > 1 \times 10^{-7} > [H^+]$ moles/litre.

$[H^+] = [OH^-] = 10^{-7} M$

pH value:

acid $[H^+] > 10^{-7}$ M

$\cancel{-\log H^+ > -\log 10^{-7}}$

The acidity or the basicity of a solution can be expressed in terms of hydrogen ion concentration.

$$[H^+] = \boxed{\frac{K_w}{[OH^-]} = \frac{1\times10^{-14}}{[OH^-]}} \quad \text{and } [OH^-] = \boxed{\frac{K_w}{[H^+]} = \frac{1\times10^{-14}}{[H^+]}}$$

pH of a solution is the negative logarithm of hydrogen ion concentration (called pH scale, Sorensen in 1909).

pH value (contd.)

$H^+ > 10^{-7}$ $OH^- > 10^{-7}$

$pH < 7$ $pH > 7$

$$pH = \boxed{-\log_{10}[H^+] = \log_{10}\frac{1}{[H^+]}}$$

$pH > 7$

pOH

$$pOH = \boxed{-\log_{10}[OH^-] = \log_{10}\frac{1}{[OH^-]}}$$

For pure water, $[H^+] = [OH^-] = 1 \times 10^{-7}$ moles/litre

$$\therefore \quad pH = \boxed{-\log_{10}[1\times 10^{-7}] = -(-7) = 7}$$

$$\therefore \quad pOH = \boxed{-\log_{10}[1\times 10^{-7}] = -(-7) = 7}$$

$$\boxed{\therefore \quad pH + pOH = 7 + 7 = 14}$$

$pH + pOH = 14$

6 8

Example-2:

Calculate the pH of 0.001 M HCl.

10^{-3} M

$HCl \rightarrow H^+ + Cl^-$

0.001

$pH = -\log(10^{-3})$

$= 3$

Solution:

HCl is a strong acid and it is completely dissociated in aqueous solution.

HCl	$\leftrightarrows$	H^+	+	Cl^-
0.001 M		0.001 M		

For every molecule of HCl, there is one H^+, therefore

$[H^+] = [HCl]$

Solution (contd)

or $[H^+] = 0.001\ M$

$$\therefore \quad pH = -\log(0.001)$$

$$= -\log(1 \times 10^{-3})$$

$$= -\log 1 + 3 \log 10$$

$$= 3$$

Therefore the pH of 0.001 M HCl is 3. **Ans.**

3

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

$$\Rightarrow \text{Antilog}(-pH)$$

$$= -2.699$$

$$= 0.002\,M$$

Problem 6. Calculate pH and pOH of 0.02 M H_2SO_4 solution. $K_w = 1 \times 10^{-14}$ at 25^0C.

- $H_2SO_4 \leftrightarrow 2H^+ + SO_4^-$
- *equilib. conc.* 1M 2M 1M

  0.02 0.04

  $(2H_3O^+)$

$pH + pOH = 14$

$pH = -\log(0.04) = 1.40$

If H_2SO_4 in 1M solution ionizes completely, $[H_3O^+]$ will be 2M.

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

$-\log(1 \times 10^{-14}) = -\log H^+ + pOH$

$= pH + pOH$

- Therefore, in a 0.02 M H_2SO_4 solution
- $[H_3O^+] = 0.04$ M
- $\therefore [OH^-] = K_w / [H_3O^+] = (1 \times 10^{-14}) / 0.04 = 2.5 \times 10^{-13}$ M

  14

  $= 12.60$
- $\therefore pH = -\log [H_3O^+] = -\log (0.04) = 1.40$
- $\therefore pOH = -\log [OH^-] = -\log (2.5 \times 10^{-13}) = 12.60$ Ans.

Problem -7. pH of an aqueous solution of HCl is 2.699 at 25^{0}C. Calculate the molarity of the solution.

- We know from the definition of pH,

$HCl \rightarrow H^+ + Cl^-$

$pH = -\log H^+$

$$pH = \boxed{-\log_{10}[H^+] = \log_{10}\frac{1}{[H^+]}}$$

$2.669 = -\log H^+$

$[H^+] = \text{antilog } 6.699$

$= 0.002$

- $\therefore$ 2.699 = -log $[H_3O^+]$
- or, $[H_3O^+]$ = antilog (- 2.699) = 0.002 M
- As HCl is a strong acid, it will ionize completely in the aqueous solution. So the molarity of HCl in the solution will be equal to the concentration of H_3O^+.
- $\therefore$ Molarity of HCl in the solution is 0.002. <u>Ans</u>.

pH 1 to 6

Importance of pH in our daily Life

- **All living organisms are pH sensitive and can survive only in a narrow range of pH.**

- **Most foods are slightly acidic; our "bodily fluids" are slightly alkaline,** as is seawater— not surprising, since early animal life began in the oceans. The pH of freshly-distilled water will go downward as it takes up carbon dioxide from the air. "Acid" rain is by definition more acidic than pure water in equilibrium with atmospheric CO_2, owing mainly to sulfuric and nitric acids that originate from fossil-fuel emissions of nitrogen oxides and SO_2.
- **pH of the soil:** Plants require a specific pH range for their healthy growth.

MCQ

	Environmental Effects	pH Value	Examples
ACIDIC		pH = 0	Battery acid
		pH = 1	Sulfuric acid
		pH = 2	Lemon juice, Vinegar
		pH = 3	Orange juice, Soda
	All fish die (4.2)	pH = 4	Acid rain (4.2-4.4) Acidic lake (4.5)
	Frog eggs, tadpoles, crayfish, and mayflies die (5.5)	pH = 5	Bananas (5.0-5.3) Clean rain (5.6)
NEUTRAL	Rainbow trout begin to die (6.0)	pH = 6	Healthy lake (6.5) Milk (6.5-6.8)
		pH = 7	Pure water
		pH = 8	Sea water, Eggs
		pH = 9	Baking soda
		pH = 10	Milk of Magnesia
		pH = 11	Ammonia
		pH = 12	Soapy water
		pH = 13	Bleach
BASIC		pH = 14	Liquid drain cleaner

HCl

Importance of pH in our daily Life…

- **Plants and animals are pH sensitive**: Our body works within the pH range of 7.0 to 7.8. When pH of rain water is less than 5.6, it is called acid rain. When acid rain flows into the rivers, it lowers the pH of the river water. The survival of aquatic life in such rivers becomes difficult.

- **pH in our digestive system**: It is very interesting to note that our stomach produces hydrochloric acid. It helps in the digestion of food without harming the stomach. During indigestion the stomach produces too much acid and this causes pain and irritation. To get rid of this pain, people use bases called antacids. These antacids neutralise the excess acid.

Importance of pH in our daily Life…

- **pH change as the cause of tooth decay:** Tooth decay starts when the pH of the mouth is lower than 5.5. Tooth enamel, made up of calcium phosphate is the hardest substance in the body. It does not dissolve in water, but is corroded when the pH in the mouth is below 5.5. Bacteria present in the mouth produce acids by degradation of sugar and food particles remaining in the mouth after eating. The best way to prevent this is to clean the mouth after eating food. Using toothpastes, which are generally basic, for cleaning the teeth can neutralize the excess acid and prevent tooth decay.

Importance of pH in our daily Life…

- **Self defence by animals and plants through chemical warfare:** Wasps (insect) and jellyfish have an alkaline sting and bees have an acidic sting. So with wasps stung area can be treated with vinegar, and bees with soap or baking soda. Stinging hair of nettle (plant) leaves inject methanoic acid causing burning pain.

- **The balance of pH** in our body also helps to regulate our breathing rate (carbonic acid in our blood), controls microorganisms on skin, and activates enzymes. Blood has a pH which needs to be maintained between 7.35 and 7.45, or else serious illness and death may occur.

Next Class: Electrochemistry & Battery

Syllabus for Quiz-5

(pH & Problems, Electrochemistry & Battery)

Thank you