Solubility Product

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 is known as *solubility product law*.

For example, lead sulphate is a sparingly soluble electrolyte.

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

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. (Mol.wt. of $PbSO_4$ is 303.37)

Solution: The molecular weight of $PbSO_4$ = 303.37

$\therefore$ The solubility of $PbSO_4$ = 0.0037g/100g H_2O = 0.0037g/100ml H_2O

= 0.037g/1000ml H_2O = 0.037 gm/liter H_2O

$= \dfrac{0.037}{303.37}$ mole/liter H_2O

$= 1.2\times10^{-4}$ mole/liter H_2O

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

$\therefore$ $K_{sp} = [Pb^{+2}]\ [SO_4^{-2}] = (1.2\times10^{-4})(1.2\times10^{-4}) = 1.44\times10^{-8}$ <u>Ans.</u>

<u>Problem-2</u>. The solubility product of $CuCl_2$ is 3.2×10^{-7} at 25^0C. Calculate the solubility of $CuCl_2$ in. (Answer: 4.3×10^{-3} mole litre^{-1})

<u>Problem-3</u>. 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? (Answer: 2.9 litre)

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.

Common-ion effect: 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.

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

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

APPLICATION OF SOLUBILITY PRODUCT PRINCIPLE:

The concept of solubility product mentioned above finds a number of applications:

(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

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

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.

(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.

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

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.

IONIC PRODUCT OF WATER: IONIZATION OF WATER

Water is known to be slightly ionized,

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

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

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

Applying law of chemical equilibrium,

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

In case of dilute solution,

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

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

$$K\,[H_2O] = K_w,$$

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

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.

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

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

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

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.

Now hydrogen ion concentration and hydroxide ion concentration can expressed in terms of ionic product of water by the following way--

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

pH value: The acidity or the basicity of a solution can be expressed in terms of hydrogen ion concentration. pH of a solution is the negative logarithm of hydrogen ion concentration (called pH scale, Sorensen in 1909).

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

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

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

$\therefore$ pH = $-\log_{10}[1\times10^{-7}] = -(-7) = 7$

$\therefore$ pOH = $-\log_{10}[1\times10^{-7}] = -(-7) = 7$

$\therefore$ pH + pOH = 7 + 7 = 14

Example-2: Calculate the pH of 0.001 M HCl.

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]

or $[H^+]$ = 0.001 M

$\therefore$ pH = -log (0.001)
= -log (1×10^{-3})
= - log 1 + 3 log 10
= 3

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

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

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

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.
- **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 of the soil:** Plants require a specific pH range for their healthy growth.
- **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.
- **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 neutralise the excess acid and prevent tooth decay.
- **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.