

## Equilibrium

$$\text{Buffer capacity} = \frac{\text{No. of moles of acids or base added}}{\text{Change in pH}} \text{ per litre of buffer}$$

The range of pH over which the buffer solutions remain effective is called buffer range.

**Buffer Buffer range in pH**

Acidic  $pK_a \pm 1$

Basic  $(pK_w - pK_b) \pm 1$

*Example* :  $pK_a$  of acetic acid is 4.74, then the range of buffer solution of acetic acid is

$$pH = 4.74 \pm 1, \text{ i.e., } 3.74 \text{ to } 5.74$$

### Illustration 9

Calculate the amount of  $NH_3$  and  $NH_4Cl$  required to prepare a buffer solution of  $pH = 9.0$  when total concentration of buffering reagents is  $0.6 \text{ mol litre}^{-1}$ . ( $pK_b$  for  $NH_3 = 4.7$ ,  $\log 2 = 0.30$ ).

**Soln.:** Applying,  $pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$

$$pOH = 14 - pH = 14 - 9 = 5.0$$

$$5.0 = 4.7 + \log \frac{[\text{Salt}]}{[\text{Base}]}, \quad \log \frac{[\text{Salt}]}{[\text{Base}]} = 5.0 - 4.7 = 0.3$$

Taking antilog,

$$\frac{[\text{Salt}]}{[\text{Base}]} = 2, \quad [\text{Salt}] = 2 \times [\text{Base}]$$

But it is given that  $[\text{Salt}] + [\text{Base}] = 0.6 \text{ M}$

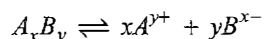
On solving two above equations

$$[\text{Base}] = 0.2 \text{ mol litre}^{-1}$$

$$[\text{Salt}] = 0.4 \text{ mol litre}^{-1}$$

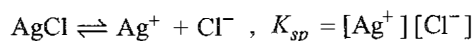
## SOLUBILITY PRODUCT

- Solubility product of a sparingly soluble salt at a given temperature is defined as the product of molar concentration of its ions in a saturated solution, with each concentration term raised to the power equal to number of ions present in the chemical equation representing the equilibrium of dissociation of one molecule of the salt. It is represented as  $K_{sp}$ .



$$\text{Solubility product } (K_{sp}) = [A^{y+}]^x [B^{x-}]^y$$

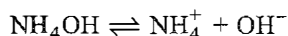
For example,



### Common Ion Effect

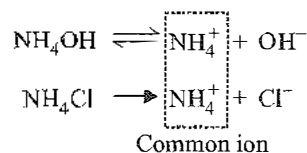
- Common ion effect is defined as the suppression of ionization of weak electrolytes by addition of strong electrolytes having an ion common to the weak electrolyte.

For example weak base  $NH_4OH$  ionizes to a small extent



- When a strong electrolyte like  $NH_4Cl$  or  $NaOH$  is added to this solution, a common ion  $NH_4^+$  and  $OH^-$  respectively is furnished so that the equilibrium is

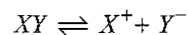
shifted to the right, according to Le Chatelier's principle and ionization of  $NH_4OH$  is suppressed.



Thus, degree of dissociation of an electrolyte decreases by common ion effect but dissociation constant of that electrolyte remains constant.

### Applications of solubility product

- Predicting precipitate formation:** if ionic product  $> K_{sp}$  precipitation takes place if ionic product  $< K_{sp}$  no precipitation takes place
- Predicting solubility of sparingly soluble salt:** Solubility of a sparingly soluble salt can be calculated from its solubility product at a given temperature.



Let solubility is  $s$   $s$   $s$

$$K_{sp} = [X^+][Y^-] = (s)(s) = s^2, \quad s = \sqrt{K_{sp}}$$

**Type of salt Solubility product**

$AB$  type  $K_{sp} = s^2$

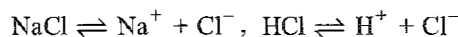
$AB_2$  or  $A_2B$  type  $K_{sp} = 4s^3$

$AB_3$  or  $A_3B$   $K_{sp} = 27s^4$

$AB_4$  or  $A_4B$   $K_{sp} = 256s^5$

where,  $s$  = solubility (mole/litre)

- Precipitation of common salt:** When HCl gas is passed through saturated solution of impure common salt, the concentration of  $Cl^-$  increases due to ionization of HCl.



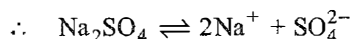
Thus ionic product  $[Na^+][Cl^-]$  exceeds solubility product and pure NaCl precipitates out.

- Qualitative Analysis:** Various basic radicals are identified and separated by the principle of solubility product and common ion effect.

### Illustration 10

Predict whether a precipitate will be formed or not on mixing equal volumes of  $2 \times 10^{-4} \text{ M}$   $BaCl_2$  solution and  $2 \times 10^{-5} \text{ M}$   $Na_2SO_4$  solution if solubility product of  $BaSO_4$  is  $1 \times 10^{-10}$ .

**Soln.:**  $BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$ ,



Since equal volumes of  $BaCl_2$  and  $Na_2SO_4$  are mixed, concentration of  $Ba^{2+}$  and  $SO_4^{2-}$  after mixing would be

$$[Ba^{2+}] = \frac{[BaCl_2]}{2} = \frac{2 \times 10^{-4}}{2} = 10^{-4} \text{ M}$$

$$[SO_4^{2-}] = \frac{[Na_2SO_4]}{2} = \frac{2 \times 10^{-5}}{2} = 10^{-5} \text{ M}$$

Ionic product of  $BaSO_4$

$$= [Ba^{2+}][SO_4^{2-}] = [10^{-4}][10^{-5}] = 10^{-9} \text{ M}$$

Ionic product ( $10^{-9} \text{ M}$ )  $> K_{sp}$  ( $1 \times 10^{-10}$ )

Hence, precipitation will take place.